

A New Dimension to Quantum Chemistry: Analytic Derivative Methods in *Ab Initio* Molecular Electronic Structure Theory

**Yukio Yamaguchi
John D. Goddard**

**Yoshihiro Osamura
Henry F. Schaefer III**

New York Oxford
OXFORD UNIVERSITY PRESS
1994

Oxford University Press

Oxford New York Toronto
Delhi Bombay Calcutta Madras Karachi
Kuala Lumpur Singapore Hong Kong Tokyo
Nairobi Dar es Salaam Cape Town
Melbourne Auckland Madrid
and associated companies in
Berlin Ibadan

Copyright © 1994 by Oxford University Press, Inc.

Published by Oxford University Press, Inc.,
200 Madison Avenue, New York, New York 10016

Oxford is a registered trademark of Oxford University Press

All rights reserved. No part of this publication may be reproduced,
stored in a retrieval system, or transmitted, in any form or by any means,
electronic, mechanical, photocopying, recording, or otherwise,
without the prior permission of Oxford University Press.

Library of Congress Cataloging-in-Publication Data
The new dimension to quantum chemistry: analytic derivative methods in
ab initio molecular electronic structure theory / Yukio Yamaguchi ... [et al.].
p. cm. — (International series of monographs on chemistry: [#29])
Includes bibliographical references and index.
ISBN 0-19-507028-3
1. Quantum chemistry. I. Yamaguchi, Y. (Yukio) II. Series.
QD462.N49 1994 541.2'8'015118—dc20 93-31798

9 8 7 6 5 4 3 2 1
Printed in the United States of America
on acid-free paper

Preface

In modern theoretical chemistry, the importance of the analytic evaluation of energy derivatives from reliable wavefunctions can hardly be overestimated. The first and second energy derivatives of the total energy of a system with respect to geometrical variables are absolutely essential to interrogate reactive potential energy hypersurfaces unambiguously, efficiently, and accurately. The third and fourth energy derivatives are related very directly to the anharmonicity of the potential energy. These higher derivatives are crucial for a true understanding of the internal motions of molecules. The formulation and implementation of analytic energy derivative methods has been one of the “hottest” topics in *ab initio* quantum chemistry over the past two decades and remains today an area of great importance and activity.

There are many excellent books that handle the fundamental concepts involved in elementary linear combination of atomic orbital-molecular orbital (LCAO-MO) theory. However, there are few sources that explain in detail recent developments in analytic derivative methods in *ab initio* quantum chemistry. This book aims to enlighten beginning graduate students and young researchers who are interested in the development and implementation of analytic derivative methods in *ab initio* quantum chemistry. In this book we limit ourselves to derivative methods for wavefunctions based on the variational principle, namely, restricted Hartree-Fock (RHF), configuration interaction (CI) and multiconfiguration self-consistent-field (MCSCF) wavefunctions. Thus, we exclude, with some reluctance, methods based on perturbation theory such as Møller-Plesset perturbation theory to second-order, MP2. A recent development in derivative methods, the derivatives for the coupled cluster method, is omitted as well. Some references to these nonvariational derivative schemes are given in the bibliographical survey, and a brief discussion of the future of coupled cluster derivative methods is given in the final chapter on the Future.

Even the most casual observer will appreciate that the analytic evaluation of derivatives involves a vast amount of algebra. We have endeavored to put down in a permanent record a systematic presentation of the necessary algebraic formulae. Critical to such a permanent record is that it be error-free, and much effort has been expended to this end. We especially thank Oxford University Press for their good efforts in the computerized transfer of equations to the text. Of course, all human efforts are prone to error, and we would be greatly appreciative if readers would bring any errors to our attention.

It is our pleasure to thank our former and present co-workers for their significant contributions to the subjects discussed in this book, namely, Drs. Russell M. Pitzer, Nicholas C. Handy, Peter Pulay, Bernard R. Brooks, Michel Dupuis, William D. Laidig, Paul Saxe, Douglas J. Fox, Mark A. Vincent, Michael J. Frisch, Jeffrey F. Gaw, George Fitzgerald, Mark R. Hoffmann, Timothy J. Lee, Michael E. Colvin, Julia E. Rice, Miquel Duran, Peter J. Knowles, Gustavo E. Scuseria, Roger S. Grev, Richard B. Remington, Wesley D. Allen, Andrew C. Scheiner, Tracy P. Hamilton, Ian L. Alberts, Neil A. Burton, Curtis L. Janssen, Edward T. Seidl, and Seung-Joon Kim. The authors also thank Dr. Cynthia Meredith for careful proofreading of the entire manuscript.

July, 1993

Yukio Yamaguchi
Yoshihiro Osamura
John D. Goddard
Henry F. Schaefer III

Contents

Preface	i
List of Abbreviations	xvii
1 Introduction	3
References	7
Suggested Reading	8
2 Basic Concepts and Definitions	9
2.1 The Schrödinger Equation and the Hamiltonian Operator	9
2.2 The Variation Method	10
2.3 The Linear Combination of Atomic Orbitals-Molecular Orbital (LCAO-MO) Approximation	11
2.4 Basis Sets	12
2.5 The Hartree-Fock and Self-Consistent-Field Wavefunctions	13
2.6 The Configuration Interaction (CI) Wavefunction	16
2.7 The Multiconfiguration (MC) SCF Wavefunction	18
2.8 Energy Expressions in MO and AO Bases	20
2.8.1 One-Electron MO Integral	20
2.8.2 Two-Electron MO Integral	21

2.8.3	The Electronic Energy for a Closed-Shell SCF Wavefunction	22
2.8.4	The Electronic Energy for a CI Wavefunction	23
2.9	Potential Energy Surface	24
2.10	Wigner's 2n+1 Theorem	25
References	27
Suggested Reading	28
3	Derivative Expressions for Integrals and Molecular Orbital Coefficients	29
3.1	Expansions of the Hamiltonian Operator and the Atomic Orbital Integrals .	29
3.2	Expansion of the Molecular Orbital Coefficients	30
3.3	A Relationship between U^a , U^b , and U^{ab}	31
3.4	The Derivative Expressions for Overlap AO Integrals	32
3.5	The Derivative Expressions for One-Electron AO Integrals	33
3.6	The Derivative Expressions for Two-Electron AO Integrals	33
3.7	The Derivative Expressions for Overlap MO Integrals	34
3.7.1	The First and Second Derivatives of Overlap MO Integrals	34
3.7.2	An Alternative Derivation of the First Derivatives of Overlap MO Integrals	37
3.7.3	A Derivative Expression for the Skeleton (Core) Overlap Derivative Integrals	38
3.7.4	An Alternative Derivation of the Second Derivatives of Overlap MO Integrals	39
3.8	The Derivative Expressions for One-Electron MO Integrals	39
3.8.1	The First and Second Derivatives of One-Electron MO Integrals . .	39
3.8.2	An Alternative Derivation of the First Derivatives of One-Electron MO Integrals	41

3.8.3 A Derivative Expression for the Skeleton (Core) One-Electron Derivative Integrals	42
3.8.4 An Alternative Derivation of the Second Derivatives of One-Electron MO Integrals	42
3.9 The Derivative Expressions for Two-Electron MO Integrals	43
3.9.1 The First and Second Derivatives of the Two-Electron MO Integrals	43
3.9.2 An Alternative Derivation of the First Derivatives of Two-Electron MO Integrals	47
3.9.3 The Derivative Expression for the Skeleton (Core) Two-Electron Derivative Integrals	48
3.9.4 An Alternative Derivation of the Second Derivatives of Two-Electron MO Integrals	49
3.10 The Derivatives of the Nuclear Repulsion Energy	51
3.10.1 The First Derivative of the Nuclear Repulsion Energy	51
3.10.2 The Second Derivative of the Nuclear Repulsion Energy	51
References	52
4 Closed-Shell Self-Consistent-Field Wavefunctions	53
4.1 The SCF Energy	53
4.2 The Closed-Shell Fock Operator and the Variational Conditions	54
4.3 The First Derivative of the Electronic Energy	55
4.4 The Evaluation of the Energy First Derivative	57
4.5 The First Derivative of the Fock Matrix	58
4.6 The Second Derivative of the Electronic Energy	60
4.7 An Alternative Derivation of the Second Derivative of the Electronic Energy	63
References	66

Suggested Reading	66
5 General Restricted Open-Shell Self-Consistent-Field Wavefunctions	68
5.1 The SCF Energy	68
5.2 The Generalized Fock Operator and the Variational Conditions	70
5.3 The First Derivative of the Electronic Energy	71
5.4 The Evaluation of the First Derivative	73
5.5 The First Derivative of the Lagrangian Matrix	74
5.6 The Second Derivative of the Electronic Energy	76
5.7 An Alternative Derivation of the Second Derivative of the Electronic Energy	79
References	81
Suggested Reading	82
6 Configuration Interaction Wavefunctions	83
6.1 The CI Wavefunction, Energy and the Variational Conditions	83
6.2 The First Derivative of the Electronic Energy	84
6.3 The Evaluation of the First Derivative	87
6.4 The First Derivative of the Hamiltonian Matrix	89
6.5 The First Derivative of the “Bare” Lagrangian Matrix	90
6.6 The Second Derivative of the Hamiltonian Matrix	92
6.7 The Second Derivative of the Electronic Energy	94
References	96
Suggested Reading	97

7 Two-Configuration Self-Consistent-Field Wavefunctions	98
7.1 The Two-Configuration Self-Consistent-Field (TCSCF) Wavefunction and Energy	98
7.2 The Generalized Fock Operator and the Variational Conditions	101
7.3 The First Derivative of the Electronic Energy	102
7.4 The First Derivative of the Hamiltonian Matrix	103
7.5 The Second Derivative of the Hamiltonian Matrix	104
7.6 The Second Derivative of the Electronic Energy	106
References	109
Suggested Reading	109
8 Paired Excitation Multiconfiguration Self-Consistent-Field Wavefunctions	110
8.1 The Paired Excitation Multiconfiguration Self-Consistent-Field (PEMCSCF) Wavefunction and Energy	110
8.2 The Generalized Fock Operator and the Variational Conditions	114
8.3 The First Derivative of the Electronic Energy	115
8.4 The Second Derivative of the Electronic Energy	116
References	118
Suggested Reading	118
9 Multiconfiguration Self-Consistent-Field Wavefunctions	119
9.1 The MCSCF Wavefunction and Energy	119
9.2 The Variational Conditions	120
9.3 The First Derivative of the Electronic Energy	121
9.4 The Evaluation of the First Derivative	123
9.5 The Second Derivative of the Electronic Energy	124

References	126
Suggested Reading	127
10 Closed-Shell Coupled Perturbed Hartree-Fock Equations	128
10.1 The First-Order CPHF Equations	128
10.2 The Derivatives of the F^a Matrices	132
10.3 The First Derivative of the A matrix	133
10.4 The Second-Order CPHF Equations	134
10.5 An Alternative Derivation of the Second Derivative of the Fock Matrix	138
References	142
Suggested Reading	143
11 General Restricted Open-Shell Coupled Perturbed Hartree-Fock Equations	144
11.1 The First-Order CPHF Equations	144
11.2 The Averaged Fock Operator	150
11.3 The Derivative of the ϵ^a Matrices	153
11.4 The First Derivative of the Generalized Lagrangian Matrix	154
11.5 The First Derivative of the τ Matrices	155
11.6 The Second Derivative of the Lagrangian Matrix	156
11.7 The Second-Order CPHF Equations	158
11.8 An Alternative Derivation of the Second Derivative of the Lagrangian Matrix	162
References	165
Suggested Reading	165

12 Coupled Perturbed Configuration Interaction Equations	166
12.1 The First-Order Coupled Perturbed Configuration Interaction Equations	166
12.2 The Second-Order Coupled Perturbed Configuration Interaction Equations	169
References	171
Suggested Reading	171
13 Coupled Perturbed Paired Excitation Multiconfiguration Hartree-Fock Equations	172
13.1 The First-Order CPPEMCHF Equations	172
13.1.1 The Molecular Orbital (MO) Part	172
13.1.2 The Configuration Interaction (CI) Part	177
13.1.3 A Complete Expression for the First-Order CPPEMCHF Equations	179
13.2 The Averaged Fock Operator	180
13.3 The Second-Order CPPEMCHF Equations	182
13.3.1 The Molecular Orbital (MO) Part	182
13.3.2 The Configuration Interaction (CI) Part	187
13.3.3 A Complete Expression for the Second-Order CPPEMCHF Equations	189
References	191
Suggested Reading	192
14 Coupled Perturbed Multiconfiguration Hartree-Fock Equations	193
14.1 The First-Order CPMCHF Equations	194
14.1.1 The Molecular Orbital (MO) Part	194
14.1.2 The Configuration Interaction (CI) Part	198
14.1.3 A Complete Expression for the First-Order CPMCHF Equations	201

14.2 The Averaged Fock Operator	202
14.3 The First Derivative of the “Bare” γ Matrix	206
14.4 The Second-Order CPMCHF Equations	208
14.4.1 The Molecular Orbital (MO) Part	208
14.4.2 The Configuration Interaction (CI) Part	213
14.4.3 A Complete Expression for the Second-Order CPMCHF Equations .	215
References	217
Suggested Reading	217
15 Third and Fourth Energy Derivatives for Configuration Interaction Wavefunctions	218
15.1 The First and Second Derivatives of the Electronic Energy for a CI Wavefunction	219
15.2 The Third Derivative of the Electronic Energy for a CI Wavefunction	222
15.3 The Fourth Derivative of the Electronic Energy for the CI Wavefunction	224
15.4 The Third Derivative of the Hamiltonian Matrix	228
15.5 An Explicit Expression for the Third Derivative of the Electronic Energy .	233
15.6 The First Derivative Expression for the “Bare” Z Matrix	234
15.7 The Fourth Derivative of the Hamiltonian Matrix	235
15.8 An Explicit Expression for the Fourth Derivative of the Electronic Energy .	246
References	248
Suggested Reading	248
16 Correspondence Between Correlated and Restricted Hartree-Fock Wavefunctions	249
16.1 Configuration Interaction (CI) Wavefunctions	249
16.1.1 Electronic Energy and the Variational Condition	249

16.1.2 First Derivative	250
16.1.3 Second Derivative	251
16.1.4 Third Derivative	251
16.1.5 Fourth Derivative	253
16.2 Correspondence Equations	256
16.3 Multiconfiguration Self-Consistent-Field (MCSCF) Wavefunctions	258
16.3.1 Electronic Energy and the Variational Condition	258
16.3.2 First Derivative	259
16.3.3 Second Derivative	259
16.3.4 Third Derivative	260
16.3.5 Fourth Derivative	264
16.4 Paired Excitation Multiconfiguration Self-Consistent-Field (PEMCSCF) Wavefunctions	270
16.4.1 Electronic Energy and the Variational Condition	270
16.4.2 First Derivative	272
16.4.3 Second Derivative	272
16.4.4 Third Derivative	274
16.4.5 Fourth Derivative	278
16.5 General Restricted Open-Shell Self-Consistent-Field (GRSCF) Wavefunctions	285
16.5.1 Electronic Energy and the Variational Condition	285
16.5.2 First Derivative	286
16.5.3 Second Derivative	286
16.5.4 Third Derivative	288
16.5.5 Fourth Derivative	290
16.6 Closed-Shell Self-Consistent-Field (CLSCF) Wavefunctions	293

16.6.1 Electronic Energy and the Variational Condition	293
16.6.2 First Derivative	295
16.6.3 Second Derivative	296
16.6.4 Third Derivative	298
16.6.5 Fourth Derivative	300
16.7 Energy Derivative Expressions Using Orbital Energies	304
Suggested Reading	307
17 Analytic Derivatives Involving Electric Field Perturbations	308
17.1 The Electric Field Perturbation	308
17.1.1 The Hamiltonian Operator with Mixed Perturbations	308
17.1.2 The Derivative of the Molecular Orbital Coefficients	309
17.1.3 The Derivative One-Electron AO Integrals	309
17.1.4 The Derivative One-Electron MO Integrals	310
17.1.5 Constraints on the Molecular Orbitals	311
17.2 The Electric Dipole Moment	312
17.2.1 The Closed-Shell SCF Wavefunction	312
17.2.2 The General Restricted Open-Shell SCF Wavefunction	313
17.2.3 The Configuration Interaction (CI) Wavefunction	313
17.2.4 The Multiconfiguration (MC) SCF Wavefunction	314
17.3 The Electric Polarizability	314
17.3.1 The Closed-Shell SCF Wavefunction	315
17.3.2 The General Restricted Open-Shell SCF Wavefunction	317
17.3.3 The Configuration Interaction (CI) Wavefunction	320
17.3.4 The Multiconfiguration (MC) SCF Wavefunction	323

17.4 The Dipole Moment Derivative	326
17.4.1 The Closed-Shell SCF Wavefunction	327
17.4.2 The General Restricted Open-Shell SCF Wavefunction	328
17.4.3 The Configuration Interaction (CI) Wavefunction	329
17.4.4 The Multiconfiguration (MC) SCF Wavefunction	331
17.5 The Coupled Perturbed Hartree-Fock (CPHF) Equations Involving Electric Field Perturbations	332
17.5.1 The First-Order CPHF Equations for a Closed-Shell SCF Wavefunction	332
17.5.2 The Second-Order CPHF Equations for a Closed-Shell SCF Wavefunction	333
17.5.3 The First-Order CPHF Equations for a General Restricted Open-Shell Wavefunction	335
17.5.4 The Second-Order CPHF Equations for a General Restricted Open-Shell Wavefunction	336
17.6 The Coupled Perturbed Configuration Interaction Equations Involving Electric Field Perturbations	340
17.6.1 The First-Order CPCI Equations	340
17.6.2 The Second-Order CPCI Equations	341
17.7 The Coupled Perturbed Multiconfiguration Hartree-Fock Equations Involving Electric Field Perturbations	343
17.7.1 The First-Order CPMCHF Equations	343
17.7.2 The Second-Order CPMCHF Equations	345
17.8 The Coupled Perturbed Equations for Multiple Perturbations	349
References	354
Suggested Reading	354

18 The Z Vector Method	355
18.1 The Z Vector Method and First Derivative Properties for the CI Wavefunction	355
18.2 The Z Vector Method and Second Derivative Properties for the CI Wavefunction	358
References	362
19 Applications of Analytic Derivatives	363
19.1 Unimolecular Isomerization of HCN	365
19.2 Formaldehyde Dissociation	367
19.3 Dissociation of <i>cis</i> -Glyoxal → H ₂ + 2 CO	371
19.4 The Hydrogen Fluoride Dimer, (HF) ₂	373
19.5 Systematics of Molecular Properties	376
19.6 Vibrational Analysis: Anharmonic Effects	379
19.7 Larger Molecules: Structural Certainty	381
References	383
Suggested Reading	384
20 The Future	385
References	386
Appendix A Some Elementary Definitions	387
Appendix B Definition of Integrals	388
Appendix C Electronic Energy Expressions	390
Appendix D Relationships between Reduced Density Matrices and Coupling Constant Matrices	392

CONTENTS	xix
Appendix E Fock and Lagrangian Matrices	394
Appendix F Variational Conditions and Constraints	396
Appendix G Definition of U Matrices	398
Appendix H Relationships among U Matrices	399
Appendix I Definition of Skeleton (Core) Derivative Integrals	400
Appendix J First Derivative Expressions for MO Integrals	402
Appendix K Expressions for Skeleton (Core) Derivatives	403
Appendix L Second Derivative Expressions for MO Integrals	405
Appendix M Definition of Skeleton (Core) Derivative Matrices for Closed-Shell SCF Wavefunctions	407
Appendix N Expressions for Skeleton (Core) Derivative Matrices for Closed-Shell SCF Wavefunctions	409
Appendix O Definition of Skeleton (Core) Derivative Matrices for General Restricted Open-Shell SCF Wavefunctions	411
Appendix P Expressions for Skeleton (Core) Derivative Matrices for General Restricted Open-Shell SCF Wavefunctions	414
Appendix Q Definition of Skeleton (Core) Derivative “Bare” Matrices for CI and MCSCF Wavefunctions	417
Appendix R Expressions for Skeleton (Core) Derivative Hamiltonian Matrices for CI and MCSCF Wavefunctions	419
Appendix S Definition of Skeleton (Core) Derivative Lagrangian and Y Matrices for CI and MCSCF Wavefunctions	420

Appendix T Derivative Expressions for Skeleton (Core) “Bare” Matrices for CI and MCSCF Wavefunctions	423
Appendix U Derivative Expressions for Hamiltonian Matrices for CI and MCSCF Wavefunctions	425
Appendix V First and Second Electronic Energy Derivatives	428
Appendix W First and Second Derivatives of Fock and Lagrangian Matrices	433
Appendix X Coupled Perturbed Hartree-Fock (CPHF) Equations for Closed-Shell SCF Wavefunctions	437
Appendix Y Coupled Perturbed Hartree-Fock (CPHF) Equations for General Restricted Open-Shell SCF Wavefunctions	439
Appendix Z Coupled Perturbed Configuration Interaction (CPCI) Equations	441
Appendix AA Coupled Perturbed Paired Excitation Multiconfiguration Hartree-Fock (CPPEMCHF) Equations	442
Appendix BB Coupled Perturbed Multiconfiguration Hartree-Fock (CPMCHF) Equations	445
Bibliographical Survey on Analytic Energy Derivatives	448
Index	463

List of Abbreviations

AO	atomic orbital
CASSCF	complete active space self-consistent-field
CI	configuration interaction
CISD	configuration interaction with single and double excitations
CLSCF	closed-shell self-consistent-field
CPCI	coupled perturbed configuration interaction
CPHF	coupled perturbed Hartree-Fock
CPMCHF	coupled perturbed multiconfiguration Hartree-Fock
CPPEMCHF	coupled perturbed paired excitation multiconfiguration Hartree-Fock
CPTCHF	coupled perturbed two-configuration Hartree-Fock
CSF	configuration state function
GRSCF	general restricted open-shell self-consistent-field
GTO	Gaussian-type orbital
GVB	generalized valence bond
HF	Hartree-Fock
LCAO	linear combination of atomic orbitals
lhs	left hand side
MO	molecular orbital
MCSCF	multiconfiguration self-consistent-field
PEMCSCF	paired excitation multiconfiguration self-consistent-field
PES	potential energy (hyper) surface
RHF	restricted Hartree-Fock
rhs	right hand side
SCF	self-consistent-field
STO	Slater-type orbital
TCSCF	two-configuration self-consistent-field
ZPVE	zero-point vibrational energy

A New Dimension to Quantum Chemistry:
Analytic Derivative Methods in *Ab Initio*
Molecular Electronic Structure Theory

Chapter 1

Introduction

In modern theoretical chemistry, the importance of evaluating force fields from reliable wavefunctions has become increasingly apparent. The second derivative matrix (Hessian) of the total energy of a system with respect to geometrical variables is used not only to evaluate vibrational frequencies and related properties, but also to interrogate reactive potential energy hypersurfaces. Following the arguments of Murrell and Laidler [1] and McIver and Komornicki [2], it is essential to demonstrate that the stationary points for a molecule containing N nuclei have $3N-6$ real harmonic vibrational frequencies ($3N-5$ for linear molecules) for energy minima and $3N-7$ ($3N-6$ for linear molecules) real frequencies plus a single imaginary frequency (corresponding to the reaction coordinate) for transition states.

Explicit implementation of the analytic first derivative of the energy with respect to geometrical variables was first proposed by Pulay [3] in 1969 and the significance of his force method was immediately recognized by the computational quantum chemistry community. In the last two decades, the analytic first and second derivative techniques for *ab initio* single configuration self-consistent-field (SCF) and correlated wavefunctions have been developed by several research groups and applied to the investigation of a large variety of chemical phenomena. In principle, energy derivatives may be evaluated from total energies by the finite difference method. However, such a scheme is prone to numerical difficulties and is computationally expensive. Thus the advantages in accuracy and inherent efficiency are continually propelling theoretical chemists to further development of analytic derivative techniques.

In *ab initio* derivative studies, Gaussian-type orbitals (GTOs) [4] have been invariably used, predominantly because of the relatively simple recurring character of their derivatives. In an early stage of development, however, only s and p orbitals were included in the derivative formalism, since the derivatives of d or higher orbitals become significantly more complicated. A major breakthrough in this regard was the work of Dupuis and King, using Rys polynomials to evaluate GTO integrals and their derivatives [5]. The important next

step to the analytic second derivative technique for SCF wavefunctions by Pople et al. [6] was due, in part, to the Rys polynomial technique.

It is well established that electron correlation strongly affects the potential energy surfaces of reactive systems. The unitary group approach (UGA) laid out for electronic systems by Paldus [7] and reformulated for practical applications by Shavitt [8], Brooks and Schaefer [9], and Siegbahn [10], provides a remarkably efficient scheme for the evaluation of Hamiltonian matrix elements between configuration state functions (CSFs). With respect to configuration interaction (CI) wavefunctions for closed-shell molecules, analytic gradient methods have been formulated by Pople's group [11] and in our laboratory [12]. Later we also reported the determination of analytic energy first derivatives for open-shell correlated wavefunctions [13]. These studies employed the coupled perturbed Hartree-Fock (CPHF) theory, first outlined in a classic paper by Gerratt and Mills in 1968 [14], to evaluate the changes in molecular orbitals caused by the perturbation of a nuclear position in a molecule.

One of the most intensely studied methods in theoretical chemistry today is certainly the multiconfiguration SCF (MCSCF) technique. One motivation for this emphasis is the well-known fact that single configuration SCF theory fails to properly describe the separated fragments arising in many reactive processes. Accordingly, it is desirable to use MCSCF wavefunctions. While slow convergence in iterative MCSCF procedures has been a significant barrier to the construction of reliable MCSCF wavefunctions for quite some time, this problem is now practically solved in many cases by employing the Newton-Raphson technique, which is quadratically convergent [15,16].

Within a chosen, finite basis set the exact solution to Schrödinger's equation is the full CI wavefunction. Although recent methodological developments and advances in computer technology have allowed some breakthroughs in computational quantum chemistry, it is highly unlikely that full CI wavefunctions will become available in the near future for systems of greater complexity than 10 to 12 electrons, even if modest basis sets are used. In contrast, using techniques developed to date, MCSCF wave functions including a fairly large number of configurations may be routinely obtained. This procedure is still a difficult one and probably not the best available approach for the quantitative description of molecular systems. Experience does suggest, however, that in most cases chemical systems may be described qualitatively using a small MCSCF reference function. An eminently reasonable approach at the present time, therefore, is to obtain a small MCSCF wavefunction by some quadratically convergent procedure, for example via the complete active space (CAS) SCF technique [17], and then carry out a large multireference CI treatment based on these MCSCF orbitals. The analytic energy second derivative method for MCSCF wavefunctions was first implemented in our laboratory [18] and the first derivative of MCSCF-CI wavefunctions by Page and coworkers [19]. Considering the practical significance of such MCSCF and MCSCF-CI wavefunctions, further efforts toward the improvement of these analytic derivative techniques will be very important.

The rest of this book is divided into nineteen chapters. The contents of each chapter are previewed briefly in the remainder of this chapter. The basic concepts involved in the

ab initio linear combination of atomic orbitals-molecular orbital (LCAO-MO) method are reviewed briefly and the fundamental equations necessary for future discussion are introduced in Chapter 2. Using these concepts, expressions for the derivatives of integrals and molecular orbital (MO) coefficients are derived in Chapter 3. The results obtained in this chapter are quite general and thus applicable to any type of wavefunction.

Moving from the general to the specific, the first and second energy derivative expressions for the simplest and most frequently used case, the closed-shell (CL) SCF wavefunction, are discussed in Chapter 4, building upon the equations derived in Chapter 3. At a somewhat greater level of complexity, the first and second energy derivative expressions for the general restricted open-shell (GR) SCF wavefunction are presented in Chapter 5. The equations given there are applicable to any type of single configuration SCF wavefunction.

Chapters 6 through 9 discuss analytic derivatives for methods that go beyond the single configuration SCF level. Chapter 6 deals with the first and second energy derivatives of CI wavefunctions. The configurations included in a CI wavefunction are constructed using a set of molecular orbitals defined with respect to a reference wavefunction, and the derivatives of the MO coefficients of the reference wavefunction are required to evaluate the derivatives of properties computed from the CI wavefunction. In Chapter 7, the first and second energy derivatives for the simplest case of a multiconfiguration (MC) SCF wavefunction, the two-configuration (TC) SCF wavefunction, are given. For the TCSCF wavefunction, it is important to realize that the MO and CI coefficients must be optimized simultaneously to satisfy the variational conditions. During the evaluation of the first derivative of the energy no information concerning the derivatives of the MO and CI coefficients is required. However, explicit evaluation of such derivatives is necessary to obtain the second derivatives of the TCSCF energy. In Chapter 8 the first and second derivative energy expressions are extended to a more general paired excitation (PE) MCSCF wavefunction. This type of wavefunction is one of the most complicated that does not require a full four-index MO transformation of the electron repulsion integrals. The generalized valence bond (GVB) wavefunction may be viewed as a special case of a PEMCSCF wavefunction. Chapter 9 treats the first and second energy derivatives for even more general MCSCF wavefunctions. The widely used complete active space (CAS) SCF wavefunctions are considered as special cases of these general MCSCF wavefunctions.

The determination of the energy gradient (first derivative) at the SCF or MCSCF levels of theory does not require information concerning the first-order changes in the molecular orbitals. However, this is not the case for the CI wavefunction that uses an SCF or MCSCF wavefunction as a reference. In the CI case, the first-order changes in the molecular orbital coefficients must be evaluated. Usually they are determined by solving the coupled perturbed Hartree-Fock (CPHF) equations for the SCF case and the coupled perturbed multi-configuration Hartree-Fock (CPMCHF) equations for MCSCF reference wavefunctions. The CPHF and CPMCHF equations are also required to evaluate analytic second derivatives of the SCF and MCSCF wavefunctions. Chapters 10 through 14 deal with the solutions of such coupled perturbed equations for increasingly complex wavefunctions. Chapter 10 begins with the first- and second-order CPHF equations for the closed-shell SCF wave-

function. Chapter 11 extends the CPHF equations to the general restricted open-shell (GR) SCF wavefunction. The equations involved with the GRSCF wavefunction are formally equivalent to those for the MO part of the TCSCF and PEMCSCF wavefunctions described in Chapter 13. In order to evaluate the second derivatives for configuration interaction (CI) wavefunctions, it is necessary to evaluate the first-order changes of the CI coefficients. They usually are obtained by solving the coupled perturbed configuration interaction (CPCI) equations. In Chapter 12 the first- and second-order CPCI equations are derived. Chapter 13 discusses the CPHF equations for PEMCSCF wavefunctions. Those CPPEMCHF equations associated with the CI space are formally the same as the CPCI equations described in Chapter 12. It should be noted that the CPHF equations for the TCSCF wavefunction are considered as a special case of the CPPEMCHF equations. In Chapter 14, the CPHF equations for more general MCSCF wavefunctions are elaborated. It should be emphasized again that the CPMCHF equations are constructed from elements involving both the MO and CI spaces. While the CI parts of the CPMCHF equations are formally equivalent to the CPCI equations in Chapter 12, a new derivation is required for the MO part of the CPMCHF equations.

Up to this point only the first and second energy derivatives have been considered. The next three chapters extend the analytical derivative approach to higher derivatives and to quantities due to other than nuclear perturbations. The third and fourth energy derivatives are important as they are directly related to the anharmonicity of the vibrational motions of molecules. In Chapter 15, analytic third and fourth derivatives for CI wavefunctions are derived using a convenient recurrence technique. The results obtained in Chapter 15 are used to derive analytic third and fourth derivatives for MCSCF, PEMCSCF, GRSCF, and CLSCF wavefunctions in Chapter 16. To interrelate the above-mentioned wavefunctions, a series of correspondence equations is introduced.

All derivative equations discussed through Chapter 16 in the text are equally applicable to any “real” perturbations including electric field perturbations. For electric field perturbations derivative expressions are greatly simplified since the derivatives of the two-electron integrals are *not* involved. In Chapter 17 analytic derivatives involving electric field perturbations are described in detail.

In the first implementation of the analytic first derivative of the CI wavefunction, the CPHF equations were solved for $3N$ (N being the number of nuclei) sets of nuclear perturbations [12]. However, Handy and Schaefer have presented a technique in which only one set of perturbations, in the present case the CI energy change with respect to the MO rotations, is solved [20]. This new technique is called the Z vector method and proves very powerful whenever applicable. In Chapter 18, the Z vector method is discussed along with some of its applications.

Chapter 19 provides several case studies of the use of analytic derivative methods in applied quantum chemistry. This discussion is in no sense exhaustive but seeks to illustrate the great practical importance of the theoretical techniques discussed in the book to actual studies of chemically interesting problems.

In Chapter 20 we present our perspective on future directions for analytic derivative methods and make some concluding remarks. At the end of the book, a selection of literature references related to analytic derivative methods, mostly directly associated with implementation of these techniques, are collected in a bibliography. The important derivative expressions for each chapter are summarized in the Appendices for the reader's convenience. We encourage readers to carefully follow through the derivations in each chapter with pencil, paper, and patience.

References

1. J.N. Murrell and K.J. Laidler, *Trans. Faraday Soc.* **64**, 371 (1968).
2. J.W. McIver, Jr. and A. Komornicki, *J. Am. Chem. Soc.* **94**, 2625 (1972).
3. P. Pulay, *Mol. Phys.* **17**, 197 (1969).
4. S.F. Boys, *Proc. Roy. Soc. London A* **200**, 542 (1950).
5. M. Dupuis, J. Rys, and H.F. King, *J. Chem. Phys.* **65**, 111 (1976).
6. J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, *Int. J. Quantum Chem.* **S13**, 225 (1979).
7. J. Paldus, in *Theoretical Chemistry : Advances and Perspectives*, H. Eyring and D.J. Henderson editors, Academic Press, New York, Vol.2, p.131 (1976).
8. I. Shavitt, *Int. J. Quantum Chem.* **S11**, 131 (1977); **S12**, 5 (1978).
9. B.R. Brooks and H.F. Schaefer, *J. Chem. Phys.* **70**, 5092 (1979).
10. P.E.M. Siegbahn, *J. Chem. Phys.* **70**, 5391 (1979).
11. R. Krishnan, H.B. Schlegel, and J.A. Pople, *J. Chem. Phys.* **72**, 4654 (1980).
12. B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **72**, 4652 (1980).
13. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **75**, 2919 (1981).
14. J. Gerratt and I.M. Mills, *J. Chem. Phys.* **49**, 1719 (1968).
15. H.-J. Werner, in *Advances in Chemical Physics : Ab Initio Methods in Quantum Chemistry Part II.*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 69, p.1 (1987).
16. R. Shepard, in *Advances in Chemical Physics : Ab Initio Methods in Quantum Chemistry Part II.*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 69, p.63 (1987).
17. B.O. Roos, in *Advances in Chemical Physics : Ab Initio Methods in Quantum Chemistry Part II.*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 69, p.399 (1987).
18. M.R. Hoffmann, D.J. Fox, J.F. Gaw, Y. Osamura, Y. Yamaguchi, R.S. Grev, G. Fitzgerald, H.F. Schaefer, P.J. Knowles, and N.C. Handy, *J. Chem. Phys.* **80**, 2660 (1984).
19. M. Page, P. Saxe, G.F. Adams, and B.H. Lengsfield, *J. Chem. Phys.* **81**, 434 (1984).
20. N.C. Handy and H.F. Schaefer, *J. Chem. Phys.* **81**, 5031 (1984).

Suggested Reading

1. H.F. Schaefer editor, *Modern Theoretical Chemistry*, Vols. 3 and 4, Plenum, New York, 1977.
2. P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry*, Academic Press, New York, 1981.
3. H.F. Schaefer, *Quantum Chemistry: The Development of Ab Initio Methods in Molecular Electronic Structure Theory*, Clarendon Press, Oxford, 1984.
4. P. Jørgensen and J. Simons editors, *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, NATO ASI Series C166, D. Reidel, 1985.
5. H.F. Schaefer and Y. Yamaguchi, *J. Mol. Struct.* **135**, 369 (1986).
6. P. Pulay, in *Advances in Chemical Physics : Ab Initio Methods in Quantum Chemistry Part II*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 69, p.241 (1987).
7. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986.
8. C.E. Dykstra, *Ab Initio Calculation of the Structures and Properties of Molecules*, Elsevier, Amsterdam, 1988.
9. T. Helgaker and P. Jørgensen, in *Advances in Quantum Chemistry*, P.O. Löwdin, J.H. Sabin, and M.C. Zerner editors, Academic Press, New York, Vol. 19, p.183 (1988).
10. J. Gauss and D. Cremer, in *Advances in Quantum Chemistry*, P.O. Löwdin, J.H. Sabin, and M.C. Zerner editors, Academic Press, New York, Vol. 23, p.205 (1992).
11. T. Helgaker and P. Jørgensen, in *Methods in Computational Molecular Physics*, NATO ASI Series B293, S. Wilson and G.H.F. Diercksen editors, Plenum, New York, p.353 (1992).

Chapter 2

Basic Concepts and Definitions

This chapter briefly reviews the basic concepts and definitions needed in molecular quantum mechanics beginning with the linear combination of atomic orbitals-molecular orbital (LCAO-MO) approach. Readers who require a more elementary introduction to these fundamental topics in quantum chemistry or their applications to specific chemical problems should consult the books listed at the end of this chapter as Suggested Reading.

2.1 The Schrödinger Equation and the Hamiltonian Operator

For a given molecular system the Schrödinger equation [1], the most important equation in modern science, is

$$\mathbf{H}\Psi = E\Psi \quad (2.1)$$

where \mathbf{H} is the Hamiltonian operator, Ψ is the total wavefunction, and E is the energy eigenvalue. The non-relativistic time-independent Hamiltonian operator of concern in most *ab initio* computations is given (in atomic units) by

$$\begin{aligned} \mathbf{H} = & -\frac{1}{2} \sum_i^n \nabla_i^2 - \frac{1}{2} \sum_A^N \frac{1}{M_A} \nabla_A^2 - \sum_i^n \sum_A^N \frac{Z_A}{r_{iA}} \\ & + \sum_{i>j}^n \frac{1}{r_{ij}} + \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}} \quad , \end{aligned} \quad (2.2)$$

for n electrons and N nuclei. ∇_i^2 is the Laplacian operator for the i th electron, ∇_A^2 is the Laplacian operator for the A th nucleus, M_A is the ratio of the mass of nucleus A to the mass of the electron, Z_A is the atomic number of nucleus A , r_{iA} is the distance between the i th electron and nucleus A , r_{ij} is the distance between the i th and j th electrons, and R_{AB} is the distance between nuclei A and B . In the Hamiltonian \mathbf{H} the first term represents

the kinetic energy of the electrons, the second term the kinetic energy of the nuclei, and the third through fifth terms are the contributions to the potential energy arising from nuclear-electronic, electronic, and nuclear interactions, respectively. The indices $i > j$ and $A > B$ in the fourth and fifth terms are necessary to prevent counting the same interaction twice.

Using the standard Born-Oppenheimer approximation [2] we consider the electronic Hamiltonian

$$\mathbf{H}_{elec} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_A^N \frac{Z_A}{r_{iA}} + \sum_{i>j}^n \frac{1}{r_{ij}} \quad (2.3)$$

$$= \sum_i^n \mathbf{h}(i) + \sum_{i>j}^n \frac{1}{r_{ij}} \quad (2.4)$$

and solve

$$\mathbf{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \quad (2.5)$$

where the one-electron operator $\mathbf{h}(i)$ is

$$\mathbf{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A^N \frac{Z_A}{r_{iA}} \quad (2.6)$$

The total energy at fixed nuclear coordinates is expressed within this approximation as

$$E_{total} = E_{elec} + \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}} \quad (2.7)$$

It should be noted that the second term in eq. (2.7), the contribution from the nuclear repulsion energy, is a constant at a fixed geometry.

2.2 The Variation Method

For any arbitrary wavefunction Ψ satisfying the appropriate boundary conditions the energy expectation value W is described by

$$W = \frac{\int \Psi^* \mathbf{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \quad (2.8)$$

$$\equiv \frac{\langle \Psi | \mathbf{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.9)$$

where \mathbf{H} is the Hamiltonian operator defined in eq. (2.2) and Ψ^* denotes the complex conjugate of the wavefunction. It may be shown that the expectation value of the energy may approach but never be less (lower) than the true ground state energy, E_0 , of the system

$$W \geq E_0 . \quad (2.10)$$

Let us assume that an approximate wavefunction Ψ can be constructed as an expansion in the “true” orthonormal eigenfunctions of the Hamiltonian operator, i.e.,

$$\Psi = \sum_I C_I \psi_I \quad (2.11)$$

with

$$\sum_I C_I^* C_I = 1 \quad . \quad (2.12)$$

The expectation value of the energy is given by

$$W = \sum_I \sum_J C_I^* C_J \langle \psi_I | \mathbf{H} | \psi_J \rangle \quad (2.13)$$

$$= \sum_I C_I^* C_I E_I \quad (2.14)$$

using the orthogonality of the “true” wavefunctions. If the lowest energy level E_0 is subtracted from both sides of eq. (2.14), we obtain

$$W - E_0 = \sum_I C_I^* C_I (E_I - E_0) \quad . \quad (2.15)$$

E_0 is the lowest energy, and therefore $E_I - E_0$ must always be zero or positive. In addition the products of the coefficients $C_I^* C_I$ are all zero or positive. Thus, we can state that

$$W \geq E_0 \quad . \quad (2.16)$$

This theorem was proved first by Eckart [3] and is called the variation principle. It states that the energy expectation value is a rigorous upper bound to the true ground state energy.

The essential problem in the variation method is to find a wavefunction which gives the *lowest possible* value of W . For this purpose the variational condition

$$\delta W = 0 \quad (2.17)$$

is usually employed. In this equation δ refers to an infinitesimal change in the given function. If the wavefunctions are chosen with care, it may be possible to approach the true energy very closely. Generally, the more variational parameters the wavefunction (when constructed in a judicious manner) includes, the closer the true energy can be approached as these variables are optimized.

2.3 The Linear Combination of Atomic Orbitals-Molecular Orbital (LCAO-MO) Approximation

In *ab initio* quantum chemistry the most frequently used molecular model is the Hartree-Fock approximation [4,5]. The Hartree-Fock wavefunction is usually constructed from an antisymmetrized product of spin-orbitals, ψ_i ,

$$\Psi_{elec} = A \prod_i^n \psi_i \quad (2.18)$$

where A is the antisymmetrizer and each spin-orbital is a product of a spatial molecular orbital (MO), ϕ_i , and a one-electron spin function, α or β ,

$$\psi_i(1) = \begin{cases} \phi_i(1)\alpha(1) \\ \text{or} \\ \phi_i(1)\beta(1) \end{cases} \quad (2.19)$$

Each molecular orbital is conventionally expanded as a linear combination of one-electron basis functions, usually termed atomic orbitals (AOs), which are normally centered on each nucleus,

$$\phi_i(1) = \sum_{\mu}^{AO} C_{\mu}^i \chi_{\mu}(1) \quad . \quad (2.20)$$

C_{μ}^i is the coefficient of the μ th atomic orbital χ_{μ} in the i th MO. The simplest antisymmetrized wavefunction for a closed-shell molecule with $2n$ electrons is described using a Slater determinant [6]

$$\Psi = \frac{1}{\sqrt{2n!}} \left| \begin{array}{ccccc} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \dots & \phi_n(1)\alpha(1) & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \dots & \phi_n(2)\alpha(2) & \phi_n(2)\beta(2) \\ \dots & \dots & \dots & \dots & \dots \\ \phi_1(2n)\alpha(2n) & \phi_1(2n)\beta(2n) & \dots & \phi_n(2n)\alpha(2n) & \phi_n(2n)\beta(2n) \end{array} \right| \quad (2.21)$$

$$\equiv \frac{1}{\sqrt{2n!}} \left| \begin{array}{ccccc} \phi_1\alpha & \phi_1\beta & \phi_2\alpha & \phi_2\beta & \dots \\ \phi_n\alpha & \phi_n\beta & & & \end{array} \right| \quad . \quad (2.22)$$

Using a characteristic of determinants, it is easily shown that the Slater determinant in eq. (2.21) satisfies the Pauli exclusion principle [7].

2.4 Basis Sets

The set of atomic orbitals (AOs) appearing in the LCAO-MO formalism given in eq. (2.20) is called a basis set. The most frequently used basis sets are Slater-type orbitals (STOs) [8] and Gaussian-type orbitals (GTOs) [9]. In these basis sets the angular part is described by powers of cartesian coordinates, while the radial part is expressed by either $\exp(-\zeta r)$ for a STO or $\exp(-\alpha r^2)$ for a GTO. The variables ζ and α are orbital exponents. Thus, the two most frequently used basis sets are

$$\chi_{\mu}^{STO}(r) = Nx^l y^m z^n \exp(-\zeta r) \quad (2.23)$$

and

$$\chi_{\mu}^{GTO}(r) = Nx^l y^m z^n \exp(-\alpha r^2) \quad (2.24)$$

where N is a normalization constant. In these equations the superscripts l , m , and n denote angular quantum numbers for the associated cartesian coordinates. Very popular

GTO basis sets were developed in 1965 by Huzinaga [10]. Later, efficient contractions of these primitive GTO basis sets were carried out by Dunning [11]

$$\chi_{\mu}^{GTO}(r) = \sum_i^{n_G} C_i \chi_{\mu}^{GTO}(r) \quad (2.25)$$

where n_G is the number of primitive (original) Gaussian basis functions included in the contraction. Pople and coworkers [12] have developed a series of minimal basis sets in which STOs were least squares fit by expansions in Gaussian-type functions,

$$\chi_{\mu}^{STO}(r) = \sum_i^{n_G} C_i \chi_{\mu}^{GTO}(r) \quad . \quad (2.26)$$

The case of $n_G = 3$, i.e., the STO-3G basis, was used with remarkable success in early studies on many organic molecules by Pople and his collaborators as detailed in reference 8 of the Suggested Reading. Today split valence sets, i.e., a double zeta representation of the valence orbitals and a minimal basis for the core orbitals, such as 3-21G and 6-31G* are the most widely employed Gaussian basis sets. Whole books have been devoted to the topic of optimized Gaussian basis sets of various sizes and types for many elements [13,14] and obviously no lengthy discussion is required here. A very helpful review of basis sets has recently appeared [15].

While the STO basis set is better able to describe the motion of electrons, especially near the nucleus, relative to the GTO basis, the evaluation of AO integrals and their derivatives is much more difficult with STO functions. The recurrence relations for GTO make integral and integral derivative computation much easier than for STO [16]. Any deficiency of the GTO basis can ultimately be overcome by using a larger number of basis functions, usually without great increases in computation time.

2.5 The Hartree-Fock and Self-Consistent-Field Wavefunctions

In a variational sense, the Hartree-Fock (HF) wavefunction is the best wavefunction that can be constructed by assigning each electron to a separate orbital. An orbital is a function depending on the coordinates of only one electron (see eqs. (2.19) to (2.21)). The expectation value (the electronic energy) of the single determinant wavefunction for the closed-shell system given by eq. (2.21) is

$$E_{elec} = \langle \Psi_{HF} | \mathbf{H}_{elec} | \Psi_{HF} \rangle \quad (2.27)$$

$$= 2 \sum_i^n H_i + \sum_{ij}^n \left\{ 2J_{ij} - K_{ij} \right\} \quad (2.28)$$

$$= 2 \sum_i^n h_{ii} + \sum_{ij}^n \left\{ 2(ii|jj) - (ij|ij) \right\} \quad . \quad (2.29)$$

The one-electron, Coulomb and exchange molecular orbital (MO) integrals are defined by

$$H_i = h_{ii} = \int \phi_i^*(1)\mathbf{h}(1)\phi_i(1)d\tau_1 \quad (2.30)$$

$$\equiv \langle \phi_i | \mathbf{h} | \phi_i \rangle \quad (2.31)$$

$$J_{ij} = (ii|jj) = \int \int \phi_i^*(1)\phi_i(1) \frac{1}{r_{12}} \phi_j^*(2)\phi_j(2) d\tau_1 d\tau_2 \quad (2.32)$$

$$K_{ij} = (ij|ij) = \int \int \phi_i^*(1)\phi_j(1) \frac{1}{r_{12}} \phi_i^*(2)\phi_j(2) d\tau_1 d\tau_2 \quad . \quad (2.33)$$

Usually all the orbitals occupied in the Slater determinant in eq. (2.21) are orthonormalized

$$\langle \phi_i | \phi_j \rangle = S_{ij} = \delta_{ij} \quad (2.34)$$

where S_{ij} stands for an element of the overlap matrix in the MO basis and δ is the Kronecker delta function:

$$\delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases} \quad . \quad (2.35)$$

The “best” wavefunction is obtained from the variational conditions

$$\delta E_{elec} = \delta \langle \Psi_{HF} | \mathbf{H}_{elec} | \Psi_{HF} \rangle = 0 \quad (2.36)$$

under the orthonormalization constraint of eq. (2.34). In this equation δ refers to an infinitesimal change of the electronic energy. Equation (2.36) leads to the following Hartree-Fock equations [4,5]

$$F\phi_i = \epsilon_i \phi_i \quad (2.37)$$

where ϵ_i are the orbital energies and the Fock operator, \mathbf{F} , is given by

$$\mathbf{F}(1) = \mathbf{h}(1) + \sum_i^n (2\mathbf{J}_i(1) - \mathbf{K}_i(1)) \quad . \quad (2.38)$$

The one-electron operator, $\mathbf{h}(1)$, has already been defined in eq. (2.6). The Coulomb and exchange operators are

$$\mathbf{J}_i(1) = \int \phi_i^*(2)\phi_i(2) \frac{1}{r_{12}} d\tau_2 \quad , \quad (2.39)$$

$$\mathbf{K}_i(1) = \int \phi_i^*(2)\phi_i(1) \mathbf{P}_{12} \frac{1}{r_{12}} d\tau_2 \quad . \quad (2.40)$$

In eq. (2.40), \mathbf{P}_{12} is a permutation operator which exchanges electrons 1 and 2. An element of the Fock matrix may be expressed as

$$F_{ij} = \langle \phi_i | \mathbf{F} | \phi_j \rangle \quad (2.41)$$

$$= \langle \phi_i | \mathbf{h} + \sum_k^n (2\mathbf{J}_k - \mathbf{K}_k) | \phi_j \rangle \quad (2.42)$$

$$= h_{ij} + \sum_k^n \left\{ 2(ij|kk) - (ik|jk) \right\} \quad . \quad (2.43)$$

The orbital energy appearing in eq. (2.37) is a diagonal element of the Fock matrix

$$\epsilon_i = \langle \phi_i | \mathbf{F} | \phi_i \rangle = F_{ii} = h_{ii} + \sum_j^n \left\{ 2(ii|jj) - (ij|ij) \right\} . \quad (2.44)$$

Since it is never possible in practice to use a mathematically rigorous complete set of basis functions in molecular computations, one obtains approximate solutions to the Hartree-Fock equations. The best single configuration wavefunction within a finite basis set is the self-consistent-field (SCF) wavefunction. Clearly, as the size of a basis set is increased, the SCF energy and wavefunction will approach the Hartree-Fock limits. For the self-consistent-field (SCF) wavefunction the electronic energy is minimized with respect to changes of the molecular orbital coefficients under the constraint of orthonormality. This problem was solved by Roothaan and Hall in 1951 for the closed-shell case using the LCAO molecular orbital approach [17,18]

$$\phi_i = \sum_{\mu}^{AO} C_{\mu}^i \chi_{\mu} . \quad (2.45)$$

The resulting secular equation is

$$\sum_i \left[F_{\mu\nu} - \epsilon_i S_{\mu\nu} \right] C_{\mu}^i = 0 . \quad (2.46)$$

The Fock matrix F and the overlap matrix S are defined in the atomic orbital (AO) basis to have the elements

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma}^{AO} D_{\rho\sigma} \left\{ 2(\mu\nu|\rho\sigma) - (\mu\rho|\nu\sigma) \right\} \quad (2.47)$$

and

$$S_{\mu\nu} = \int \chi_{\mu}^{*}(1) \chi_{\nu}(1) d\tau_1 \quad (2.48)$$

$$\equiv \langle \chi_{\mu} | \chi_{\nu} \rangle . \quad (2.49)$$

In eq. (2.47) the one- and two-electron AO integrals are

$$h_{\mu\nu} = \int \chi_{\mu}^{*}(1) \mathbf{h}(1) \chi_{\nu}(1) d\tau_1 \quad (2.50)$$

$$\equiv \langle \chi_{\mu} | \mathbf{h} | \chi_{\nu} \rangle \quad (2.51)$$

and

$$(\mu\nu|\rho\sigma) = \int \int \chi_{\mu}^{*}(1) \chi_{\nu}(1) \frac{1}{r_{12}} \chi_{\rho}^{*}(2) \chi_{\sigma}(2) d\tau_1 d\tau_2 . \quad (2.52)$$

The density matrix D (in the AO basis) is defined by its elements

$$D_{\mu\nu} = \sum_i^{d.o.} C_{\mu}^{i*} C_{\nu}^i \quad (2.53)$$

where *d.o.* refers to the doubly occupied molecular orbitals. The normalization condition for each molecular orbital is:

$$\sum_{\mu\nu}^{AO} C_{\mu}^{i*} S_{\mu\nu} C_{\nu}^i = 1 \quad . \quad (2.54)$$

The SCF theory for open-shell cases was rigorously developed by Roothaan in 1960 [19] and later by many others [20,21]. For open-shell systems it is conventional to use the generalized Fock operator [20,21]

$$\mathbf{F}_i(1) = f_i \mathbf{h}(1) + \sum_k^{occ} (\alpha_{ik} \mathbf{J}_k(1) + \beta_{ik} \mathbf{K}_k(1)) \quad (2.55)$$

where f , α , and β are one- and two-electron coupling constants (see Chapter 5) and *occ* stands for both doubly and partially occupied molecular orbitals. It should be noted that there is more than one Fock operator in the open-shell equations. Defining the Lagrangian matrix as

$$\epsilon_{ij} = \langle \phi_i | \mathbf{F}_i | \phi_j \rangle \quad (2.56)$$

$$= \langle \phi_i | f_i \mathbf{h} + \sum_k^{occ} (\alpha_{ik} \mathbf{J}_k + \beta_{ik} \mathbf{K}_k) | \phi_j \rangle \quad (2.57)$$

$$= f_i h_{ij} + \sum_k^{occ} \left\{ \alpha_{ik} (ij|kk) + \beta_{ik} (ik|jk) \right\} \quad , \quad (2.58)$$

the variational conditions for an open-shell SCF wavefunction are

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad . \quad (2.59)$$

2.6 The Configuration Interaction (CI) Wavefunction

In closed-shell SCF theory, a wavefunction is constructed as a single determinant. In the configuration interaction (CI) method [22] the wavefunction is expressed as a linear combination of a finite number of either Slater determinants or configuration state functions (CSFs, which are constructed as linear combinations of determinants to be eigenfunctions of the square of the total electronic spin angular momentum operator, \mathbf{S}^2)

$$\Psi_{CI} = \sum_I^{CI} C_I \Phi_I \quad . \quad (2.60)$$

The C_I are the CI expansion coefficients and Φ_I the CSFs. Assuming that the *real* wavefunction is employed, it is common to normalize the CI coefficients such that

$$\sum_I^{CI} C_I^2 = 1 \quad . \quad (2.61)$$

The electronic energy (expectation value) for such a wavefunction is

$$E_{elec} = \langle \Psi_{CI} | \mathbf{H}_{elec} | \Psi_{CI} \rangle \quad (2.62)$$

$$= \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (2.63)$$

where \mathbf{H}_{elec} is the usual Hamiltonian given by eq. (2.3). The CI Hamiltonian matrix H_{IJ} is

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (2.64)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl) \quad . \quad (2.65)$$

Q^{IJ} and G^{IJ} are the one- and two-electron coupling constants between configurations and molecular orbitals [23]. The one- and two-electron MO integrals are

$$h_{ij} = \int \phi_i^*(1) \mathbf{h}(1) \phi_j(1) d\tau_1 \quad (2.66)$$

and

$$(ij|kl) = \int \int \phi_i^*(1) \phi_j(1) \frac{1}{r_{12}} \phi_k^*(2) \phi_l(2) d\tau_1 d\tau_2 \quad . \quad (2.67)$$

The electronic energy is given alternatively in the MO expansion as

$$E_{elec} = \sum_{ij}^{MO} Q_{ij} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl) \quad (2.68)$$

where the one- and two-electron reduced density matrices [23] appearing in the equation are related to the corresponding coupling constants through

$$Q_{ij} = \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} \quad (2.69)$$

and

$$G_{ijkl} = \sum_{IJ}^{CI} C_I C_J G_{ijkl}^{IJ} \quad . \quad (2.70)$$

The following symmetric relationships hold for elements of the one- and two-electron reduced density matrices provided *real* MOs are used:

$$Q_{ij} = Q_{ji} \quad (2.71)$$

and

$$G_{ijkl} = G_{ijlk} = G_{jikl} = G_{jilk} = G_{klij} = G_{klji} = G_{lkij} = G_{lkji} \quad . \quad (2.72)$$

Each configuration is constructed using a set of molecular orbitals from a given wavefunction, commonly called the *reference wavefunction*. In most cases the reference configuration is either an SCF or a multiconfiguration (MC) SCF wavefunction (see Section 2.7).

The CI wavefunction is determined by the variational conditions

$$\delta E_{elec} = \delta \langle \Psi_{CI} | \mathbf{H}_{elec} | \Psi_{CI} \rangle = 0 \quad (2.73)$$

which lead to the following eigenvalue problem

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad . \quad (2.74)$$

When all possible configurations (with all possible electronic excitations) are included in the CI expansion (2.60), the procedure is called a *full CI*. The full CI method is the best possible variational treatment for a given basis set. In practice, however, the full CI wavefunction cannot presently be obtained for systems with more than 10 to 12 electrons using a basis set of reasonable size. Among limited CI methods the most frequently used technique is called *configuration interaction with singles and doubles (CISD)*. The CISD wavefunction includes all possible single and double excitations with respect to the reference configuration.

In constructing a CI wavefunction the *frozen core* and *deleted virtual* approximations are quite often employed. In the frozen core approximation electrons occupying a limited number of the low-lying occupied molecular orbitals are kept “frozen” and excitations of these electrons are not included in the CI expansion. In the deleted virtual approximation a limited number of the high-lying virtual (unoccupied) orbitals are “deleted” and electrons are not allowed to occupy these orbitals. The frozen core orbitals are usually selected from core (inside valence-shell) atomic-orbital-like occupied orbitals, and the deleted virtual orbitals from the corresponding core-counterpart orbitals. Employing these approximations the number of possible excitations in the CI space may be substantially reduced and great reductions in computation time are expected, usually without significantly lowering the quality of the CI wavefunction.

2.7 The Multiconfiguration (MC) SCF Wavefunction

In constructing the CI wavefunctions described in the preceding section, the set of molecular orbitals is determined in advance. In the multiconfiguration (MC) SCF method [24,25] the electronic energy is minimized with respect to both the molecular orbitals and the CI coefficients. The MCSCF wavefunction is expressed as a linear combination of a finite number of Slater determinants or configuration state functions (CSFs)

$$\Psi_{MCSCF} = \sum_I^{CI} C_I \Phi_I \quad (2.75)$$

where the C_I are the CI expansion coefficients and Φ_I the configuration state functions. The CI coefficients are usually normalized as

$$\sum_I^{CI} C_I^2 = 1 \quad . \quad (2.76)$$

The electronic energy for such a wavefunction is

$$E_{elec} = \langle \Psi_{MCSCF} | \mathbf{H}_{elec} | \Psi_{MCSCF} \rangle \quad (2.77)$$

$$= \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (2.78)$$

with the CI Hamiltonian matrix H_{IJ} being

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (2.79)$$

$$= \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl) \quad . \quad (2.80)$$

In the equation above the γ^{IJ} and Γ^{IJ} are one- and two-electron coupling constants between configurations and molecular orbitals [23]. The electronic energy is given in the MO basis as

$$E_{elec} = \sum_{ij}^{MO} \gamma_{ij} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl) \quad . \quad (2.81)$$

The one- and two-electron reduced density matrices [23] appearing in the equation are related to the corresponding coupling constants through the expressions

$$\gamma_{ij} = \sum_{IJ}^{CI} C_I C_J \gamma_{ij}^{IJ} \quad (2.82)$$

and

$$\Gamma_{ijkl} = \sum_{IJ}^{CI} C_I C_J \Gamma_{ijkl}^{IJ} \quad . \quad (2.83)$$

The coupling constants γ^{IJ} and Γ^{IJ} and reduced density matrices γ and Γ for the MCSCF wavefunction have the same meaning as the corresponding quantities for the CI wavefunction. Different notations (Q and G for CI; γ and Γ for MCSCF) are used in this book in order to avoid any possible confusion.

The molecular orbitals are usually orthonormalized giving

$$S_{ij} = \delta_{ij} \quad . \quad (2.84)$$

The true MCSCF wavefunction is determined from the variational conditions

$$\delta E_{elec} = \delta \langle \Psi_{MCSCF} | \mathbf{H}_{elec} | \Psi_{MCSCF} \rangle = 0 \quad (2.85)$$

which lead to equations for the CI space formally the same as eq. (2.74)

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad . \quad (2.86)$$

If the Lagrangian matrix for the MCSCF wavefunction is defined as

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl) \quad (2.87)$$

then the variational conditions on the MO space are

$$x_{ij} - x_{ji} = 0 \quad . \quad (2.88)$$

These equations are in a form very similar to those for the open-shell SCF wavefunction in eq. (2.59). It should be emphasized that two sets of variational conditions, eqs. (2.86) and (2.88), have to be satisfied simultaneously to obtain an MCSCF wavefunction under the two sets of constraints, eqs. (2.76) and (2.84).

Among MCSCF methods, the most frequently used technique is the complete active space (CAS) SCF method [26]. The CASSCF formalism yields MCSCF wavefunctions corresponding to a full CI within a limited configuration space (active space) and a limited number of electrons. This type of MCSCF wavefunction is relatively easily obtained due to the full CI procedure in the active space and proves to be a very powerful starting point in the investigation of a wide variety of chemical systems [26]. The problem with the CASSCF method, however, is that the number of configurations in the full CI increases drastically with the number of electrons. For example, with no spatial symmetry restrictions, CASSCF with 12 electrons and 12 active orbitals generates 226,512 singlet CSFs.

2.8 Energy Expressions in MO and AO Bases

Using the definition of an LCAO-MO in eq. (2.20), the one- and two-electron MO integrals may be related to the AO integrals. These transformations will be extensively used later in the practical implementation of analytic derivative methods.

2.8.1 One-Electron MO Integral

The one-electron MO integral h_{ij} is

$$h_{ij} = \int \phi_i^*(1) \mathbf{h}(1) \phi_j(1) d\tau_1 \quad (2.89)$$

$$\equiv \langle \phi_i | \mathbf{h} | \phi_j \rangle \quad (2.90)$$

$$= \sum_{\mu\nu}^{AO} C_\mu^{i*} C_\nu^j \int \chi_\mu^*(1) \mathbf{h}(1) \chi_\nu(1) d\tau_1 \quad (2.91)$$

$$= \sum_{\mu\nu}^{AO} C_\mu^{i*} C_\nu^j h_{\mu\nu} \quad . \quad (2.92)$$

The one-electron AO integral $h_{\mu\nu}$ is defined by

$$h_{\mu\nu} = \int \chi_\mu^*(1) \mathbf{h}(1) \chi_\nu(1) d\tau_1 \quad (2.93)$$

$$\equiv \langle \chi_\mu | \mathbf{h} | \chi_\nu \rangle \quad (2.94)$$

where \mathbf{h} is the one-electron operator defined in eq. (2.6). The following symmetries exist for the AO and MO integrals provided *real* basis functions are used:

$$h_{\mu\nu} = h_{\nu\mu} \quad (2.95)$$

and

$$h_{ij} = h_{ji} \quad . \quad (2.96)$$

2.8.2 Two-Electron MO Integral

The two-electron MO integrals ($ij|kl$) are related to the AO integrals through

$$(ij|kl) = \int \int \phi_i^*(1) \phi_j(1) \frac{1}{r_{12}} \phi_k^*(2) \phi_l(2) d\tau_1 d\tau_2 \quad (2.97)$$

$$= \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^{i*} C_\nu^j C_\rho^{k*} C_\sigma^l \int \int \chi_\mu^*(1) \chi_\nu(1) \frac{1}{r_{12}} \chi_\rho^*(2) \chi_\sigma(2) d\tau_1 d\tau_2 \quad (2.98)$$

$$= \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^{i*} C_\nu^j C_\rho^{k*} C_\sigma^l (\mu\nu|\rho\sigma) \quad . \quad (2.99)$$

The two-electron AO integral ($\mu\nu|\rho\sigma$) is

$$(\mu\nu|\rho\sigma) = \int \int \chi_\mu^*(1) \chi_\nu(1) \frac{1}{r_{12}} \chi_\rho^*(2) \chi_\sigma(2) d\tau_1 d\tau_2 \quad (2.100)$$

with $1/r_{12}$ being the two-electron Coulomb repulsion operator defined in Section 2.1. The following very useful symmetric relationships hold for the AO and MO integrals provided *real* basis functions are used:

$$(\mu\nu|\rho\sigma) = (\mu\nu|\sigma\rho) = (\nu\mu|\rho\sigma) = (\nu\mu|\sigma\rho) = (\rho\sigma|\mu\nu) = (\rho\sigma|\nu\mu) = (\sigma\rho|\mu\nu) = (\sigma\rho|\nu\mu) \quad (2.101)$$

and

$$(ij|kl) = (ij|lk) = (ji|kl) = (ji|lk) = (kl|ij) = (kl|ji) = (lk|ij) = (lk|ji) \quad . \quad (2.102)$$

2.8.3 The Electronic Energy for a Closed-Shell SCF Wavefunction

The electronic energy for a closed-shell SCF wavefunction is expressed in the MO basis,

$$E_{elec} = 2 \sum_i^{d.o.} h_{ii} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj) - (ij|ij) \right\} \quad (2.103)$$

where *d.o.* denotes doubly occupied molecular orbitals. Using eqs. (2.92) and (2.99), eq. (2.103) can be rewritten as

$$\begin{aligned} E_{elec} &= 2 \sum_i^{d.o.} \left\{ \sum_{\mu\nu}^{AO} C_\mu^{i*} C_\nu^i h_{\mu\nu} \right\} \\ &+ \sum_{ij}^{d.o.} \left[\sum_{\mu\nu\rho\sigma}^{AO} \left\{ 2C_\mu^{i*} C_\nu^i C_\rho^{j*} C_\sigma^j - C_\mu^{i*} C_\nu^j C_\rho^{j*} C_\sigma^i \right\} (\mu\nu|\rho\sigma) \right] \end{aligned} \quad (2.104)$$

$$\begin{aligned} &= 2 \sum_{\mu\nu}^{AO} \left\{ \sum_i^{d.o.} C_\mu^{i*} C_\nu^i \right\} h_{\mu\nu} \\ &+ \sum_{\mu\nu\rho\sigma}^{AO} \left[2 \left\{ \sum_i^{d.o.} C_\mu^{i*} C_\nu^i \right\} \left\{ \sum_j^{d.o.} C_\rho^{j*} C_\sigma^j \right\} (\mu\nu|\rho\sigma) \right. \\ &\quad \left. - \left\{ \sum_i^{d.o.} C_\mu^{i*} C_\nu^i \right\} \left\{ \sum_j^{d.o.} C_\rho^{j*} C_\sigma^j \right\} (\mu\rho|\nu\sigma) \right] \end{aligned} \quad (2.105)$$

$$= 2 \sum_{\mu\nu}^{AO} D_{\mu\nu} h_{\mu\nu} + \sum_{\mu\nu\rho\sigma}^{AO} \left[D_{\mu\nu} D_{\rho\sigma} \left\{ 2(\mu\nu|\rho\sigma) - (\mu\rho|\nu\sigma) \right\} \right] \quad (2.106)$$

$$= \sum_{\mu\nu}^{AO} D_{\mu\nu} \left[2h_{\mu\nu} + \sum_{\rho\sigma}^{AO} D_{\rho\sigma} \left\{ 2(\mu\nu|\rho\sigma) - (\mu\rho|\nu\sigma) \right\} \right] \quad (2.107)$$

$$= \sum_{\mu\nu}^{AO} D_{\mu\nu} \left(h_{\mu\nu} + F_{\mu\nu} \right) . \quad (2.108)$$

The density matrix *D* and the Fock matrix *F* in the AO basis are given by

$$D_{\mu\nu} = \sum_i^{d.o.} C_\mu^{i*} C_\nu^i \quad (2.109)$$

and

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma}^{AO} D_{\rho\sigma} \left\{ 2(\mu\nu|\rho\sigma) - (\mu\rho|\nu\sigma) \right\} . \quad (2.110)$$

2.8.4 The Electronic Energy for a CI Wavefunction

The electronic energy for a configuration interaction (CI) wavefunction in MO form is

$$E_{elec} = \sum_{ij}^{MO} Q_{ij} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl) \quad (2.111)$$

where Q_{ij} and G_{ijkl} are elements of the one- and two-electron reduced (particle) density matrices [23]. Using eqs. (2.92) and (2.99), the electronic energy may be transformed into the AO basis as

$$E_{elec} = \sum_{ij}^{MO} Q_{ij} \sum_{\mu\nu}^{AO} C_{\mu}^{i*} C_{\nu}^j h_{\mu\nu} + \sum_{ijkl}^{MO} G_{ijkl} \sum_{\mu\nu\rho\sigma}^{AO} C_{\mu}^{i*} C_{\nu}^j C_{\rho}^{k*} C_{\sigma}^l (\mu\nu|\rho\sigma) \quad (2.112)$$

$$\begin{aligned} &= \sum_{\mu\nu}^{AO} \left(\sum_{ij}^{MO} C_{\mu}^{i*} C_{\nu}^j Q_{ij} \right) h_{\mu\nu} \\ &+ \sum_{\mu\nu\rho\sigma}^{AO} \left\{ \sum_{ijkl}^{MO} C_{\mu}^{i*} C_{\nu}^j C_{\rho}^{k*} C_{\sigma}^l G_{ijkl} \right\} (\mu\nu|\rho\sigma) \end{aligned} \quad (2.113)$$

$$= \sum_{\mu\nu}^{AO} Q_{\mu\nu} h_{\mu\nu} + \sum_{\mu\nu\rho\sigma}^{AO} G_{\mu\nu\rho\sigma} (\mu\nu|\rho\sigma) \quad (2.114)$$

The one- and two-electron reduced (particle) density matrices in the AO basis are:

$$Q_{\mu\nu} = \sum_{ij}^{MO} C_{\mu}^{i*} C_{\nu}^j Q_{ij} \quad (2.115)$$

and

$$G_{\mu\nu\rho\sigma} = \sum_{ijkl}^{MO} C_{\mu}^{i*} C_{\nu}^j C_{\rho}^{k*} C_{\sigma}^l G_{ijkl} \quad (2.116)$$

The following symmetric relationships hold for elements of the one- and two-electron reduced density matrices in the AO basis provided *real* basis functions are used:

$$Q_{\mu\nu} = Q_{\nu\mu} \quad (2.117)$$

and

$$G_{\mu\nu\rho\sigma} = G_{\mu\nu\sigma\rho} = G_{\nu\mu\rho\sigma} = G_{\nu\mu\sigma\rho} = G_{\rho\sigma\mu\nu} = G_{\rho\sigma\nu\mu} = G_{\sigma\rho\mu\nu} = G_{\sigma\rho\nu\mu} . \quad (2.118)$$

2.9 Potential Energy Surface

The energy expressions described in the preceding sections are defined at certain fixed nuclear coordinates of a given molecule. Using the Born-Oppenheimer approximation [2] the total energy of a system may be described as a function of nuclear coordinates (see Section 2.1). The surface formed by the potential energy vs. nuclear coordinates is usually termed a *potential energy hypersurface (PES)*. One of the most important goals of quantum chemists is to locate equilibrium and transition state structures along a reaction coordinate. In order to locate stationary points, where all the energy gradients (first derivatives of total energy) with respect to nuclear coordinates become zero, the force method by Pulay [27] and/or some standard mathematical optimization techniques [28], e.g., quasi-Newton-Raphson or Newton-Raphson methods, are widely employed. In this light development of the derivative methods in *ab initio* electronic structure theory has already made significant contributions to the deeper understanding of chemical reactions.

Minimization of the total energy, E_{total} , with respect to a set of nuclear coordinates, “ a ”, leads to a stationary value of E_{total} , that is,

$$\frac{\partial E_{total}}{\partial a} = 0 \quad . \quad (2.119)$$

In order to characterize the nature of the stationary point as a local minimum or local maximum (in one or more dimensions) it is necessary to examine the second-order variation (Hessian) of E_{total} with respect to all normal coordinates q ,

$$\frac{\partial^2 E_{total}}{\partial^2 q} \begin{cases} > 0 & \text{for all normal coordinates} \\ & (\text{local minimum}) \\ < 0 & \text{for at least one normal coordinate} \\ & (\text{local saddle point}) \end{cases} \quad . \quad (2.120)$$

This situation is shown schematically in Figure 2.1 for a one-dimensional case, with the extension to multi-dimensional cases being apparent.

It is possible that a Hessian for a particular wavefunction has more than one negative eigenvalue. The number of negative eigenvalues of the Hessian is, therefore, sometimes called the Hessian index. When the Hessian index is zero, i.e., there are no negative eigenvalues, the wavefunction describes an equilibrium structure of the system. On the other hand, when the Hessian index is one, i.e., there is *only one* negative eigenvalue, the wavefunction represents a genuine transition state. For the efficient and accurate localization of stationary points and characterization of the PES it is inevitably desirable to develop analytic first and second derivatives for various wavefunctions. The remaining chapters will describe analytic derivatives of variational wavefunctions widely used in *ab initio* molecular electronic structure theory.

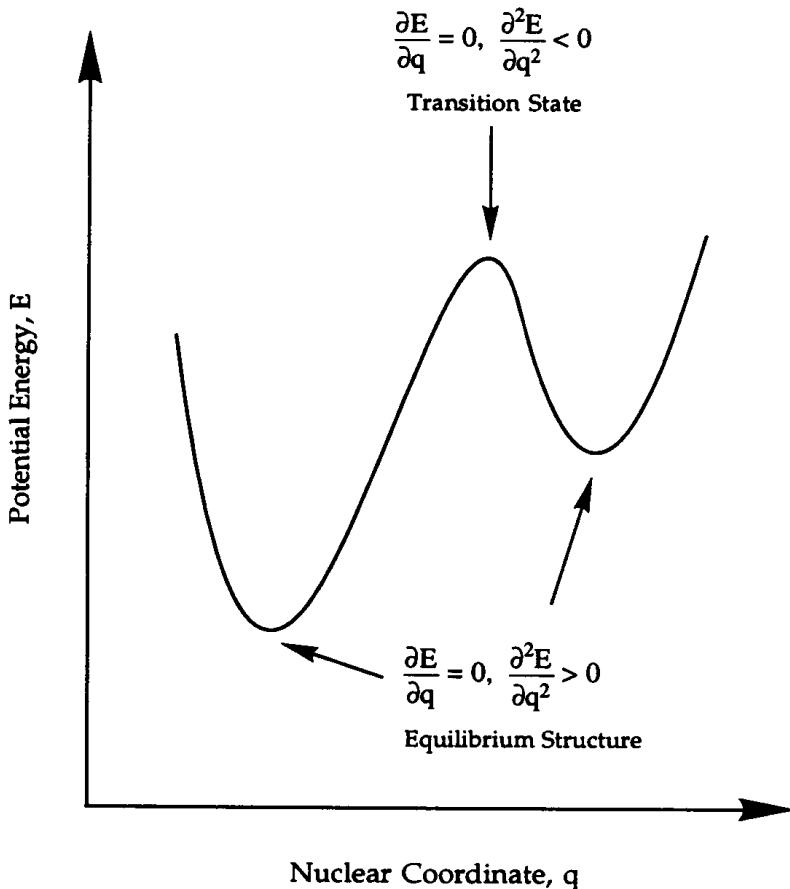


Figure 2.1 Energy derivatives on the potential energy surface.

2.10 Wigner's 2n+1 Theorem

When the wavefunction is determined up to the n th order, the expectation value (electronic energy) of the system is resolved, according to the results of perturbation theory, up to the $(2n+1)$ st order. This principle is called Wigner's $2n+1$ theorem [29-31].

In molecular electronic structure theory, the total energy of a system is given as a sum of the electronic and nuclear repulsion energies,

$$E_{total} = E_{elec} + E_{nuc} \quad (2.121)$$

using the Born-Oppenheimer approximation [2]. The n th derivative of the total energy with respect to nuclear coordinates may also be separated into two parts involving electronic and nuclear derivatives,

$$\frac{\partial^n E_{total}}{\partial x_1 \partial x_2 \dots \partial x_n} = \frac{\partial^n E_{elec}}{\partial x_1 \partial x_2 \dots \partial x_n} + \frac{\partial^n E_{nuc}}{\partial x_1 \partial x_2 \dots \partial x_n} . \quad (2.122)$$

Table 2.1 A classification of the derivatives of the variational parameters required to straightforwardly evaluate energy derivatives for CI, MCSCF, and RHF wavefunctions. Note that in Chapter 18 the Handy-Schaefer Z vector method is discussed which simplifies the analytic evaluation of energy derivatives.

	CI Method		MCSCF Method	RHF Method
	MO space	CI space	MO/CI space	MO space
Energy, E	C_μ^i	C_I	C_μ^i, C_I	C_μ^i
First Derivative, $\frac{\partial E}{\partial a}$	U^a	C_I	C_μ^i, C_I	C_μ^i
Second Derivative, $\frac{\partial^2 E}{\partial a \partial b}$	U^{ab}	$\frac{\partial C_I}{\partial a}$	$U^a, \frac{\partial C_I}{\partial a}$	U^a
Third Derivative, $\frac{\partial^3 E}{\partial a \partial b \partial c}$	U^{abc}	$\frac{\partial C_I}{\partial a}$	$U^a, \frac{\partial C_I}{\partial a}$	U^a
Fourth Derivative, $\frac{\partial^4 E}{\partial a \partial b \partial c \partial d}$	U^{abcd}	$\frac{\partial^2 C_I}{\partial a \partial b}$	$U^{ab}, \frac{\partial^2 C_I}{\partial a \partial b}$	U^{ab}
Fifth Derivative, $\frac{\partial^5 E}{\partial a \partial b \partial c \partial d \partial e}$	U^{abcde}	$\frac{\partial^2 C_I}{\partial a \partial b}$	$U^{ab}, \frac{\partial^2 C_I}{\partial a \partial b}$	U^{ab}

The derivatives of the nuclear repulsion energy are trivial and will be described briefly in the next chapter.

The electronic energy of a variational wavefunction can be expressed as a function of the AO integrals and the MO and CI coefficients. The derivatives of the electronic energy with respect to nuclear coordinates, therefore, involve the corresponding derivatives for the AO integrals, and of the MO and CI coefficients. Derivatives of the AO integrals are discussed briefly in the next chapter.

Now let us assume that the variational conditions are satisfied, as is the case for SCF or MCSCF wavefunctions. Then it is possible to evaluate the $(2n+1)$ st energy derivatives by determining the n th-order derivatives of the MO coefficients. The derivatives of the MO coefficients may be obtained by solving the coupled perturbed Hartree-Fock (CPHF) or the coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) equations. Let us further assume that the variational conditions are satisfied, as is the case for a CI wavefunction. Then it is possible to evaluate the $(2n+1)$ st energy derivatives by determining the n th-order derivatives of the CI coefficients and the $(2n+1)$ st derivatives of the MO coefficients. The derivatives of the CI coefficients may be obtained by solving the coupled perturbed configuration interaction (CPCI) equations. Table 2.1 illustrates the derivatives of the variational parameters necessary to evaluate the derivatives of the energy for various wavefunctions.

The U matrices in the table are generally defined by,

$$\frac{\partial C_{\mu}^i}{\partial a} = \sum_m^{MO} U_{mi}^a C_{\mu}^i \quad (2.123)$$

and will be discussed in detail in Chapter 3.

References

1. E. Schrödinger, Ann. Physik **79**, 361, 489, 734; **80**, 437; **81**, 109 (1926).
2. M. Born and J.R. Oppenheimer, Ann. Physik **84**, 457 (1927).
3. C.E. Eckart, Phys. Rev. **36**, 878 (1930).
4. D.R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89, 111, 426 (1928).
5. V. Fock, Z. Physik **61**, 126 (1930).
6. J.C. Slater, Phys. Rev. **34**, 1293 (1929); **35**, 509 (1930).
7. W. Pauli, Z. Physik **31**, 765 (1925).
8. J.C. Slater, Phys. Rev. **36**, 57 (1930).
9. S.F. Boys, Proc. Roy. Soc. London **A200**, 542 (1950).
10. S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).
11. T.H. Dunning, J. Chem. Phys. **53**, 2823 (1970).
12. W.J. Hehre, R.F. Stewart, and J.A. Pople, J. Chem. Phys. **51**, 2657 (1969).
13. J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, S. Huzinaga editor, Elsevier, Amsterdam, 1984.
14. R. Poirier, R. Kari, and I.G. Csizmadia, *Handbook of Gaussian Basis Sets*, Elsevier, New York, 1985.
15. D. Feller and E.R. Davidson, Chapter 1 in *Reviews in Computational Chemistry*, K.B. Lipkowitz and D.B. Boyd editors, VCH Publishers, New York, 1990.
16. V.R. Saunders, in *Methods in Computational Molecular Physics*, G.H.F. Diercksen and S. Wilson editors, D. Reidel Publishing Co., Dordrecht, p.1 (1983).
17. C.C.J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
18. G.G. Hall, Proc. Roy. Soc. London, **A205**, 541 (1951).
19. C.C.J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).
20. F.W. Bobrowicz and W.A. Goddard, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.79 (1977).
21. R. Carbo and J.M. Riera, *A General SCF Theory*, Springer-Verlag, Berlin, 1978.
22. I. Shavitt, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.189 (1977).

23. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.
24. H.-J. Werner, in *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry Part II*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 69, p.1 (1987).
25. R. Shepard, in *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry Part II*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 69, p.63 (1987).
26. B.O. Roos, in *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry Part II*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 69, p.399 (1987).
27. P. Pulay, *Mol. Phys.* **17**, 197 (1969).
28. H.B. Schlegel, in *Advances in Chemical Physics :Ab Initio Methods in Quantum Chemistry Part I*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 67, p.249 (1987).
29. S.T. Epstein, *The Variation Method in Quantum Chemistry*, Academic Press, New York, 1974.
30. S.T. Epstein, *J. Chem. Phys.* **48**, 4725 (1968).
31. S.T. Epstein, *Chem. Phys. Lett.* **70**, 311 (1980).

Suggested Reading

1. L. Pauling and E.B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Co., New York, 1935.
2. H. Eyring, J. Walter, and G.E. Kimball, *Quantum Chemistry*, John Wiley & Sons, New York, 1944.
3. H.F. Schaefer, *The Electronic Structure of Atoms and Molecules*, Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, 1972.
4. D.B. Cook, *Ab Initio Valence Calculations in Chemistry*, John Wiley & Sons, New York, 1974.
5. H.F. Schaefer editor, *Modern Theoretical Chemistry*, Vols. 3 and 4, Plenum, New York, 1977.
6. P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry*, Academic Press, New York, 1981.
7. H.F. Schaefer, *Quantum Chemistry: The Development of Ab Initio Methods in Molecular Electronic Structure Theory*, Clarendon Press, Oxford, 1984.
8. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986.
9. C.E. Dykstra, *Ab Initio Calculation of the Structures and Properties of Molecules*, Elsevier, Amsterdam, 1988.
10. A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry*, First Edition, Revised, McGraw-Hill, New York, 1989.
11. Ralph E. Christoffersen, *Basic Principles and Techniques of Molecular Quantum Mechanics*, Springer-Verlag, New York, 1989.
12. R. McWeeny, *Methods of Molecular Quantum Mechanics*, Second Edition, Academic Press, New York, 1989.
13. F.L. Pilar, *Elementary Quantum Chemistry*, Second Edition, McGraw-Hill, New York, 1990.
14. I.N. Levine, *Quantum Chemistry*, 4th Edition, Prentice Hall, Englewood Cliffs, 1991.

Chapter 3

Derivative Expressions for Integrals and Molecular Orbital Coefficients

In methods beginning with the linear combination of atomic orbitals (LCAO) molecular orbital (MO) approach, the electronic energy of a variational wavefunction at a fixed geometry is minimized with respect to the variational parameters, namely the MO coefficients (C_μ^i) and/or CI coefficients (C_I). Thus, it is evident that the derivatives of the electronic energy with respect to geometrical variables are described as a function of atomic orbital (AO) integrals, the MO and CI coefficients, and their derivatives. In this chapter derivative expressions of AO and MO integrals and MO coefficients are presented.

In the first three sections, the expansions of one- and two-electron AO integrals and MO coefficients with respect to *real* perturbations, including nuclear perturbations, are described. The subsequent sections present detailed derivations of one- and two-electron derivative AO and MO integrals. In the last section the derivatives of the nuclear repulsion energy are described.

3.1 Expansions of the Hamiltonian Operator and the Atomic Orbital Integrals

Let us consider the effects of real perturbations (e.g., a nuclear coordinate or an electric field), “ a ” and “ b ”, on the Hamiltonian operator, \mathbf{H} ,

$$\begin{aligned}\mathbf{H} &= \mathbf{H}_0 + \lambda_a \mathbf{H}'_a + \lambda_b \mathbf{H}'_b \\ &+ \frac{1}{2} \lambda_a^2 \mathbf{H}''_{aa} + \frac{1}{2} \lambda_b^2 \mathbf{H}''_{bb} + \lambda_a \lambda_b \mathbf{H}''_{ab} + \dots .\end{aligned}\quad (3.1)$$

\mathbf{H}_0 is the unperturbed Hamiltonian operator, while \mathbf{H}' and \mathbf{H}'' are the first-order and second-order perturbed Hamiltonians. λ_a and λ_b are first-order, and λ_a^2 , λ_b^2 and $\lambda_a\lambda_b$ are second-order perturbations, respectively.

All variables involved in describing an expectation value of the Hamiltonian operator may be expanded with respect to perturbations in a manner similar to eq. (3.1). As a function of these perturbations the overlap AO integrals, $S_{\mu\nu}$, and the one-electron AO integrals, $h_{\mu\nu}$, are

$$\begin{aligned} S_{\mu\nu}^{pert} &= S_{\mu\nu} + \lambda_a \frac{\partial S_{\mu\nu}}{\partial a} + \lambda_b \frac{\partial S_{\mu\nu}}{\partial b} \\ &+ \frac{1}{2} \lambda_a^2 \frac{\partial^2 S_{\mu\nu}}{\partial a^2} + \frac{1}{2} \lambda_b^2 \frac{\partial^2 S_{\mu\nu}}{\partial b^2} + \lambda_a \lambda_b \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} + \dots , \end{aligned} \quad (3.2)$$

$$\begin{aligned} h_{\mu\nu}^{pert} &= h_{\mu\nu} + \lambda_a \frac{\partial h_{\mu\nu}}{\partial a} + \lambda_b \frac{\partial h_{\mu\nu}}{\partial b} \\ &+ \frac{1}{2} \lambda_a^2 \frac{\partial^2 h_{\mu\nu}}{\partial a^2} + \frac{1}{2} \lambda_b^2 \frac{\partial^2 h_{\mu\nu}}{\partial b^2} + \lambda_a \lambda_b \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} + \dots . \end{aligned} \quad (3.3)$$

The two-electron AO integrals, $(\mu\nu|\rho\sigma)$, may be expanded in a similar manner,

$$\begin{aligned} (\mu\nu|\rho\sigma)^{pert} &= (\mu\nu|\rho\sigma) + \lambda_a \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + \lambda_b \frac{\partial(\mu\nu|\rho\sigma)}{\partial b} \\ &+ \frac{1}{2} \lambda_a^2 \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a^2} + \frac{1}{2} \lambda_b^2 \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial b^2} + \lambda_a \lambda_b \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a \partial b} + \dots . \end{aligned} \quad (3.4)$$

Although a perturbation like an electric field does not change the overlap or the two-electron AO integrals provided field independent basis functions are used (as is normally the case), expressions (3.2) and (3.4) will be included hereafter to keep the derivation general. The derivative expressions involving electric field perturbations will be described in detail in Chapter 17.

3.2 Expansion of the Molecular Orbital Coefficients

The μ th coefficient of the i th perturbed molecular orbital (MO), C_μ^i , is

$$\begin{aligned} C_\mu^{i,pert} &= C_\mu^i + \lambda_a \frac{\partial C_\mu^i}{\partial a} + \lambda_b \frac{\partial C_\mu^i}{\partial b} \\ &+ \frac{1}{2} \lambda_a^2 \frac{\partial^2 C_\mu^i}{\partial a^2} + \frac{1}{2} \lambda_b^2 \frac{\partial^2 C_\mu^i}{\partial b^2} + \lambda_a \lambda_b \frac{\partial^2 C_\mu^i}{\partial a \partial b} + \dots . \end{aligned} \quad (3.5)$$

The changes in C_μ^i due to perturbations can be expanded in the basis of the unperturbed MOs. Thus,

$$C_\mu^{i,pert} = C_\mu^i + \lambda_a \sum_m^{MO} U_{mi}^a C_\mu^m + \lambda_b \sum_m^{MO} U_{mi}^b C_\mu^m$$

$$+ \frac{1}{2} \lambda_a^2 \sum_m^{MO} U_{mi}^{aa} C_\mu^m + \frac{1}{2} \lambda_b^2 \sum_m^{MO} U_{mi}^{bb} C_\mu^m + \lambda_a \lambda_b \sum_m^{MO} U_{mi}^{ab} C_\mu^m + \dots . \quad (3.6)$$

"MO" here implies a sum over all occupied and virtual molecular orbitals. U^a and U^{ab} are defined by [1-4]:

$$\frac{\partial C_\mu^i}{\partial a} = \sum_m^{MO} U_{mi}^a C_\mu^m \quad (3.7)$$

and

$$\frac{\partial^2 C_\mu^i}{\partial a \partial b} = \sum_m^{MO} U_{mi}^{ab} C_\mu^m . \quad (3.8)$$

Equations (3.6) to (3.8) expand the molecular orbitals including the effects of the perturbations λ_a and λ_b in terms of the unperturbed MOs. The higher-order U matrices are defined similarly and are summarized in Appendix G.

3.3 A Relationship between U^a , U^b , and U^{ab}

Recall from eq. (3.7) in the previous section that the U^a are the weights of the MO coefficients C in the expansion of the partial derivatives of the C 's with respect to a perturbation "a". The U^{ab} in eq. (3.8) are the analogous weights in the expansion of the mixed partial derivative of the C 's with respect to "a" and "b". A relationship between U^a , U^b , and U^{ab} may be derived in the following manner:

$$\frac{\partial^2 C_\mu^i}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial C_\mu^i}{\partial a} \right) = \frac{\partial}{\partial b} \left(\sum_m^{MO} U_{mi}^a C_\mu^m \right) \quad (3.9)$$

$$= \sum_m^{MO} \left(\frac{\partial U_{mi}^a}{\partial b} C_\mu^m + U_{mi}^a \frac{\partial C_\mu^m}{\partial b} \right) \quad (3.10)$$

$$= \sum_m^{MO} \left(\frac{\partial U_{mi}^a}{\partial b} C_\mu^m + U_{mi}^a \sum_n^{MO} U_{nm}^b C_\mu^n \right) . \quad (3.11)$$

The indices m and n can be interchanged as the summation runs over all molecular orbitals, to give:

$$\frac{\partial^2 C_\mu^i}{\partial a \partial b} = \sum_m^{MO} \left(\frac{\partial U_{mi}^a}{\partial b} + \sum_n^{MO} U_{ni}^a U_{mn}^b \right) C_\mu^m . \quad (3.12)$$

Using (3.8), the following equation is obtained:

$$U_{mi}^{ab} = \frac{\partial U_{mi}^a}{\partial b} + \sum_n^{MO} U_{ni}^a U_{mn}^b \quad (3.13)$$

which may be rewritten in the more convenient form,

$$\frac{\partial U_{ij}^a}{\partial b} = U_{ij}^{ab} - \sum_k^{MO} U_{ik}^b U_{kj}^a . \quad (3.14)$$

It should be noted that the derivative of U^a with respect to a variable “ b ” is not simply equal to U^{ab} . Relationships for the higher-order U matrices may be obtained in a similar manner. They are summarized in Appendix H.

3.4 The Derivative Expressions for Overlap AO Integrals

The overlap AO integral is defined as follows:

$$S_{\mu\nu} = \int \chi_\mu^*(1) \chi_\nu(1) d\tau_1 \quad (3.15)$$

$$= \langle \chi_\mu | \chi_\nu \rangle . \quad (3.16)$$

Since only “real” perturbations are considered in this book, real AOs will be used in the following derivation. The first derivative of the overlap AO integral with respect to a geometrical variable “ a ” is,

$$\frac{\partial S_{\mu\nu}}{\partial a} = \frac{\partial}{\partial a} \langle \chi_\mu | \chi_\nu \rangle \quad (3.17)$$

$$= \left\langle \frac{\partial \chi_\mu}{\partial a} | \chi_\nu \right\rangle + \left\langle \chi_\mu | \frac{\partial \chi_\nu}{\partial a} \right\rangle . \quad (3.18)$$

The second derivative expression of the overlap AO integrals may be obtained by differentiating eq. (3.18) with respect to a second variable “ b ”,

$$\frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} = \frac{\partial^2}{\partial a \partial b} \langle \chi_\mu | \chi_\nu \rangle \quad (3.19)$$

$$= \frac{\partial}{\partial b} \left(\frac{\partial S_{\mu\nu}}{\partial a} \right) \quad (3.20)$$

$$= \left\langle \frac{\partial^2 \chi_\mu}{\partial a \partial b} | \chi_\nu \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial a} | \frac{\partial \chi_\nu}{\partial b} \right\rangle \\ + \left\langle \frac{\partial \chi_\mu}{\partial b} | \frac{\partial \chi_\nu}{\partial a} \right\rangle + \left\langle \chi_\mu | \frac{\partial^2 \chi_\nu}{\partial a \partial b} \right\rangle . \quad (3.21)$$

It is seen that the first and second derivatives of the overlap AO integrals involve the derivatives of the basis set or AO.

3.5 The Derivative Expressions for One-Electron AO Integrals

The one-electron AO integral is defined by,

$$h_{\mu\nu} = \int \chi_{\mu}^{*}(1) \mathbf{h}(1) \chi_{\nu}(1) d\tau_1 \quad (3.22)$$

$$= \langle \chi_{\mu} | \mathbf{h} | \chi_{\nu} \rangle \quad . \quad (3.23)$$

The first derivative of the one-electron AO integral is then

$$\frac{\partial h_{\mu\nu}}{\partial a} = \frac{\partial}{\partial a} \langle \chi_{\mu} | \mathbf{h} | \chi_{\nu} \rangle \quad (3.24)$$

$$= \left\langle \frac{\partial \chi_{\mu}}{\partial a} | \mathbf{h} | \chi_{\nu} \right\rangle + \left\langle \chi_{\mu} | \frac{\partial \mathbf{h}}{\partial a} | \chi_{\nu} \right\rangle + \left\langle \chi_{\mu} | \mathbf{h} | \frac{\partial \chi_{\nu}}{\partial a} \right\rangle \quad . \quad (3.25)$$

The second derivative of the one-electron AO integral is obtained by differentiating eq. (3.25),

$$\frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} = \frac{\partial^2}{\partial a \partial b} \langle \chi_{\mu} | \mathbf{h} | \chi_{\nu} \rangle \quad (3.26)$$

$$= \frac{\partial}{\partial b} \left(\frac{\partial h_{\mu\nu}}{\partial a} \right) \quad (3.27)$$

$$\begin{aligned} &= \left\langle \frac{\partial^2 \chi_{\mu}}{\partial a \partial b} | \mathbf{h} | \chi_{\nu} \right\rangle + \left\langle \frac{\partial \chi_{\mu}}{\partial a} | \frac{\partial \mathbf{h}}{\partial b} | \chi_{\nu} \right\rangle + \left\langle \frac{\partial \chi_{\mu}}{\partial a} | \mathbf{h} | \frac{\partial \chi_{\nu}}{\partial b} \right\rangle \\ &+ \left\langle \frac{\partial \chi_{\mu}}{\partial b} | \frac{\partial \mathbf{h}}{\partial a} | \chi_{\nu} \right\rangle + \left\langle \chi_{\mu} | \frac{\partial^2 \mathbf{h}}{\partial a \partial b} | \chi_{\nu} \right\rangle + \left\langle \chi_{\mu} | \frac{\partial \mathbf{h}}{\partial a} | \frac{\partial \chi_{\nu}}{\partial b} \right\rangle \\ &+ \left\langle \frac{\partial \chi_{\mu}}{\partial b} | \mathbf{h} | \frac{\partial \chi_{\nu}}{\partial a} \right\rangle + \left\langle \chi_{\mu} | \frac{\partial \mathbf{h}}{\partial b} | \frac{\partial \chi_{\nu}}{\partial a} \right\rangle + \left\langle \chi_{\mu} | \mathbf{h} | \frac{\partial^2 \chi_{\nu}}{\partial a \partial b} \right\rangle \quad . \quad (3.28) \end{aligned}$$

The derivatives of the one-electron AO integrals involve the derivatives of the one-electron operator as well as the derivatives of the basis set.

3.6 The Derivative Expressions for Two-Electron AO Integrals

A standard two-electron AO integral is defined by,

$$(\mu\nu|\rho\sigma) = \int \int \chi_{\mu}^{*}(1) \chi_{\nu}(1) \frac{1}{r_{12}} \chi_{\rho}^{*}(2) \chi_{\sigma}(2) d\tau_1 d\tau_2 \quad (3.29)$$

$$= \left[\chi_{\mu} \chi_{\nu} | \frac{1}{r_{12}} | \chi_{\rho} \chi_{\sigma} \right] \quad . \quad (3.30)$$

The first derivative of the two-electron AO integral is obtained by differentiating eq. (3.30) with respect to a geometrical variable "a"

$$\frac{\partial(\mu\nu|\rho\sigma)}{\partial a} = \frac{\partial}{\partial a} \left[\chi_{\mu} \chi_{\nu} | \frac{1}{r_{12}} | \chi_{\rho} \chi_{\sigma} \right] \quad (3.31)$$

$$\begin{aligned}
&= \left[\frac{\partial \chi_\mu}{\partial a} \chi_\nu | \frac{1}{r_{12}} | \chi_\rho \chi_\sigma \right] + \left[\chi_\mu \frac{\partial \chi_\nu}{\partial a} | \frac{1}{r_{12}} | \chi_\rho \chi_\sigma \right] \\
&+ \left[\chi_\mu \chi_\nu | \frac{1}{r_{12}} | \frac{\partial \chi_\rho}{\partial a} \chi_\sigma \right] + \left[\chi_\mu \chi_\nu | \frac{1}{r_{12}} | \chi_\rho \frac{\partial \chi_\sigma}{\partial a} \right]
\end{aligned} \tag{3.32}$$

Of course, the two-electron operator $1/r_{12}$ explicitly involves only electronic coordinates and thus derivatives of this operator with respect to nuclear variables such as “ a ” are zero.

The second derivatives of the two-electron AO integrals may be obtained by differentiating eq. (3.32) with respect to a second variable “ b ”,

$$\frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a \partial b} = \frac{\partial^2}{\partial a \partial b} \left[\chi_\mu \chi_\nu | \frac{1}{r_{12}} | \chi_\rho \chi_\sigma \right] \tag{3.33}$$

$$= \frac{\partial}{\partial b} \left(\frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right) \tag{3.34}$$

$$\begin{aligned}
&= \left[\frac{\partial^2 \chi_\mu}{\partial a \partial b} \chi_\nu | \frac{1}{r_{12}} | \chi_\rho \chi_\sigma \right] + \left[\frac{\partial \chi_\mu}{\partial a} \frac{\partial \chi_\nu}{\partial b} | \frac{1}{r_{12}} | \chi_\rho \chi_\sigma \right] \\
&+ \left[\frac{\partial \chi_\mu}{\partial a} \chi_\nu | \frac{1}{r_{12}} | \frac{\partial \chi_\rho}{\partial b} \chi_\sigma \right] + \left[\frac{\partial \chi_\mu}{\partial a} \chi_\nu | \frac{1}{r_{12}} | \chi_\rho \frac{\partial \chi_\sigma}{\partial b} \right] \\
&+ \left[\frac{\partial \chi_\mu}{\partial b} \frac{\partial \chi_\nu}{\partial a} | \frac{1}{r_{12}} | \chi_\rho \chi_\sigma \right] + \left[\chi_\mu \frac{\partial^2 \chi_\nu}{\partial a \partial b} | \frac{1}{r_{12}} | \chi_\rho \chi_\sigma \right] \\
&+ \left[\chi_\mu \frac{\partial \chi_\nu}{\partial a} | \frac{1}{r_{12}} | \frac{\partial \chi_\rho}{\partial b} \chi_\sigma \right] + \left[\chi_\mu \frac{\partial \chi_\nu}{\partial a} | \frac{1}{r_{12}} | \chi_\rho \frac{\partial \chi_\sigma}{\partial b} \right] \\
&+ \left[\frac{\partial \chi_\mu}{\partial b} \chi_\nu | \frac{1}{r_{12}} | \frac{\partial \chi_\rho}{\partial a} \chi_\sigma \right] + \left[\chi_\mu \frac{\partial \chi_\nu}{\partial b} | \frac{1}{r_{12}} | \frac{\partial \chi_\rho}{\partial a} \chi_\sigma \right] \\
&+ \left[\chi_\mu \chi_\nu | \frac{1}{r_{12}} | \frac{\partial^2 \chi_\rho}{\partial a \partial b} \chi_\sigma \right] + \left[\chi_\mu \chi_\nu | \frac{1}{r_{12}} | \frac{\partial \chi_\rho}{\partial a} \frac{\partial \chi_\sigma}{\partial b} \right] \\
&+ \left[\frac{\partial \chi_\mu}{\partial b} \chi_\nu | \frac{1}{r_{12}} | \chi_\rho \frac{\partial \chi_\sigma}{\partial a} \right] + \left[\chi_\mu \frac{\partial \chi_\nu}{\partial b} | \frac{1}{r_{12}} | \chi_\rho \frac{\partial \chi_\sigma}{\partial a} \right] \\
&+ \left[\chi_\mu \chi_\nu | \frac{1}{r_{12}} | \frac{\partial \chi_\rho}{\partial b} \frac{\partial \chi_\sigma}{\partial a} \right] + \left[\chi_\mu \chi_\nu | \frac{1}{r_{12}} | \chi_\rho \frac{\partial^2 \chi_\sigma}{\partial a \partial b} \right]
\end{aligned} \tag{3.35}$$

The first and second derivatives of the two-electron AO integrals thus are seen to require the first and second derivatives of the basis functions.

3.7 The Derivative Expressions for Overlap MO Integrals

3.7.1 The First and Second Derivatives of Overlap MO Integrals

Although the overlap AO integrals are crucial pieces of information for our theoretical development, the actual quantities that are initially differentiated are integrals over MOs.

The overlap MO integrals, S_{ij} for real MO, are defined as follows:

$$S_{ij} = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j S_{\mu\nu} . \quad (3.36)$$

“AO” means a sum over all atomic orbitals. A derivative expression for the overlap MO integrals may be obtained straightforwardly using eqs. (3.2), (3.6), and (3.36):

$$S_{ij}^{pert} = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j S_{\mu\nu}^{pert} \quad (3.37)$$

$$\begin{aligned} &= \sum_{\mu\nu}^{AO} \left(C_{\mu}^i + \lambda_a \sum_m^{MO} U_{mi}^a C_{\mu}^m + \lambda_b \sum_m^{MO} U_{mi}^b C_{\mu}^m + \lambda_a \lambda_b \sum_m^{MO} U_{mi}^{ab} C_{\mu}^m + \dots \right) \\ &\quad \times \left(C_{\nu}^j + \lambda_a \sum_n^{MO} U_{nj}^a C_{\nu}^n + \lambda_b \sum_n^{MO} U_{nj}^b C_{\nu}^n + \lambda_a \lambda_b \sum_n^{MO} U_{nj}^{ab} C_{\nu}^n + \dots \right) \\ &\quad \times \left(S_{\mu\nu} + \lambda_a \frac{\partial S_{\mu\nu}}{\partial a} + \lambda_b \frac{\partial S_{\mu\nu}}{\partial b} + \lambda_a \lambda_b \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} + \dots \right) . \end{aligned} \quad (3.38)$$

Collection of terms according to the order of the perturbation yields:

$$\begin{aligned} S_{ij}^{pert} &= \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j S_{\mu\nu} \\ &+ \lambda_a \sum_{\mu\nu}^{AO} \left(C_{\mu}^i C_{\nu}^j \frac{\partial S_{\mu\nu}}{\partial a} + \sum_m^{MO} U_{mi}^a C_{\mu}^m C_{\nu}^j S_{\mu\nu} + \sum_n^{MO} U_{nj}^a C_{\mu}^i C_{\nu}^n S_{\mu\nu} \right) \\ &+ \lambda_a \lambda_b \sum_{\mu\nu}^{AO} \left(C_{\mu}^i C_{\nu}^j \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} + \sum_m^{MO} U_{mi}^{ab} C_{\mu}^m C_{\nu}^j S_{\mu\nu} + \sum_n^{MO} U_{nj}^{ab} C_{\mu}^i C_{\nu}^n S_{\mu\nu} \right. \\ &\quad \left. + \sum_m^{MO} U_{mi}^a C_{\mu}^m C_{\nu}^j \frac{\partial S_{\mu\nu}}{\partial b} + \sum_m^{MO} U_{mi}^b C_{\mu}^m C_{\nu}^j \frac{\partial S_{\mu\nu}}{\partial a} \right. \\ &\quad \left. + \sum_n^{MO} U_{nj}^a C_{\mu}^i C_{\nu}^n \frac{\partial S_{\mu\nu}}{\partial b} + \sum_n^{MO} U_{nj}^b C_{\mu}^i C_{\nu}^n \frac{\partial S_{\mu\nu}}{\partial a} \right. \\ &\quad \left. + \sum_{mn}^{MO} U_{mi}^a U_{nj}^b C_{\mu}^m C_{\nu}^n S_{\mu\nu} + \sum_{mn}^{MO} U_{mi}^b U_{nj}^a C_{\mu}^m C_{\nu}^n S_{\mu\nu} \right) + \dots . \end{aligned} \quad (3.39)$$

The MO overlap integral S_{ij} is given in eq. (3.36) and the terms S_{ij}^a , and S_{ij}^{ab} are defined by

$$S_{ij}^a = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j \frac{\partial S_{\mu\nu}}{\partial a} \quad (3.40)$$

and

$$S_{ij}^{ab} = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} . \quad (3.41)$$

Thus equation (3.39) may be reformulated as

$$\begin{aligned}
 S_{ij}^{pert} = & S_{ij} \\
 & + \lambda_a \left(S_{ij}^a + \sum_m^{MO} U_{mi}^a S_{mj} + \sum_n^{MO} U_{nj}^a S_{in} \right) \\
 & + \lambda_a \lambda_b \left(S_{ij}^{ab} + \sum_m^{MO} U_{mi}^{ab} S_{mj} + \sum_n^{MO} U_{nj}^{ab} S_{in} \right. \\
 & \quad + \sum_m^{MO} U_{mi}^a S_{mj}^b + \sum_m^{MO} U_{mi}^b S_{mj}^a \\
 & \quad + \sum_n^{MO} U_{nj}^a S_{in}^b + \sum_n^{MO} U_{nj}^b S_{in}^a \\
 & \quad \left. + \sum_{mn}^{MO} U_{mi}^a U_{nj}^b S_{mn} + \sum_{mn}^{MO} U_{mi}^b U_{nj}^a S_{mn} \right) + \dots . \quad (3.42)
 \end{aligned}$$

In the final expression eq. (3.42), the terms in λ_b , λ_a^2 and λ_b^2 are excluded for the sake of brevity. The derivative integrals, S_{ij}^a and S_{ij}^{ab} , defined by eqs. (3.40) and (3.41), will be called the *skeleton (core)* derivative overlap integrals throughout this book. These terms are due purely to AO changes, i.e., no derivatives of the MO coefficients are involved.

It is immaterial whether the summations run over the m or n subscripts and thus the first-order derivatives of the overlap MO integrals are:

$$\frac{\partial S_{ij}}{\partial a} = S_{ij}^a + \sum_m^{MO} \left(U_{mi}^a S_{mj} + U_{mj}^a S_{im} \right) . \quad (3.43)$$

The orthonormality of the molecular orbitals and their derivatives gives the following equations:

$$S_{ij} = \delta_{ij} , \quad (3.44)$$

and

$$\frac{\partial S_{ij}}{\partial a} = \frac{\partial^2 S_{ij}}{\partial a \partial b} = 0 . \quad (3.45)$$

In eq. (3.44) δ_{ij} is the Kronecker delta function. Using eqs. (3.44) and (3.45), equation (3.43) becomes:

$$\frac{\partial S_{ij}}{\partial a} = S_{ij}^a + U_{ji}^a + U_{ij}^a = 0 , \quad (3.46)$$

a simple result which turns out to be very important. The second-order derivatives of the overlap MO integrals are:

$$\begin{aligned}
 \frac{\partial^2 S_{ij}}{\partial a \partial b} = & S_{ij}^{ab} + \sum_m^{MO} \left(U_{mi}^{ab} S_{mj} + U_{mj}^{ab} S_{im} \right) \\
 & + \sum_m^{MO} \left(U_{mi}^a S_{mj}^b + U_{mi}^b S_{mj}^a + U_{mj}^a S_{im}^b + U_{mj}^b S_{im}^a \right)
 \end{aligned}$$

$$+ \sum_{mn}^{MO} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) S_{mn} . \quad (3.47)$$

Using eqs. (3.44) to (3.46), the latter equation may be reformulated as:

$$\begin{aligned} \frac{\partial^2 S_{ij}}{\partial a \partial b} &= S_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} \\ &+ \sum_m^{MO} \left(U_{mi}^a S_{mj}^b + U_{mi}^b S_{mj}^a + U_{mj}^a S_{im}^b + U_{mj}^b S_{im}^a \right) \\ &+ \sum_m^{MO} \left(U_{mi}^a U_{mj}^b + U_{mi}^b U_{mj}^a \right) \end{aligned} \quad (3.48)$$

$$\begin{aligned} &= S_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} \\ &+ \sum_m^{MO} \left(-U_{mi}^a U_{jm}^b - U_{mi}^b U_{jm}^a + U_{mj}^a S_{im}^b + U_{mj}^b S_{im}^a \right) \end{aligned} \quad (3.49)$$

$$\begin{aligned} &= S_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} \\ &+ \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) = 0 . \end{aligned} \quad (3.50)$$

The ξ^{ab} and η^{ab} matrices are defined by their matrix elements:

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \quad (3.51)$$

$$= S_{ij}^{ab} + \eta_{ij}^{ab} \quad (3.52)$$

and

$$\eta_{ij}^{ab} = \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) . \quad (3.53)$$

Using these quantities equation (3.50) becomes:

$$\frac{\partial^2 S_{ij}}{\partial a \partial b} = \xi_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} \quad (3.54)$$

$$= S_{ij}^{ab} + \eta_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} = 0 . \quad (3.55)$$

3.7.2 An Alternative Derivation of the First Derivatives of Overlap MO Integrals

Alternatively, the first derivative expression for the overlap MO integrals may be derived by directly differentiating eq. (3.36),

$$\frac{\partial S_{ij}}{\partial a} = \frac{\partial}{\partial a} \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j S_{\mu\nu} \quad (3.56)$$

$$= \sum_{\mu\nu}^{AO} \left(\frac{\partial C_\mu^i}{\partial a} C_\nu^j S_{\mu\nu} + C_\mu^i \frac{\partial C_\nu^j}{\partial a} S_{\mu\nu} + C_\mu^i C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} \right) \quad (3.57)$$

The definitions in equations (3.7), (3.36), and (3.40) may then be used to give:

$$\frac{\partial S_{ij}}{\partial a} = \sum_{\mu\nu}^{AO} \left(\sum_m^{MO} U_{mi}^a C_\mu^m C_\nu^j S_{\mu\nu} + \sum_m^{MO} U_{mj}^a C_\mu^i C_\nu^m S_{\mu\nu} + C_\mu^i C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} \right) \quad (3.58)$$

$$= \sum_m^{MO} \left(U_{mi}^a S_{mj} + U_{mj}^a S_{im} \right) + S_{ij}^a . \quad (3.59)$$

Using the orthonormality of the molecular orbitals, eq. (3.44), equation (3.59) becomes:

$$\frac{\partial S_{ij}}{\partial a} = U_{ji}^a + U_{ij}^a + S_{ij}^a . \quad (3.60)$$

Equation (3.60) is identical to eq. (3.46) which was derived differently in the preceding subsection.

3.7.3 A Derivative Expression for the Skeleton (Core) Overlap Derivative Integrals

The first derivative of the overlap MO integral contains terms due both to the AO changes (third term, 3.57) and MO changes (first and second terms, 3.57) as shown in the preceding subsections. In Subsection 3.7.1 the part due to purely AO changes was identified as arising from the skeleton (core) derivative overlap integrals. The derivative of the skeleton (core) derivative overlap integral (3.40) may be found using a similar manipulation to that in the preceding subsection,

$$\frac{\partial S_{ij}^a}{\partial b} = \frac{\partial}{\partial b} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} \quad (3.61)$$

$$= \sum_{\mu\nu}^{AO} \left(\frac{\partial C_\mu^i}{\partial b} C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} + C_\mu^i \frac{\partial C_\nu^j}{\partial b} \frac{\partial S_{\mu\nu}}{\partial a} + C_\mu^i C_\nu^j \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} \right) . \quad (3.62)$$

Equations (3.7), (3.40) and (3.41) are used to yield:

$$\frac{\partial S_{ij}^a}{\partial b} = \sum_{\mu\nu}^{AO} \left(\sum_m^{MO} U_{mi}^b C_\mu^m C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} + \sum_m^{MO} U_{mj}^b C_\mu^i C_\nu^m \frac{\partial S_{\mu\nu}}{\partial a} + C_\mu^i C_\nu^j \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} \right) \quad (3.63)$$

$$= \sum_m^{MO} \left(U_{mi}^b S_{mj}^a + U_{mj}^b S_{im}^a \right) + S_{ij}^{ab} . \quad (3.64)$$

It should be noted that elements of the skeleton (core) derivative overlap matrices S^a and S^{ab} are generally *not* equal to zero. Derivative expressions for the skeleton (core) overlap higher derivative integrals may be obtained in a similar way and are summarized in Appendix K.

3.7.4 An Alternative Derivation of the Second Derivatives of Overlap MO Integrals

An alternative derivation of the second derivative expression for overlap MO integrals is obtained by directly differentiating eq. (3.60):

$$\frac{\partial^2 S_{ij}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial S_{ij}}{\partial a} \right) \quad (3.65)$$

$$= \frac{\partial}{\partial b} \left(U_{ji}^a + U_{ij}^a + S_{ij}^a \right) \quad (3.66)$$

$$= \frac{\partial U_{ji}^a}{\partial b} + \frac{\partial U_{ij}^a}{\partial b} + \frac{\partial S_{ij}^a}{\partial b} \quad (3.67)$$

$$= \left(U_{ji}^{ab} - \sum_m^{MO} U_{jm}^b U_{mi}^a \right) + \left(U_{ij}^{ab} - \sum_m^{MO} U_{im}^b U_{mj}^a \right) \\ + \sum_m^{MO} \left(U_{mi}^b S_{mj}^a + U_{mj}^b S_{im}^a \right) + S_{ij}^{ab} \quad . \quad (3.68)$$

Relationships (3.14) and (3.64) were used in deriving eq. (3.68). Equation (3.68) can be further simplified to yield

$$\frac{\partial^2 S_{ij}}{\partial a \partial b} = U_{ji}^{ab} + U_{ij}^{ab} + S_{ij}^{ab} \\ + \sum_m^{MO} \left(-U_{jm}^b U_{mi}^a - U_{im}^b U_{mj}^a + U_{mi}^b S_{mj}^a + U_{mj}^b S_{im}^a \right) \quad (3.69)$$

$$= U_{ji}^{ab} + U_{ij}^{ab} + S_{ij}^{ab} \\ + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \quad . \quad (3.70)$$

which is identical to eq. (3.50).

The equality $\partial^2 S_{ij}/\partial a \partial b = \partial^2 S_{ij}/\partial b \partial a$ is proved easily by taking the derivative of $\partial S_{ij}/\partial b$ with respect to a variable "a".

3.8 The Derivative Expressions for One-Electron MO Integrals

3.8.1 The First and Second Derivatives of One-Electron MO Integrals

One-electron MO integrals, h_{ij} , for real MOs, are:

$$h_{ij} = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j h_{\mu\nu} \quad (3.71)$$

A derivative expression for the one-electron MO integrals may be obtained straightforwardly using eqs. (3.3), (3.6), and (3.71):

$$h_{ij}^{pert} = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j h_{\mu\nu}^{pert} \quad (3.72)$$

$$\begin{aligned} &= \sum_{\mu\nu}^{AO} \left(C_{\mu}^i + \lambda_a \sum_m^{MO} U_{mi}^a C_{\mu}^m + \lambda_b \sum_m^{MO} U_{mi}^b C_{\mu}^m + \lambda_a \lambda_b \sum_m^{MO} U_{mi}^{ab} C_{\mu}^m + \dots \right) \\ &\quad \times \left(C_{\nu}^j + \lambda_a \sum_n^{MO} U_{nj}^a C_{\nu}^n + \lambda_b \sum_n^{MO} U_{nj}^b C_{\nu}^n + \lambda_a \lambda_b \sum_n^{MO} U_{nj}^{ab} C_{\nu}^n + \dots \right) \\ &\quad \times \left(h_{\mu\nu} + \lambda_a \frac{\partial h_{\mu\nu}}{\partial a} + \lambda_b \frac{\partial h_{\mu\nu}}{\partial b} + \lambda_a \lambda_b \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} + \dots \right) . \end{aligned} \quad (3.73)$$

Collection of terms according to the order of the perturbation yields:

$$\begin{aligned} h_{ij}^{pert} &= \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j h_{\mu\nu} \\ &+ \lambda_a \sum_{\mu\nu}^{AO} \left(C_{\mu}^i C_{\nu}^j \frac{\partial h_{\mu\nu}}{\partial a} + \sum_m^{MO} U_{mi}^a C_{\mu}^m C_{\nu}^j h_{\mu\nu} + \sum_n^{MO} U_{nj}^a C_{\mu}^i C_{\nu}^n h_{\mu\nu} \right) \\ &+ \lambda_a \lambda_b \sum_{\mu\nu}^{AO} \left(C_{\mu}^i C_{\nu}^j \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} + \sum_m^{MO} U_{mi}^{ab} C_{\mu}^m C_{\nu}^j h_{\mu\nu} + \sum_n^{MO} U_{nj}^{ab} C_{\mu}^i C_{\nu}^n h_{\mu\nu} \right. \\ &\quad \left. + \sum_m^{MO} U_{mi}^a C_{\mu}^m C_{\nu}^j \frac{\partial h_{\mu\nu}}{\partial b} + \sum_m^{MO} U_{mi}^b C_{\mu}^m C_{\nu}^j \frac{\partial h_{\mu\nu}}{\partial a} \right. \\ &\quad \left. + \sum_n^{MO} U_{nj}^a C_{\mu}^i C_{\nu}^n \frac{\partial h_{\mu\nu}}{\partial b} + \sum_n^{MO} U_{nj}^b C_{\mu}^i C_{\nu}^n \frac{\partial h_{\mu\nu}}{\partial a} \right. \\ &\quad \left. + \sum_{mn}^{MO} U_{mi}^a U_{nj}^b C_{\mu}^m C_{\nu}^n h_{\mu\nu} + \sum_{mn}^{MO} U_{mi}^b U_{nj}^a C_{\mu}^m C_{\nu}^n h_{\mu\nu} \right) + \dots . \end{aligned} \quad (3.74)$$

h_{ij} was given in eq. (3.71) and h_{ij}^a , and h_{ij}^{ab} are defined by

$$h_{ij}^a = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j \frac{\partial h_{\mu\nu}}{\partial a} \quad (3.75)$$

and

$$h_{ij}^{ab} = \sum_{\mu\nu}^{AO} C_{\mu}^i C_{\nu}^j \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} . \quad (3.76)$$

Thus the equation may be reformulated as

$$h_{ij}^{pert} = h_{ij}$$

$$\begin{aligned}
& + \lambda_a \left(h_{ij}^a + \sum_m^{MO} U_{mi}^a h_{mj} + \sum_n^{MO} U_{nj}^a h_{in} \right) \\
& + \lambda_a \lambda_b \left(h_{ij}^{ab} + \sum_m^{MO} U_{mi}^{ab} h_{mj} + \sum_n^{MO} U_{nj}^{ab} h_{in} \right. \\
& \quad + \sum_m^{MO} U_{mi}^a h_{mj}^b + \sum_m^{MO} U_{mi}^b h_{mj}^a \\
& \quad + \sum_n^{MO} U_{nj}^a h_{in}^b + \sum_n^{MO} U_{nj}^b h_{in}^a \\
& \quad \left. + \sum_{mn}^{MO} U_{mi}^a U_{nj}^b h_{mn} + \sum_{mn}^{MO} U_{mi}^b U_{nj}^a h_{mn} \right) + \dots . \quad (3.77)
\end{aligned}$$

In the final expression eq. (3.77), the terms in λ_b , λ_a^2 and λ_b^2 are excluded for the sake of brevity. It is immaterial whether the summations run over the m or n subscripts, and thus the first- and second-order derivatives of the one-electron MO integrals are:

$$\frac{\partial h_{ij}}{\partial a} = h_{ij}^a + \sum_m^{MO} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \quad (3.78)$$

and

$$\begin{aligned}
\frac{\partial^2 h_{ij}}{\partial a \partial b} &= h_{ij}^{ab} + \sum_m^{MO} \left(U_{mi}^{ab} h_{mj} + U_{mj}^{ab} h_{im} \right) \\
&+ \sum_m^{MO} \left(U_{mi}^a h_{mj}^b + U_{mi}^b h_{mj}^a + U_{mj}^a h_{im}^b + U_{mj}^b h_{im}^a \right) \\
&+ \sum_{mn}^{MO} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) h_{mn} . \quad (3.79)
\end{aligned}$$

The derivative integrals, h^a and h^{ab} , defined by eqs. (3.75) and (3.76), will be called the *skeleton (core)* derivative one-electron integrals throughout this book. These terms are due purely to AO changes.

3.8.2 An Alternative Derivation of the First Derivatives of One-Electron MO Integrals

Alternatively, the first derivative expression for the one-electron MO integrals may be derived by directly differentiating eq. (3.71),

$$\frac{\partial h_{ij}}{\partial a} = \frac{\partial}{\partial a} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j h_{\mu\nu} \quad (3.80)$$

$$= \sum_{\mu\nu}^{AO} \left(\frac{\partial C_\mu^i}{\partial a} C_\nu^j h_{\mu\nu} + C_\mu^i \frac{\partial C_\nu^j}{\partial a} h_{\mu\nu} + C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} \right) . \quad (3.81)$$

The definitions in equations (3.7), (3.71), and (3.75) may then be used to give:

$$\frac{\partial h_{ij}^a}{\partial a} = \sum_{\mu\nu}^{AO} \left(\sum_m^{MO} U_{mi}^a C_\mu^m C_\nu^j h_{\mu\nu} + \sum_m^{MO} U_{mj}^a C_\mu^i C_\nu^m h_{\mu\nu} + C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} \right) \quad (3.82)$$

$$= \sum_m^{MO} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) + h_{ij}^a . \quad (3.83)$$

3.8.3 A Derivative Expression for the Skeleton (Core) One-Electron Derivative Integrals

The derivative form of the skeleton (core) derivative one-electron integral (3.75) may be found using a similar manipulation to that in the preceding subsection,

$$\frac{\partial h_{ij}^a}{\partial b} = \frac{\partial}{\partial b} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} \quad (3.84)$$

$$= \sum_{\mu\nu}^{AO} \left(\frac{\partial C_\mu^i}{\partial b} C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} + C_\mu^i \frac{\partial C_\nu^j}{\partial b} \frac{\partial h_{\mu\nu}}{\partial a} + C_\mu^i C_\nu^j \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} \right) . \quad (3.85)$$

Equations (3.7), (3.75) and (3.76) are used to yield:

$$\frac{\partial h_{ij}^a}{\partial b} = \sum_{\mu\nu}^{AO} \left(\sum_m^{MO} U_{mi}^b C_\mu^m C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} + \sum_m^{MO} U_{mj}^b C_\mu^i C_\nu^m \frac{\partial h_{\mu\nu}}{\partial a} + C_\mu^i C_\nu^j \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} \right) \quad (3.86)$$

$$= \sum_m^{MO} \left(U_{mi}^b h_{mj}^a + U_{mj}^b h_{im}^a \right) + h_{ij}^{ab} . \quad (3.87)$$

Derivative expressions for the skeleton (core) one-electron higher derivative integrals may be obtained in a similar way and are summarized in Appendix K.

3.8.4 An Alternative Derivation of the Second Derivatives of One-Electron MO Integrals

An alternative derivation of the second derivative expression for one-electron MO integrals results from directly differentiating eq. (3.83):

$$\frac{\partial^2 h_{ij}^a}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial h_{ij}^a}{\partial a} \right) \quad (3.88)$$

$$= \frac{\partial}{\partial b} \left[\sum_m^{MO} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) + h_{ij}^a \right] \quad (3.89)$$

$$= \sum_m^{MO} \left\{ \frac{\partial U_{mi}^a}{\partial b} h_{mj} + U_{mi}^a \frac{\partial h_{mj}}{\partial b} + \frac{\partial U_{mj}^a}{\partial b} h_{im} + U_{mj}^a \frac{\partial h_{im}}{\partial b} \right\} + \frac{\partial h_{ij}^a}{\partial b} \quad (3.90)$$

$$\begin{aligned} = & \sum_m^{MO} \left[\left(U_{mi}^{ab} - \sum_n^{MO} U_{mn}^b U_{ni}^a \right) h_{mj} \right. \\ & + U_{mi}^a \left\{ \sum_n^{MO} \left(U_{nm}^b h_{nj} + U_{nj}^b h_{mn} \right) + h_{mj}^b \right\} \\ & + \left(U_{mj}^{ab} - \sum_n^{MO} U_{mn}^b U_{nj}^a \right) h_{im} \\ & \left. + U_{mj}^a \left\{ \sum_n^{MO} \left(U_{ni}^b h_{nm} + U_{nm}^b h_{in} \right) + h_{im}^b \right\} \right] \\ & + \sum_m^{MO} \left(U_{mi}^b h_{mj}^a + U_{mj}^b h_{im}^a \right) + h_{ij}^{ab} . \end{aligned} \quad (3.91)$$

Relationships (3.14), (3.83) and (3.87) were used in deriving eq. (3.91). Equation (3.91) can be further simplified to yield

$$\begin{aligned} \frac{\partial^2 h_{ij}}{\partial a \partial b} = & \sum_m^{MO} \left(U_{mi}^{ab} h_{mj} + U_{mj}^{ab} h_{im} \right) \\ & + \sum_m^{MO} \left(U_{mi}^a h_{mj}^b + U_{mj}^a h_{im}^b + U_{mi}^b h_{mj}^a + U_{mj}^b U_{im}^a \right) \\ & + \sum_{mn}^{MO} \left(U_{mi}^a U_{nj}^b + U_{nj}^a U_{mi}^b \right) h_{mn} + h_{ij}^{ab} \end{aligned} \quad (3.92)$$

which is equal to eq. (3.79). It should be noted that the interchange of the indices m and n does not alter the equation, since the summations run over all molecular orbitals.

The equality $\partial^2 h_{ij}/\partial a \partial b = \partial^2 h_{ij}/\partial b \partial a$ is proved easily by taking the derivative of $\partial h_{ij}/\partial b$ with respect to the second variable “ a ”.

3.9 The Derivative Expressions for Two-Electron MO Integrals

3.9.1 The First and Second Derivatives of the Two-Electron MO Integrals

Since the electron repulsion integrals involve four orbitals, their derivative expressions are the most complicated. The two-electron MO integrals, $(ij|kl)$ for real MO, are defined by,

$$(ij|kl) = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) . \quad (3.93)$$

For the two-electron MO integrals the same techniques used above to derive the expressions for S_{ij} and h_{ij} can be extended,

$$(ij|kl)^{pert} = \sum_{\mu\nu\rho\sigma}^{AO} C_{\mu}^i C_{\nu}^j C_{\rho}^k C_{\sigma}^l (\mu\nu|\rho\sigma)^{pert} \quad (3.94)$$

$$= \sum_{\mu\nu\rho\sigma}^{AO} \left(C_{\mu}^i + \lambda_a \sum_r^{MO} U_{ri}^a C_{\mu}^r + \lambda_b \sum_r^{MO} U_{ri}^b C_{\mu}^r \right. \\ \left. + \lambda_a \lambda_b \sum_r^{MO} U_{ri}^{ab} C_{\mu}^r + \dots \right)$$

$$\times \left(C_{\nu}^j + \lambda_a \sum_s^{MO} U_{sj}^a C_{\nu}^s + \lambda_b \sum_s^{MO} U_{sj}^b C_{\nu}^s \right. \\ \left. + \lambda_a \lambda_b \sum_s^{MO} U_{sj}^{ab} C_{\nu}^s + \dots \right)$$

$$\times \left(C_{\rho}^k + \lambda_a \sum_t^{MO} U_{tk}^a C_{\rho}^t + \lambda_b \sum_t^{MO} U_{tk}^b C_{\rho}^t \right. \\ \left. + \lambda_a \lambda_b \sum_t^{MO} U_{tk}^{ab} C_{\rho}^t + \dots \right)$$

$$\times \left(C_{\sigma}^l + \lambda_a \sum_u^{MO} U_{ul}^a C_{\sigma}^u + \lambda_b \sum_u^{MO} U_{ul}^b C_{\sigma}^u \right. \\ \left. + \lambda_a \lambda_b \sum_u^{MO} U_{ul}^{ab} C_{\sigma}^u + \dots \right)$$

$$\times \left\{ (\mu\nu|\rho\sigma) + \lambda_a \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + \lambda_b \frac{\partial(\mu\nu|\rho\sigma)}{\partial b} \right. \\ \left. + \lambda_a \lambda_b \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a \partial b} + \dots \right\}$$

(3.95)

$$= \sum_{\mu\nu\rho\sigma}^{AO} C_{\mu}^i C_{\nu}^j C_{\rho}^k C_{\sigma}^l (\mu\nu|\rho\sigma) \\ + \lambda_a \sum_{\mu\nu\rho\sigma}^{AO} \left\{ C_{\mu}^i C_{\nu}^j C_{\rho}^k C_{\sigma}^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right. \\ \left. + \sum_r^{MO} U_{ri}^a C_{\mu}^r C_{\nu}^j C_{\rho}^k C_{\sigma}^l (\mu\nu|\rho\sigma) + \sum_s^{MO} U_{sj}^a C_{\mu}^i C_{\nu}^s C_{\rho}^k C_{\sigma}^l (\mu\nu|\rho\sigma) \right. \\ \left. + \sum_t^{MO} U_{tk}^a C_{\mu}^i C_{\nu}^j C_{\rho}^t C_{\sigma}^l (\mu\nu|\rho\sigma) + \sum_u^{MO} U_{ul}^a C_{\mu}^i C_{\nu}^j C_{\rho}^k C_{\sigma}^u (\mu\nu|\rho\sigma) \right\}$$

$$\begin{aligned}
& + \lambda_a \lambda_b \sum_{\mu\nu\rho\sigma}^{AO} \left\{ C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a \partial b} \right. \\
& + \sum_r^{MO} U_{ri}^{ab} C_\mu^r C_\nu^j C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) + \sum_s^{MO} U_{sj}^{ab} C_\mu^i C_\nu^s C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) \\
& + \sum_t^{MO} U_{tk}^{ab} C_\mu^i C_\nu^j C_\rho^t C_\sigma^l (\mu\nu|\rho\sigma) + \sum_u^{MO} U_{ul}^{ab} C_\mu^i C_\nu^j C_\rho^k C_\sigma^u (\mu\nu|\rho\sigma) \\
& + \sum_r^{MO} U_{ri}^a C_\mu^r C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial b} + \sum_s^{MO} U_{sj}^a C_\mu^i C_\nu^s C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial b} \\
& + \sum_t^{MO} U_{tk}^a C_\mu^i C_\nu^j C_\rho^t C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial b} + \sum_u^{MO} U_{ul}^a C_\mu^i C_\nu^j C_\rho^k C_\sigma^u \frac{\partial(\mu\nu|\rho\sigma)}{\partial b} \\
& + \sum_r^{MO} U_{ri}^b C_\mu^r C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + \sum_s^{MO} U_{sj}^b C_\mu^i C_\nu^s C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\
& + \sum_t^{MO} U_{tk}^b C_\mu^i C_\nu^j C_\rho^t C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + \sum_u^{MO} U_{ul}^b C_\mu^i C_\nu^j C_\rho^k C_\sigma^u \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\
& + \sum_{rs}^{MO} U_{ri}^a U_{sj}^b C_\mu^r C_\nu^s C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) + \sum_{rt}^{MO} U_{ri}^a U_{tk}^b C_\mu^r C_\nu^j C_\rho^t C_\sigma^l (\mu\nu|\rho\sigma) \\
& + \sum_{ru}^{MO} U_{ri}^a U_{ul}^b C_\mu^r C_\nu^j C_\rho^k C_\sigma^u (\mu\nu|\rho\sigma) + \sum_{st}^{MO} U_{sj}^a U_{tk}^b C_\mu^i C_\nu^s C_\rho^t C_\sigma^l (\mu\nu|\rho\sigma) \\
& + \sum_{su}^{MO} U_{sj}^a U_{ul}^b C_\mu^i C_\nu^s C_\rho^k C_\sigma^u (\mu\nu|\rho\sigma) + \sum_{tk}^{MO} U_{tk}^a U_{ul}^b C_\mu^i C_\nu^j C_\rho^t C_\sigma^u (\mu\nu|\rho\sigma) \\
& + \sum_{ts}^{MO} U_{ri}^b U_{sj}^a C_\mu^r C_\nu^s C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) + \sum_{rt}^{MO} U_{ri}^b U_{tk}^a C_\mu^r C_\nu^j C_\rho^t C_\sigma^l (\mu\nu|\rho\sigma) \\
& + \sum_{ru}^{MO} U_{ri}^b U_{ul}^a C_\mu^r C_\nu^j C_\rho^k C_\sigma^u (\mu\nu|\rho\sigma) + \sum_{st}^{MO} U_{sj}^b U_{tk}^a C_\mu^i C_\nu^s C_\rho^t C_\sigma^l (\mu\nu|\rho\sigma) \\
& \left. + \sum_{su}^{MO} U_{sj}^b U_{ul}^a C_\mu^i C_\nu^s C_\rho^k C_\sigma^u (\mu\nu|\rho\sigma) + \sum_{tu}^{MO} U_{tk}^b U_{ul}^a C_\mu^i C_\nu^j C_\rho^t C_\sigma^u (\mu\nu|\rho\sigma) \right\} \\
& + \dots .
\end{aligned} \tag{3.96}$$

The series is terminated to exclude cubic and higher terms in λ . The expression (3.96) is meant to implicitly include terms in λ_b , λ_a^2 , and λ_b^2 .

Collecting terms by order of perturbation gives:

$$\begin{aligned}
(ij|kl)^{pert} &= (ij|kl) \\
&+ \lambda_a \left\{ (ij|kl)^a + \sum_r^{MO} U_{ri}^a (rj|kl) + \sum_s^{MO} U_{sj}^a (is|kl) \right.
\end{aligned}$$

$$\begin{aligned}
& + \sum_t^{MO} U_{tk}^a(ij|tl) + \sum_u^{MO} U_{ul}^a(ij|ku) \Big\} \\
& + \lambda_a \lambda_b \left\{ (ij|kl)^{ab} + \sum_r^{MO} U_{ri}^{ab}(rj|kl) + \sum_s^{MO} U_{sj}^{ab}(is|kl) \right. \\
& + \sum_t^{MO} U_{tk}^{ab}(ij|tl) + \sum_u^{MO} U_{ul}^{ab}(ij|ku) \\
& + \sum_r^{MO} U_{ri}^a(rj|kl)^b + \sum_s^{MO} U_{sj}^a(is|kl)^b \\
& + \sum_t^{MO} U_{tk}^a(ij|tl)^b + \sum_u^{MO} U_{ul}^a(ij|ku)^b \\
& + \sum_r^{MO} U_{ri}^b(rj|kl)^a + \sum_s^{MO} U_{sj}^b(is|kl)^a \\
& + \sum_t^{MO} U_{tk}^b(ij|tl)^a + \sum_u^{MO} U_{ul}^b(ij|ku)^a \\
& + \sum_{rs}^{MO} U_{ri}^a U_{sj}^b(rs|kl) + \sum_{rt}^{MO} U_{ri}^a U_{tk}^b(rj|tl) \\
& + \sum_{ru}^{MO} U_{ri}^a U_{ul}^b(rj|ku) + \sum_{st}^{MO} U_{sj}^a U_{tk}^b(is|tl) \\
& + \sum_{su}^{MO} U_{sj}^a U_{ul}^b(is|ku) + \sum_{tu}^{MO} U_{tk}^a U_{ul}^b(ij|tu) \\
& + \sum_{rs}^{MO} U_{ri}^b U_{sj}^a(rs|kl) + \sum_{rt}^{MO} U_{ri}^b U_{tk}^a(rj|tl) \\
& + \sum_{ru}^{MO} U_{ri}^b U_{ul}^a(rj|ku) + \sum_{st}^{MO} U_{sj}^b U_{tk}^a(is|tl) \\
& \left. + \sum_{su}^{MO} U_{sj}^b U_{ul}^a(is|ku) + \sum_{tu}^{MO} U_{tk}^b U_{ul}^a(ij|tu) \right\} \\
& + \dots .
\end{aligned} \tag{3.97}$$

The purely AO parts of the MO derivative two-electron integrals $(ij|kl)^a$ and $(ij|kl)^{ab}$ are defined by

$$(ij|kl)^a = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \tag{3.98}$$

and

$$(ij|kl)^{ab} = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a \partial b} . \tag{3.99}$$

In deriving eq. (3.97), terms in λ_b , λ_a^2 and λ_b^2 were excluded for the sake of brevity. Since the summations run over all molecular orbitals, the interchange of the indices r , s , t , and u does not alter the equation. Thus, the first- and second-order derivatives of the two-electron MO integrals are

$$\begin{aligned} \frac{\partial(ij|kl)}{\partial a} &= (ij|kl)^a \\ &+ \sum_m^{MO} \left(U_{mi}^a(mj|kl) + U_{mj}^a(im|kl) + U_{mk}^a(ij|ml) + U_{ml}^a(ij|km) \right) \end{aligned} \quad (3.100)$$

and

$$\begin{aligned} \frac{\partial^2(ij|kl)}{\partial a \partial b} &= (ij|kl)^{ab} \\ &+ \sum_m^{MO} \left(U_{mi}^{ab}(mj|kl) + U_{mj}^{ab}(im|kl) + U_{mk}^{ab}(ij|ml) + U_{ml}^{ab}(ij|km) \right) \\ &+ \sum_m^{MO} \left(U_{mi}^a(mj|kl)^b + U_{mj}^a(im|kl)^b + U_{mk}^a(ij|ml)^b + U_{ml}^a(ij|km)^b \right. \\ &\quad \left. + U_{mi}^b(mj|kl)^a + U_{mj}^b(im|kl)^a + U_{mk}^b(ij|ml)^a + U_{ml}^b(ij|km)^a \right) \\ &+ \sum_{mn}^{MO} \left[\left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mn|kl) + \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mj|nl) \right. \\ &\quad \left. + \left(U_{mi}^a U_{nl}^b + U_{mi}^b U_{nl}^a \right) (mj|kn) + \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (im|nl) \right. \\ &\quad \left. + \left(U_{mj}^a U_{nl}^b + U_{mj}^b U_{nl}^a \right) (im|kn) + \left(U_{mk}^a U_{nl}^b + U_{mk}^b U_{nl}^a \right) (ij|mn) \right] \end{aligned} \quad (3.101)$$

The derivative integrals, $(ij|kl)^a$ and $(ij|kl)^{ab}$, defined in eqs. (3.98) and (3.99), will be called the *skeleton (core)* derivative two-electron integrals throughout this book. These terms are due purely to AO changes.

3.9.2 An Alternative Derivation of the First Derivatives of Two-Electron MO Integrals

The first derivative expression for two-electron MO integrals may also be derived by directly differentiating eq. (3.93),

$$\frac{\partial(ij|kl)}{\partial a} = \frac{\partial}{\partial a} \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) \quad (3.102)$$

$$\begin{aligned}
&= \sum_{\mu\nu\rho\sigma}^{AO} \left\{ \frac{\partial C_\mu^i}{\partial a} C_\nu^j C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) + C_\mu^i \frac{\partial C_\nu^j}{\partial a} C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) \right. \\
&\quad + C_\mu^i C_\nu^j \frac{\partial C_\rho^k}{\partial a} C_\sigma^l (\mu\nu|\rho\sigma) + C_\mu^i C_\nu^j C_\rho^k \frac{\partial C_\sigma^l}{\partial a} (\mu\nu|\rho\sigma) \\
&\quad \left. + C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right\} . \tag{3.103}
\end{aligned}$$

The definitions in eqs. (3.7), (3.93) and (3.98) may be employed to rewrite (3.103) as:

$$\begin{aligned}
\frac{\partial(ij|kl)}{\partial a} &= \sum_{\mu\nu\rho\sigma}^{AO} \left\{ \sum_m^{MO} U_{mi}^a C_\mu^m C_\nu^j C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) + \sum_m^{MO} U_{mj}^a C_\mu^i C_\nu^m C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) \right. \\
&\quad + \sum_m^{MO} U_{mk}^a C_\mu^i C_\nu^j C_\rho^m C_\sigma^l (\mu\nu|\rho\sigma) + \sum_m^{MO} U_{ml}^a C_\mu^i C_\nu^j C_\rho^k C_\sigma^m (\mu\nu|\rho\sigma) \\
&\quad \left. + C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right\} \tag{3.104}
\end{aligned}$$

$$\begin{aligned}
&= \sum_m^{MO} \left(U_{mi}^a (mj|kl) + U_{mj}^a (im|kl) + U_{mk}^a (ij|ml) + U_{ml}^a (ij|km) \right) \\
&+ (ij|kl)^a . \tag{3.105}
\end{aligned}$$

3.9.3 The Derivative Expression for the Skeleton (Core) Two-Electron Derivative Integrals

The derivative form of the skeleton (core) derivative two-electron integral (3.98) may be obtained in a manner similar to that in the preceding subsection,

$$\frac{\partial(ij|kl)^a}{\partial b} = \frac{\partial}{\partial b} \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \tag{3.106}$$

$$\begin{aligned}
&= \sum_{\mu\nu\rho\sigma}^{AO} \left\{ \frac{\partial C_\mu^i}{\partial b} C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + C_\mu^i \frac{\partial C_\nu^j}{\partial b} C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right. \\
&\quad + C_\mu^i C_\nu^j \frac{\partial C_\rho^k}{\partial b} C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + C_\mu^i C_\nu^j C_\rho^k \frac{\partial C_\sigma^l}{\partial b} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\
&\quad \left. + C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a \partial b} \right\} . \tag{3.107}
\end{aligned}$$

This equation may be modified using eqs. (3.7), (3.98), and (3.99) to yield:

$$\frac{\partial(ij|kl)^a}{\partial b} = \sum_{\mu\nu\rho\sigma}^{AO} \left\{ \sum_m^{MO} U_{mi}^b C_\mu^m C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + \sum_m^{MO} U_{mj}^b C_\mu^i C_\nu^m C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right. \tag{3.108}$$

$$\begin{aligned}
& + \sum_m^{MO} U_{mk}^b C_\mu^i C_\nu^j C_\rho^m C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + \sum_m^{MO} U_{ml}^b C_\mu^i C_\nu^j C_\rho^k C_\sigma^m \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\
& + C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a \partial b} \Big\} \quad (3.108)
\end{aligned}$$

$$\begin{aligned}
& = \sum_m^{MO} \left(U_{mi}^b (mj|kl)^a + U_{mj}^b (im|kl)^a + U_{mk}^b (ij|ml)^a + U_{ml}^b (ij|km)^a \right) \\
& + (ij|kl)^{ab} \quad (3.109)
\end{aligned}$$

Derivative expressions for the skeleton (core) two-electron higher derivative integrals may be obtained in a similar manner and are summarized in Appendix K.

3.9.4 An Alternative Derivation of the Second Derivatives of Two-Electron MO Integrals

An alternative derivation of the second derivative expression for two-electron MO integrals may be obtained by directly differentiating eq. (3.105),

$$\frac{\partial^2(ij|kl)}{\partial a \partial b} = \frac{\partial}{\partial b} \left[\frac{\partial(ij|kl)}{\partial a} \right] \quad (3.110)$$

$$\begin{aligned}
& = \frac{\partial}{\partial b} \left[\sum_m^{MO} \left\{ U_{mi}^a (mj|kl) + U_{mj}^a (im|kl) + U_{mk}^a (ij|ml) + U_{ml}^a (ij|km) \right\} \right. \\
& \quad \left. + (ij|kl)^a \right] \quad (3.111)
\end{aligned}$$

$$\begin{aligned}
& = \sum_m^{MO} \left\{ \frac{\partial U_{mi}^a}{\partial b} (mj|kl) + U_{mi}^a \frac{\partial(mj|kl)}{\partial b} \right. \\
& \quad + \frac{\partial U_{mj}^a}{\partial b} (im|kl) + U_{mj}^a \frac{\partial(im|kl)}{\partial b} \\
& \quad + \frac{\partial U_{mk}^a}{\partial b} (ij|ml) + U_{mk}^a \frac{\partial(ij|ml)}{\partial b} \\
& \quad \left. + \frac{\partial U_{ml}^a}{\partial b} (ij|km) + U_{ml}^a \frac{\partial(ij|km)}{\partial b} \right\} \\
& + \frac{\partial(ij|kl)^a}{\partial b} . \quad (3.112)
\end{aligned}$$

Relationships (3.14), (3.105) and (3.109) may then be employed to give

$$\begin{aligned}
\frac{\partial^2(ij|kl)}{\partial a \partial b} & = \sum_m^{MO} \left[\left(U_{mi}^{ab} - \sum_n^{MO} U_{mn}^b U_{ni}^a \right) (mj|kl) \right. \\
& \quad \left. + U_{mi}^a \left\{ \sum_n^{MO} \left[U_{nm}^b (nj|kl) + U_{nj}^b (mn|kl) \right] \right. \right. \\
& \quad \left. \left. + (ij|kl)^{ab} \right\} \right]
\end{aligned}$$

$$\begin{aligned}
& + U_{nk}^b(mj|nl) + U_{nl}^b(mj|kn) \Big] + (mj|kl)^b \Big\} \\
& + \left(U_{mj}^{ab} - \sum_n U_{mn}^b U_{nj}^a \right) (im|kl) \\
& + U_{mj}^a \left\{ \sum_n^{MO} \left[U_{ni}^b(nm|kl) + U_{nm}^b(in|kl) \right. \right. \\
& \left. \left. + U_{nk}^b(im|nl) + U_{nl}^b(im|kn) \right] + (im|kl)^b \right\} \\
& + \left(U_{mk}^{ab} - \sum_n^{MO} U_{mn}^b U_{nk}^a \right) (ij|ml) \\
& + U_{mk}^a \left\{ \sum_n^{MO} \left[U_{ni}^b(nj|ml) + U_{nj}^b(in|ml) \right. \right. \\
& \left. \left. + U_{nm}^b(ij|nl) + U_{nl}^b(ij|mn) \right] + (ij|ml)^b \right\} \\
& + \left(U_{ml}^{ab} - \sum_n^{MO} U_{mn}^b U_{nl}^a \right) (ij|km) \\
& + U_{ml}^a \left\{ \sum_n^{MO} \left[U_{ni}^b(nj|km) + U_{nj}^b(in|km) \right. \right. \\
& \left. \left. + U_{nk}^b(ij|nm) + U_{nm}^b(ij|kn) \right] + (ij|km)^b \right\} \\
& + \sum_m^{MO} \left\{ U_{mi}^b(mj|kl)^a + U_{mj}^b(im|kl)^a + U_{mk}^b(ij|ml)^a + U_{ml}^b(ij|km)^a \right\} \\
& + (ij|kl)^{ab} . \tag{3.113}
\end{aligned}$$

Equation (3.113) may then be simplified further to

$$\begin{aligned}
\frac{\partial^2(ij|kl)}{\partial a \partial b} & = \sum_m^{MO} \left(U_{mi}^{ab}(mj|kl) + U_{mj}^{ab}(im|kl) + U_{mk}^{ab}(ij|ml) + U_{ml}^{ab}(ij|km) \right) \\
& + \sum_m^{MO} \left(U_{mi}^a(mj|kl)^b + U_{mj}^a(im|kl)^b + U_{mk}^a(ij|ml)^b + U_{ml}^a(ij|km)^b \right. \\
& \quad \left. + U_{mi}^b(mj|kl)^a + U_{mj}^b(im|kl)^a + U_{mk}^b(ij|ml)^a + U_{ml}^b(ij|km)^a \right) \\
& + \sum_{mn}^{MO} \left[\left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mn|kl) + \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mj|nl) \right. \\
& \quad \left. + \left(U_{mj}^a U_{nl}^b + U_{mj}^b U_{nl}^a \right) (mj|kn) + \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (im|nl) \right. \\
& \quad \left. + \left(U_{mj}^a U_{nl}^b + U_{mj}^b U_{nl}^a \right) (im|kn) + \left(U_{mk}^a U_{nl}^b + U_{mk}^b U_{nl}^a \right) (ij|mn) \right]
\end{aligned}$$

$$+ (ij|kl)^{ab} \quad (3.114)$$

which equals eq. (3.101). The equality $\partial^2(ij|kl)/\partial a\partial b = \partial^2(ij|kl)/\partial b\partial a$ may be proved simply by taking the derivative of $\partial(ij|kl)/\partial b$ with respect to the variable "a".

3.10 The Derivatives of the Nuclear Repulsion Energy

As mentioned in Section 2.1, only the electronic part of the Hamiltonian and total wavefunction are considered in detail in this book. The contribution of the nuclear repulsion energy to the total energy of a system is given by

$$E_{nuc} = \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}} . \quad (3.115)$$

Although this term is constant at a fixed geometry, a geometrical perturbation changes the value of E_{nuc} . It is convenient to note the relationships

$$R_{AB}^2 = (X_A - X_B)^2 + (Y_A - Y_B)^2 + (Z_A - Z_B)^2 \quad (3.116)$$

and

$$\frac{\partial R_{AB}}{\partial X_A} = \frac{X_A - X_B}{R_{AB}} = - \frac{\partial R_{AB}}{\partial X_B} \quad (3.117)$$

for manipulating the derivatives of the nuclear repulsion energy.

3.10.1 The First Derivative of the Nuclear Repulsion Energy

The first derivative of E_{nuc} is obtained easily by differentiating eq. (3.115) with respect to a nuclear cartesian coordinate X_A ,

$$\frac{\partial E_{nuc}}{\partial X_A} = \frac{\partial}{\partial X_A} \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}} \quad (3.118)$$

$$= - \sum_{B \neq A}^N (X_A - X_B) \frac{Z_A Z_B}{R_{AB}^3} . \quad (3.119)$$

3.10.2 The Second Derivative of the Nuclear Repulsion Energy

There are four different types of second derivatives of the nuclear repulsion energy. They may be obtained by directly differentiating eq. (3.119) with respect to a second variable, X_A or X_B .

Type I

$$\frac{\partial^2 E_{nuc}}{\partial X_A^2} = \frac{\partial}{\partial X_A} \left(\frac{\partial E_{nuc}}{\partial X_A} \right) \quad (3.120)$$

$$= - \sum_{B \neq A}^N \frac{Z_A Z_B}{R_{AB}^3} + 3 \sum_{B \neq A}^N (X_A - X_B)^2 \frac{Z_A Z_B}{R_{AB}^5} \quad (3.121)$$

Type II

$$\frac{\partial^2 E_{nuc}}{\partial X_A \partial X_B} = \frac{\partial}{\partial X_B} \left(\frac{\partial E_{nuc}}{\partial X_A} \right) \quad (3.122)$$

$$= \frac{Z_A Z_B}{R_{AB}^3} - 3 (X_A - X_B)^2 \frac{Z_A Z_B}{R_{AB}^5} \quad (3.123)$$

Type III

$$\frac{\partial^2 E_{nuc}}{\partial X_A \partial Y_A} = \frac{\partial}{\partial Y_A} \left(\frac{\partial E_{nuc}}{\partial X_A} \right) \quad (3.124)$$

$$= 3 \sum_{B \neq A}^N (X_A - X_B)(Y_A - Y_B) \frac{Z_A Z_B}{R_{AB}^5} \quad (3.125)$$

Type IV

$$\frac{\partial^2 E_{nuc}}{\partial X_A \partial Y_B} = \frac{\partial}{\partial Y_B} \left(\frac{\partial E_{nuc}}{\partial X_A} \right) \quad (3.126)$$

$$= -3 (X_A - X_B)(Y_A - Y_B) \frac{Z_A Z_B}{R_{AB}^5} \quad (3.127)$$

The nuclear derivative should be added to the corresponding electronic part to obtain the total energy derivative.

References

1. J. Gerratt and I.M. Mills, *J. Chem. Phys.* **49**, 1719 (1968).
2. J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, *Int. J. Quantum Chem.* **S13**, 225 (1979).
3. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *Chem. Phys.* **103**, 227 (1986).
4. Y. Yamaguchi, M.J. Frisch, J.F. Gaw, H.F. Schaefer, and J.S. Binkley, *J. Chem. Phys.* **84**, 2262 (1986).

Chapter 4

Closed-Shell Self-Consistent-Field Wavefunctions

The quantum mechanical concepts and most elementary derivative quantities have been introduced in Chapters 2 and 3 and allow us to proceed to the simplest practical example of energy derivatives. Closed-shell self-consistent-field (CLSCF) wavefunctions are very frequently used in *ab initio* quantum chemistry. The electronic energy of the system is determined using only one set of doubly occupied orbitals. Although this single-configuration approximation is oversimplified in a quantum mechanical sense, it is well defined and accepted at least as a conceptual and computational starting point by most chemists. Indeed there are many chemical phenomena, e.g., equilibrium geometries, vibrational frequencies, and infrared intensities of various molecules, that have been explained quite successfully using such methods. In this chapter the energy expression for a closed-shell system is given first and then the Fock operator and the variational conditions are described. Starting from these basic concepts detailed derivations of the first and second derivatives with respect to nuclear perturbations (in terms of cartesian coordinates) are presented.

4.1 The SCF Energy

In restricted Hartree-Fock (RHF) theory, the electronic energy for a single configuration closed-shell SCF (CLSCF) wavefunction is [1]:

$$E_{elec} = 2 \sum_i^{d.o.} h_{ii} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj) - (ij|ij) \right\} . \quad (4.1)$$

h_{ii} are the one-electron integrals, and $(ii|jj)$ and $(ij|ij)$ are the Coulomb and exchange integrals in the MO basis. The summations are over doubly occupied (*d.o.*) orbitals. Alternatively the electronic energy may be expressed using one-electron integrals and closed-shell

orbital energies as

$$E_{elec} = \sum_i^{d.o.} (h_{ii} + \epsilon_i) , \quad (4.2)$$

where the orbital energies, ϵ_i , are defined by

$$\epsilon_i = h_{ii} + \sum_k^{d.o.} \left\{ 2(ij|kk) - (ik|ik) \right\} . \quad (4.3)$$

The total energy of the system at the SCF level is a sum of the electronic energy and the nuclear repulsion energy:

$$E_{SCF} = E_{elec} + E_{nuc} . \quad (4.4)$$

It is important to realize that the electronic energy is defined using *only* the doubly occupied orbitals. Only these doubly occupied orbitals are well defined physically in single-configuration Hartree-Fock theory. The virtual or unoccupied orbitals exist as eigenfunctions of the Fock operator (see next section) and are mathematically well defined but of limited value as far as the physical model is concerned.

4.2 The Closed-Shell Fock Operator and the Variational Conditions

In restricted Hartree-Fock (RHF) theory, the Fock operator for a single configuration closed-shell SCF wavefunction is [1]:

$$\mathbf{F} = \mathbf{h} + \sum_k^{d.o.} (2\mathbf{J}_k - \mathbf{K}_k) . \quad (4.5)$$

\mathbf{h} is the one-electron operator and \mathbf{J} and \mathbf{K} are the Coulomb and exchange operators. The Fock matrix elements involve a sum over doubly occupied (*d.o.*) orbitals

$$F_{ij} = \langle \phi_i | \mathbf{F} | \phi_j \rangle = h_{ij} + \sum_k^{d.o.} \left\{ 2(ij|kk) - (ik|jk) \right\} \quad (4.6)$$

where h_{ij} are the one-electron integrals, and $(ij|kk)$ and $(ik|jk)$ are the two-electron integrals in the MO basis. Using eq. (4.6), the variational conditions for the system are

$$F_{ij} = \delta_{ij} \epsilon_i \quad (4.7)$$

where δ_{ij} is the Kronecker delta function and ϵ_i are the orbital energies defined by eq. (4.3). According to the variational conditions (4.7), the CLSCF wavefunction has converged when the Fock matrix in the MO basis becomes diagonal. Each diagonal element is an orbital energy defined by eq. (4.3). It should be noted, however, that the choice of variational condition (4.7) is only possible for the CLSCF wavefunction with one Fock operator for all the closed-shell occupied orbitals. The expression of the variational conditions for an SCF wavefunction of more general form is given by the symmetric character of the Lagrangian matrix, as will be shown later.

4.3 The First Derivative of the Electronic Energy

Within the Born-Oppenheimer approximation [2] the nuclear repulsion energy and its derivatives are trivial to evaluate at a fixed geometry for the molecule under consideration and were described in Chapter 3. Therefore, only the electronic part of the SCF energy is considered here. An expression for the first derivative of the electronic energy of the system may be obtained by differentiating eq. (4.1) with respect to a cartesian nuclear coordinate “ a ”:

$$\frac{\partial E_{elec}}{\partial a} = 2 \sum_i^{d.o.} \frac{\partial h_{ii}}{\partial a} + \sum_{ij}^{d.o.} \left\{ 2 \frac{\partial(ii|jj)}{\partial a} - \frac{\partial(ij|ij)}{\partial a} \right\} . \quad (4.8)$$

Using the results of Sections 3.8 and 3.9 (or Appendix J) the derivative expressions for the relevant one- and two-electron MO integrals are:

$$\frac{\partial h_{ii}}{\partial a} = h_{ii}^a + 2 \sum_m^{all} U_{mi}^a h_{mi} \quad (4.9)$$

$$\frac{\partial(ii|jj)}{\partial a} = (ii|jj)^a + 2 \sum_m^{all} \left\{ U_{mi}^a (mi|jj) + U_{mj}^a (ii|mj) \right\} \quad (4.10)$$

$$\frac{\partial(ij|ij)}{\partial a} = (ij|ij)^a + 2 \sum_m^{all} \left\{ U_{mi}^a (mj|ij) + U_{mj}^a (im|ij) \right\} . \quad (4.11)$$

“all” implies a sum over both occupied and virtual molecular orbitals. Using eqs. (4.9) to (4.11), the derivative expression (4.8) may be expanded to yield

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{d.o.} \left\{ h_{ii}^a + 2 \sum_m^{all} U_{mi}^a h_{mi} \right\} \\ &+ \sum_{ij}^{d.o.} \left[2(ii|jj)^a + 4 \sum_m^{all} \left\{ U_{mi}^a (mi|jj) + U_{mj}^a (ii|mj) \right\} \right. \\ &\quad \left. - (ij|ij)^a - 2 \sum_m^{all} \left\{ U_{mi}^a (mj|ij) + U_{mj}^a (im|ij) \right\} \right] . \end{aligned} \quad (4.12)$$

This equation may be manipulated in the following manner,

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{d.o.} h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &+ 2 \sum_i^{d.o.} \sum_m^{all} U_{mi}^a h_{mi} + 2 \sum_j^{d.o.} \sum_m^{all} U_{mj}^a h_{mj} \\ &+ 4 \sum_{ij}^{d.o.} \sum_m^{all} U_{mi}^a (mi|jj) + 4 \sum_{ij}^{d.o.} \sum_m^{all} U_{mj}^a (mj|ii) \end{aligned}$$

$$- 2 \sum_{ij}^{\text{d.o.}} \sum_m^{\text{all}} U_{mi}^a(mj|ij) - 2 \sum_{ij}^{\text{d.o.}} \sum_m^{\text{all}} U_{mj}^a(mi|ji) \quad (4.13)$$

$$\begin{aligned} &= 2 \sum_i^{\text{d.o.}} h_{ii}^a + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &+ 2 \sum_i^{\text{d.o.}} \sum_m^{\text{all}} U_{mi}^a \left[h_{mi} + \sum_j^{\text{d.o.}} \left\{ 2(mi|jj) - (mj|ij) \right\} \right] \\ &+ 2 \sum_j^{\text{d.o.}} \sum_m^{\text{all}} U_{mj}^a \left[h_{mj} + \sum_i^{\text{d.o.}} \left\{ 2(mj|ii) - (mi|ji) \right\} \right] . \end{aligned} \quad (4.14)$$

The definition of the Fock matrix, (4.6), can be used to simplify the terms in square brackets:

$$\begin{aligned} \frac{\partial E_{\text{elec}}}{\partial a} &= 2 \sum_i^{\text{d.o.}} h_{ii}^a + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &+ 2 \sum_i^{\text{d.o.}} \sum_m^{\text{all}} U_{mi}^a F_{mi} + 2 \sum_j^{\text{d.o.}} \sum_m^{\text{all}} U_{mj}^a F_{mj} . \end{aligned} \quad (4.15)$$

The equivalence of the summations over i or j then yields:

$$\begin{aligned} \frac{\partial E_{\text{elec}}}{\partial a} &= 2 \sum_i^{\text{d.o.}} h_{ii}^a + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &+ 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^a F_{ij} . \end{aligned} \quad (4.16)$$

Equation (4.16) is applicable to any CLSCF wavefunction whose Fock matrix is constructed using eq. (4.6).

The third term in equation (4.16) may be simplified further due to the diagonal nature of the Fock matrix (4.7):

$$\begin{aligned} \frac{\partial E_{\text{elec}}}{\partial a} &= 2 \sum_i^{\text{d.o.}} h_{ii}^a + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &+ 4 \sum_i^{\text{d.o.}} U_{ii}^a \epsilon_i . \end{aligned} \quad (4.17)$$

As mentioned in Section 3.7, the molecular orbitals are orthonormal

$$S_{ij} = \delta_{ij} . \quad (4.18)$$

Recalling one of the most important results of Section 3.7, the first derivative of equation (4.18) is

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 . \quad (4.19)$$

The diagonal terms satisfy the even simpler relationship

$$U_{ii}^a = -\frac{1}{2} S_{ii}^a \quad . \quad (4.20)$$

Using equation (4.20), the final expression for the first derivative of the electronic energy becomes:

$$\frac{\partial E_{elec}}{\partial a} = 2 \sum_i^{d.o.} h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} - 2 \sum_i^{d.o.} S_{ii}^a \epsilon_i \quad . \quad (4.21)$$

One should realize that the first derivative expression (4.21) does not require the explicit evaluation of the changes in the MO coefficients (the U^a defined in Section 3.2). Thus the coupled perturbed Hartree-Fock equations need not be solved if only first derivatives of the CLSCF wavefunction are of interest. Such a simplification is not possible for the second or higher derivatives as will be discussed in Section 4.6.

4.4 The Evaluation of the Energy First Derivative

In the practical evaluation of the first derivative, expression (4.21) usually is reduced to the AO basis. The first derivative is rewritten accordingly as:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{d.o.} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^i \frac{\partial h_{\mu\nu}}{\partial a} \\ &+ \sum_{ij}^{d.o.} \sum_{\mu\nu\rho\sigma}^{AO} \left\{ 2C_\mu^i C_\nu^i C_\rho^j C_\sigma^j \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} - C_\mu^i C_\nu^j C_\rho^i C_\sigma^j \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right\} \\ &- 2 \sum_i^{d.o.} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^i \epsilon_i \frac{\partial S_{\mu\nu}}{\partial a} \quad . \end{aligned} \quad (4.22)$$

Defining the density matrix D by its elements,

$$D_{\mu\nu} = \sum_i^{d.o.} C_\mu^i C_\nu^i \quad (4.23)$$

and the “energy weighted” density matrix W by its elements,

$$W_{\mu\nu} = \sum_i^{d.o.} C_\mu^i C_\nu^i \epsilon_i \quad (4.24)$$

eq. (4.22) becomes

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_{\mu\nu}^{AO} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} + \sum_{\mu\nu\rho\sigma}^{AO} \left\{ 2D_{\mu\nu} D_{\rho\sigma} - D_{\mu\rho} D_{\nu\sigma} \right\} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ &- 2 \sum_{\mu\nu}^{AO} W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} \quad . \end{aligned} \quad (4.25)$$

In practice the derivative integrals, $\frac{\partial h_{\mu\nu}}{\partial a}$, $\frac{\partial S_{\mu\nu}}{\partial a}$, and $\frac{\partial(\mu\nu|\rho\sigma)}{\partial a}$, are evaluated only for unique combinations of the AOs ($\mu \geq \nu$ and $\rho \geq \sigma$) in order to minimize computation.

Thus, the first derivative of the electronic energy is given in an efficiently programmable form by

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} = & 4 \sum_{\mu \geq \nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} \\ & + 4 \sum_{\substack{\mu \geq \nu, \rho \geq \sigma \\ \mu\nu \geq \rho\sigma}}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) \left(1 - \frac{\delta_{\rho\sigma}}{2} \right) \left(1 - \frac{\delta_{\mu\nu, \rho\sigma}}{2} \right) \\ & \times \left\{ 4 D_{\mu\nu} D_{\rho\sigma} - D_{\mu\rho} D_{\nu\sigma} - D_{\mu\sigma} D_{\nu\rho} \right\} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ & - 4 \sum_{\mu \geq \nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a}, \end{aligned} \quad (4.26)$$

in which $\delta_{\mu\nu}$ is again the Kronecker delta function. In the second term of this equation the summations run over the indices that satisfy the conditions $\mu\nu \geq \rho\sigma$, where $\mu\nu = \frac{1}{2} \mu(\mu-1) + \nu$ and $\rho\sigma = \frac{1}{2} \rho(\rho-1) + \sigma$.

4.5 The First Derivative of the Fock Matrix

At this point a first derivative expression of the elements of the Fock matrix will be obtained for future use. Differentiation of eq. (4.6) with respect to a cartesian coordinate “ a ”

$$\frac{\partial F_{ij}}{\partial a} = \frac{\partial h_{ij}}{\partial a} + \sum_k^{\text{d.o.}} \left\{ 2 \frac{\partial(ij|kk)}{\partial a} - \frac{\partial(ik|jk)}{\partial a} \right\} \quad (4.27)$$

is required. The relevant derivative expressions for the one- and two-electron MO integrals are given in Sections 3.8 and 3.9 (or Appendix J) as,

$$\frac{\partial h_{ij}}{\partial a} = h_{ij}^a + \sum_m^{\text{all}} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \quad (4.28)$$

$$\begin{aligned} \frac{\partial(ij|kk)}{\partial a} = & (ij|kk)^a + \sum_m^{\text{all}} \left\{ U_{mi}^a (mj|kk) + U_{mj}^a (im|kk) \right. \\ & \left. + 2U_{mk}^a (ij|mk) \right\} \end{aligned} \quad (4.29)$$

and

$$\frac{\partial(ik|jk)}{\partial a} = (ik|jk)^a + \sum_m^{\text{all}} \left\{ U_{mi}^a (mk|jk) + U_{mk}^a (im|jk) \right.$$

$$+ U_{mj}^a(i k | m k) + U_{mk}^a(i k | j m) \} . \quad (4.30)$$

Inserting eqs. (4.28) to (4.30) into eq. (4.27) one obtains

$$\begin{aligned} \frac{\partial F_{ij}}{\partial a} &= h_{ij}^a + \sum_m^{all} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \\ &+ \sum_k^{d.o.} \left[2(i j | k k)^a + 2 \sum_m^{all} \left\{ U_{mi}^a(m j | k k) + U_{mj}^a(i m | k k) + 2U_{mk}^a(i j | m k) \right\} \right. \\ &\quad \left. - (i k | j k)^a - \sum_m^{all} \left\{ U_{mi}^a(m k | j k) + U_{mk}^a(i m | j k) \right. \right. \\ &\quad \left. \left. + U_{mj}^a(i k | m k) + U_{mk}^a(i k | j m) \right\} \right] \end{aligned} \quad (4.31)$$

$$\begin{aligned} &= h_{ij}^a + \sum_k^{d.o.} \left\{ 2(i j | k k)^a - (i k | j k)^a \right\} \\ &+ \sum_m^{all} U_{mi}^a \left[h_{mj} + \sum_k^{d.o.} \left\{ 2(m j | k k) - (m k | j k) \right\} \right] \\ &+ \sum_m^{all} U_{mj}^a \left[h_{im} + \sum_k^{d.o.} \left\{ 2(i m | k k) - (i k | m k) \right\} \right] \\ &+ \sum_m^{all} \sum_k^{d.o.} U_{mk}^a \left\{ 4(i j | m k) - (i m | j k) - (i k | j m) \right\} . \end{aligned} \quad (4.32)$$

Using the definition of the Fock matrix in eq. (4.6), this equation becomes

$$\begin{aligned} \frac{\partial F_{ij}}{\partial a} &= F_{ij}^a + \sum_m^{all} U_{mi}^a F_{mj} + \sum_m^{all} U_{mj}^a F_{im} \\ &+ \sum_m^{all} \sum_k^{d.o.} U_{mk}^a \left\{ 4(i j | m k) - (i m | j k) - (i k | j m) \right\} \end{aligned} \quad (4.33)$$

$$\begin{aligned} &= F_{ij}^a + \sum_k^{all} U_{ki}^a F_{kj} + \sum_k^{all} U_{kj}^a F_{ik} \\ &+ \sum_k^{all} \sum_l^{d.o.} U_{kl}^a \left\{ 4(i j | k l) - (i k | j l) - (i l | j k) \right\} \end{aligned} \quad (4.34)$$

$$= F_{ij}^a + \sum_k^{all} \left(U_{ki}^a F_{kj} + U_{kj}^a F_{ik} \right) + \sum_k^{all} \sum_l^{d.o.} U_{kl}^a A_{ij,kl} . \quad (4.35)$$

The skeleton (core) first derivative Fock matrix appearing in this equation is defined by

$$F_{ij}^a = h_{ij}^a + \sum_k^{d.o.} \left\{ 2(i j | k k)^a - (i k | j k)^a \right\} \quad (4.36)$$

and the A matrix by

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) \quad . \quad (4.37)$$

4.6 The Second Derivative of the Electronic Energy

An expression for the second derivative of the electronic energy is obtained by differentiating eq. (4.16) with respect to a second cartesian coordinate “ b ”,

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial E_{elec}}{\partial a} \right) \quad (4.38)$$

$$\begin{aligned} &= 2 \sum_i^{d.o.} \frac{\partial h_{ii}^a}{\partial b} + \sum_{ij}^{d.o.} \left\{ 2 \frac{\partial(ii|jj)^a}{\partial b} - \frac{\partial(ij|ij)^a}{\partial b} \right\} \\ &+ 4 \sum_i^{all} \sum_j^{d.o.} \left\{ \frac{\partial U_{ij}^a}{\partial b} F_{ij} + U_{ij}^a \frac{\partial F_{ij}}{\partial b} \right\} \quad . \end{aligned} \quad (4.39)$$

The derivative expressions for the one- and two-electron skeleton (core) derivative integrals were given in Sections 3.8 and 3.9 (or Appendix K) as,

$$\frac{\partial h_{ii}^a}{\partial b} = h_{ii}^{ab} + 2 \sum_m^{all} U_{mi}^b h_{mi}^a \quad (4.40)$$

$$\frac{\partial(ii|jj)^a}{\partial b} = (ii|jj)^{ab} + 2 \sum_m^{all} \left\{ U_{mi}^b (mi|jj)^a + U_{mj}^b (ii|mj)^a \right\} \quad (4.41)$$

$$\frac{\partial(ij|ij)^a}{\partial b} = (ij|ij)^{ab} + 2 \sum_m^{all} \left\{ U_{mi}^b (mj|ij)^a + U_{mj}^b (im|ij)^a \right\} \quad . \quad (4.42)$$

Using eqs. (4.40) to (4.42), the first two terms in eq. (4.39) may be written as

$$\begin{aligned} &2 \sum_i^{d.o.} \frac{\partial h_{ii}^a}{\partial b} + \sum_{ij}^{d.o.} \left\{ 2 \frac{\partial(ii|jj)^a}{\partial b} - \frac{\partial(ij|ij)^a}{\partial b} \right\} \\ &= 2 \sum_i^{d.o.} \left\{ h_{ii}^{ab} + 2 \sum_m^{all} U_{mi}^b h_{mi}^a \right\} \\ &+ \sum_{ij}^{d.o.} \left[2(ii|jj)^{ab} + 4 \sum_m^{all} \left\{ U_{mi}^b (mi|jj)^a + U_{mj}^b (ii|mj)^a \right\} \right. \\ &\quad \left. - (ij|ij)^{ab} - 2 \sum_m^{all} \left\{ U_{mi}^b (mj|ij)^a + U_{mj}^b (im|ij)^a \right\} \right] \quad (4.43) \\ &= 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_i^{\text{d.o.}} \sum_m^{\text{all}} U_{mi}^b \left[h_{mi}^a + \sum_j^{\text{d.o.}} \left\{ 2(mi|jj)^a - (mj|ij)^a \right\} \right] \\
& + 2 \sum_j^{\text{d.o.}} \sum_m^{\text{all}} U_{mj}^b \left[h_{mj}^a + \sum_i^{\text{d.o.}} \left\{ 2(mj|ii)^a - (mi|ji)^a \right\} \right]
\end{aligned} \tag{4.44}$$

$$\begin{aligned}
& = 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
& + 2 \sum_i^{\text{d.o.}} \sum_m^{\text{all}} U_{mi}^b F_{mi}^a + 2 \sum_j^{\text{d.o.}} \sum_m^{\text{all}} U_{mj}^b F_{mj}^a
\end{aligned} \tag{4.45}$$

$$\begin{aligned}
& = 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^b F_{ij}^a .
\end{aligned} \tag{4.46}$$

In deriving eq. (4.46), we use the definition of the skeleton derivative Fock matrix, eq. (4.36), and the fact that it is immaterial whether the summations run over i or j . The third term in eq. (4.39) may be manipulated using results of Section 3.3 and eq. (4.35) to give

$$\begin{aligned}
& 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \left\{ \frac{\partial U_{ij}^a}{\partial b} F_{ij} + U_{ij}^a \frac{\partial F_{ij}}{\partial b} \right\} \\
& = 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \left(U_{ij}^{ab} - \sum_k^{\text{all}} U_{ik}^b U_{kj}^a \right) F_{ij} \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^a \left[F_{ij}^b + \sum_k^{\text{all}} \left(U_{ki}^b F_{kj} + U_{kj}^b F_{ik} \right) + \sum_l^{\text{all d.o.}} U_{kl}^b A_{ij,kl} \right]
\end{aligned} \tag{4.47}$$

$$\begin{aligned}
& = 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^{ab} F_{ij} + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^a F_{ij}^b \\
& + 4 \sum_{ij}^{\text{all}} F_{ij} \sum_k^{\text{d.o.}} U_{ik}^a U_{jk}^b \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{all d.o.}} \sum_k^{\text{all d.o.}} \sum_l^{\text{all d.o.}} U_{ij}^a U_{kl}^b A_{ij,kl} .
\end{aligned} \tag{4.48}$$

Combining equations (4.46) and (4.48), the expression for the second derivative of the electronic energy becomes

$$\begin{aligned}
\frac{\partial^2 E_{\text{elec}}}{\partial a \partial b} & = 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^{ab} F_{ij}
\end{aligned}$$

$$\begin{aligned}
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
& + 4 \sum_{ij}^{\text{all}} F_{ij} \sum_k^{\text{d.o.}} U_{ik}^a U_{jk}^b \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} U_{ij}^a U_{kl}^b A_{ij,kl} .
\end{aligned} \tag{4.49}$$

Equation (4.49) involves the second derivatives of the MO coefficients, and this equation is applicable to any CLSCF wavefunction whose Fock matrix is constructed from eq. (4.6).

In order to eliminate U_{ij}^{ab} in eq. (4.49), the second derivative form of the orthonormality condition of the molecular orbitals described in Section 3.7 (or Appendix L) is used,

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \tag{4.50}$$

where ξ_{ij}^{ab} is defined by

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{\text{all}} \left\{ U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right\} . \tag{4.51}$$

It is evident that the diagonal terms of the U^{ab} matrix satisfy

$$U_{ii}^{ab} = -\frac{1}{2} \xi_{ii}^{ab} \tag{4.52}$$

Using the relationships (4.7) and (4.52), a final expression for the second derivative of the electronic energy is found:

$$\begin{aligned}
\frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
&- 2 \sum_i^{\text{d.o.}} \xi_{ii}^{ab} \epsilon_i \\
&+ 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
&+ 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^a U_{ij}^b \epsilon_i \\
&+ 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} U_{ij}^a U_{kl}^b A_{ij,kl} \\
&= 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\}
\end{aligned} \tag{4.53}$$

$$\begin{aligned}
& - 2 \sum_i^{d.o.} S_{ii}^{ab} \epsilon_i - 2 \sum_i^{d.o.} \eta_{ii}^{ab} \epsilon_i \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
& + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^a U_{ij}^b \epsilon_i \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} U_{ij}^a U_{kl}^b \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} . \quad (4.54)
\end{aligned}$$

The η^{ab} matrices in eq. (4.54) were defined in Section 3.7 by their elements:

$$\eta_{ij}^{ab} = \sum_m^{all} \left\{ U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right\} . \quad (4.55)$$

Equation (4.54) is in a form that is symmetric with respect to the differential variables "a" and "b".

For the evaluation of the second derivative of the electronic energy, information about the changes in the molecular orbitals due to perturbations U^a is required as seen clearly in eq. (4.54). The elements of the U^a matrices may be readily obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations, which will be discussed in detail in Chapter 10.

4.7 An Alternative Derivation of the Second Derivative of the Electronic Energy

Another expression for the second derivative of the electronic energy of the system can be obtained by directly differentiating eq. (4.1) with respect to two cartesian coordinates "a" and "b",

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = 2 \sum_i^{d.o.} \frac{\partial^2 h_{ii}}{\partial a \partial b} + \sum_{ij}^{d.o.} \left\{ 2 \frac{\partial^2(ii|jj)}{\partial a \partial b} - \frac{\partial^2(ij|ij)}{\partial a \partial b} \right\} . \quad (4.56)$$

The relevant second derivative expressions for the one- and two-electron integrals were given in Sections 3.8 and 3.9 (or Appendix L) as,

$$\begin{aligned}
\frac{\partial^2 h_{ii}}{\partial a \partial b} &= h_{ii}^{ab} + 2 \sum_m^{all} U_{mi}^{ab} h_{mi} \\
&+ 2 \sum_m^{all} \left(U_{mi}^a h_{mi}^b + U_{mi}^b h_{mi}^a \right) + 2 \sum_{mn}^{all} U_{mi}^a U_{ni}^b h_{mn} , \quad (4.57)
\end{aligned}$$

$$\frac{\partial^2(ii|jj)}{\partial a \partial b} = (ii|jj)^{ab} + 2 \sum_m^{all} \left(U_{mi}^{ab}(mi|jj) + U_{mj}^{ab}(ii|mj) \right)$$

$$\begin{aligned}
& + 2 \sum_m^{\text{all}} \left(U_{mi}^a (mi|jj)^b + U_{mj}^a (ii|mj)^b + U_{mi}^b (mi|jj)^a + U_{mj}^b (ii|mj)^a \right) \\
& + 2 \sum_{mn}^{\text{all}} U_{mi}^a U_{ni}^b (mn|jj) + 2 \sum_{mn}^{\text{all}} U_{mj}^a U_{nj}^b (ii|mn) \\
& + 4 \sum_{mn}^{\text{all}} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (im|jn) ,
\end{aligned} \tag{4.58}$$

and

$$\begin{aligned}
\frac{\partial^2 (ij|ij)}{\partial a \partial b} & = (ij|ij)^{ab} + 2 \sum_m^{\text{all}} \left(U_{mi}^{ab} (mj|ij) + U_{mj}^{ab} (im|ij) \right) \\
& + 2 \sum_m^{\text{all}} \left(U_{mi}^a (mj|ij)^b + U_{mj}^a (im|ij)^b + U_{mi}^b (mj|ij)^a + U_{mj}^b (im|ij)^a \right) \\
& + 4 \sum_{mn}^{\text{all}} U_{mi}^a U_{nj}^b (mn|ij) \\
& + 2 \sum_{mn}^{\text{all}} U_{mi}^a U_{ni}^b (mj|nj) + 2 \sum_{mn}^{\text{all}} U_{mj}^a U_{nj}^b (im|in) \\
& + 2 \sum_{mn}^{\text{all}} U_{mi}^a U_{nj}^b (mj|in) + 2 \sum_{mn}^{\text{all}} U_{mj}^a U_{ni}^b (im|nj) .
\end{aligned} \tag{4.59}$$

Using eqs. (4.57) to (4.59), the second derivative expression (4.56) is then:

$$\begin{aligned}
\frac{\partial^2 E_{\text{elec}}}{\partial a \partial b} & = 2 \sum_i^{\text{d.o.}} \left[h_{ii}^{ab} + 2 \sum_m^{\text{all}} U_{mi}^{ab} h_{mi} \right. \\
& \quad \left. + 2 \sum_m^{\text{all}} \left(U_{mi}^a h_{mi}^b + U_{mi}^b h_{mi}^a \right) + 2 \sum_{mn}^{\text{all}} U_{mi}^a U_{ni}^b h_{mn} \right] \\
& + 2 \sum_{ij}^{\text{d.o.}} \left[(ii|jj)^{ab} + 2 \sum_m^{\text{all}} \left(U_{mi}^{ab} (mi|jj) + U_{mj}^{ab} (ii|mj) \right) \right. \\
& \quad \left. + 2 \sum_m^{\text{all}} \left(U_{mi}^a (mi|jj)^b + U_{mj}^a (ii|mj)^b + U_{mi}^b (mi|jj)^a + U_{mj}^b (ii|mj)^a \right) \right. \\
& \quad \left. + 2 \sum_{mn}^{\text{all}} U_{mi}^a U_{ni}^b (mn|jj) + 2 \sum_{mn}^{\text{all}} U_{mj}^a U_{nj}^b (ii|mn) \right. \\
& \quad \left. + 4 \sum_{mn}^{\text{all}} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (im|jn) \right] \\
& - \sum_{ij}^{\text{d.o.}} \left[(ij|ij)^{ab} + 2 \sum_m^{\text{all}} \left(U_{mi}^{ab} (mj|ij) + U_{mj}^{ab} (im|ij) \right) \right. \\
& \quad \left. + 2 \sum_m^{\text{all}} \left(U_{mi}^a (mj|ij)^b + U_{mj}^a (im|ij)^b + U_{mi}^b (mj|ij)^a + U_{mj}^b (im|ij)^a \right) \right]
\end{aligned}$$

$$\begin{aligned}
& + 4 \sum_{mn}^{all} U_{mi}^a U_{nj}^b (mn|ij) \\
& + 2 \sum_{mn}^{all} U_{mi}^a U_{ni}^b (mj|nj) + 2 \sum_{mn}^{all} U_{mj}^a U_{nj}^b (im|in) \\
& + 2 \sum_{mn}^{all} U_{mi}^a U_{nj}^b (mj|in) + 2 \sum_{mn}^{all} U_{mj}^a U_{ni}^b (im|nj) \Big] \\
= & 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
& + 2 \sum_i^{d.o.} \sum_m^{all} U_{mi}^{ab} \left[h_{mi} + \sum_j^{d.o.} \left\{ 2(mi|jj) - (mj|ij) \right\} \right] \\
& + 2 \sum_j^{d.o.} \sum_m^{all} U_{mj}^{ab} \left[h_{mj} + \sum_i^{d.o.} \left\{ 2(mj|ii) - (mi|ji) \right\} \right] \\
& + 2 \sum_i^{d.o.} \sum_m^{all} U_{mi}^b \left[h_{mi}^a + \sum_j^{d.o.} \left\{ 2(mi|jj)^a - (mj|ij)^a \right\} \right] \\
& + 2 \sum_j^{d.o.} \sum_m^{all} U_{mj}^b \left[h_{mj}^a + \sum_i^{d.o.} \left\{ 2(mj|ii)^a - (mi|ji)^a \right\} \right] \\
& + 2 \sum_i^{d.o.} \sum_m^{all} U_{mi}^a \left[h_{mi}^b + \sum_j^{d.o.} \left\{ 2(mi|jj)^b - (mj|ij)^b \right\} \right] \\
& + 2 \sum_j^{d.o.} \sum_m^{all} U_{mj}^a \left[h_{mj}^b + \sum_i^{d.o.} \left\{ 2(mj|ii)^b - (mi|ji)^b \right\} \right] \\
& + 2 \sum_i^{d.o.} \sum_{mn}^{all} U_{mi}^a U_{ni}^b \left[h_{mn} + \sum_j^{d.o.} \left\{ 2(mn|jj) - (mj|nj) \right\} \right] \\
& + 2 \sum_j^{d.o.} \sum_{mn}^{all} U_{mj}^a U_{ni}^b \left[h_{mn} + \sum_i^{d.o.} \left\{ 2(mn|ii) - (mi|ni) \right\} \right] \\
& + 4 \sum_{ij}^{d.o.} \sum_{mn}^{all} U_{mi}^a U_{nj}^b \left[4(im|jn) - (ij|mn) - (in|jm) \right]
\end{aligned} \tag{4.61}$$

The definitions of the F , F^a , and A matrices (eqs. (4.6), (4.36), and (4.37)) may be employed to give:

$$\begin{aligned}
\frac{\partial^2 E_{elec}}{\partial a \partial b} = & 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
& + 2 \sum_i^{d.o.} \sum_m^{all} U_{mi}^{ab} F_{mi} + 2 \sum_j^{d.o.} \sum_m^{all} U_{mj}^{ab} F_{mj}
\end{aligned}$$

$$\begin{aligned}
& + 2 \sum_i^{\text{d.o.}} \sum_m^{\text{all}} U_{mi}^b F_{mi}^a + 2 \sum_j^{\text{d.o.}} \sum_m^{\text{all}} U_{mj}^b F_{mj}^a \\
& + 2 \sum_i^{\text{d.o.}} \sum_m^{\text{all}} U_{mi}^a F_{mi}^b + 2 \sum_j^{\text{d.o.}} \sum_m^{\text{all}} U_{mj}^a F_{mj}^b \\
& + 2 \sum_i^{\text{d.o.}} \sum_{mn}^{\text{all}} U_{mi}^a U_{ni}^b F_{mn} + 2 \sum_j^{\text{d.o.}} \sum_{mn}^{\text{all}} U_{mj}^a U_{nj}^b F_{mn} \\
& + 4 \sum_{ij}^{\text{d.o.}} \sum_{mn}^{\text{all}} U_{mi}^a U_{nj}^b A_{im,jn} \\
& = 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\}
\end{aligned} \tag{4.62}$$

$$\begin{aligned}
& + 4 \sum_i^{\text{all}} \sum_j^{\text{d.o.}} U_{ij}^{ab} F_{ij} \\
& + 4 \sum_i^{\text{all}} \sum_j^{\text{d.o.}} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
& + 4 \sum_{ij}^{\text{all}} F_{ij} \sum_k^{\text{d.o.}} U_{ik}^a U_{jk}^b \\
& + 4 \sum_i^{\text{all}} \sum_j^{\text{d.o.}} \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{ij}^a U_{kl}^b A_{ij,kl} .
\end{aligned} \tag{4.63}$$

Equation (4.63) is equivalent to eq. (4.49) which was derived in two steps in the preceding section.

References

1. C.C.J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
2. M. Born and J.R. Oppenheimer, Ann. Physik **84**, 457 (1927).

Suggested Reading

1. P. Pulay, Mol. Phys. **17**, 197 (1969).
2. H.B. Schlegel, S. Wolfe, and F. Bernardi, J. Chem. Phys. **63**, 3632 (1975).
3. P. Pulay, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 4, p.153 (1977).
4. A. Komornicki, K. Ishida, K. Morokuma, R. Ditchfield, and M. Conrad, Chem. Phys. Lett. **45**, 595 (1977).

5. M. Dupuis and H.F. King, *J. Chem. Phys.* **68**, 3998 (1978).
6. J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, *Int. J. Quantum Chem.* **S13**, 225 (1979).
7. T. Takada, M. Dupuis, and H.F. King, *J. Chem. Phys.* **75**, 332 (1981).
8. P. Saxe, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 5647 (1982).

Chapter 5

General Restricted Open-Shell Self-Consistent-Field Wavefunctions

An open-shell wavefunction, which is described by a single determinant (or two determinants for the open-shell singlet case) and is an eigenfunction of the square of the total spin angular momentum operator (S^2), is termed a general restricted open-shell SCF (GRSCF) wavefunction. This chapter extends derivative SCF theory to such general restricted open-shell systems. The closed-shell system treated thus far may be considered as a special case of general restricted open-shell SCF theory. Once an explicit energy expression and the necessary coupling constants are given, the formalism is applicable to almost any single configuration wavefunction.

5.1 The SCF Energy

Within the framework of RHF theory, the electronic energy for a single-configuration restricted open-shell SCF wavefunction is [1-3]:

$$E_{elec} = 2 \sum_i^{all} f_i h_{ii} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} . \quad (5.1)$$

f_i is the occupation number of the i th molecular orbital, and α_{ij} and β_{ij} are coupling constants unique to the i th and j th MOs. The term “*all*” implies a sum over all occupied and virtual (unoccupied) molecular orbitals. The total SCF energy of the system is

$$E_{SCF} = E_{elec} + E_{nuc} . \quad (5.2)$$

The explicit electronic energy expressions and the coupling constants for the three most

frequently encountered cases are:

A. Closed-shell:

$$E_{elec} = 2 \sum_k^{d.o.} h_{kk} + \sum_{kl}^{d.o.} \{2(kk|ll) - (kl|kl)\} , \quad (5.3)$$

where *d.o.* denotes doubly occupied orbitals.

$$f_i = \begin{matrix} \text{closed} \\ \text{virtual} \end{matrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} , \quad (5.4)$$

$$\alpha_{ij} = \begin{matrix} \text{closed} \\ \text{virtual} \end{matrix} \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} , \quad (5.5)$$

and

$$\beta_{ij} = \begin{matrix} \text{closed} \\ \text{virtual} \end{matrix} \begin{bmatrix} -1 & 0 \\ 0 & 0 \end{bmatrix} . \quad (5.6)$$

B. High-spin open-shell: The doublet, triplet, and quartet states possessing unpaired electrons with parallel spins are the most common examples of this case.

$$\begin{aligned} E_{elec} = & 2 \sum_k^{d.o.} h_{kk} + \sum_m^{h.o.} h_{mm} \\ & + \sum_{kl}^{d.o.} \{2(kk|ll) - (kl|kl)\} \\ & + \sum_k^{d.o.} \sum_m^{h.o.} \{2(kk|mm) - (km|km)\} \\ & + \frac{1}{2} \sum_{mn}^{h.o.} \{(mm|nn) - (mn|mn)\} , \end{aligned} \quad (5.7)$$

where *h.o.* denotes singly occupied orbitals.

$$f_i = \begin{matrix} \text{closed} \\ \text{open} \\ \text{virtual} \end{matrix} \begin{bmatrix} 1 \\ 1/2 \\ 0 \end{bmatrix} , \quad (5.8)$$

$$\alpha_{ij} = \begin{matrix} \text{closed} \\ \text{open} \\ \text{virtual} \end{matrix} \begin{bmatrix} 2 & 1 & 0 \\ 1 & 1/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} , \quad (5.9)$$

and

$$\beta_{ij} = \begin{matrix} \text{closed} \\ \text{open} \\ \text{virtual} \end{matrix} \begin{bmatrix} -1 & -1/2 & 0 \\ -1/2 & -1/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} . \quad (5.10)$$

C. Open-shell singlet:

$$\begin{aligned}
 E_{elec} = & 2 \sum_k^{d.o.} h_{kk} + h_{mm} + h_{nn} \\
 & + \sum_{kl}^{d.o.} \left\{ 2(kk|ll) - (kl|kl) \right\} \\
 & + \sum_k^{d.o.} \left\{ 2(kk|mm) - (km|km) \right\} + \sum_k^{d.o.} \left\{ 2(kk|nn) - (kn|kn) \right\} \\
 & + (mm|nn) + (mn|mn) ,
 \end{aligned} \tag{5.11}$$

where m and n are singly occupied orbitals possessing electrons with α and β spin functions, respectively.

$$f_i = \begin{array}{l} \text{closed} \\ \text{alpha} \\ \text{beta} \\ \text{virtual} \end{array} \begin{bmatrix} 1 \\ 1/2 \\ 1/2 \\ 0 \end{bmatrix} , \tag{5.12}$$

$$\alpha_{ij} = \begin{array}{l} \text{closed} \\ \text{alpha} \\ \text{beta} \\ \text{virtual} \end{array} \begin{bmatrix} 2 & 1 & 1 & 0 \\ 1 & 1/2 & 1/2 & 0 \\ 1 & 1/2 & 1/2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} , \tag{5.13}$$

and

$$\beta_{ij} = \begin{array}{l} \text{closed} \\ \text{alpha} \\ \text{beta} \\ \text{virtual} \end{array} \begin{bmatrix} -1 & -1/2 & -1/2 & 0 \\ -1/2 & -1/2 & 1/2 & 0 \\ -1/2 & 1/2 & -1/2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} . \tag{5.14}$$

The above three cases are the most frequently used wavefunctions. However, eq. (5.1) is generally applicable to single-configuration wavefunctions.

5.2 The Generalized Fock Operator and the Variational Conditions

Within the framework of RHF theory, the generalized Fock operator for a single-configuration SCF wavefunction is [1-3]:

$$\mathbf{F}_i = f_i \mathbf{h} + \sum_l^{all} \left(\alpha_{il} \mathbf{J}_l + \beta_{il} \mathbf{K}_l \right) . \tag{5.15}$$

\mathbf{h} is the one-electron operator, while \mathbf{J}_l and \mathbf{K}_l are the Coulomb and exchange operators, respectively. The Lagrangian matrix ϵ was described in Section 2.5:

$$\epsilon_{ij} = \langle \phi_i | \mathbf{F}_i | \phi_j \rangle = f_i h_{ij} + \sum_l^{all} \left\{ \alpha_{il} (ij|ll) + \beta_{il} (il|jl) \right\} . \tag{5.16}$$

The RHF variational conditions for the system become

$$\epsilon_{ij} - \epsilon_{ji} = 0 . \quad (5.17)$$

According to these variational conditions, the general restricted open-shell SCF (GRSCF) procedure has converged when the Lagrangian matrix in the MO basis becomes symmetric. In contrast to the simpler closed-shell case, the “orbital energies” are not uniquely defined for the open-shell system with more than one type of occupied orbital.

When an explicit energy expression and the appropriate set of coupling constants are known, all the results of this chapter are applicable. It is important to realize that the Fock operator is defined explicitly for the virtual (unoccupied) orbitals as well, although the coupling constants involving these virtual orbitals are all zero.

5.3 The First Derivative of the Electronic Energy

An expression for the first derivative of the general restricted open-shell Hartree-Fock electronic energy is obtained by differentiating eq. (5.1) with respect to a cartesian coordinate “a” in a similar manner to that for the closed-shell SCF wavefunction in Chapter 4

$$\frac{\partial E_{elec}}{\partial a} = 2 \sum_i^{\text{all}} f_i \frac{\partial h_{ii}}{\partial a} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij} \frac{\partial(ii|jj)}{\partial a} + \beta_{ij} \frac{\partial(ij|ij)}{\partial a} \right\} . \quad (5.18)$$

Using results from Sections 3.8 and 3.9 (see also Section 4.3), this derivative expression may be rewritten as

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{\text{all}} f_i \left\{ h_{ii}^a + 2 \sum_m^{\text{all}} U_{mi}^a h_{mi} \right\} \\ &+ \sum_{ij}^{\text{all}} \left[\alpha_{ij} \left((ii|jj)^a + 2 \sum_m^{\text{all}} \left\{ U_{mi}^a (mi|jj) + U_{mj}^a (ii|mj) \right\} \right) \right. \\ &\quad \left. + \beta_{ij} \left((ij|ij)^a + 2 \sum_m^{\text{all}} \left\{ U_{mi}^a (mj|ij) + U_{mj}^a (im|ij) \right\} \right) \right] . \end{aligned} \quad (5.19)$$

This equation may be manipulated in the following manner:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{\text{all}} f_i h_{ii}^a + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij} (ii|jj)^a + \beta_{ij} (ij|ij)^a \right\} \\ &+ 2 \sum_i^{\text{all}} f_i \sum_m^{\text{all}} U_{mi}^a h_{mi} + 2 \sum_j^{\text{all}} f_j \sum_m^{\text{all}} U_{mj}^a h_{mj} \\ &+ 2 \sum_{ij}^{\text{all}} \alpha_{ij} \sum_m^{\text{all}} U_{mi}^a (mi|jj) + 2 \sum_{ij}^{\text{all}} \alpha_{ij} \sum_m^{\text{all}} U_{mj}^a (mj|ii) \end{aligned}$$

$$+ 2 \sum_{ij}^{\text{all}} \beta_{ij} \sum_m^{\text{all}} U_{mi}^a(mj|ij) + 2 \sum_{ij}^{\text{all}} \beta_{ij} \sum_m^{\text{all}} U_{mj}^a(mi|ji) \quad (5.20)$$

$$\begin{aligned} &= 2 \sum_i^{\text{all}} f_i h_{ii}^a + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &+ 2 \sum_{im}^{\text{all}} U_{mi}^a \left[f_i h_{mi} + \sum_j^{\text{all}} \left\{ \alpha_{ij}(mi|jj) + \beta_{ij}(mj|ij) \right\} \right] \\ &+ 2 \sum_{jm}^{\text{all}} U_{mj}^a \left[f_j h_{mj} + \sum_i^{\text{all}} \left\{ \alpha_{ij}(mj|ii) + \beta_{ij}(mi|ji) \right\} \right] \end{aligned} \quad (5.21)$$

Introducing the definition of the Lagrangian matrix (5.16) and recognizing the interchangeability of the summations over i or j gives:

$$\begin{aligned} \frac{\partial E_{\text{elec}}}{\partial a} &= 2 \sum_i^{\text{all}} f_i h_{ii}^a + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &+ 2 \sum_{im}^{\text{all}} U_{mi}^a \epsilon_{im} + 2 \sum_{jm}^{\text{all}} U_{mj}^a \epsilon_{jm} \end{aligned} \quad (5.22)$$

$$\begin{aligned} &= 2 \sum_i^{\text{all}} f_i h_{ii}^a + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &+ 4 \sum_{ij}^{\text{all}} U_{ij}^a \epsilon_{ji} . \end{aligned} \quad (5.23)$$

The last term of this equation is simplified further by employing the symmetric character of the Lagrangian matrix, eq. (5.17), and the first derivative form of the orthonormality condition given in Section 3.7 (also see Section 4.3):

$$4 \sum_{ij}^{\text{all}} U_{ij}^a \epsilon_{ji} = 2 \sum_{ij}^{\text{all}} \left(U_{ij}^a + U_{ji}^a \right) \epsilon_{ij} \quad (5.24)$$

$$= -2 \sum_{ij}^{\text{all}} S_{ij}^a \epsilon_{ij} . \quad (5.25)$$

Using equation (5.25), the final expression for the first derivative of the electronic energy becomes:

$$\begin{aligned} \frac{\partial E_{\text{elec}}}{\partial a} &= 2 \sum_i^{\text{all}} f_i h_{ii}^a + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{\text{all}} S_{ij}^a \epsilon_{ij} . \end{aligned} \quad (5.26)$$

The first derivative expression (5.26) for the GRSCF wavefunction does not require the explicit evaluation of the changes in the MO coefficients (the U^a in Section 3.2) as was also the case for the CLSCF wavefunction in the preceding chapter.

5.4 The Evaluation of the First Derivative

In the practical evaluation of the first derivatives, expression (5.26) is usually transformed into the AO basis. The first derivative of the electronic energy in this context is

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} = & 2 \sum_i^{\text{all AO}} f_i C_\mu^i C_\nu^i \frac{\partial h_{\mu\nu}}{\partial a} \\ & + \sum_{ij}^{\text{all AO}} \sum_{\mu\nu\rho\sigma} \left\{ \alpha_{ij} C_\mu^i C_\nu^i C_\rho^j C_\sigma^j \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} + \beta_{ij} C_\mu^i C_\nu^j C_\rho^i C_\sigma^j \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \right\} \\ & - 2 \sum_{ij}^{\text{all AO}} C_\mu^i C_\nu^j \epsilon_{ij} \frac{\partial S_{\mu\nu}}{\partial a} . \end{aligned} \quad (5.27)$$

It is convenient to define the density matrix D^I for the I th shell:

$$D_{\mu\nu}^I = \sum_{i \in I}^{\text{all}} C_\mu^i C_\nu^i \quad (5.28)$$

where the summation runs over all molecular orbitals that belong to the I th shell. The term “shell” is used to describe a set of molecular orbitals that involve the same Fock operator (i.e., share a common set of coupling constants). The total density matrix of the system, D^T , is then defined by its elements as:

$$D_{\mu\nu}^T = \sum_i^{\text{all}} f_i C_\mu^i C_\nu^i = \sum_I^{\text{shell}} f^I D_{\mu\nu}^I \quad (5.29)$$

where f^I denotes an occupation number for the I th shell. The elements of the “energy weighted” density matrix for a GRSCF wavefunction are

$$W_{\mu\nu} = \sum_{ij}^{\text{all}} C_\mu^i C_\nu^j \epsilon_{ij} . \quad (5.30)$$

Using these density matrices, the first derivative expression becomes

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} = & 2 \sum_{\mu\nu}^{\text{AO}} D_{\mu\nu}^T \frac{\partial h_{\mu\nu}}{\partial a} \\ & + \sum_{\mu\nu\rho\sigma}^{\text{AO}} \sum_I^{\text{shell}} \sum_J^{\text{shell}} \left\{ \alpha^{IJ} D_{\mu\nu}^I D_{\rho\sigma}^J + \beta^{IJ} D_{\mu\rho}^I D_{\nu\sigma}^J \right\} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ & - 2 \sum_{\mu\nu}^{\text{AO}} W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} . \end{aligned} \quad (5.31)$$

Here α^{IJ} and β^{IJ} denote the Coulomb and exchange coupling constants for the I and J th shells, respectively. In practice, the derivative integrals are evaluated only for unique combinations of AOs ($\mu \geq \nu$ and $\rho \geq \sigma$) in order to minimize computational effort. The first derivative of the electronic energy in a directly applicable form is then

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} = & 4 \sum_{\mu \geq \nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2}\right) D_{\mu\nu}^T \frac{\partial h_{\mu\nu}}{\partial a} \\ & + 4 \sum_{\substack{\mu \geq \nu, \rho \geq \sigma \\ \mu\nu \geq \rho\sigma}}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2}\right) \left(1 - \frac{\delta_{\rho\sigma}}{2}\right) \left(1 - \frac{\delta_{\mu\nu, \rho\sigma}}{2}\right) \\ & \times \sum_I^{\text{shell}} \sum_J^{\text{shell}} \left\{ 2\alpha^{IJ} D_{\mu\nu}^I D_{\rho\sigma}^J + \beta^{IJ} (D_{\mu\rho}^I D_{\nu\sigma}^J + D_{\mu\sigma}^I D_{\nu\rho}^J) \right\} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ & - 4 \sum_{\mu \geq \nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2}\right) W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} . \end{aligned} \quad (5.32)$$

In eq. (5.32) $\delta_{\mu\nu}$ is the usual Kronecker delta function. In the second term of this equation the summations run over the indices that satisfy the conditions $\mu\nu \geq \rho\sigma$, where $\mu\nu = \frac{1}{2} \mu(\mu-1) + \nu$ and $\rho\sigma = \frac{1}{2} \rho(\rho-1) + \sigma$.

5.5 The First Derivative of the Lagrangian Matrix

At this point we obtain the first derivative of the Lagrangian matrix for future use. In particular, differentiation of eq. (5.16) with respect to a cartesian nuclear coordinate “ a ”

$$\frac{\partial \epsilon_{ij}}{\partial a} = f_i \frac{\partial h_{ij}}{\partial a} + \sum_l^{\text{all}} \left\{ \alpha_{il} \frac{\partial(ij|ll)}{\partial a} + \beta_{il} \frac{\partial(il|jl)}{\partial a} \right\} \quad (5.33)$$

will be required in subsequent developments. Using the derivative expressions for the one- and two-electron MO integrals from Sections 3.8 and 3.9 (see also Section 4.5), we obtain

$$\begin{aligned} \frac{\partial \epsilon_{ij}}{\partial a} = & f_i \left[h_{ij}^a + \sum_m^{\text{all}} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \right] \\ & + \sum_l^{\text{all}} \left[\alpha_{il} \left((ij|ll)^a + \sum_m^{\text{all}} \left\{ U_{mi}^a (mj|ll) + U_{mj}^a (im|ll) + 2U_{ml}^a (ij|ml) \right\} \right) \right. \\ & \left. + \beta_{il} \left((il|jl)^a + \sum_m^{\text{all}} \left\{ U_{mi}^a (ml|jl) + U_{ml}^a (im|jl) \right. \right. \right. \\ & \left. \left. \left. + U_{mj}^a (il|ml) + U_{ml}^a (il|jm) \right\} \right) \right] \end{aligned} \quad (5.34)$$

$$\begin{aligned}
&= f_i h_{ij}^a + \sum_l^{all} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} \\
&+ \sum_m^{all} U_{mi}^a \left[f_i h_{mj} + \sum_l^{all} \left\{ \alpha_{il}(mj|ll) + \beta_{il}(ml|jl) \right\} \right] \\
&+ \sum_m^{all} U_{mj}^a \left[f_i h_{im} + \sum_l^{all} \left\{ \alpha_{il}(im|ll) + \beta_{il}(il|ml) \right\} \right] \\
&+ \sum_{ml}^{all} U_{ml}^a \left[2\alpha_{il}(ij|ml) + \beta_{il} \left\{ (im|jl) + (il|jm) \right\} \right] . \tag{5.35}
\end{aligned}$$

The definition of the Lagrangian matrix may be recalled from equation (5.16). The skeleton (core) first derivative Lagrangian ϵ^a and the *generalized* Lagrangian matrices ζ^l may then be defined by

$$\epsilon_{ij}^a = f_i h_{ij}^a + \sum_l^{all} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} \tag{5.36}$$

and

$$\zeta_{ij}^l = f_l h_{ij} + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk) + \beta_{lk}(ik|jk) \right\} . \tag{5.37}$$

Thus, eq. (5.35) may be rewritten as

$$\begin{aligned}
\frac{\partial \epsilon_{ij}}{\partial a} &= \epsilon_{ij}^a + \sum_m^{all} U_{mi}^a \zeta_{mj}^i + \sum_m^{all} U_{mj}^a \epsilon_{im} \\
&+ \sum_{ml}^{all} U_{ml}^a \left[2\alpha_{il}(ij|ml) + \beta_{il} \left\{ (im|jl) + (il|jm) \right\} \right] . \tag{5.38}
\end{aligned}$$

Note that the skeleton (core) first derivative Lagrangian ϵ^a matrices are *not* symmetric in general. The τ matrix may be defined by its elements:

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl) + \beta_{mn} \left\{ (ik|jl) + (il|jk) \right\} . \tag{5.39}$$

With this definition equation (5.38) becomes

$$\begin{aligned}
\frac{\partial \epsilon_{ij}}{\partial a} &= \epsilon_{ij}^a + \sum_k^{all} \left(U_{ki}^a \zeta_{kj}^i + U_{kj}^a \epsilon_{ik} \right) \\
&+ \sum_{kl}^{all} U_{kl}^a \left[2\alpha_{il}(ij|kl) + \beta_{il} \left\{ (ik|jl) + (il|jk) \right\} \right] \tag{5.40}
\end{aligned}$$

$$= \epsilon_{ij}^a + \sum_k^{all} \left(U_{ki}^a \zeta_{kj}^i + U_{kj}^a \epsilon_{ik} \right) + \sum_{kl}^{all} U_{kl}^a \tau_{ij,kl}^{ii} . \tag{5.41}$$

The following relationship holds between the generalized Lagrangian ζ^i and Lagrangian ϵ matrices when the SCF variational conditions are satisfied:

$$\zeta_{ij}^i = \zeta_{ij}^j = \epsilon_{ij} . \quad (5.42)$$

This equality is easily proven as follows:

$$\zeta_{ij}^i = f_i h_{ij} + \sum_k^{all} \left\{ \alpha_{ik}(ij|kk) + \beta_{ik}(ik|jk) \right\} = \epsilon_{ij} \quad (5.43)$$

$$\zeta_{ij}^j = f_j h_{ij} + \sum_k^{all} \left\{ \alpha_{jk}(ij|kk) + \beta_{jk}(ik|jk) \right\} = \epsilon_{ji} = \epsilon_{ij} . \quad (5.44)$$

In these proofs the definition of the Lagrangian matrix (5.16) and its symmetric character (5.17) are employed.

5.6 The Second Derivative of the Electronic Energy

The second derivative of the general restricted open-shell Hartree-Fock electronic energy may be obtained by differentiating eq. (5.23) with respect to a second nuclear coordinate “ b ”,

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial E_{elec}}{\partial a} \right) \quad (5.45)$$

$$= 2 \sum_i^{all} f_i \frac{\partial h_{ii}^a}{\partial b} + \sum_{ij}^{all} \left\{ \alpha_{ij} \frac{\partial(ii|jj)^a}{\partial b} + \beta_{ij} \frac{\partial(ij|ij)^a}{\partial b} \right\} \\ + 4 \sum_{ij}^{all} \left\{ \frac{\partial U_{ij}^a}{\partial b} \epsilon_{ji} + U_{ij}^a \frac{\partial \epsilon_{ji}}{\partial b} \right\} . \quad (5.46)$$

Using the derivative expressions for the one- and two-electron skeleton (core) derivative integrals from Sections 3.8 and 3.9 (see also Section 4.6), the first and second terms of eq. (5.46) may be manipulated as follows:

$$2 \sum_i^{all} f_i \frac{\partial h_{ii}^a}{\partial b} + \sum_{ij}^{all} \left\{ \alpha_{ij} \frac{\partial(ii|jj)^a}{\partial b} + \beta_{ij} \frac{\partial(ij|ij)^a}{\partial b} \right\} \\ = 2 \sum_i^{all} f_i \left\{ h_{ii}^{ab} + 2 \sum_m^{all} U_{mi}^b h_{mi}^a \right\} \\ + \sum_{ij}^{all} \left[\alpha_{ij} \left((ii|jj)^{ab} + 2 \sum_m^{all} \left\{ U_{mi}^b (mi|jj)^a + U_{mj}^b (ii|mj)^a \right\} \right) \right. \\ \left. + \beta_{ij} \left((ij|ij)^{ab} + 2 \sum_m^{all} \left\{ U_{mi}^b (mj|ij)^a + U_{mj}^b (im|ij)^a \right\} \right) \right] \quad (5.47)$$

$$\begin{aligned}
&= 2 \sum_i^{\text{all}} f_i h_{ii}^{ab} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
&+ 2 \sum_{im}^{\text{all}} U_{mi}^b \left[f_i h_{mi}^a + \sum_j^{\text{all}} \left\{ \alpha_{ij}(mi|jj)^a + \beta_{ij}(mj|ij)^a \right\} \right] \\
&+ 2 \sum_{jm}^{\text{all}} U_{mj}^b \left[f_j h_{mj}^a + \sum_i^{\text{all}} \left\{ \alpha_{ij}(mj|ii)^a + \beta_{ij}(mi|ji)^a \right\} \right] . \quad (5.48)
\end{aligned}$$

The definition of the skeleton (core) derivative Lagrangian matrix and the fact that summations over i and j are equivalent leads to an alternative form for these two terms of:

$$\begin{aligned}
&2 \sum_i^{\text{all}} f_i h_{ii}^{ab} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
&+ 2 \sum_{im}^{\text{all}} U_{mi}^b \epsilon_{im}^a + 2 \sum_{jm}^{\text{all}} U_{mj}^b \epsilon_{jm}^a \quad (5.49)
\end{aligned}$$

$$\begin{aligned}
&= 2 \sum_i^{\text{all}} f_i h_{ii}^{ab} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
&+ 4 \sum_{ij}^{\text{all}} U_{ij}^b \epsilon_{ji}^a . \quad (5.50)
\end{aligned}$$

The third term of eq. (5.46) may be rewritten using results from Section 3.3 and eq. (5.41) as

$$\begin{aligned}
&4 \sum_{ij}^{\text{all}} \left\{ \frac{\partial U_{ij}^a}{\partial b} \epsilon_{ji} + U_{ij}^a \frac{\partial \epsilon_{ji}}{\partial b} \right\} \\
&= 4 \sum_{ij}^{\text{all}} \left(U_{ij}^{ab} - \sum_k^{\text{all}} U_{ik}^b U_{kj}^a \right) \epsilon_{ji} \\
&+ 4 \sum_{ij}^{\text{all}} U_{ij}^a \left[\epsilon_{ji}^b + \sum_k^{\text{all}} \left(U_{kj}^b \zeta_{ki}^j + U_{ki}^b \epsilon_{jk} \right) + \sum_{kl}^{\text{all}} U_{kl}^b \tau_{ji,kl}^{jl} \right] \quad (5.51)
\end{aligned}$$

$$\begin{aligned}
&= 4 \sum_{ij}^{\text{all}} U_{ij}^{ab} \epsilon_{ji} + 4 \sum_{ij}^{\text{all}} U_{ij}^a \epsilon_{ji}^b \\
&+ 4 \sum_{ijk}^{\text{all}} U_{ij}^a U_{kj}^b \zeta_{ki}^j + 4 \sum_{ijkl}^{\text{all}} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} . \quad (5.52)
\end{aligned}$$

Combining eqs. (5.50) and (5.52), the expression for the second derivative of the electronic energy becomes

$$\frac{\partial^2 E_{\text{elec}}}{\partial a \partial b} = 2 \sum_i^{\text{all}} f_i h_{ii}^{ab} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\}$$

$$\begin{aligned}
& + 4 \sum_{ij}^{all} U_{ij}^{ab} \epsilon_{ji} \\
& + 4 \sum_{ij}^{all} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\
& + 4 \sum_{ijk}^{all} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{all} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} .
\end{aligned} \quad (5.53)$$

It should be noted that eq. (5.53) involves terms related to the second derivatives of the MO coefficients. For the computational procedure to be practical, these second derivative terms must be removed from the formalism. In order to eliminate the U_{ij}^{ab} in eq. (5.53), the second derivative form of the orthonormality condition of the molecular orbitals described in Section 3.7, may be used. The final expression for the second derivative of the electronic energy is

$$\begin{aligned}
\frac{\partial^2 E_{elec}}{\partial a \partial b} & = 2 \sum_i^{all} f_i h_{ii}^{ab} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
& - 2 \sum_{ij}^{all} \xi_{ij}^{ab} \epsilon_{ij} \\
& + 4 \sum_{ij}^{all} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\
& + 4 \sum_{ijk}^{all} U_{ij}^a U_{kj}^b \zeta_{ik}^j \\
& + 4 \sum_{ijkl}^{all} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} .
\end{aligned} \quad (5.54)$$

$$\begin{aligned}
& = 2 \sum_i^{all} f_i h_{ii}^{ab} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
& - 2 \sum_{ij}^{all} S_{ij}^{ab} \epsilon_{ij} - 2 \sum_{ij}^{all} \eta_{ij}^{ab} \epsilon_{ij} \\
& + 4 \sum_{ij}^{all} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\
& + 4 \sum_{ijk}^{all} U_{ij}^a U_{kj}^b \zeta_{ik}^j \\
& + 4 \sum_{ijkl}^{all} U_{ij}^a U_{kl}^b \left[2\alpha_{jl}(ij|kl) + \beta_{jl} \left\{ (ik|jl) + (il|jk) \right\} \right] .
\end{aligned} \quad (5.55)$$

ξ^{ab} and η^{ab} were defined in Section 3.7 (see also Section 4.6). Equation (5.55) is given in a form which is symmetric with respect to the variables "a" and "b". The summations run over all (occupied and unoccupied) molecular orbitals. It should be noted that the constants, f_i , α_{ij} , and β_{ij} , involving unoccupied orbitals, should be set to zero explicitly. It is very difficult to derive a symmetric expression for the derivatives without allowing these summations to run over all molecular orbitals.

For the evaluation of the second derivative of the electronic energy, it is necessary to determine the changes of the molecular orbital coefficients (i.e., the elements of the U^a matrices) as seen clearly in eq. (5.55). These U^a matrices are evaluated by solving the general restricted open-shell coupled perturbed Hartree-Fock (CPHF) equations, which will be discussed in detail in Chapter 11.

5.7 An Alternative Derivation of the Second Derivative of the Electronic Energy

Another expression for the second derivative of the electronic energy of the system may be obtained by differentiating eq. (5.1) with respect to the two cartesian coordinates "a" and "b",

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = 2 \sum_i^{\text{all}} f_i \frac{\partial^2 h_{ii}}{\partial a \partial b} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij} \frac{\partial^2 (ii|jj)}{\partial a \partial b} + \beta_{ij} \frac{\partial^2 (ij|ij)}{\partial a \partial b} \right\} . \quad (5.56)$$

Using results developed in Sections 3.8 and 3.9 (see also Section 4.7), the second derivative expression (5.56) may be expanded as:

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{\text{all}} f_i \left[h_{ii}^{ab} + 2 \sum_m^{\text{all}} U_{mi}^{ab} h_{mi} \right. \\ &\quad \left. + 2 \sum_m^{\text{all}} \left(U_{mi}^a h_{mi}^b + U_{mi}^b h_{mi}^a \right) + 2 \sum_{mn}^{\text{all}} U_{mi}^a U_{ni}^b h_{mn} \right] \\ &\quad + \sum_{ij}^{\text{all}} \alpha_{ij} \left[(ii|jj)^{ab} + 2 \sum_m^{\text{all}} \left(U_{mi}^{ab} (mi|jj) + U_{mj}^{ab} (ii|mj) \right) \right. \\ &\quad \left. + 2 \sum_m^{\text{all}} \left(U_{mi}^a (mi|jj)^b + U_{mj}^a (ii|mj)^b \right. \right. \\ &\quad \left. \left. + U_{mi}^b (mi|jj)^a + U_{mj}^b (ii|mj)^a \right) \right. \\ &\quad \left. + 2 \sum_{mn}^{\text{all}} U_{mi}^a U_{ni}^b (mn|jj) + 2 \sum_{mn}^{\text{all}} U_{mj}^a U_{nj}^b (ii|mn) \right. \\ &\quad \left. + 4 \sum_{mn}^{\text{all}} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (im|jn) \right] \end{aligned}$$

$$\begin{aligned}
& + \sum_{ij}^{all} \beta_{ij} \left[(ij|ij)^{ab} + 2 \sum_m^{all} \left(U_{mi}^{ab}(mj|ij) + U_{mj}^{ab}(im|ij) \right) \right. \\
& \quad + 2 \sum_m^{all} \left(U_{mi}^a(mj|ij)^b + U_{mj}^a(im|ij)^b + U_{mi}^b(mj|ij)^a + U_{mj}^b(im|ij)^a \right) \\
& \quad + 4 \sum_{mn}^{all} U_{mi}^a U_{nj}^b (mn|ij) \\
& \quad + 2 \sum_{mn}^{all} U_{mi}^a U_{ni}^b (mj|nj) + 2 \sum_{mn}^{all} U_{mj}^a U_{nj}^b (im|in) \\
& \quad \left. + 2 \sum_{mn}^{all} U_{mi}^a U_{nj}^b (mj|in) + 2 \sum_{mn}^{all} U_{mj}^a U_{ni}^b (im|nj) \right] \tag{5.57}
\end{aligned}$$

$$\begin{aligned}
& = 2 \sum_i^{all} f_i h_{ii}^{ab} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
& + 2 \sum_{im}^{all} U_{mi}^{ab} \left[f_i h_{mi} + \sum_j^{all} \left\{ \alpha_{ij}(mi|jj) + \beta_{ij}(mj|ij) \right\} \right] \\
& + 2 \sum_{jm}^{all} U_{mj}^{ab} \left[f_j h_{mj} + \sum_i^{all} \left\{ \alpha_{ij}(mj|ii) + \beta_{ij}(mi|ji) \right\} \right] \\
& + 2 \sum_{im}^{all} U_{mi}^b \left[f_i h_{mi}^a + \sum_j^{all} \left\{ \alpha_{ij}(mi|jj)^a + \beta_{ij}(mj|ij)^a \right\} \right] \\
& + 2 \sum_{jm}^{all} U_{mj}^b \left[f_j h_{mj}^a + \sum_i^{all} \left\{ \alpha_{ij}(mj|ii)^a + \beta_{ij}(mi|ji)^a \right\} \right] \\
& + 2 \sum_{im}^{all} U_{mi}^a \left[f_i h_{mi}^b + \sum_j^{all} \left\{ \alpha_{ij}(mi|jj)^b + \beta_{ij}(mj|ij)^b \right\} \right] \\
& + 2 \sum_{jm}^{all} U_{mj}^a \left[f_j h_{mj}^b + \sum_i^{all} \left\{ \alpha_{ij}(mj|ii)^b + \beta_{ij}(mi|ji)^b \right\} \right] \\
& + 2 \sum_{imn}^{all} U_{mi}^a U_{ni}^b \left[f_i h_{mn} + \sum_j^{all} \left\{ \alpha_{ij}(mn|jj) + \beta_{ij}(mj|nj) \right\} \right] \\
& + 2 \sum_{jmn}^{all} U_{mj}^a U_{nj}^b \left[f_j h_{mn} + \sum_i^{all} \left\{ \alpha_{ij}(mn|ii) + \beta_{ij}(im|in) \right\} \right] \\
& + 4 \sum_{ijmn}^{all} U_{mi}^a U_{nj}^b \left[2\alpha_{ij}(im|jn) + \beta_{ij}\{(mn|ij) + (mj|in)\} \right] \tag{5.58}
\end{aligned}$$

The definitions of ϵ , ϵ^a , ζ , and τ , which are found in eqs. (5.16), (5.36), (5.37) and (5.39), allow this equation to be rewritten as:

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{all} f_i h_{ii}^{ab} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &+ 2 \sum_{im}^{all} U_{mi}^{ab} \epsilon_{im} + 2 \sum_{jm}^{all} U_{mj}^{ab} \epsilon_{jm} \\ &+ 2 \sum_{im}^{all} U_{mi}^b \epsilon_{im}^a + 2 \sum_{jm}^{all} U_{mj}^b \epsilon_{jm}^a \\ &+ 2 \sum_{im}^{all} U_{mi}^a \epsilon_{im}^b + 2 \sum_{jm}^{all} U_{mj}^a \epsilon_{jm}^b \\ &+ 2 \sum_{imn}^{all} U_{mi}^a U_{ni}^b \zeta_{mn}^i + 2 \sum_{jmn}^{all} U_{mj}^a U_{nj}^b \zeta_{mn}^j \\ &+ 4 \sum_{ijmn}^{all} U_{mi}^a U_{nj}^b \tau_{im,jn}^{ij} \end{aligned} \quad (5.59)$$

$$\begin{aligned} &= 2 \sum_i^{all} f_i h_{ii}^{ab} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &+ 4 \sum_{ij}^{all} U_{ij}^{ab} \epsilon_{ji} \\ &+ 4 \sum_{ij}^{all} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{all} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{all} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} . \end{aligned} \quad (5.60)$$

Equation (5.60) is equivalent to eq. (5.53), which was derived independently in the preceding section.

References

1. C.C.J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).
2. F.W. Bobrowicz and W.A. Goddard, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.79 (1977).
3. R. Carbo and J.M. Riera, *A General SCF Theory*, Springer-Verlag, Berlin, 1978.

Suggested Reading

1. J.D. Goddard, N.C. Handy, and H.F. Schaefer, *J. Chem. Phys.* **71**, 1525 (1979).
2. S. Kato and K. Morokuma, *Chem. Phys. Lett.* **65**, 19 (1979).
3. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **75**, 2919 (1981).
4. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 383 (1982).
5. P. Saxe, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 5647 (1982).
6. Y. Osamura, Y. Yamaguchi, P. Saxe, M.A. Vincent, J.F. Gaw, and H.F. Schaefer, *Chem. Phys.* **72**, 131 (1982).
7. Y. Osamura, Y. Yamaguchi, P. Saxe, D.J. Fox, M.A. Vincent, and H.F. Schaefer, *J. Mol. Struct.* **103**, 183 (1983).
8. G. Fitzgerald and H.F. Schaefer, *J. Chem. Phys.* **83**, 1162 (1985).

Chapter 6

Configuration Interaction Wavefunctions

The configuration interaction (CI) method has been the most commonly used approach to include electron correlation effects in electronic wavefunctions. Many important chemical problems have been solved by quantum chemists using the CI method. A number of electronic configurations are included in the wavefunction, constructed using a particular set of molecular orbitals, which usually are obtained by an SCF or MCSCF procedure. Of course, the MO coefficients are not variationally optimized in the CI procedure. Thus, the derivatives (to any order) based on the CI wavefunction necessarily require information on the derivatives (to the same order) of the MO coefficients. In this chapter the first and second derivatives of the CI wavefunction are discussed.

6.1 The CI Wavefunction, Energy and the Variational Conditions

The configuration interaction (CI) wavefunction is a linear combination of electronic configurations Φ_I that are constructed from an appropriate fixed set of reference molecular orbitals [1]

$$\Psi_{CI} = \sum_I^{CI} C_I \Phi_I \quad . \quad (6.1)$$

The summation runs over electronic configurations. The C_I are the CI coefficients which are to be variationally determined. The wavefunction is normalized, giving the condition

$$\sum_I^{CI} C_I^2 = 1 \quad (6.2)$$

on the CI coefficients. The electronic energy of the CI wavefunction is:

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} . \quad (6.3)$$

The CI Hamiltonian matrix appearing in eq. (6.3) is defined by

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (6.4)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl) . \quad (6.5)$$

Q_{ij}^{IJ} and G_{ijkl}^{IJ} are one- and two-electron coupling constants between electronic configurations and molecular orbitals [2]. \mathbf{H}_{elec} is the usual electronic Hamiltonian. The one- and two-electron reduced density matrices are defined in terms of their elements by:

$$Q_{ij} = \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} \quad (6.6)$$

and

$$G_{ijkl} = \sum_{IJ}^{CI} C_I C_J G_{ijkl}^{IJ} . \quad (6.7)$$

Using these quantities the electronic energy of the CI wavefunction is given in MO form by

$$E_{elec} = \sum_{ij}^{MO} Q_{ij} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl) . \quad (6.8)$$

The total CI energy of the system is the sum of the electronic energy and the nuclear repulsion energy

$$E_{CI} = E_{elec} + E_{nuc} . \quad (6.9)$$

The variational conditions for the determination of the CI wavefunction (6.1) are:

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 . \quad (6.10)$$

The CI Hamiltonian matrix in eq. (6.10) is defined by eq. (6.5). δ_{IJ} is again the Kronecker delta function.

6.2 The First Derivative of the Electronic Energy

The differentiation of eq. (6.3) with respect to a nuclear coordinate “ a ” gives:

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} H_{IJ} C_J + \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} H_{IJ} + \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} . \quad (6.11)$$

It is immaterial whether the summations initially run over the I or J subscripts and thus this equation becomes:

$$\frac{\partial E_{elec}}{\partial a} = 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} H_{IJ} C_J + \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} . \quad (6.12)$$

From the variational conditions, eq. (6.10), the following equation is obtained:

$$\sum_J^{CI} H_{IJ} C_J = E_{elec} C_I . \quad (6.13)$$

Using this equation eq. (6.12) may be rewritten as:

$$\frac{\partial E_{elec}}{\partial a} = 2E_{elec} \sum_I^{CI} \frac{\partial C_I}{\partial a} C_I + \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} . \quad (6.14)$$

The first derivative of the normalization condition gives:

$$\sum_I^{CI} \frac{\partial C_I}{\partial a} C_I = 0 . \quad (6.15)$$

Using this condition the first term in eq. (6.14) vanishes and a simpler (in fact, deceptively simple) expression for the CI gradient is found:

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} . \quad (6.16)$$

Since the H_{IJ} matrix is defined in eq. (6.5) without using the CI coefficients, the first derivative of the electronic energy for the wavefunction, eq. (6.16), which satisfies the CI variational condition (6.10) may be obtained by differentiating the energy expression in only the MO space.

An expression for the first derivative of the electronic energy of the CI wavefunction is obtained by differentiating the MO part of eq. (6.8) with respect to a cartesian coordinate “ a ”:

$$\frac{\partial E_{elec}}{\partial a} = \sum_{ij}^{MO} Q_{ij} \frac{\partial h_{ij}}{\partial a} + \sum_{ijkl}^{MO} G_{ijkl} \frac{\partial (ij|kl)}{\partial a} . \quad (6.17)$$

Using the results given in Sections 3.8 and 3.9, this derivative expression becomes:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} Q_{ij} \left\{ h_{ij}^a + \sum_m^{MO} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \right\} \\ &+ \sum_{ijkl}^{MO} G_{ijkl} \left[(ij|kl)^a + \sum_m^{MO} \left\{ U_{mi}^a (mj|kl) + U_{mj}^a (im|kl) \right\} \right] \end{aligned}$$

$$+ U_{mk}^a(ij|ml) + U_{ml}^a(ij|km) \Big\} \Big] \quad (6.18)$$

$$\begin{aligned} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a \\ &+ \sum_{ijm}^{MO} \left(Q_{ij} U_{mi}^a h_{mj} + Q_{ij} U_{mj}^a h_{im} \right) \\ &+ \sum_{ijklm}^{MO} \left\{ G_{ijkl} U_{mi}^a(mj|kl) + G_{ijkl} U_{mj}^a(im|kl) \right. \\ &\quad \left. + G_{ijkl} U_{mk}^a(ij|ml) + G_{ijkl} U_{ml}^a(ij|km) \right\} . \end{aligned} \quad (6.19)$$

Interchange of i, j, k, l , and m does not change the value of the first derivative as the summations run over all molecular orbitals. Focusing attention on the third and fourth terms in this equation, the first derivative of the electronic energy becomes:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a \\ &+ \sum_{ijm}^{MO} \left(Q_{jm} U_{ij}^a h_{im} + Q_{mj} U_{ij}^a h_{mi} \right) \\ &+ \sum_{ijklm}^{MO} \left\{ G_{jmkl} U_{ij}^a(im|kl) + G_{mjkl} U_{ij}^a(mi|kl) \right. \\ &\quad \left. + G_{kljm} U_{ij}^a(kl|im) + G_{klmj} U_{ij}^a(kl|mi) \right\} \end{aligned} \quad (6.20)$$

$$\begin{aligned} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a \\ &+ 2 \sum_{ijm}^{MO} Q_{jm} U_{ij}^a h_{im} + 4 \sum_{ijklm}^{MO} G_{jmkl} U_{ij}^a(im|kl) \end{aligned} \quad (6.21)$$

$$\begin{aligned} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a \\ &+ 2 \sum_{ij}^{MO} U_{ij}^a \left\{ \sum_m^{MO} Q_{jm} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl) \right\} \end{aligned} \quad (6.22)$$

$$\begin{aligned} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a \\ &+ 2 \sum_{ij}^{MO} U_{ij}^a X_{ij} . \end{aligned} \quad (6.23)$$

The particular Lagrangian matrix X in eq. (6.23) is defined by

$$X_{ij} = \sum_m^{MO} Q_{jm} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl) . \quad (6.24)$$

This Lagrangian matrix indicates the changes in the CI energy with respect to the changes in the MO coefficients. Note that the symmetry properties of the MO integrals in Section 2.8 and reduced density matrices in Section 2.6 were used in deriving eq. (6.23). The first derivative expression (6.23) requires the explicit evaluation of changes in the MO coefficients or U^a matrices. These U^a matrices are evaluated by solving the coupled perturbed Hartree-Fock (CPHF) or the coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) equations, depending on the reference wavefunction employed to construct the electronic configurations. These methods are nontrivial and will be described in Chapters 10, 11, 13 and 14. The related subject of the evaluation of the third term in eq. (6.23) (using the \tilde{Z} vector method) will be treated in Chapter 18.

6.3 The Evaluation of the First Derivative

In the practical evaluation of the first derivative for CI wavefunctions, the first two terms in eq. (6.23) are usually transformed into the AO basis. The first derivative of the electronic energy is

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} \sum_{\mu\nu}^{AO} Q_{ij} C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} + \sum_{ijkl}^{MO} \sum_{\mu\nu\rho\sigma}^{AO} G_{ijkl} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^a X_{ij} . \end{aligned} \quad (6.25)$$

The one- and two-electron reduced density matrices in the AO basis are defined by (see Section 2.8)

$$Q_{\mu\nu} = \sum_{ij}^{MO} C_\mu^i C_\nu^j Q_{ij} \quad (6.26)$$

and

$$G_{\mu\nu\rho\sigma} = \sum_{ijkl}^{MO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l G_{ijkl} . \quad (6.27)$$

Using these AO reduced density matrices, eq. (6.25) becomes:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{\mu\nu}^{AO} Q_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} + \sum_{\mu\nu\rho\sigma}^{AO} G_{\mu\nu\rho\sigma} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^a X_{ij} . \end{aligned} \quad (6.28)$$

The third term of this equation requires the solutions to the CPHF equations for the reference wavefunction. This term may be modified as follows:

$$2 \sum_{ij}^{MO} U_{ij}^a X_{ij} = 2 \sum_{i>j}^{MO} U_{ij}^a X_{ij} + 2 \sum_{i<j}^{MO} U_{ij}^a X_{ij} + 2 \sum_i^{MO} U_{ii}^a X_{ii} \quad (6.29)$$

$$= 2 \sum_{i>j}^{MO} (U_{ij}^a X_{ij} + U_{ji}^a X_{ji}) + 2 \sum_i^{MO} U_{ii}^a X_{ii} \quad . \quad (6.30)$$

Using the first derivative of the orthonormality condition from Section 3.7,

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \quad (6.31)$$

eq. (6.30) is further manipulated:

$$2 \sum_{ij}^{MO} U_{ij}^a X_{ij} = 2 \sum_{i>j}^{MO} U_{ij}^a (X_{ij} - X_{ji}) - 2 \sum_{i>j}^{MO} S_{ij}^a X_{ji} - \sum_i^{MO} S_{ii}^a X_{ii} \quad . \quad (6.32)$$

The last two terms of eq. (6.32) may be transformed into the AO basis as:

$$2 \sum_{i>j}^{MO} S_{ij}^a X_{ji} + \sum_i^{MO} S_{ii}^a X_{ii} = 2 \sum_{i>j}^{MO} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} X_{ji} + \sum_i^{MO} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^i \frac{\partial S_{\mu\nu}}{\partial a} X_{ii} \quad (6.33)$$

$$= 2 \sum_{i>j}^{MO} \sum_{\mu\nu}^{AO} \left(1 - \frac{\delta_{ij}}{2}\right) C_\mu^i C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} X_{ji} \quad . \quad (6.34)$$

Defining the “energy weighted” density matrix as

$$W_{\mu\nu} = \sum_{i>j}^{MO} \left(1 - \frac{\delta_{ij}}{2}\right) C_\mu^i C_\nu^j X_{ji} \quad (6.35)$$

eq. (6.34) becomes

$$2 \sum_{i>j}^{MO} S_{ij}^a X_{ji} + \sum_i^{MO} S_{ii}^a X_{ii} = 2 \sum_{\mu\nu}^{AO} W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} \quad . \quad (6.36)$$

Combining eqs. (6.28), (6.32), and (6.36), the electronic energy first derivative for a CI wavefunction is given by

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{\mu\nu}^{AO} Q_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} + \sum_{\mu\nu\rho\sigma}^{AO} G_{\mu\nu\rho\sigma} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ &- 2 \sum_{\mu\nu}^{AO} W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} + 2 \sum_{i>j}^{MO} U_{ij}^a (X_{ij} - X_{ji}) \end{aligned} \quad . \quad (6.37)$$

In practice, the derivative integrals are evaluated only for unique combinations of AOs ($\mu \geq \nu$ and $\rho \geq \sigma$) in order to minimize computational effort. The first derivative of the electronic energy in a directly applicable form is:

$$\begin{aligned}
\frac{\partial E_{elec}}{\partial a} = & 2 \sum_{\mu \geq \nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) Q_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} \\
& + 4 \sum_{\substack{\mu \geq \nu, \rho \geq \sigma \\ \mu\nu \geq \rho\sigma}}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) \left(1 - \frac{\delta_{\rho\sigma}}{2} \right) \left(1 - \frac{\delta_{\mu\nu, \rho\sigma}}{2} \right) \\
& \quad \times \left\{ 2G_{\mu\nu\rho\sigma} \right\} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\
& - 4 \sum_{\mu \geq \nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} \\
& + 2 \sum_{i>j}^{MO} U_{ij}^a \left(X_{ij} - X_{ji} \right) . \tag{6.38}
\end{aligned}$$

In the second term of this equation the summations run over the indices that satisfy the conditions $\mu\nu \geq \rho\sigma$, where $\mu\nu = \frac{1}{2} \mu(\mu-1) + \nu$ and $\rho\sigma = \frac{1}{2} \rho(\rho-1) + \sigma$. The last term of eq. (6.38) indicates that the CPHF equations need to be solved only for the $i-j$ pairs whose elements of the Lagrangian matrix are not symmetric, i.e., for the pairs with $X_{ij} \neq X_{ji}$. When a molecule has point group symmetry higher than C_1 , the number of contributing derivative MO pairs will decrease.

6.4 The First Derivative of the Hamiltonian Matrix

An explicit expression for the first derivative of the Hamiltonian matrix was not required in the preceding section. However, such a result will be necessary for the evaluation of the second derivative of the energy. The explicit first derivative of the CI Hamiltonian matrix is given in this section.

Differentiating eq. (6.5) with respect to a cartesian coordinate “ a ”, gives

$$\frac{\partial H_{IJ}}{\partial a} = \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial h_{ij}}{\partial a} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial(ij|kl)^a}{\partial a} . \tag{6.39}$$

Since the coupling constants, Q_{ij}^{IJ} and G_{ijkl}^{IJ} , in eq. (6.5) are independent of the CI coefficients and nuclear coordinates, this derivation is essentially the same as that starting from eq. (6.17) and working to eq. (6.23). Using results from the preceding section:

$$\frac{\partial H_{IJ}}{\partial a} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^a$$

$$+ 2 \sum_{ij}^{MO} U_{ij}^a \left\{ \sum_m^{MO} Q_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl) \right\} \quad (6.40)$$

$$= H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} . \quad (6.41)$$

The skeleton (core) first derivative Hamiltonian matrices H_{IJ}^a and the “bare” Lagrangian matrices X^{IJ} are defined by

$$H_{IJ}^a = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^a \quad (6.42)$$

and

$$X_{ij}^{IJ} = \sum_m^{MO} Q_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl) . \quad (6.43)$$

The relationship between the Lagrangian X and the “bare” Lagrangian X^{IJ} matrices is:

$$X_{ij} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ} . \quad (6.44)$$

This equation is reminiscent of that for the one- and two-electron reduced density matrices and the coupling constants given in eqs. (6.6) and (6.7).

The various “bare” quantities, Q^{IJ} , G^{IJ} , H_{IJ} , H_{IJ}^a , and X^{IJ} do *not* contain the CI coefficients by definition. Using eq. (6.41) it is easily shown that eq. (6.16) is equivalent to eq. (6.23) by:

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad (6.45)$$

$$= \sum_{IJ}^{CI} C_I C_J \left\{ H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \right\} \quad (6.46)$$

$$= \sum_{IJ}^{CI} C_I C_J \left\{ \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \right\} \quad (6.47)$$

$$= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij} \quad . \quad (6.48)$$

The relationships (6.6), (6.7) and (6.44) were used in this proof.

6.5 The First Derivative of the “Bare” Lagrangian Matrix

It is appropriate to find a first derivative expression for the elements of the “bare” Lagrangian matrix for future use. Differentiation of eq. (6.43) with respect to a cartesian

coordinate "a"

$$\frac{\partial X_{ij}^{IJ}}{\partial a} = \sum_m^{MO} Q_{jm}^{IJ} \frac{\partial h_{im}}{\partial a} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} \frac{\partial (im|kl)}{\partial a} \quad (6.49)$$

is required. Using results developed in Sections 3.8 and 3.9 one obtains

$$\begin{aligned} \frac{\partial X_{ij}^{IJ}}{\partial a} &= \sum_m^{MO} Q_{jm}^{IJ} \left[h_{im}^a + \sum_n^{MO} \left\{ U_{ni}^a h_{nm} + U_{nm}^a h_{in} \right\} \right] \\ &+ 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} \left[(im|kl)^a + \sum_n^{MO} \left\{ U_{ni}^a (nm|kl) + U_{nm}^a (in|kl) \right. \right. \\ &\quad \left. \left. + U_{nk}^a (im|nl) + U_{nl}^a (im|kn) \right\} \right] \end{aligned} \quad (6.50)$$

$$\begin{aligned} &= \sum_m^{MO} Q_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (im|kl)^a \\ &+ \sum_n^{MO} U_{ni}^a \left\{ \sum_m^{MO} Q_{jm}^{IJ} h_{nm} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (nm|kl) \right\} \\ &+ \sum_{nm}^{MO} U_{nm}^a \left\{ Q_{jm}^{IJ} h_{in} + 2 \sum_{kl}^{MO} G_{jmkl}^{IJ} (in|kl) \right\} \\ &+ 2 \sum_{nmkl}^{MO} \left\{ U_{nk}^a G_{jmkl}^{IJ} (im|nl) + U_{nl}^a G_{jmkl}^{IJ} (im|kn) \right\} . \end{aligned} \quad (6.51)$$

In eq. (6.51), the summation runs over all molecular orbitals. Interchange of the m, n, k , and l indices does not change the value of the first derivative of the "bare" Lagrangian matrix. Thus,

$$\begin{aligned} \frac{\partial X_{ij}^{IJ}}{\partial a} &= X_{ij}^{IJa} + \sum_n^{MO} U_{ni}^a X_{nj}^{IJ} \\ &+ \sum_{kl}^{MO} U_{kl}^a \left\{ Q_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ} (ik|mn) + 4 \sum_{mn}^{MO} G_{jmfn}^{IJ} (im|kn) \right\} \end{aligned} \quad (6.52)$$

$$= X_{ij}^{IJa} + \sum_k^{MO} U_{ki}^a X_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^a Y_{ijkl}^{IJ} . \quad (6.53)$$

In deriving eq. (6.53), the symmetry properties of the MO integrals and reduced density matrices and the definition of the "bare" Lagrangian matrix (6.43) were employed. The skeleton (core) first derivative "bare" Lagrangian matrices X^a and the "bare" Y matrix appearing in eq. (6.53) are

$$X_{ij}^{IJa} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (im|kl)^a \quad (6.54)$$

and

$$Y_{ijkl}^{IJ} = Q_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ}(ik|mn) + 4 \sum_{mn}^{MO} G_{jmln}^{IJ}(im|kn) . \quad (6.55)$$

These two matrices are related to their “parent” quantities by

$$X_{ij}^a = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJa} \quad (6.56)$$

and

$$Y_{ijkl} = \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJ} . \quad (6.57)$$

6.6 The Second Derivative of the Hamiltonian Matrix

It is advantageous to have an explicit expression for the second derivative of the Hamiltonian matrix at this point. The second derivative of the Hamiltonian matrix may be obtained by differentiating eq. (6.5) with respect to the two variables “ a ” and “ b ”:

$$\frac{\partial^2 H_{IJ}}{\partial a \partial b} = \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial^2 h_{ij}}{\partial a \partial b} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial^2 (ij|kl)}{\partial a \partial b} \quad (6.58)$$

$$= \frac{\partial}{\partial b} \left(\frac{\partial H_{IJ}}{\partial a} \right) . \quad (6.59)$$

Recalling eq. (6.41), the equation (6.59) may be rewritten to yield

$$\frac{\partial^2 H_{IJ}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \right) \quad (6.60)$$

$$= \frac{\partial H_{IJ}^a}{\partial b} + 2 \sum_{ij}^{MO} \frac{\partial U_{ij}^a}{\partial b} X_{ij}^{IJ} + 2 \sum_{ij}^{MO} U_{ij}^a \frac{\partial X_{ij}^{IJ}}{\partial b} . \quad (6.61)$$

The first term of eq. (6.61) is manipulated as in Sections 6.2 and 6.4. Using results from Sections 3.8 and 3.9,

$$\frac{\partial H_{IJ}^a}{\partial b} = \frac{\partial}{\partial b} \left[\sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^a \right] \quad (6.62)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial h_{ij}^a}{\partial b} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial (ij|kl)^a}{\partial b} \quad (6.63)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} \left[h_{ij}^{ab} + \sum_m^{MO} \left\{ U_{mi}^b h_{mj}^a + U_{mj}^b h_{im}^a \right\} \right]$$

$$\begin{aligned}
& + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \left[(ij|kl)^{ab} + \sum_m^M \left\{ U_{mi}^b (mj|kl)^a + U_{mj}^b (im|kl)^a \right. \right. \\
& \quad \left. \left. + U_{mk}^b (ij|ml)^a + U_{ml}^b (ij|km)^a \right\} \right] \quad (6.64)
\end{aligned}$$

$$\begin{aligned}
& = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{ab} \\
& + 2 \sum_{ij}^{MO} U_{ij}^b \left\{ \sum_m^M Q_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (im|kl)^a \right\} \quad (6.65)
\end{aligned}$$

$$= H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJa} . \quad (6.66)$$

The skeleton (core) second derivative Hamiltonian matrices H_{IJ}^{ab} are defined by

$$H_{IJ}^{ab} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{ab} . \quad (6.67)$$

The second term of eq. (6.61) may be rewritten using the relationship given in Section 3.3 as

$$2 \sum_{ij}^{MO} \frac{\partial U_{ij}^a}{\partial b} X_{ij}^{IJ} = 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} - \sum_k^M U_{ik}^b U_{kj}^a \right) X_{ij}^{IJ} . \quad (6.68)$$

Using the results given in eq. (6.53) the third term of eq. (6.61) is

$$\begin{aligned}
2 \sum_{ij}^{MO} U_{ij}^a \frac{\partial X_{ij}^{IJ}}{\partial b} & = 2 \sum_{ij}^{MO} U_{ij}^a \left[X_{ij}^{IJb} + \sum_k^M U_{ki}^b X_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^b Y_{ijkl}^{IJ} \right] \quad (6.69) \\
& = 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJb} + 2 \sum_{ijk}^{MO} U_{ik}^b U_{kj}^a X_{ij}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} .
\end{aligned} \quad (6.70)$$

The “bare” Y matrices were defined by eq. (6.55). In deriving eq. (6.70), the interchangeability of the summations over MO indices and the symmetry properties of the integrals and reduced density matrices were used.

The explicit expression for the second derivative of the H_{IJ} matrix is obtained by substituting eqs. (6.66), (6.68) and (6.70) into eq. (6.61):

$$\begin{aligned}
\frac{\partial^2 H_{IJ}}{\partial a \partial b} & = H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJa} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} - \sum_k^M U_{ik}^b U_{kj}^a \right) X_{ij}^{IJ}
\end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJb} + 2 \sum_{ijk}^{MO} U_{ik}^b U_{kj}^a X_{ij}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ}
\end{aligned} \tag{6.71}$$

$$\begin{aligned}
& = H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJa} + U_{ij}^a X_{ij}^{IJb} \right) \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ}
\end{aligned} \tag{6.72}$$

6.7 The Second Derivative of the Electronic Energy

The second derivative of the CI energy expression may be obtained by the differentiation of eq. (6.16) with respect to a second nuclear coordinate “*b*”:

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial E_{elec}}{\partial a} \right) \tag{6.73}$$

$$= \frac{\partial}{\partial b} \left(\sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \right) \tag{6.74}$$

$$= \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} + 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \frac{\partial H_{IJ}}{\partial a} . \tag{6.75}$$

This equation does not appear to be symmetric with respect to the interchange of the variables “*a*” and “*b*”. However, it may be shown to be equivalent to the symmetric form in the following manner. The differentiation of the variational condition (6.10) gives important relationships between the derivatives of the CI coefficients and those of the Hamiltonian matrix elements

$$\sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 . \tag{6.76}$$

These conditions are equivalent to the coupled perturbed configuration interaction (CPCI) equations which will be discussed in detail in Chapter 12. Multiplying by $(\sum_I^{CI} \partial C_I / \partial b)$ on both sides of eq. (6.76) gives

$$\begin{aligned}
& \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \\
& + \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 .
\end{aligned} \tag{6.77}$$

Using eq. (6.15), equation (6.75) may be rewritten as

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} + 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) . \quad (6.78)$$

Employing the relationship in eq. (6.77) the second derivative of the CI energy becomes

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (6.79)$$

An explicit expression for the second derivative of the CI energy results from combining eqs. (6.72) and (6.79):

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{IJ}^{CI} C_I C_J \left[H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \right. \\ &\quad \left. + 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJ^a} + U_{ij}^a X_{ij}^{IJ^b} \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} \right] \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \end{aligned} \quad (6.80)$$

$$\begin{aligned} &= \sum_{ij}^{MO} \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} \sum_{IJ}^{CI} C_I C_J G_{ijkl}^{IJ}(ij|kl)^{ab} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^{ab} \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} \left\{ U_{ij}^b \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ^a} + U_{ij}^a \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ^b} \right\} \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJ} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (6.81)$$

Equations (6.6) and (6.7) relate the reduced density matrices Q_{ij} and G_{ijkl} to the coupling constants. The relationships between the “bare” and the corresponding “parent” quantities in eqs. (6.44), (6.56) and (6.57) are used to rewrite (6.81) as

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{ij}^{MO} Q_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}$$

$$\begin{aligned}
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^a + U_{ij}^a X_{ij}^b \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl} \\
 & - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (6.82)
 \end{aligned}$$

The third term of this equation requires the solutions to the second-order CPHF equations of the reference wavefunction. This term may be modified in a similar manner as was done in Section 6.3:

$$2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} = 2 \sum_{i>j}^{MO} U_{ij}^{ab} X_{ij} + 2 \sum_{i<j}^{MO} U_{ij}^{ab} X_{ij} + 2 \sum_i^{MO} U_{ii}^{ab} X_{ii} \quad (6.83)$$

$$= 2 \sum_{i>j}^{MO} \left(U_{ij}^{ab} X_{ij} + U_{ji}^{ab} X_{ji} \right) + 2 \sum_i^{MO} U_{ii}^{ab} X_{ii} . \quad (6.84)$$

Using the second derivative of the orthonormality condition of the molecular orbitals from Section 3.7

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad (6.85)$$

where

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) , \quad (6.86)$$

eq. (6.84) is further manipulated:

$$2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} = 2 \sum_{i>j}^{MO} U_{ij}^{ab} \left(X_{ij} - X_{ji} \right) - 2 \sum_{i>j}^{MO} \xi_{ij}^{ab} X_{ji} - \sum_i^{MO} \xi_{ii}^{ab} X_{ii} . \quad (6.87)$$

The first term of eq. (6.87) indicates that the second-order CPHF equations need to be solved only for the MO pairs whose elements of the Lagrangian matrix are not symmetric, i.e., for pairs with $X_{ij} \neq X_{ji}$. These second-order CPHF equations will be discussed in Chapters 10, 11, 13 and 14. A related subject, the evaluation of the third term in eq. (6.82) by the Z vector method, will be treated in Chapter 18. The derivative of the CI coefficients can be determined by solving the first-order CPCI equations, as will be shown in Chapter 12.

References

1. I. Shavitt, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.189 (1977).
2. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.

Suggested Reading

1. B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **72**, 4652 (1980).
2. R. Krishnan, H.B. Schlegel, and J.A. Pople, *J. Chem. Phys.* **72**, 4654 (1980).
3. B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, and H.F. Schaefer, in *Lecture Notes in Chemistry*, J. Hinze editor, Springer-Verlag, Berlin, Vol. 22, p. 158 (1981).
4. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **75**, 2919 (1981).
5. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 383 (1982).
6. D.J. Fox, Y. Osamura, M.R. Hoffmann, J.F. Gaw, G. Fitzgerald, Y. Yamaguchi, and H.F. Schaefer, *Chem. Phys. Lett.* **102**, 17 (1983).
7. J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, and H.F. Schaefer, *J. Chem. Phys.* **85**, 963 (1986).
8. T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, *J. Chem. Phys.* **85**, 3930 (1986).

Chapter 7

Two-Configuration Self-Consistent-Field Wavefunctions

The two-configuration self-consistent-field (TCSCF) wavefunction is a simple but useful correlated wavefunction. Specifically, TCSCF wavefunctions provide reasonable starting points for the description of singlet carbenes and other organic biradicals. They are also useful in the classical problem of the proper description of the dissociation of a single bond in a molecule. Theoretically, TCSCF is a simple case of the generalized valence bond (GVB), paired excitation multiconfiguration SCF (PEMCSCF), complete active space SCF (CASSCF) and general multiconfiguration SCF (MCSCF) wavefunctions. Here, unlike the simpler single configuration SCF cases, one must consider constraints involving both the molecular orbital (MO) and configuration interaction (CI) spaces in deriving the analytic energy derivative expressions. Thus, this simplified multiconfiguration wavefunction provides an excellent introduction to the analytic derivative techniques needed for the more elaborate wavefunctions considered in the immediately following chapters.

7.1 The Two-Configuration Self-Consistent-Field (TCSCF) Wavefunction and Energy

The two-configuration self-consistent-field (TCSCF) wavefunction Ψ [1-5] of interest is:

$$\Psi_{TCSCF} = C_1\Phi_1 + C_2\Phi_2 \quad . \quad (7.1)$$

It consists of two configurations

$$\Phi_1 = | (closed)(open)mm | \quad (7.2)$$

and

$$\Phi_2 = |(closed)(open)nn| \quad (7.3)$$

where *(closed)* and *(open)* designate the fixed closed shells and open shells in molecular orbital spaces, and m and n are the molecular orbitals with variable electronic occupation. The CI coefficients are normalized according to

$$C_1^2 + C_2^2 = 1 \quad . \quad (7.4)$$

The electronic energy of the TCSCF wavefunction in CI form is

$$E_{elec} = \langle \Psi_{TCSCF} | \mathbf{H}_{elec} | \Psi_{TCSCF} \rangle \quad (7.5)$$

$$= \sum_{IJ}^2 C_I C_J H_{IJ} \quad (7.6)$$

and the CI Hamiltonian matrix element H_{IJ} is

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (7.7)$$

$$= 2 \sum_i^{MO} f_i^{IJ} h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj) + \beta_{ij}^{IJ}(ij|ij) \right\} \quad . \quad (7.8)$$

The summation runs over all orbitals including m and n . f_i^{IJ} is the one-electron and α_{ij}^{IJ} and β_{ij}^{IJ} are the two-electron coupling constants. Explicitly, these coupling constants for a high-spin open-shell TCSCF wavefunction, which would represent the most complicated of the commonly employed TCSCF procedures, are:

$$f_i^{11} = \begin{array}{l} \text{closed} \\ \text{open} \\ m \\ n \end{array} \begin{bmatrix} 1 \\ 1/2 \\ 1 \\ 0 \end{bmatrix} \quad (7.9)$$

$$f_i^{22} = \begin{array}{l} \text{closed} \\ \text{open} \\ m \\ n \end{array} \begin{bmatrix} 1 \\ 1/2 \\ 0 \\ 1 \end{bmatrix} \quad (7.10)$$

$$\alpha_{ij}^{11} = \begin{array}{l} \text{closed} \\ \text{open} \\ m \\ n \end{array} \begin{bmatrix} 2 & 1 & 2 & 0 \\ 1 & 1/2 & 1 & 0 \\ 2 & 1 & 2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (7.11)$$

$$\alpha_{ij}^{22} = \begin{array}{l} \text{closed} \\ \text{open} \\ m \\ n \end{array} \begin{bmatrix} 2 & 1 & 0 & 2 \\ 1 & 1/2 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 2 & 1 & 0 & 2 \end{bmatrix} \quad (7.12)$$

$$\beta_{ij}^{11} = \begin{array}{ll} \text{closed} & \begin{bmatrix} -1 & -1/2 & -1 & 0 \\ -1/2 & -1/2 & -1/2 & 0 \\ -1 & -1/2 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \\ \text{open} & \end{array} \quad (7.13)$$

$$\beta_{ij}^{22} = \begin{array}{ll} \text{closed} & \begin{bmatrix} -1 & -1/2 & 0 & -1 \\ -1/2 & -1/2 & 0 & -1/2 \\ 0 & 0 & 0 & 0 \\ -1 & -1/2 & 0 & -1 \end{bmatrix} \\ \text{open} & \end{array} \quad (7.14)$$

$$\beta_{ij}^{12} = \begin{array}{ll} \text{closed} & \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2 \\ 0 & 0 & 1/2 & 0 \end{bmatrix} \\ \text{open} & \end{array} \quad . \quad (7.15)$$

The coupling constants involving the virtual orbitals are zero as are all the elements of f^{12} and α^{12} . Explicit expressions for the elements of the CI Hamiltonian matrix in eq. (7.8) are:

$$\begin{aligned} H_{11} = & 2 \sum_{i \neq m, n}^{MO} f_i h_{ii} + \sum_{i, j \neq m, n}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \\ & + 2 h_{mm} + 2 \sum_{i \neq m, n}^{MO} f_i \left\{ 2(ii|mm) - (im|im) \right\} \\ & + (mm|mm) \end{aligned} \quad (7.16)$$

$$\begin{aligned} H_{22} = & 2 \sum_{i \neq m, n}^{MO} f_i h_{ii} + \sum_{i, j \neq m, n}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \\ & + 2 h_{nn} + 2 \sum_{i \neq m, n}^{MO} f_i \left\{ 2(ii|nn) - (in|in) \right\} \\ & + (nn|nn) \end{aligned} \quad (7.17)$$

$$H_{12} = H_{21} = (mn|mn) \quad . \quad (7.18)$$

In the above equations, the summations run over all molecular orbitals. The reduced density (coefficient) matrix elements for the high-spin open-shell TCSCF wavefunction for which the coupling constants were written out above are given by

$$f_i = \begin{array}{ll} \text{closed} & \begin{bmatrix} 1 \\ 1/2 \\ C_1^2 \\ C_2^2 \\ 0 \end{bmatrix} \\ \text{open} & \\ m & \\ n & \\ \text{virtual} & \end{array} \quad (7.19)$$

$$\alpha_{ij} = \begin{matrix} \text{closed} \\ \text{open} \\ m \\ n \\ \text{virtual} \end{matrix} \begin{bmatrix} 2 & 1 & 2C_1^2 & 2C_2^2 & 0 \\ 1 & 1/2 & C_1^2 & C_2^2 & 0 \\ 2C_1^2 & C_1^2 & C_1^2 & 0 & 0 \\ 2C_2^2 & C_2^2 & 0 & C_2^2 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (7.20)$$

$$\beta_{ij} = \begin{matrix} \text{closed} \\ \text{open} \\ m \\ n \\ \text{virtual} \end{matrix} \begin{bmatrix} -1 & -1/2 & -C_1^2 & -C_2^2 & 0 \\ -1/2 & -1/2 & -1/2C_1^2 & -1/2C_2^2 & 0 \\ -C_1^2 & -1/2C_1^2 & 0 & C_1C_2 & 0 \\ -C_2^2 & -1/2C_2^2 & C_1C_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad . \quad (7.21)$$

The reduced density matrix elements involving the virtual orbitals are all zero.

The relationships between the elements of the one- and two-electron reduced density matrices and the coupling constants are

$$f_i = \sum_{IJ}^2 C_I C_J f_i^{IJ} \quad (7.22)$$

$$\alpha_{ij} = \sum_{IJ}^2 C_I C_J \alpha_{ij}^{IJ} \quad (7.23)$$

$$\beta_{ij} = \sum_{IJ}^2 C_I C_J \beta_{ij}^{IJ} \quad . \quad (7.24)$$

Using these equations, the electronic energy of the TCSCF wavefunction in the MO form is

$$E_{elec} = 2 \sum_i^{MO} f_i h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad . \quad (7.25)$$

Finally, the total energy is simply the sum of this electronic energy and the nuclear repulsion energy:

$$E_{TCSCF} = E_{elec} + E_{nuc} \quad . \quad (7.26)$$

7.2 The Generalized Fock Operator and the Variational Conditions

The generalized Fock operator for the TCSCF case is formally the same as for the general restricted open-shell SCF wavefunction in Section 5.2 [4],

$$\mathbf{F}_i = f_i \mathbf{h} + \sum_l^{MO} \left(\alpha_{il} \mathbf{J}_l + \beta_{il} \mathbf{K}_l \right) \quad . \quad (7.27)$$

The variational conditions in the MO space are formally identical to those for the general restricted open-shell SCF wavefunction,

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad (7.28)$$

where the Lagrangian matrix is defined by

$$\epsilon_{ij} = \langle \phi_i | \mathbf{F}_i | \phi_j \rangle = f_i h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} . \quad (7.29)$$

Since the CI coefficients, C_1 and C_2 in eq. (7.1), are optimized simultaneously with the MO coefficients, the variational conditions in the CI space also are involved:

$$\sum_J^2 C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 . \quad (7.30)$$

In the above equation the H_{IJ} are the elements of the CI Hamiltonian matrix and were defined by eqs. (7.16) through (7.18).

7.3 The First Derivative of the Electronic Energy

For a TCSCF wavefunction, the variational conditions on both the MO and CI spaces, eqs. (7.28) and (7.30), must be satisfied simultaneously. Thus, the first derivative of the electronic energy can be obtained without explicit information on the derivatives of the MO and CI coefficients. The expression for the first derivative of the electronic energy of the TCSCF wavefunction is equivalent to that of the general restricted open-shell SCF wavefunction in Section 5.3:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &\quad + 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji} \end{aligned} \quad (7.31)$$

$$\begin{aligned} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &\quad - 2 \sum_{ij}^{MO} S_{ij}^a \epsilon_{ij} . \end{aligned} \quad (7.32)$$

An alternative expression in terms of the CI coefficients and Hamiltonian matrix elements is

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^2 C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad (7.33)$$

and may be compared with the result for the CI wavefunction in Section 6.2. The equivalence between eqs. (7.31) and (7.33) will be shown in the next section. The practical evaluation of the first derivative may be carried out in the same manner as was described in Section 5.4.

7.4 The First Derivative of the Hamiltonian Matrix

Although the first derivative of the TCSCF Hamiltonian matrix was not required in the manipulations in Section 7.3, it will be needed for the second derivative of the energy. Therefore an explicit expression for the first derivative of the Hamiltonian matrix is derived in this section. Differentiating eq. (7.8) with respect to a cartesian coordinate “ a ”, yields

$$\frac{\partial H_{IJ}}{\partial a} = 2 \sum_i^{MO} f_i^{IJ} \frac{\partial h_{ii}}{\partial a} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ} \frac{\partial(ii|jj)}{\partial a} + \beta_{ij}^{IJ} \frac{\partial(ij|ij)}{\partial a} \right\} . \quad (7.34)$$

Since the coupling constants, f_i^{IJ} , α_{ij}^{IJ} and β_{ij}^{IJ} , in eq. (7.34) are constant (independent of the CI coefficients), the manipulation is essentially the same as that for the GRSCF wavefunction described in Section 5.3. Thus,

$$\begin{aligned} \frac{\partial H_{IJ}}{\partial a} &= 2 \sum_i^{MO} f_i^{IJ} h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ} (ii|jj)^a + \beta_{ij}^{IJ} (ij|ij)^a \right\} \\ &+ 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} \end{aligned} \quad (7.35)$$

$$= H_{IJ}^a + 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} . \quad (7.36)$$

The skeleton (core) first derivative Hamiltonian matrices, H_{IJ}^a , and the “bare” Lagrangian matrices, ϵ_{ij}^{IJ} , appearing in eq. (7.36) are defined by

$$H_{IJ}^a = 2 \sum_i^{MO} f_i^{IJ} h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ} (ii|jj)^a + \beta_{ij}^{IJ} (ij|ij)^a \right\} \quad (7.37)$$

and

$$\epsilon_{ij}^{IJ} = f_i^{IJ} h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}^{IJ} (ij|ll) + \beta_{il}^{IJ} (il|jl) \right\} . \quad (7.38)$$

The relationship between the Lagrangian matrix elements and the “bare” Lagrangian matrix elements is given by

$$\epsilon_{ij} = \sum_{IJ}^2 C_I C_J \epsilon_{ij}^{IJ} . \quad (7.39)$$

Using equations (7.22) to (7.24) and (7.35) to (7.39), eq. (7.33) can be shown to be equivalent to eq. (7.31):

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{IJ}^2 C_I C_J \frac{\partial H_{IJ}}{\partial a} \\ &= \sum_{IJ}^2 C_I C_J \left[2 \sum_i^{MO} f_i^{IJ} h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ} (ii|jj)^a + \beta_{ij}^{IJ} (ij|ij)^a \right\} \right] \end{aligned} \quad (7.40)$$

$$+ 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} \Big] \quad (7.41)$$

$$\begin{aligned} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &+ 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji} \quad . \end{aligned} \quad (7.42)$$

7.5 The Second Derivative of the Hamiltonian Matrix

The second derivative of the TCSCF Hamiltonian matrix will be derived here. The second derivative of this Hamiltonian matrix is obtained by differentiating eq. (7.8) with respect to the variables “ a ” and “ b ”:

$$\frac{\partial^2 H_{IJ}}{\partial a \partial b} = 2 \sum_i^{MO} f_i^{IJ} \frac{\partial^2 h_{ii}}{\partial a \partial b} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ} \frac{\partial^2(ii|jj)}{\partial a \partial b} + \beta_{ij}^{IJ} \frac{\partial^2(ij|ij)}{\partial a \partial b} \right\} \quad (7.43)$$

$$= \frac{\partial}{\partial b} \left[\frac{\partial H_{IJ}}{\partial a} \right] \quad . \quad (7.44)$$

Recalling that the expression in square brackets was given by eq. (7.36), yields

$$\frac{\partial^2 H_{IJ}}{\partial a \partial b} = \frac{\partial}{\partial b} \left[H_{IJ}^a + 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} \right] \quad (7.45)$$

$$= \frac{\partial H_{IJ}^a}{\partial b} + 4 \sum_{ij}^{MO} \frac{\partial U_{ij}^a}{\partial b} \epsilon_{ji}^{IJ} + 4 \sum_{ij}^{MO} U_{ij}^a \frac{\partial \epsilon_{ji}^{IJ}}{\partial b} \quad . \quad (7.46)$$

The first term of eq. (7.46) is manipulated as was done for the GRSCF wavefunction in Section 5.6, since the f_i^{IJ} , α_{ij}^{IJ} and β_{ij}^{IJ} are all constants.

$$\frac{\partial H_{IJ}^a}{\partial b} = \frac{\partial}{\partial b} \left[2 \sum_i^{MO} f_i^{IJ} h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^a + \beta_{ij}^{IJ}(ij|ij)^a \right\} \right] \quad (7.47)$$

$$\begin{aligned} &= 2 \sum_i^{MO} f_i^{IJ} h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^{ab} + \beta_{ij}^{IJ}(ij|ij)^{ab} \right\} \\ &+ 4 \sum_{ij}^{MO} U_{ij}^b \epsilon_{ji}^{IJ^a} \end{aligned} \quad (7.48)$$

$$= H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^b \epsilon_{ji}^{IJ^a} \quad . \quad (7.49)$$

The skeleton (core) second derivative Hamiltonian matrices, H_{IJ}^{ab} , and skeleton (core) first derivative “bare” Lagrangian matrices, $\epsilon_{ij}^{IJ^a}$, are:

$$H_{IJ}^{ab} = 2 \sum_i^{MO} f_i^{IJ} h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^{ab} + \beta_{ij}^{IJ}(ij|ij)^{ab} \right\} \quad (7.50)$$

and

$$\epsilon_{ij}^{IJ^a} = f_i^{IJ} h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll)^a + \beta_{il}^{IJ}(il|jl)^a \right\} \quad . \quad (7.51)$$

The skeleton (core) first derivative “bare” Lagrangian matrices are related to their “parent” quantities through the expression

$$\epsilon_{ij}^a = \sum_{IJ}^2 C_I C_J \epsilon_{ij}^{IJ^a} \quad (7.52)$$

where

$$\epsilon_{ij}^a = f_i h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} \quad . \quad (7.53)$$

The second term in eq. (7.46) is rewritten using a result from Section 3.3 to become

$$4 \sum_{ij}^{MO} \frac{\partial U_{ij}^a}{\partial b} \epsilon_{ji}^{IJ} = 4 \sum_{ij}^{MO} \left[U_{ij}^{ab} - \sum_k^{MO} U_{ik}^b U_{kj}^a \right] \epsilon_{ji}^{IJ} \quad . \quad (7.54)$$

The third term of eq. (7.46) is treated in a manner similar to that in Section 5.5. The derivative expression of the “bare” Lagrangian matrix is manipulated in the same way as its parent. After a similar derivation to that performed in Section 5.5, the third term becomes:

$$4 \sum_{ij}^{MO} U_{ij}^a \frac{\partial \epsilon_{ji}^{IJ}}{\partial b} = 4 \sum_{ij}^{MO} U_{ij}^a \left[\epsilon_{ji}^{IJ^b} + \sum_k^{MO} \left(U_{kj}^b \zeta_{ki}^{jIJ} + U_{ki}^b \epsilon_{jk}^{IJ} \right) + \sum_{kl}^{MO} U_{kl}^b \tau_{ji,kl}^{jIJ} \right] \quad (7.55)$$

$$= 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ^b} + 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ki}^{jIJ} + 4 \sum_{ijk}^{MO} U_{ij}^a U_{ki}^b \epsilon_{jk}^{IJ} \\ + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jIJ} \quad . \quad (7.56)$$

The “bare” generalized Lagrangian and τ matrices are defined by

$$\zeta_{ij}^{lIJ} = f_l^{IJ} h_{ij} + \sum_k^{MO} \left\{ \alpha_{lk}^{IJ}(ij|kk) + \beta_{lk}^{IJ}(ik|jk) \right\} \quad (7.57)$$

and

$$\tau_{ij,kl}^{mnIJ} = 2\alpha_{mn}^{IJ}(ij|kl) + \beta_{mn}^{IJ} \left\{ (ik|jl) + (il|jk) \right\} \quad . \quad (7.58)$$

They are related to their “parent” quantities through the following expressions:

$$\zeta_{ij}^l = \sum_{IJ}^2 C_I C_J \zeta_{ij}^{IJ} \quad (7.59)$$

$$\tau_{ij,kl}^{mn} = \sum_{IJ}^2 C_I C_J \tau_{ij,kl}^{mnIJ} . \quad (7.60)$$

Thus, the second derivative of the H_{IJ} matrix is obtained by substituting eqs. (7.49), (7.54) and (7.56) into eq. (7.46) to yield the final expression,

$$\begin{aligned} \frac{\partial^2 H_{IJ}}{\partial a \partial b} &= H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^b \epsilon_{ji}^{IJ^a} \\ &+ 4 \sum_{ij}^{MO} \left[U_{ij}^{ab} - \sum_k^{MO} U_{ik}^b U_{kj}^a \right] \epsilon_{ji}^{IJ} \\ &+ 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ^b} + 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ki}^{jIJ} \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{ki}^b \epsilon_{jk}^{IJ} \\ &+ 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlIJ} \\ &= H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji}^{IJ} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ki}^{jIJ} \\ &+ 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlIJ} . \end{aligned} \quad (7.61)$$

(7.62)

7.6 The Second Derivative of the Electronic Energy

An expression for the second derivative of the electronic energy of the TCSCF wavefunction is formally the same as that for the CI wavefunction in Section 6.7:

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^2 C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} - 2 \sum_{IJ}^2 \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (7.63)$$

The last equation of Section 7.5 allows us to rewrite this expression as:

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{IJ}^2 C_I C_J \left[H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji}^{IJ} \right. \\ &\quad + 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\ &\quad \left. + 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{ij} + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \right] \\ &- 2 \sum_{IJ}^2 \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (7.64)$$

The relationships between the one- and two-electron reduced density matrices and the coupling constants given by eqs. (7.22) to (7.24) and the relations between the “bare” matrices and their “parent” matrices in eqs. (7.39), (7.52), (7.59) and (7.60) are used to rewrite (7.64) as:

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{MO} \sum_{IJ}^2 C_I C_J f_i^{IJ} h_{ii}^{ab} + \sum_{ij}^{MO} \sum_{IJ}^2 C_I C_J \left\{ \alpha_{ij}^{IJ} (ii|jj)^{ab} + \beta_{ij}^{IJ} (ij|ij)^{ab} \right\} \\ &\quad + 4 \sum_{ij}^{MO} \sum_{IJ}^2 C_I C_J U_{ij}^{ab} \epsilon_{ji}^{IJ} \\ &\quad + 4 \sum_{ij}^{MO} \sum_{IJ}^2 C_I C_J \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) + 4 \sum_{ijk}^{MO} \sum_{IJ}^2 C_I C_J U_{ij}^a U_{kj}^b \zeta_{ik}^{ij} \\ &\quad + 4 \sum_{ijkl}^{MO} \sum_{IJ}^2 C_I C_J U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \\ &- 2 \sum_{IJ}^2 \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \end{aligned} \quad (7.65)$$

$$\begin{aligned} &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij} (ii|jj)^{ab} + \beta_{ij} (ij|ij)^{ab} \right\} \\ &\quad + 4 \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji} \\ &\quad + 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) + 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \\ &- 2 \sum_{IJ}^2 \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (7.66)$$

In order to eliminate U_{ij}^{ab} in eq. (7.66), the second derivative form of the orthonormality condition on the molecular orbitals from Section 3.7 may be used:

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad (7.67)$$

where

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \eta_{ij}^{ab} \quad (7.68)$$

and

$$\eta_{ij}^{ab} = \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) . \quad (7.69)$$

Thus a final expression for the second derivative of the electronic energy becomes:

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &- 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \epsilon_{ij} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \\ &- 2 \sum_{IJ}^2 \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \end{aligned} \quad (7.70)$$

$$\begin{aligned} &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &- 2 \sum_{ij}^{MO} S_{ij}^{ab} \epsilon_{ij} - 2 \sum_{ij}^{MO} \eta_{ij}^{ab} \epsilon_{ij} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j \\ &+ 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \left[2\alpha_{jl}(ij|kl) + \beta_{jl} \left\{ (ik|jl) + (il|jk) \right\} \right] \\ &- 2 \sum_{IJ}^2 \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (7.71)$$

It should be noted that the equation for the GRSCF wavefunction in Section 5.6 and the equation for the TCSCF wavefunction, eq. (7.71), differ formally only in the last term of

the latter. The last term in eq. (7.71) involves the derivatives of the CI coefficients. It is necessary to determine the changes of both the MO and CI coefficients with respect to perturbations for the evaluation of the second derivative of the TCSCF electronic energy. These quantities come from solving the coupled perturbed two-configuration Hartree-Fock (CPTCHF) equations, which will be discussed in detail in Chapter 13.

References

1. G. Das and A.C. Wahl, *J. Chem. Phys.* **44**, 87 (1966).
2. A.C. Wahl and G. Das, *Adv. Quantum Chem.* **5**, 261 (1970).
3. A.C. Wahl and G. Das, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.51 (1977).
4. F.W. Bobrowicz and W.A. Goddard, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.79 (1977).
5. R. Carbo and J.M. Riera, *A General SCF Theory*, Springer-Verlag, Berlin, 1978.

Suggested Reading

1. S. Kato and K. Morokuma, *Chem. Phys. Lett.* **65**, 19 (1979).
2. J.D. Goddard, N.C. Handy, and H.F. Schaefer, *J. Chem. Phys.* **71**, 1525 (1979).
3. Y. Yamaguchi, Y. Osamura, G. Fitzgerald, and H.F. Schaefer, *J. Chem. Phys.* **78**, 1607 (1983).
4. Y. Yamaguchi, Y. Osamura, and H.F. Schaefer, *J. Am. Chem. Soc.* **105**, 7506 (1983).
5. M. Duran, Y. Yamaguchi, and H.F. Schaefer, *J. Phys. Chem.* **92**, 3070 (1988).

Chapter 8

Paired Excitation Multiconfiguration Self-Consistent-Field Wavefunctions

A paired excitation multiconfiguration self-consistent-field (PEMCSCF) wavefunction is another special case of more general multiconfiguration SCF (MCSCF) wavefunctions. The PEMCSCF wavefunctions provide useful simple orbital representations for describing molecular bonding and chemical reactions. The PEMCSCF molecular orbitals typically resemble those expected for bond and lone-pair orbitals. For the PEMCSCF procedure, the only configurations which are employed are derived from excitations of pairs of electrons within a limited number of molecular orbitals (MOs). The excitation of two electrons is termed “paired” in that both (one with α and one with β spin function) are excited from one MO and remain paired in another MO. The simplest case of a PEMCSCF wavefunction is the two-configuration SCF (TCSCF) wavefunction described in the preceding chapter. A generalized valence-bond (GVB) wavefunction where valence-bond-type paired electronic excitations have been employed is a more complicated example.

8.1 The Paired Excitation Multiconfiguration Self-Consistent-Field (PEMCSCF) Wavefunction and Energy

Consider a high-spin open-shell paired excitation multiconfiguration self-consistent-field (PEMCSCF) wavefunction [1,2]. Obviously the closed-shell PEMCSCF wavefunction is

a special case of this example. We partition the molecular orbitals into four sets:

<i>C</i> (<i>Closed</i>)	<i>doubly occupied MOs</i>
<i>O</i> (<i>Open</i>)	<i>singly occupied MOs</i>
<i>P</i> (<i>Pair</i>)	<i>paired excitation MOs</i>
<i>V</i> (<i>Virtual</i>)	<i>unoccupied MOs</i>

The P set involves those orbitals with fractional occupation number and is commonly called the “active space”. For each configuration, there is a subset of n molecular orbitals that are doubly occupied and belong to the set of paired excitation orbitals:

$$S_I = \{i_1, i_2, i_3, \dots, i_n\} \quad (8.1)$$

n is the total number of doubly occupied MOs and equals half the number of electrons involved in the P set given the paired excitation restriction. Using the above terminology, the PEMCSCF wavefunction is:

$$\Psi_{PEMCSCF} = \sum_I^{CI} C_I \Phi_I \quad (8.2)$$

where C_I is the coefficient of the I th configuration and each configuration state function Φ_I may be described by

$$\Phi_I = A \left| (\text{closed})(\text{open})(S_I) \right| \quad (8.3)$$

where A is the antisymmetrizer. The CI coefficients are normalized according to the usual convention as

$$\sum_I^{CI} C_I^2 = 1 \quad . \quad (8.4)$$

The electronic energy of the PEMCSCF wavefunction in CI form is

$$E_{elec} = \langle \Psi_{PEMCSCF} | \mathbf{H}_{elec} | \Psi_{PEMCSCF} \rangle \quad (8.5)$$

$$= \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad . \quad (8.6)$$

The elements of the CI Hamiltonian matrix remain relatively simple:

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (8.7)$$

$$= 2 \sum_i^{MO} f_i^{IJ} h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj) + \beta_{ij}^{IJ}(ij|ij) \right\} \quad . \quad (8.8)$$

The summation here runs over all orbitals including the paired excitation MOs. The quantity f_i^{IJ} is the one-electron, and α_{ij}^{IJ} and β_{ij}^{IJ} are the two-electron coupling constants. These

coupling constants are determined by the diagonal elements H_{II} of the CI Hamiltonian matrix,

$$f_i^{II} = \begin{array}{ll} \text{closed} & \begin{bmatrix} 1 \\ 1/2 \\ 1 \end{bmatrix} \\ \text{open} & \\ S_I & \end{array} \quad (8.9)$$

$$\alpha_{ij}^{II} = \begin{array}{ll} \text{closed} & \begin{bmatrix} 2 & 1 & 2 \\ 1 & 1/2 & 1 \\ 2 & 1 & 2 \end{bmatrix} \\ \text{open} & \\ S_I & \end{array} \quad (8.10)$$

$$\beta_{ij}^{II} = \begin{array}{ll} \text{closed} & \begin{bmatrix} -1 & -1/2 & -1 \\ -1/2 & -1/2 & -1/2 \\ -1 & -1/2 & -1 \end{bmatrix} \\ \text{open} & \\ S_I & \end{array} \quad . \quad (8.11)$$

For the off-diagonal elements H_{IJ} , the only nonvanishing coupling constants are of the exchange type and are

$$\beta_{ij}^{IJ} = \begin{array}{ll} \text{closed} & \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2 \\ 0 & 0 & 1/2 & 0 \end{bmatrix} \\ \text{open} & \\ S_I & \\ S_J & \end{array} \quad . \quad (8.12)$$

In eq. (8.12) the configurations I and J are constrained by the PEMCSCF model to have only one paired orbital different. Those coupling constants not defined above are identically zero.

The CI matrix elements in eq. (8.8) are given explicitly by :

a) For the diagonal elements,

$$H_{II} = H_{00} + 2 \sum_{i \in S_I}^P h_{ii} + 2 \sum_{i \in S_I}^P \sum_j^{C,O} f_j \left\{ 2(ii|jj) - (ij|ij) \right\} + \sum_{i,j \in S_I}^P \left\{ 2(ii|jj) - (ij|ij) \right\} \quad (8.13)$$

where H_{00} is

$$H_{00} = 2 \sum_i^{C,O} f_i h_{ii} + \sum_i^{C,O} \sum_j^{C,O} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad . \quad (8.14)$$

b) For the off-diagonal elements with one paired orbital different,

$$H_{IJ} = (pq|pq) , \quad \text{where } p \in S_I \text{ and } q \in S_J \quad . \quad (8.15)$$

In the above equation, p and q are the two unique MOs that are not common to the S_I and S_J sets.

c) For the off-diagonal elements with more than one paired orbital different,

$$H_{IJ} = 0 \quad . \quad (8.16)$$

The one-electron reduced density matrix used in the above energy expression is

$$f_i = \begin{array}{c} \text{closed} \\ \text{open} \\ \text{pair} \\ \text{virtual} \end{array} \left[\begin{array}{c} 1 \\ 1/2 \\ \omega_f \\ 0 \end{array} \right] \quad . \quad (8.17)$$

An array ω_f is defined by

$$(\omega_f)_i = \sum_I^{CI} \delta(i \in S_I) C_I^2 \quad . \quad (8.18)$$

The function δ is unity when an orbital i is in the paired excitation set; otherwise it is zero. Using this definition, the Coulombic two-electron reduced density matrix is

$$\alpha_{ij} = \begin{array}{c} \text{closed} \\ \text{open} \\ \text{pair} \\ \text{virtual} \end{array} \left[\begin{array}{cccc} 2 & 1 & 2\omega_f & 0 \\ 1 & 1/2 & \omega_f & 0 \\ 2\omega_f & \omega_f & \omega_\alpha & 0 \\ 0 & 0 & 0 & 0 \end{array} \right] \quad (8.19)$$

with the additional matrix ω_α defined by

$$(\omega_\alpha)_{ij} = 2 \sum_I^{CI} \delta(i, j \in S_I) C_I^2 \quad (8.20)$$

where i and j must both be orbitals in the set of paired excitation orbitals. The exchange two-electron reduced density matrix is

$$\beta_{ij} = \begin{array}{c} \text{closed} \\ \text{open} \\ \text{pair} \\ \text{virtual} \end{array} \left[\begin{array}{cccc} -1 & -1/2 & -\omega_f & 0 \\ -1/2 & -1/2 & -1/2\omega_f & 0 \\ -\omega_f & -1/2\omega_f & -\omega_\beta & 0 \\ 0 & 0 & 0 & 0 \end{array} \right] \quad (8.21)$$

where the matrix ω_β is defined by

$$(\omega_\beta)_{ij} = \sum_I^{CI} \delta(i, j \in S_I) C_I^2 - \sum_{IJ}^{CI*} \delta(i \in S_I, j \in S_J) C_I C_J \quad . \quad (8.22)$$

In the first term i and j must be in the same set of paired excitation orbitals and in the second term one must belong to each of the two sets. In this equation \sum_{IJ}^{CI*} means that the summation runs over only those pairs of configurations that differ by at most one electron pair.

The relationships between the elements of the one- and two-electron reduced density matrices and the coupling constants are

$$f_i = \sum_{IJ}^{CI} C_I C_J f_i^{IJ} \quad (8.23)$$

$$\alpha_{ij} = \sum_{IJ}^{CI} C_I C_J \alpha_{ij}^{IJ} \quad (8.24)$$

and

$$\beta_{ij} = \sum_{IJ}^{CI} C_I C_J \beta_{ij}^{IJ} \quad . \quad (8.25)$$

Using these equations the electronic energy of the PEMCSCF wavefunction in MO form is

$$E_{elec} = 2 \sum_i^{MO} f_i h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad . \quad (8.26)$$

The total PEMCSCF energy of the system is:

$$E_{PEMCSCF} = E_{elec} + E_{nuc} \quad . \quad (8.27)$$

The total energy and its derivatives for the PEMCSCF wavefunction are formally the same as those for the TCSCF wavefunction, the difference being the contents of the f^{IJ} , α^{IJ} , β^{IJ} and f , α and β matrices.

8.2 The Generalized Fock Operator and the Variational Conditions

The PEMCSCF generalized Fock operator [1] is formally the same as for the general restricted open-shell SCF and TCSCF wavefunctions, the difference being the elements of the one- (f) and two-electron (α and β) reduced density matrices:

$$\mathbf{F}_i = f_i \mathbf{h} + \sum_l^{MO} \left(\alpha_{il} \mathbf{J}_l + \beta_{il} \mathbf{K}_l \right) \quad . \quad (8.28)$$

The variational conditions on the MO space are formally the same as for a TCSCF wavefunction:

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad . \quad (8.29)$$

The Lagrangian matrix is

$$\epsilon_{ij} = \langle \phi_i | \mathbf{F}_i | \phi_j \rangle = f_i h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} \quad . \quad (8.30)$$

The variational condition on the CI space is

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad . \quad (8.31)$$

The elements of the CI Hamiltonian matrix appearing in eq. (8.31) were defined by eqs. (8.13) to (8.16).

8.3 The First Derivative of the Electronic Energy

The expression for the first derivative of the electronic energy of the PEMCSCF wavefunction is formally equivalent to that for the TCSCF wavefunction:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &+ 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji} \\ &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \end{aligned} \quad (8.32)$$

$$- 2 \sum_{ij}^{MO} S_{ij}^a \epsilon_{ij} \quad . \quad (8.33)$$

The first derivative of this energy in CI form is

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad (8.34)$$

where the first derivative Hamiltonian matrices are

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} \quad . \quad (8.35)$$

The skeleton (core) first derivative Hamiltonian matrices, H_{IJ}^a , and the “bare” Lagrangian matrices, ϵ^{IJ} , in the preceding equation are

$$H_{IJ}^a = 2 \sum_i^{MO} f_i^{IJ} h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^a + \beta_{ij}^{IJ}(ij|ij)^a \right\} \quad (8.36)$$

and

$$\epsilon_{ij}^{IJ} = f_i^{IJ} h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll) + \beta_{il}^{IJ}(il|jl) \right\} \quad . \quad (8.37)$$

The relationship between a Lagrangian matrix and the “bare” Lagrangian matrices is

$$\epsilon_{ij} = \sum_{IJ}^{CI} C_I C_J \epsilon_{ij}^{IJ} . \quad (8.38)$$

A proof of the equivalence of eq. (8.32) and eq. (8.34) was given in Section 7.4. The practical evaluation of the first derivative may be performed in the same manner as was described in Section 5.4.

8.4 The Second Derivative of the Electronic Energy

The form of the second derivative of the electronic energy for a PEMCSCF wavefunction is formally the same as that for a TCSCF wavefunction, the difference being the elements of the one- (f) and two-electron (α and β) matrices:

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) . \quad (8.39)$$

The second derivative of the Hamiltonian matrix is

$$\begin{aligned} \frac{\partial^2 H_{IJ}}{\partial a \partial b} &= H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji}^{IJ} \\ &+ 4 \sum_{ij}^{MO} (U_{ij}^b \epsilon_{ji}^{IJa} + U_{ij}^a \epsilon_{ji}^{IJb}) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{jIJ} \\ &+ 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlIJ} . \end{aligned} \quad (8.40)$$

The skeleton (core) second derivative Hamiltonian matrices H_{IJ}^{ab} are defined by

$$H_{IJ}^{ab} = 2 \sum_i^{MO} f_i^{IJ} h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ} (ii|jj)^{ab} + \beta_{ij}^{IJ} (ij|ij)^{ab} \right\} . \quad (8.41)$$

Similarly the skeleton (core) “bare” first derivative Lagrangian matrices ϵ^{IJa} are

$$\epsilon_{ij}^{IJa} = f_i^{IJ} h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}^{IJ} (ij|ll)^a + \beta_{il}^{IJ} (il|jl)^a \right\} . \quad (8.42)$$

Finally the “bare” generalized Lagrangian and τ matrices are

$$\zeta_{ij}^{lIJ} = f_l^{IJ} h_{ij} + \sum_k^{MO} \left\{ \alpha_{lk}^{IJ} (ij|kk) + \beta_{lk}^{IJ} (ik|jk) \right\} \quad (8.43)$$

and

$$\tau_{ij,kl}^{mnIJ} = 2\alpha_{mn}^{IJ}(ij|kl) + \beta_{mn}^{IJ}\{(ik|jl) + (il|jk)\} . \quad (8.44)$$

These "bare" quantities are related to their "parents" through:

$$\epsilon_{ij}^a = \sum_{IJ}^{CI} C_I C_J \epsilon_{ij}^{IJa} \quad (8.45)$$

$$\zeta_{ij}^l = \sum_{IJ}^{CI} C_I C_J \zeta_{ij}^{IJl} \quad (8.46)$$

and

$$\tau_{ij,kl}^{mn} = \sum_{IJ}^{CI} C_I C_J \tau_{ij,kl}^{mnIJ} . \quad (8.47)$$

Combining equations (8.39) and (8.40) gives the final working expression:

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &- 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \epsilon_{ij} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \\ &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &- 2 \sum_{ij}^{MO} S_{ij}^{ab} \epsilon_{ij} - 2 \sum_{ij}^{MO} \eta_{ij}^{ab} \epsilon_{ij} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j \\ &+ 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \left[2\alpha_{jl}(ij|kl) + \beta_{jl}\{(ik|jl) + (il|jk)\} \right] \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (8.48)$$

In these equations the ξ^{ab} and η^{ab} matrices were defined in Section 3.7 as:

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \eta_{ij}^{ab} , \quad (8.50)$$

where

$$\eta_{ij}^{ab} = \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \quad (8.51)$$

and satisfy the following relationship,

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 . \quad (8.52)$$

It is necessary to determine the changes in both the MO and CI coefficients with respect to perturbations in order to evaluate the second derivative of the electronic energy. These quantities are by no means trivial to determine but may be found by solving the coupled perturbed paired excitation multiconfiguration Hartree-Fock (CPPEMCHF) equations. The latter equations will be discussed in detail in Chapter 13.

References

1. F.W. Bobrowicz and W.A. Goddard, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.79 (1977).
2. R. Carbo and J.M. Riera, *A General SCF Theory*, Springer-Verlag, Berlin, 1978.

Suggested Reading

1. S. Kato and K. Morokuma, *Chem. Phys. Lett.* **65**, 19 (1979).
2. J.D. Goddard, N.C. Handy, and H.F. Schaefer, *J. Chem. Phys.* **71**, 1525 (1979).
3. Y. Yamaguchi, Y. Osamura, and H.F. Schaefer, *J. Am. Chem. Soc.* **105**, 7506 (1983).
4. M. Duran, Y. Yamaguchi, and H.F. Schaefer, *J. Phys. Chem.* **92**, 3070 (1988).
5. M. Duran, Y. Yamaguchi, R.B. Remington, and H.F. Schaefer, *Chem. Phys.* **122**, 201 (1988).

Chapter 9

Multiconfiguration Self-Consistent-Field Wavefunctions

The multiconfiguration self-consistent-field (MCSCF) method is the most powerful method to improve the quality of the molecular orbitals and to take electron correlation effects into account simultaneously. The complete active space SCF (CASSCF) wavefunction is a very important special case of still more general MCSCF wavefunctions. In the CASSCF method a full CI procedure (complete optimization of both the MO and CI spaces) is performed within a limited orbital set (usually called the *active space*). Quadratically convergent procedures developed in recent years have made it feasible, although still fairly computationally expensive, to apply MCSCF methods to a wide variety of chemical problems. In this chapter, the first and second derivatives of MCSCF wavefunctions are described.

9.1 The MCSCF Wavefunction and Energy

The multiconfiguration self-consistent-field (MCSCF) wavefunction is a linear combination of electronic configurations Φ_I that are constructed from a set of reference molecular orbitals [1-3]

$$\Psi_{MCSCF} = \sum_I^{CI} C_I \Phi_I . \quad (9.1)$$

The wavefunction is normalized, giving the condition

$$\sum_I^{CI} C_I^2 = 1 \quad (9.2)$$

on the CI coefficients.

The electronic energy of the MCSCF wavefunction in CI form is

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} . \quad (9.3)$$

The CI Hamiltonian matrix element in eq. (9.3) is defined by

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (9.4)$$

$$= \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl) . \quad (9.5)$$

The quantities γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} in the above equation are the one- and two-electron coupling constants between the electronic configurations and the molecular orbitals. The one- and two-electron reduced density matrices [4] are defined in terms of these coupling constants by

$$\gamma_{ij} = \sum_{IJ}^{CI} C_I C_J \gamma_{ij}^{IJ} \quad (9.6)$$

$$\Gamma_{ijkl} = \sum_{IJ}^{CI} C_I C_J \Gamma_{ijkl}^{IJ} . \quad (9.7)$$

Using these quantities the electronic energy of the MCSCF wavefunction is given in MO form as

$$E_{elec} = \sum_{ij}^{MO} \gamma_{ij} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl) . \quad (9.8)$$

The coupling constants γ^{IJ} and Γ^{IJ} and the reduced density matrices γ and Γ for the MCSCF wavefunction have the same meaning as for the corresponding CI wavefunction. Different notations are used in this book in order to avoid any possible confusion. The total energy of the system is finally the sum of the electronic energy and the nuclear repulsion energy

$$E_{MCSCF} = E_{elec} + E_{nuc} . \quad (9.9)$$

9.2 The Variational Conditions

The variational conditions in the CI space are formally the same as described for the CI wavefunction in Section 6.1:

$$\sum_I^{CI} C_I \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 . \quad (9.10)$$

The CI Hamiltonian matrix in eq. (9.10) is defined by eq. (9.5) and δ_{IJ} is the Kronecker delta function.

Another constraint on the MCSCF wavefunction (9.1) is the variational condition on the MO space. This condition requires a symmetric Lagrangian matrix at convergence:

$$x_{ij} - x_{ji} = 0 \quad (9.11)$$

where

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl) \quad . \quad (9.12)$$

If the Fock operator for the MCSCF wavefunction is defined as

$$\mathbf{F}_{ij} = \gamma_{ij}\mathbf{h} + 2 \sum_{kl}^{MO} \Gamma_{ijkl}\mathbf{J}_{kl} \quad , \quad (9.13)$$

then the relationship between the Fock and Lagrangian matrices is given by

$$x_{ij} = \left\langle \phi_i \left| \sum_m^{MO} \mathbf{F}_{jm} \right| \phi_m \right\rangle \quad (9.14)$$

$$= \left\langle \phi_i \left| \sum_m^{MO} \left(\gamma_{jm}\mathbf{h} + 2 \sum_{kl}^{MO} \Gamma_{jmkl}\mathbf{J}_{kl} \right) \right| \phi_m \right\rangle \quad . \quad (9.15)$$

In eq. (9.13) \mathbf{h} is the one-electron operator and \mathbf{J}_{kl} is the two-electron operator which satisfies

$$\left\langle \phi_i | \mathbf{J}_{kl} | \phi_j \right\rangle = (ij|kl) \quad . \quad (9.16)$$

9.3 The First Derivative of the Electronic Energy

The first derivative of the electronic energy of an MCSCF wavefunction can be obtained without explicit information on the derivatives of the MO and CI coefficients. The variational conditions on both spaces must be satisfied simultaneously as in eqs. (9.10) and (9.11). Thus, these coefficients are optimized explicitly in the MCSCF procedure.

The first energy derivative expression in CI form is

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad . \quad (9.17)$$

The first derivatives of the Hamiltonian matrices were obtained in Section 6.4:

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} \quad . \quad (9.18)$$

The skeleton (core) first derivative Hamiltonian matrices H_{IJ}^a and the “bare” Lagrangian matrices x^{IJ} are

$$H_{IJ}^a = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl)^a \quad (9.19)$$

$$x_{ij}^{IJ} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ}(im|kl) . \quad (9.20)$$

The following relationship holds between the Lagrangian and the “bare” Lagrangian matrices:

$$x_{ij} = \sum_{IJ}^{CI} C_I C_J x_{ij}^{IJ} . \quad (9.21)$$

This expression may be compared to that for the coupling constants in eqs. (9.6) and (9.7). It should be noted that the “bare” quantities, γ^{IJ} , Γ^{IJ} , H_{IJ} , H_{IJ}^a , and x^{IJ} do *not* contain the CI coefficients in their definition.

Using these equations, an expression for the first derivative of the electronic energy becomes

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad (9.22)$$

$$= \sum_{IJ}^{CI} C_I C_J \left\{ \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} \right\} \quad (9.23)$$

$$= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a x_{ij} . \quad (9.24)$$

Alternatively the energy first derivative expression is obtained by differentiating eq. (9.8) with respect to a cartesian coordinate “ a ”:

$$\frac{\partial E_{elec}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij} \frac{\partial h_{ij}}{\partial a} + \sum_{ijkl}^{MO} \Gamma_{ijkl} \frac{\partial (ij|kl)}{\partial a} . \quad (9.25)$$

A more explicit expression for eq. (9.25) is equivalent to that obtained for the CI wavefunction in Section 6.2:

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a \\ &+ 2 \sum_{ij}^{MO} U_{ij}^a x_{ij} \end{aligned} \quad (9.26)$$

which is identical to eq. (9.24). The Lagrangian matrix x in eq. (9.26) was defined by eq. (9.12). Using the variational condition (9.11), eq. (9.26) is simplified further to give

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a \\ &+ \sum_{ij}^{MO} \left(U_{ij}^a + U_{ji}^a \right) x_{ij} \end{aligned} \quad (9.27)$$

$$\begin{aligned}
&= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a \\
&- \sum_{ij}^{MO} S_{ij}^a x_{ij} .
\end{aligned} \tag{9.28}$$

In the last step, the first derivative form of the orthonormality condition of the MOs described in Section 3.7,

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \tag{9.29}$$

was employed. It should be emphasized again that the explicit evaluation of the changes in the MO and CI coefficients is *not* necessary for the first derivative of the energy of MCSCF wavefunctions.

9.4 The Evaluation of the First Derivative

In the practical evaluation of the first derivative, eq. (9.28) is usually transformed into the AO basis. The first derivative of the electronic energy is

$$\begin{aligned}
\frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} \sum_{\mu\nu}^{AO} \gamma_{ij} C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} + \sum_{ijkl}^{MO} \sum_{\mu\nu\rho\sigma}^{AO} \Gamma_{ijkl} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\
&- \sum_{ij}^{MO} \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} x_{ij} .
\end{aligned} \tag{9.30}$$

The one- and two-electron reduced density matrices in the AO basis are defined by (see Section 2.8)

$$\gamma_{\mu\nu} = \sum_{ij}^{MO} C_\mu^i C_\nu^j \gamma_{ij} \tag{9.31}$$

and

$$\Gamma_{\mu\nu\rho\sigma} = \sum_{ijkl}^{MO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \Gamma_{ijkl} . \tag{9.32}$$

The “energy weighted” density matrix for an MCSCF wavefunction is

$$W_{\mu\nu} = \sum_{ij}^{MO} C_\mu^i C_\nu^j x_{ij} . \tag{9.33}$$

Using these density matrices, the first derivative expression becomes

$$\frac{\partial E_{elec}}{\partial a} = \sum_{\mu\nu}^{AO} \gamma_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} + \sum_{\mu\nu\rho\sigma}^{AO} \Gamma_{\mu\nu\rho\sigma} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} - \sum_{\mu\nu}^{AO} W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} . \tag{9.34}$$

In practice, the derivative integrals are evaluated only for unique combinations of AOs ($\mu \geq \nu$ and $\rho \geq \sigma$) in order to minimize computational effort. The first derivative of the electronic energy in a directly applicable form is

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} = & 2 \sum_{\mu \geq \nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) \gamma_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} \\ & + 4 \sum_{\substack{\mu \geq \nu, \rho \geq \sigma \\ \mu\nu \geq \rho\sigma}}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) \left(1 - \frac{\delta_{\rho\sigma}}{2} \right) \left(1 - \frac{\delta_{\mu\nu, \rho\sigma}}{2} \right) \\ & \times \left\{ 2\Gamma_{\mu\nu\rho\sigma} \right\} \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \\ & - 2 \sum_{\mu\nu}^{AO} \left(1 - \frac{\delta_{\mu\nu}}{2} \right) W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial a} . \end{aligned} \quad (9.35)$$

In eq. (9.35) $\delta_{\mu\nu}$ is the Kronecker function. In the second term of this equation the summations run over the indices that satisfy $\mu\nu \geq \rho\sigma$, where $\mu\nu = \frac{1}{2}\mu(\mu - 1) + \nu$ and $\rho\sigma = \frac{1}{2}\rho(\rho - 1) + \sigma$.

9.5 The Second Derivative of the Electronic Energy

The second derivative of the electronic energy of the MCSCF wavefunction is formally the same as for the CI wavefunction in Section 6.7:

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (9.36)$$

The second derivative of the Hamiltonian matrix was derived in Section 6.6:

$$\begin{aligned} \frac{\partial^2 H_{IJ}}{\partial a \partial b} = & H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} x_{ij}^{IJ} \\ & + 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\ & + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} . \end{aligned} \quad (9.37)$$

The skeleton (core) second derivative Hamiltonian matrices H_{IJ}^{ab} and the skeleton (core) first derivative “bare” Lagrangian matrices x^{IJ^a} appearing in eq. (9.37) are defined by

$$H_{IJ}^{ab} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ} (ij|kl)^{ab} \quad (9.38)$$

and

$$x_{ij}^{IJ^a} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ} (im|kl)^a . \quad (9.39)$$

The “bare” y matrices are

$$y_{ijkl}^{IJ} = \gamma_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ} (ik|mn) + 4 \sum_{mn}^{MO} \Gamma_{jmkn}^{IJ} (im|kn) . \quad (9.40)$$

These “bare” x^a and y matrix elements are related to their “parents” through

$$x_{ij}^a = \sum_{IJ}^{CI} C_I C_J x_{ij}^{IJ^a} . \quad (9.41)$$

and

$$y_{ijkl} = \sum_{IJ}^{CI} C_I C_J y_{ijkl}^{IJ} . \quad (9.42)$$

Combining eqs. (9.36) and (9.37), gives

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl} (ij|kl)^{ab} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^{ab} x_{ij} \\ &+ 2 \sum_{ij}^{MO} (U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b) \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) . \end{aligned} \quad (9.43)$$

In deriving eq. (9.43), equations (9.6), (9.7), (9.21), (9.41) and (9.42) were employed. Using the variational condition for the symmetric Lagrangian matrix (9.11), the U^{ab} term in eq. (9.43) is conveniently eliminated:

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl} (ij|kl)^{ab} \\ &- \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij} \\ &+ 2 \sum_{ij}^{MO} (U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b) \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} \\
& - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) \quad (9.44)
\end{aligned}$$

$$\begin{aligned}
& = \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{ab} \\
& - \sum_{ij}^{MO} S_{ij}^{ab} x_{ij} - \sum_{ij}^{MO} \eta_{ij}^{ab} x_{ij} \\
& + 2 \sum_{ij}^{MO} (U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b) \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} \\
& - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) \quad . \quad (9.45)
\end{aligned}$$

In these equations the ξ^{ab} and η^{ab} matrices were defined as in Section 3.7 by,

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \eta_{ij}^{ab} \quad (9.46)$$

where

$$\eta_{ij}^{ab} = \sum_m^{MO} (U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a) \quad (9.47)$$

and satisfy the following relationship:

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad . \quad (9.48)$$

It should be emphasized that the first-order changes in both the MO and CI coefficients are required to evaluate the energy second derivative of the MCSCF wavefunction. These quantities must be evaluated by solving the coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) equations, which will be discussed in Chapter 14.

References

1. H.-J. Werner, in *Advances in Chemical Physics : Ab Initio Methods in Quantum Chemistry Part II.*, K.P. Lawley editor, John Wiley & Sons, New York, vol. 69, p.1 (1987).
2. R. Shepard, same book as reference 1, p.63 (1987).
3. B.O. Roos, same book as reference 1, p.399 (1987).
4. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.

Suggested Reading

1. P. Pulay, *J. Chem. Phys.* **78**, 5043 (1983).
2. R.N. Camp, H.F. King, J.W. McIver, Jr., and D. Mullally, *J. Chem. Phys.* **79**, 1088 (1983).
3. M.R. Hoffmann, D.J. Fox, J.F. Gaw, Y. Osamura, Y. Yamaguchi, R.S. Grev, G. Fitzgerald, H.F. Schaefer, P.J. Knowles, and N.C. Handy, *J. Chem. Phys.* **80**, 2660 (1984).
4. M. Page, P. Saxe, G.F. Adams, and B.H. Lengsfield, *J. Chem. Phys.* **81**, 434 (1984).
5. T.U. Helgaker, J. Almlöf, H. J. Aa. Jensen, and P. Jørgensen, *J. Chem. Phys.* **84**, 6266 (1986).

Chapter 10

Closed-Shell Coupled Perturbed Hartree-Fock Equations

Although the analytic derivative expressions presented in the preceding chapters are complete, many of these expressions require the solution of various coupled perturbed equations that only have been alluded to thus far in the text. The set of simultaneous equations known as the coupled perturbed Hartree-Fock (CPHF) equations provides the derivatives of the MO coefficients of the SCF wavefunction with respect to perturbations. Since the MO coefficients are determined using the variational conditions on the SCF wavefunction, the derivatives of the MO coefficients may be obtained from the derivative expressions of the variational conditions. In this chapter, the first- and second-order CPHF equations are derived for the simplest but most frequently used case, the closed-shell SCF method.

10.1 The First-Order CPHF Equations

For a closed-shell SCF wavefunction, the Fock matrix elements in restricted Hartree-Fock (RHF) theory [1,2] are

$$F_{ij} = h_{ij} + \sum_k^{\text{d.o.}} \left\{ 2(ij|kk) - (ik|jk) \right\} , \quad (10.1)$$

where the sum is over doubly occupied orbitals. The variational condition is quite simply:

$$F_{ij} = 0 \quad \text{for } i = \text{doubly occupied and } j = \text{virtual} . \quad (10.2)$$

Since the SCF energy is invariant to a unitary transformation within the occupied space, a *diagonal* Fock matrix normally is used to define the “canonical” molecular orbitals:

$$F_{ij} = \delta_{ij}\epsilon_i . \quad (10.3)$$

In eq. (10.3) δ_{ij} is the usual Kronecker delta function. The orbital energies at convergence (i.e., at the conclusion of the SCF iterative procedure) are given by

$$\epsilon_i = F_{ii} \quad (10.4)$$

and those for the occupied orbitals may be interpreted through Koopmans' theorem [3]. The first-order coupled perturbed Hartree-Fock (CPHF) equations [4] are the first derivatives of the variational condition in eq. (10.2). They are derived by differentiating eq. (10.1) with respect to an arbitrary cartesian coordinate "a":

$$\frac{\partial F_{ij}}{\partial a} = \frac{\partial h_{ij}}{\partial a} + \sum_k^{\text{d.o.}} \left\{ 2 \frac{\partial(ij|kk)}{\partial a} - \frac{\partial(ik|jk)}{\partial a} \right\} \quad . \quad (10.5)$$

This derivative was obtained in Section 4.5 (see also Appendix N) as

$$\begin{aligned} \frac{\partial F_{ij}}{\partial a} &= F_{ij}^a + \sum_k^{\text{all}} U_{ki}^a F_{kj} + \sum_k^{\text{all}} U_{kj}^a F_{ik} \\ &\quad + \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^a A_{ij,kl} \quad . \end{aligned} \quad (10.6)$$

The elements of the skeleton (core) first derivative Fock matrices are

$$F_{ij}^a = h_{ij}^a + \sum_k^{\text{d.o.}} \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} \quad (10.7)$$

and of the A matrix:

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) \quad . \quad (10.8)$$

Using the variational condition eq. (10.3), eq. (10.6) is reduced to

$$\frac{\partial F_{ij}}{\partial a} = F_{ij}^a + U_{ji}^a \epsilon_j + U_{ij}^a \epsilon_i + \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^a A_{ij,kl} \quad . \quad (10.9)$$

The important first derivative form of the orthonormality condition on the molecular orbitals was given in Section 3.7 as

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \quad . \quad (10.10)$$

Using this relationship, eq. (10.9) is reformulated as

$$\begin{aligned} \frac{\partial F_{ij}}{\partial a} &= F_{ij}^a + \left(-U_{ij}^a - S_{ij}^a \right) \epsilon_j + U_{ij}^a \epsilon_i \\ &\quad + \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^a A_{ij,kl} \end{aligned} \quad (10.11)$$

$$\begin{aligned} &= F_{ij}^a - (\epsilon_j - \epsilon_i) U_{ij}^a - S_{ij}^a \epsilon_j \\ &\quad + \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^a A_{ij,kl} \quad . \end{aligned} \quad (10.12)$$

The fourth term in eq. (10.12) may be manipulated in the following way:

$$\sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} U_{ij}^a A_{ij,kl} = \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \quad (10.13)$$

$$\begin{aligned} &= \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \\ &+ \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} . \end{aligned} \quad (10.14)$$

Using the first derivative of the orthonormality condition, eq. (10.10), allows this term to be rewritten as:

$$\begin{aligned} \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} U_{ij}^a A_{ij,kl} &= \frac{1}{2} \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} (U_{kl}^a + U_{lk}^a) \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \\ &+ \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \end{aligned} \quad (10.15)$$

$$\begin{aligned} &= -\frac{1}{2} \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} S_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \\ &+ \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \end{aligned} \quad (10.16)$$

$$\begin{aligned} &= -\sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} S_{kl}^a \left\{ 2(ij|kl) - (ik|jl) \right\} \\ &+ \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} . \end{aligned} \quad (10.17)$$

In these equations *virt.* denotes the virtual (unoccupied) orbitals. It should be noted that in the first term of eq. (10.16) the exchange of the k and l indices does not alter the summation.

Combining eqs. (10.12) and (10.17) yields the following expression:

$$\begin{aligned} \frac{\partial F_{ij}}{\partial a} &= F_{ij}^a - (\epsilon_j - \epsilon_i) U_{ij}^a - S_{ij}^a \epsilon_j \\ &- \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} S_{kl}^a \left\{ 2(ij|kl) - (ik|jl) \right\} \\ &+ \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} . \end{aligned} \quad (10.18)$$

When the Fock matrix is diagonal, then the derivatives of the Fock matrix are also diagonal:

$$\frac{\partial F_{ij}}{\partial a} = \delta_{ij} \frac{\partial \epsilon_i}{\partial a} \quad (10.19)$$

or

$$\frac{\partial F_{ij}}{\partial a} = 0 \quad \text{for } i \neq j \quad . \quad (10.20)$$

Using these conditions, eq. (10.18) becomes

$$\begin{aligned} (\epsilon_j - \epsilon_i) U_{ij}^a &= \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \\ &= F_{ij}^a - S_{ij}^a \epsilon_j - \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} S_{kl}^a \left\{ 2(ij|kl) - (ik|jl) \right\} \quad . \end{aligned} \quad (10.21)$$

This result is written commonly as

$$(\epsilon_j - \epsilon_i) U_{ij}^a - \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} A_{ij,kl} U_{kl}^a = B_{0,ij}^a \quad . \quad (10.22)$$

The A matrix was defined by eq. (10.8) and the B_0^a matrices are

$$B_{0,ij}^a = F_{ij}^a - S_{ij}^a \epsilon_j - \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} S_{kl}^a \left\{ 2(ij|kl) - (ik|jl) \right\} \quad . \quad (10.23)$$

The simultaneous equations given in eq. (10.22) are the first-order coupled perturbed Hartree-Fock (CPHF) equations, which involve the unknown variables U^a . The dimension of these CPHF equations is the product of the number of doubly occupied orbitals and the number of virtual orbitals. The CPHF equations usually are solved iteratively [5]. When the dimension is not too large (less than ~ 1000), the CPHF equations may be solved using any of the standard methods for simultaneous equations.

The first-order derivative of the orbital energy involves a diagonal term of eq. (10.18), and the results obtained from solving the CPHF equations (10.22) are

$$\frac{\partial \epsilon_i}{\partial a} = \frac{\partial F_{ii}}{\partial a} \quad (10.24)$$

$$\begin{aligned} &= F_{ii}^a - S_{ii}^a \epsilon_i - \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} S_{kl}^a \left\{ 2(ii|kl) - (ik|il) \right\} \\ &+ \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ii|kl) - (ik|il) - (il|ik) \right\} \quad . \end{aligned} \quad (10.25)$$

When the SCF condition is satisfied, the SCF energy is stationary with respect to any (real) perturbations. In other words, an infinitesimal (real) perturbation of any kind at this stationary point cannot change the SCF energy. Consequently, elements of the U^a matrix between two doubly occupied orbitals or between two virtual orbitals are not determined uniquely. Such pairs of molecular orbitals are usually called "non-independent". On the other hand, occupied-virtual pairs are uniquely determined and are termed "independent pairs".

Elements of the U^a matrix for the independent pairs of molecular orbitals are obtained by solving the CPHF equations (10.22). The non-independent pairs may be evaluated using

$$U_{ij}^a = \frac{1}{(\epsilon_j - \epsilon_i)} \left(\sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} A_{ij,kl} U_{kl}^a + B_{0,ij}^a \right) \quad . \quad (10.26)$$

The right hand side of eq. (10.26) contains the elements for the independent pairs of the U^a matrix.

It also should be realized that eq. (10.26) has been defined explicitly using the diagonal nature of the Fock matrix. Thus, this equation is not valid when a molecular system has degenerate orbital energies either by symmetry or accidentally. However, the explicit evaluation of the U^a matrix for non-independent pairs (including degenerate pairs) by eq. (10.26) can be avoided for many applications, such as second derivatives of the SCF energy and first derivatives of the CI energy [6-10].

10.2 The Derivatives of the F^a Matrices

Before studying the second-order CPHF equations, it is useful to find derivative expressions for those quantities involved in the second derivative of the Fock matrix. Examining eq. (10.6) it is obvious that these quantities include the F^a and A matrices. The next two sections are devoted to finding the derivative expressions of these two matrices. The derivatives of the F^a matrices are developed in this section. Using results from Sections 3.8 and 3.9, the derivative of eq. (10.7) with respect to a second variable “ b ” is:

$$\frac{\partial F_{ij}^a}{\partial b} = \frac{\partial h_{ij}^a}{\partial b} + \sum_k^{\text{d.o.}} \left\{ 2 \frac{\partial(ij|kk)^a}{\partial b} - \frac{\partial(ik|jk)^a}{\partial b} \right\} \quad (10.27)$$

$$\begin{aligned} &= h_{ij}^{ab} + \sum_m^{\text{all}} \left(U_{mi}^b h_{mj}^a + U_{mj}^b h_{im}^a \right) \\ &+ \sum_k^{\text{d.o.}} \left[2(ij|kk)^{ab} + 2 \sum_m^{\text{all}} \left\{ U_{mi}^b (mj|kk)^a + U_{mj}^b (im|kk)^a + 2U_{mk}^b (ij|mk)^a \right. \right. \\ &\quad \left. \left. - (ik|jk)^{ab} - \sum_m^{\text{all}} \left\{ U_{mi}^b (mk|jk)^a + U_{mk}^b (im|jk)^a + U_{mj}^b (ik|mk)^a \right. \right. \right. \\ &\quad \left. \left. \left. + U_{mk}^b (ik|jm)^a \right\} \right] \right] \end{aligned} \quad (10.28)$$

$$\begin{aligned} &= h_{ij}^{ab} + \sum_k^{\text{d.o.}} \left\{ 2(ij|kk)^{ab} - (ik|jk)^{ab} \right\} \\ &+ \sum_m^{\text{all}} U_{mi}^b \left[h_{mj}^a + \sum_k^{\text{d.o.}} \left\{ 2(mj|kk)^a - (mk|jk)^a \right\} \right] \end{aligned}$$

$$\begin{aligned}
& + \sum_m^{\text{all}} U_{mj}^b \left[h_{im}^a + \sum_k^{\text{d.o.}} \left\{ 2(im|kk)^a - (ik|mk)^a \right\} \right] \\
& + \sum_m^{\text{all}} \sum_k^{\text{d.o.}} U_{mk}^b \left[4(ij|mk)^a - (im|jk)^a - (ik|jm)^a \right]
\end{aligned} \quad . \quad (10.29)$$

Using the definition of the skeleton (core) first derivative Fock matrices from (10.7) and writing the skeleton (core) second derivative Fock matrix as

$$F_{ij}^{ab} = h_{ij}^{ab} + \sum_k^{\text{d.o.}} \left\{ 2(ij|kk)^{ab} - (ik|jk)^{ab} \right\} , \quad (10.30)$$

eq. (10.29) may be written as

$$\begin{aligned}
\frac{\partial F_{ij}^a}{\partial b} &= F_{ij}^{ab} + \sum_m^{\text{all}} U_{mi}^b F_{mj}^a + \sum_m^{\text{all}} U_{mj}^b F_{im}^a \\
&+ \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^b \left[4(ij|kl)^a - (ik|jl)^a - (il|jk)^a \right]
\end{aligned} \quad . \quad (10.31)$$

The skeleton (core) first derivative A matrices are

$$A_{ij,kl}^a = 4(ij|kl)^a - (ik|jl)^a - (il|jk)^a . \quad (10.32)$$

Thus eq. (10.31) can be written as

$$\begin{aligned}
\frac{\partial F_{ij}^a}{\partial b} &= F_{ij}^{ab} + \sum_m^{\text{all}} \left(U_{mi}^b F_{mj}^a + U_{mj}^b F_{im}^a \right) \\
&+ \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^b A_{ij,kl}^a .
\end{aligned} \quad (10.33)$$

It is noteworthy that the derivative expression for the F^a matrices in eq. (10.33) has a similar form to that for the F matrix in eq. (10.6). Derivative expressions for the skeleton (core) higher derivative Fock matrices are found in a similar manner and are summarized in Appendix N.

10.3 The First Derivative of the A matrix

In this section the derivative of the A matrix is obtained. Using the results from Section 3.9, the derivative of the A matrix (10.8) is:

$$\begin{aligned}
\frac{\partial A_{ij,kl}}{\partial a} &= 4 \frac{\partial (ij|kl)}{\partial a} - \frac{\partial (ik|jl)}{\partial a} - \frac{\partial (il|jk)}{\partial a} \\
&= 4 \left[(ij|kl)^a + \sum_m^{\text{all}} \left\{ U_{mi}^a (mj|kl) + U_{mj}^a (im|kl) \right\} \right]
\end{aligned} \quad (10.34)$$

$$\begin{aligned}
& + U_{mk}^a(ij|ml) + U_{ml}^a(ij|km) \Big\} \Big] \\
- & \left[(ik|jl)^a + \sum_m^{all} \left\{ U_{mi}^a(mk|jl) + U_{mk}^a(im|jl) \right. \right. \\
& \quad \left. \left. + U_{mj}^a(ik|ml) + U_{ml}^a(ik|jm) \right\} \right] \\
- & \left[(il|jk)^a + \sum_m^{all} \left\{ U_{mi}^a(ml|jk) + U_{ml}^a(im|jk) \right. \right. \\
& \quad \left. \left. + U_{mj}^a(il|mk) + U_{mk}^a(il|jm) \right\} \right] \quad (10.35)
\end{aligned}$$

$$\begin{aligned}
= & 4(ij|kl)^a - (ik|jl)^a - (il|jk)^a \\
+ & \sum_m^{all} U_{mi}^a \left\{ 4(mj|kl) - (mk|jl) - (ml|jk) \right\} \\
+ & \sum_m^{all} U_{mj}^a \left\{ 4(im|kl) - (ik|ml) - (il|mk) \right\} \\
+ & \sum_m^{all} U_{mk}^a \left\{ 4(ij|ml) - (im|jl) - (il|jm) \right\} \\
+ & \sum_m^{all} U_{ml}^a \left\{ 4(ij|km) - (ik|jm) - (im|jk) \right\} \quad . \quad (10.36)
\end{aligned}$$

Using the definitions of the A matrix from eq. (10.8) and the A^a matrices from eq. (10.32) gives

$$\begin{aligned}
\frac{\partial A_{ij,kl}}{\partial a} = & A_{ij,kl}^a \\
& + \sum_m^{all} \left(U_{mi}^a A_{mj,kl} + U_{mj}^a A_{im,kl} + U_{mk}^a A_{ij,ml} + U_{ml}^a A_{ij,km} \right) .
\end{aligned} \quad (10.37)$$

Derivative expressions for the skeleton (core) higher derivative A matrices are obtained in the same way and the results are summarized in Appendix N.

10.4 The Second-Order CPHF Equations

The second-order CPHF equations are the second derivatives of the variational condition in eq. (10.2). They provide the second derivatives of the MO coefficients with respect to perturbations. These second-order CPHF equations may be derived by differentiating eq.

(10.6) with respect to a second parameter "b":

$$\frac{\partial^2 F_{ij}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial F_{ij}}{\partial a} \right) \quad (10.38)$$

$$= \frac{\partial}{\partial b} \left(F_{ij}^a + \sum_k^{all} U_{ki}^a F_{kj} + \sum_k^{all} U_{kj}^a F_{ik} + \sum_k^{all} \sum_l^{d.o.} U_{kl}^a A_{ij,kl} \right) \quad (10.39)$$

$$\begin{aligned} &= \frac{\partial F_{ij}^a}{\partial b} + \sum_k^{all} \left(\frac{\partial U_{ki}^a}{\partial b} F_{kj} + U_{ki}^a \frac{\partial F_{kj}}{\partial b} \right) \\ &+ \sum_k^{all} \left(\frac{\partial U_{kj}^a}{\partial b} F_{ik} + U_{kj}^a \frac{\partial F_{ik}}{\partial b} \right) \\ &+ \sum_k^{all} \sum_l^{d.o.} \left(\frac{\partial U_{kl}^a}{\partial b} A_{ij,kl} + U_{kl}^a \frac{\partial A_{ij,kl}}{\partial b} \right) . \end{aligned} \quad (10.40)$$

The derivatives appearing in eq. (10.40) were given explicitly in Section 3.4 and in eqs. (10.6), (10.33) and (10.37). Substituting these results into eq. (10.40) yields:

$$\begin{aligned} \frac{\partial^2 F_{ij}}{\partial a \partial b} &= F_{ij}^{ab} + \sum_m^{all} \left(U_{mi}^b F_{mj}^a + U_{mj}^b F_{im}^a \right) + \sum_k^{all} \sum_l^{d.o.} U_{kl}^b A_{ij,kl}^a \\ &+ \sum_k^{all} \left(U_{ki}^{ab} - \sum_m^{all} U_{km}^b U_{mi}^a \right) F_{kj} \\ &+ \sum_k^{all} U_{ki}^a \left\{ F_{kj}^b + \sum_m^{all} U_{mk}^b F_{mj} + \sum_m^{all} U_{mj}^b F_{km} + \sum_m^{all} \sum_n^{d.o.} U_{mn}^b A_{kj,mn} \right\} \\ &+ \sum_k^{all} \left(U_{kj}^{ab} - \sum_m^{all} U_{km}^b U_{mj}^a \right) F_{ik} \\ &+ \sum_k^{all} U_{kj}^a \left\{ F_{ik}^b + \sum_m^{all} U_{mi}^b F_{mk} + \sum_m^{all} U_{mk}^b F_{im} + \sum_m^{all} \sum_n^{d.o.} U_{mn}^b A_{ik,mn} \right\} \\ &+ \sum_k^{all} \sum_l^{d.o.} \left(U_{kl}^{ab} - \sum_m^{all} U_{km}^b U_{ml}^a \right) A_{ij,kl} \\ &+ \sum_k^{all} \sum_l^{d.o.} U_{kl}^a \left\{ A_{ij,kl}^b + \sum_m^{all} U_{mi}^b A_{mj,kl} + \sum_m^{all} U_{mj}^b A_{im,kl} \right. \\ &\quad \left. + \sum_m^{all} U_{mk}^b A_{ij,ml} + \sum_m^{all} U_{ml}^b A_{ij,km} \right\} \\ &= F_{ij}^{ab} + \sum_k^{all} U_{ki}^{ab} F_{kj} + \sum_k^{all} U_{kj}^{ab} F_{ik} \\ &+ \sum_k^{all} \sum_l^{d.o.} U_{kl}^{ab} A_{ij,kl} \end{aligned} \quad (10.41)$$

$$\begin{aligned}
& + \sum_k^{\text{all}} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \\
& + \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) F_{kl} \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m U_{km}^a U_{lm}^b A_{ij,kl} \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\
& + \sum_k^{\text{all d.o.}} \sum_l \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right) . \tag{10.42}
\end{aligned}$$

Some of the summations run over all MOs while others are over doubly occupied MOs only. Using the variational condition eq. (10.3), eq. (10.42) may be reduced to

$$\begin{aligned}
\frac{\partial^2 F_{ij}}{\partial a \partial b} & = F_{ij}^{ab} + U_{ji}^{ab} \epsilon_j + U_{ij}^{ab} \epsilon_i + \sum_k^{\text{all d.o.}} U_{kl}^{ab} A_{ij,kl} \\
& + \sum_k^{\text{all}} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \\
& + \sum_k^{\text{all}} \left(U_{ki}^a U_{kj}^b + U_{ki}^b U_{kj}^a \right) \epsilon_k \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m U_{km}^a U_{lm}^b A_{ij,kl} \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\
& + \sum_k^{\text{all d.o.}} \sum_l \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right) . \tag{10.43}
\end{aligned}$$

The second derivative of the orthonormality conditions on the molecular orbitals was presented in Section 3.7 as

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \tag{10.44}$$

where

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{\text{all}} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) . \tag{10.45}$$

Using eq. (10.44), eq. (10.43) may be manipulated in a similar manner to the first-order CPHF equations to yield:

$$\begin{aligned}
 \frac{\partial^2 F_{ij}}{\partial a \partial b} = & F_{ij}^{ab} - (\epsilon_j - \epsilon_i) U_{ij}^{ab} - \xi_{ij}^{ab} \epsilon_j \\
 & - \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} \xi_{kl}^{ab} \left\{ 2(ij|kl) - (ik|jl) \right\} \\
 & + \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} U_{kl}^{ab} A_{ij,kl} \\
 & + \sum_k^{\text{all}} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \\
 & + \sum_k^{\text{all}} \left(U_{ki}^a U_{kj}^b + U_{ki}^b U_{kj}^a \right) \epsilon_k \\
 & + \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} U_{km}^a U_{lm}^b A_{ij,kl} \\
 & + \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\
 & + \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\
 & + \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right) . \tag{10.46}
 \end{aligned}$$

The second derivatives of the Fock matrix are diagonal due to the diagonality of the Fock matrix at convergence. Thus,

$$\frac{\partial^2 F_{ij}}{\partial a \partial b} = \delta_{ij} \frac{\partial^2 \epsilon_i}{\partial a \partial b} \tag{10.47}$$

or

$$\frac{\partial^2 F_{ij}}{\partial a \partial b} = 0 \quad \text{for } i \neq j . \tag{10.48}$$

By exploiting eq. (10.48), eq. (10.46) is rewritten in a familiar form as

$$(\epsilon_j - \epsilon_i) U_{ij}^{ab} - \sum_k^{\text{virt. d.o.}} \sum_l^{\text{d.o.}} A_{ij,kl} U_{kl}^{ab} = B_{0,ij}^{ab} \tag{10.49}$$

where

$$\begin{aligned}
 B_{0,ij}^{ab} = & F_{ij}^{ab} - \xi_{ij}^{ab} \epsilon_j - \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} \xi_{kl}^{ab} \left\{ 2(ij|kl) - (ik|jl) \right\} \\
 & + \sum_k^{\text{all}} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right)
 \end{aligned}$$

$$\begin{aligned}
& + \sum_k^{\text{all}} \left(U_{ki}^a U_{kj}^b + U_{ki}^b U_{kj}^a \right) \epsilon_k \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m U_{km}^a U_{lm}^b A_{ij,kl} \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\
& + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\
& + \sum_k^{\text{all d.o.}} \sum_l \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right) \quad . \tag{10.50}
\end{aligned}$$

The second-order derivative of an orbital energy, $\partial^2 \epsilon_i / \partial a \partial b$, is obtained from a diagonal term in eq. (10.46), using the results from the CPHF equations (10.49). The elements of the U^{ab} matrix for non-independent pairs are evaluated using the independent pairs as

$$U_{ij}^{ab} = \frac{1}{(\epsilon_j - \epsilon_i)} \left(\sum_k^{\text{virt. d.o.}} \sum_l A_{ij,kl} U_{kl}^{ab} + B_{0,ij}^{ab} \right) \quad . \tag{10.51}$$

It should be emphasized that the right hand side of eq. (10.51) contains elements involving the independent pairs of the U^{ab} matrix. Note that eq. (10.51) has been derived explicitly using the diagonal property of the Fock matrix in eq. (10.3). This equation is therefore not applicable when a molecular system has degenerate orbital energies either accidentally or by symmetry. However, explicit evaluation of the U^{ab} matrix for non-independent pairs (including degenerate pairs) can be avoided for many applications, such as fourth derivatives of the SCF energy or second derivatives of the CI energy [6-11].

10.5 An Alternative Derivation of the Second Derivative of the Fock Matrix

An alternative expression for the second derivative of the Fock matrix may be obtained arduously but more straightforwardly by differentiating eq. (10.1) with respect to the two cartesian coordinates “ a ” and “ b ”:

$$\frac{\partial^2 F_{ij}}{\partial a \partial b} = \frac{\partial^2 h_{ij}}{\partial a \partial b} + \sum_k^{\text{d.o.}} \left\{ 2 \frac{\partial^2 (ij|kk)}{\partial a \partial b} - \frac{\partial^2 (ik|jk)}{\partial a \partial b} \right\} \quad . \tag{10.52}$$

The relevant second derivative expression for the one-electron MO integrals was given in Section 3.8 as:

$$\frac{\partial^2 h_{ij}}{\partial a \partial b} = h_{ij}^{ab} + \sum_m^{\text{all}} \left(U_{mi}^{ab} h_{mj} + U_{mj}^{ab} h_{im} \right)$$

$$\begin{aligned}
& + \sum_m^{\text{all}} \left(U_{mi}^a h_{mj}^b + U_{mi}^b h_{mj}^a + U_{mj}^a h_{im}^b + U_{mj}^b h_{im}^a \right) \\
& + \sum_{mn}^{\text{all}} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) h_{mn} .
\end{aligned} \quad (10.53)$$

For the two-electron MO integrals, the second derivative expressions from Section 3.9 are

$$\begin{aligned}
\frac{\partial^2(ij|kk)}{\partial a \partial b} &= (ij|kk)^{ab} \\
& + \sum_m^{\text{all}} \left[U_{mi}^{ab}(mj|kk) + U_{mj}^{ab}(im|kk) + 2U_{mk}^{ab}(ij|mk) \right] \\
& + \sum_m^{\text{all}} \left[U_{mi}^a(mj|kk)^b + U_{mj}^a(im|kk)^b + 2U_{mk}^a(ij|mk)^b \right. \\
& \quad \left. + U_{mi}^b(mj|kk)^a + U_{mj}^b(im|kk)^a + 2U_{mk}^b(ij|mk)^a \right] \\
& + \sum_{mn}^{\text{all}} \left[\left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mn|kk) + \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mj|nk) \right. \\
& \quad \left. + \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mj|kn) + \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (im|nk) \right. \\
& \quad \left. + \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (im|kn) + \left(U_{mk}^a U_{nk}^b + U_{mk}^b U_{nk}^a \right) (ij|mn) \right] ,
\end{aligned} \quad (10.54)$$

and

$$\begin{aligned}
\frac{\partial^2(ik|jk)}{\partial a \partial b} &= (ik|jk)^{ab} \\
& + \sum_m^{\text{all}} \left[U_{mi}^{ab}(mk|jk) + U_{mk}^{ab}(im|jk) + U_{mj}^{ab}(ik|mk) + U_{mk}^{ab}(ik|jm) \right] \\
& + \sum_m^{\text{all}} \left[U_{mi}^a(mk|jk)^b + U_{mk}^a(im|jk)^b + U_{mj}^a(ik|mk)^b + U_{mk}^a(ik|jm)^b \right. \\
& \quad \left. + U_{mi}^b(mk|jk)^a + U_{mk}^b(im|jk)^a + U_{mj}^b(ik|mk)^a + U_{mk}^b(ik|jm)^a \right] \\
& + \sum_{mn}^{\text{all}} \left[\left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mn|jk) + \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mk|nk) \right. \\
& \quad \left. + \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mk|jn) + \left(U_{mk}^a U_{nj}^b + U_{mk}^b U_{nj}^a \right) (im|nk) \right. \\
& \quad \left. + \left(U_{mk}^a U_{nk}^b + U_{mk}^b U_{nk}^a \right) (im|jn) + \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (ik|mn) \right] ,
\end{aligned} \quad (10.55)$$

Using eqs. (10.53) to (10.55), the expression in (10.52) may then be expanded as

$$\begin{aligned}
 \frac{\partial^2 F_{ij}}{\partial a \partial b} &= h_{ij}^{ab} + \sum_m^{\text{all}} \left(U_{mi}^{ab} h_{mj} + U_{mj}^{ab} h_{im} \right) \\
 &+ \sum_m^{\text{all}} \left(U_{mi}^a h_{mj}^b + U_{mi}^b h_{mj}^a + U_{mj}^a h_{im}^b + U_{mj}^b h_{im}^a \right) \\
 &+ \sum_{mn}^{\text{all}} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) h_{mn} \\
 &+ 2 \sum_k^{\text{d.o.}} \left[(ij|kk)^{ab} + \sum_m^{\text{all}} \left(U_{mi}^{ab}(mj|kk) + U_{mj}^{ab}(im|kk) + 2U_{mk}^{ab}(ij|mk) \right) \right. \\
 &\quad + \sum_m^{\text{all}} \left(U_{mi}^a(mj|kk)^b + U_{mj}^a(im|kk)^b + 2U_{mk}^a(ij|mk)^b \right. \\
 &\quad \left. \left. + U_{mi}^b(mj|kk)^a + U_{mj}^b(im|kk)^a + 2U_{mk}^b(ij|mk)^a \right) \right] \\
 &\quad + \sum_{mn}^{\text{all}} \left\{ \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mn|kk) \right. \\
 &\quad + 2 \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mj|nk) + 2 \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (im|nk) \\
 &\quad \left. \left. + \left(U_{mk}^a U_{nk}^b + U_{mk}^b U_{nk}^a \right) (ij|mn) \right\} \right] \\
 &- \sum_k^{\text{d.o.}} \left[(ik|jk)^{ab} \right. \\
 &\quad + \sum_m^{\text{all}} \left(U_{mi}^{ab}(mk|jk) + U_{mk}^{ab}(im|jk) + U_{mj}^{ab}(ik|mk) + U_{mk}^{ab}(ik|jm) \right) \\
 &\quad + \sum_m^{\text{all}} \left(U_{mi}^a(mk|jk)^b + U_{mk}^a(im|jk)^b + U_{mj}^a(ik|mk)^b + U_{mk}^a(ik|jm)^b \right. \\
 &\quad \left. \left. + U_{mi}^b(mk|jk)^a + U_{mk}^b(im|jk)^a + U_{mj}^b(ik|mk)^a + U_{mk}^b(ik|jm)^a \right) \right] \\
 &\quad + \sum_{mn}^{\text{all}} \left\{ \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mn|jk) + \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mk|nk) \right. \\
 &\quad + \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mk|jn) + \left(U_{mk}^a U_{nj}^b + U_{mk}^b U_{nj}^a \right) (im|nk) \\
 &\quad \left. \left. + \left(U_{mk}^a U_{nk}^b + U_{mk}^b U_{nk}^a \right) (im|jn) + \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (ik|mn) \right\} \right] \\
 &= h_{ij}^{ab} + \sum_k^{\text{d.o.}} \left\{ 2(ij|kk)^{ab} - (ik|jk)^{ab} \right\}
 \end{aligned} \tag{10.56}$$

$$\begin{aligned}
& + \sum_m^{\text{all}} U_{mi}^{ab} \left[h_{mj} + \sum_k^{\text{d.o.}} \left\{ 2(mj|kk) - (mk|jk) \right\} \right] \\
& + \sum_m^{\text{all}} U_{mj}^{ab} \left[h_{im} + \sum_k^{\text{d.o.}} \left\{ 2(im|kk) - (ik|mk) \right\} \right] \\
& + \sum_m^{\text{all}} \sum_k^{\text{d.o.}} U_{mk}^{ab} \left[4(ij|mk) - (im|jk) - (ik|jm) \right] \\
& + \sum_m^{\text{all}} U_{mi}^a \left[h_{mj}^b + \sum_k^{\text{d.o.}} \left\{ 2(mj|kk)^b - (mk|jk)^b \right\} \right] \\
& + \sum_m^{\text{all}} U_{mi}^b \left[h_{mj}^a + \sum_k^{\text{d.o.}} \left\{ 2(mj|kk)^a - (mk|jk)^a \right\} \right] \\
& + \sum_m^{\text{all}} U_{mj}^a \left[h_{im}^b + \sum_k^{\text{d.o.}} \left\{ 2(im|kk)^b - (ik|mk)^b \right\} \right] \\
& + \sum_m^{\text{all}} U_{mj}^b \left[h_{im}^a + \sum_k^{\text{d.o.}} \left\{ 2(im|kk)^a - (ik|mk)^a \right\} \right] \\
& + \sum_{mn}^{\text{all}} U_{mi}^a U_{nj}^b \left[h_{mn} + \sum_k^{\text{d.o.}} \left\{ 2(mn|kk) - (mk|nk) \right\} \right] \\
& + \sum_{mn}^{\text{all}} U_{mi}^b U_{nj}^a \left[h_{mn} + \sum_k^{\text{d.o.}} \left\{ 2(mn|kk) - (mk|nk) \right\} \right] \\
& + \sum_{mn}^{\text{all}} \sum_k^{\text{d.o.}} U_{mk}^a U_{nk}^b \left[4(ij|mn) - (im|jn) - (in|jm) \right] \\
& + \sum_{mn}^{\text{all}} \sum_k^{\text{d.o.}} U_{mi}^a U_{nk}^b \left[4(mj|nk) - (mn|jk) - (mk|jn) \right] \\
& + \sum_{mn}^{\text{all}} \sum_k^{\text{d.o.}} U_{mi}^b U_{nk}^a \left[4(mj|nk) - (mn|jk) - (mk|jn) \right] \\
& + \sum_{mn}^{\text{all}} \sum_k^{\text{d.o.}} U_{mj}^a U_{nk}^b \left[4(im|nk) - (in|mk) - (ik|mn) \right] \\
& + \sum_{mn}^{\text{all}} \sum_k^{\text{d.o.}} U_{mj}^b U_{nk}^a \left[4(im|nk) - (in|mk) - (ik|mn) \right] \\
& + \sum_m^{\text{all}} \sum_k^{\text{d.o.}} U_{mk}^a \left[4(ij|mk)^b - (im|jk)^b - (ik|jm)^b \right] \\
& + \sum_m^{\text{all}} \sum_k^{\text{d.o.}} U_{mk}^b \left[4(ij|mk)^a - (im|jk)^a - (ik|jm)^a \right] \quad . \tag{10.57}
\end{aligned}$$

Finally, the definitions of the F , F^a , F^{ab} and A^a matrices given previously allow (10.57) to be rewritten as:

$$\begin{aligned}
 \frac{\partial^2 F_{ij}}{\partial a \partial b} = & F_{ij}^{ab} + \sum_k^{\text{all}} U_{ki}^{ab} F_{kj} + \sum_k^{\text{all}} U_{kj}^{ab} F_{ik} \\
 & + \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} U_{kl}^{ab} A_{ij,kl} \\
 & + \sum_k^{\text{all}} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \\
 & + \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) F_{kl} \\
 & + \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} U_{km}^a U_{lm}^b A_{ij,kl} \\
 & + \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\
 & + \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\
 & + \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right) . \tag{10.58}
 \end{aligned}$$

Equation (10.58) is equivalent to eq. (10.42), which was derived independently in the preceding section.

References

1. C.C.J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
2. G.G. Hall, Proc. Roy. Soc. London, **A205**, 541 (1951).
3. T.A. Koopmans, Physica **1**, 104 (1933).
4. J. Gerratt and I.M. Mills, J. Chem. Phys. **49**, 1719 (1968).
5. J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, Int. J. Quantum Chem. **S13**, 225 (1979).
6. Y. Osamura, Y. Yamaguchi, P. Saxe, M.A. Vincent, J.F. Gaw, and H.F. Schaefer, Chem. Phys. **72**, 131 (1982).
7. Y. Osamura, Y. Yamaguchi, P. Saxe, D.J. Fox, M.A. Vincent, and H.F. Schaefer, J. Mol. Struct. **103**, 183 (1983).
8. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, Chem. Phys. **103**, 227 (1986).

9. J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, and H.F. Schaefer, *J. Chem. Phys.* **85**, 963 (1986).
10. T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, *J. Chem. Phys.* **85**, 3930 (1986).
11. J.F. Gaw, Y. Yamaguchi, H.F. Schaefer, and N.C. Handy, *J. Chem. Phys.* **85**, 5132 (1986).

Suggested Reading

1. T. Takada, M. Dupuis, and H.F. King, *J. Comp. Chem.* **4**, 234 (1983).

Chapter 11

General Restricted Open-Shell Coupled Perturbed Hartree-Fock Equations

In this chapter, the first- and second-order CPHF equations are described for general restricted open-shell SCF wavefunctions. These equations are obtained by differentiating the variational conditions on the open-shell SCF wavefunction. The method is applicable to almost all single-configuration SCF wavefunctions and real perturbations.

11.1 The First-Order CPHF Equations

Within the framework of RHF theory, the generalized Fock operator for a single-configuration SCF wavefunction [1-3] is

$$\mathbf{F}_i = f_i \mathbf{h} + \sum_l^{all} (\alpha_{il} \mathbf{J}_l + \beta_{il} \mathbf{K}_l) \quad (11.1)$$

with the Lagrangian matrix ϵ defined in Section 5.2 by

$$\epsilon_{ij} = \langle \phi_i | \mathbf{F}_i | \phi_j \rangle = f_i h_{ij} + \sum_l^{all} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} . \quad (11.2)$$

In these equations, “*all*” implies a sum over all molecular orbitals, occupied and virtual, although the elements of the α and β coupling constants involving virtual orbitals are always zero. Using this definition, the variational condition for the general restricted open-shell SCF equation is

$$\epsilon_{ij} - \epsilon_{ji} = 0 , \quad (11.3)$$

a nontrivial result, since the order of indices is crucial. The first-order CPHF equations are derived by differentiating eq. (11.3) with respect to a cartesian coordinate “ a ”:

$$\frac{\partial \epsilon_{ij}}{\partial a} - \frac{\partial \epsilon_{ji}}{\partial a} = 0 \quad . \quad (11.4)$$

The first derivative of the Lagrangian matrix (11.2) was obtained in Section 5.5 (see also Appendix P) as

$$\begin{aligned} \frac{\partial \epsilon_{ij}}{\partial a} &= \epsilon_{ij}^a + \sum_k^{all} U_{ki}^a \zeta_{kj}^i + \sum_k^{all} U_{kj}^a \epsilon_{ik} \\ &+ \sum_{kl}^{all} U_{kl}^a \tau_{ij,kl}^{il} \quad . \end{aligned} \quad (11.5)$$

The skeleton (core) first derivative Lagrangian matrices ϵ^a , the generalized Lagrangian matrices ζ^l , and the τ matrices are defined by

$$\epsilon_{ij}^a = f_i h_{ij}^a + \sum_l^{all} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} \quad , \quad (11.6)$$

$$\zeta_{ij}^l = f_l h_{ij} + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk) + \beta_{lk}(ik|jk) \right\} \quad , \quad (11.7)$$

and

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl) + \beta_{mn} \left\{ (ik|jl) + (il|jk) \right\} \quad . \quad (11.8)$$

Substituting eq. (11.5) into eq. (11.4), gives

$$\begin{aligned} \frac{\partial \epsilon_{ij}}{\partial a} - \frac{\partial \epsilon_{ji}}{\partial a} &= \epsilon_{ij}^a + \sum_k^{all} U_{ki}^a \zeta_{kj}^i + \sum_k^{all} U_{kj}^a \epsilon_{ik} \\ &+ \sum_{kl}^{all} U_{kl}^a \tau_{ij,kl}^{il} \\ &- \epsilon_{ji}^a - \sum_k^{all} U_{kj}^a \zeta_{ki}^j - \sum_k^{all} U_{ki}^a \epsilon_{jk} \\ &- \sum_{kl}^{all} U_{kl}^a \tau_{ji,kl}^{jl} \end{aligned} \quad (11.9)$$

$$\begin{aligned} &= \epsilon_{ij}^a - \epsilon_{ji}^a \\ &+ \sum_k^{all} \left[U_{ki}^a \left(\zeta_{kj}^i - \epsilon_{jk} \right) - U_{kj}^a \left(\zeta_{ki}^j - \epsilon_{ik} \right) \right] \\ &+ \sum_{kl}^{all} U_{kl}^a \left(\tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right) \end{aligned} \quad (11.10)$$

$$\begin{aligned}
&= \epsilon_{ij}^a - \epsilon_{ji}^a \\
&+ \sum_{kl}^{all} U_{kl}^a \left[\delta_{li} (\zeta_{kj}^i - \epsilon_{jk}) - \delta_{lj} (\zeta_{ki}^j - \epsilon_{ik}) + \tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right]
\end{aligned} \tag{11.11}$$

$$\begin{aligned}
&= \epsilon_{ij}^a - \epsilon_{ji}^a \\
&+ \sum_{k>l}^{all} U_{kl}^a \left[\delta_{li} (\zeta_{kj}^i - \epsilon_{jk}) - \delta_{lj} (\zeta_{ki}^j - \epsilon_{ik}) + \tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right] \\
&+ \sum_{k>l}^{all} U_{lk}^a \left[\delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) + \tau_{ij,lk}^{ik} - \tau_{ji,lk}^{jk} \right] \\
&+ \sum_k^{all} U_{kk}^a \left[\delta_{ki} (\zeta_{kj}^i - \epsilon_{jk}) - \delta_{kj} (\zeta_{ki}^j - \epsilon_{ik}) + \tau_{ij,kk}^{ik} - \tau_{ji,kk}^{jk} \right]
\end{aligned} \tag{11.12}$$

Using the first derivative of the orthonormality condition from Section 3.7

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \tag{11.13}$$

and the following equation for the generalized Lagrangian matrices, given in Section 5.5,

$$\zeta_{ij}^i = \zeta_{ij}^j = \epsilon_{ij} \quad , \tag{11.14}$$

this expression may be rewritten as:

$$\begin{aligned}
&\frac{\partial \epsilon_{ij}}{\partial a} - \frac{\partial \epsilon_{ji}}{\partial a} = \epsilon_{ij}^a - \epsilon_{ji}^a \\
&+ \sum_{k>l}^{all} U_{kl}^a \left[\delta_{li} (\zeta_{kj}^i - \epsilon_{jk}) - \delta_{lj} (\zeta_{ki}^j - \epsilon_{ik}) + \tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right] \\
&- \sum_{k>l}^{all} U_{kl}^a \left[\delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) + \tau_{ij,lk}^{ik} - \tau_{ji,lk}^{jk} \right] \\
&- \sum_{k>l}^{all} S_{kl}^a \left[\delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) + \tau_{ij,lk}^{ik} - \tau_{ji,lk}^{jk} \right] \\
&- \frac{1}{2} \sum_k^{all} S_{kk}^a \left[\delta_{ki} (\zeta_{kj}^i - \epsilon_{jk}) - \delta_{kj} (\zeta_{ki}^j - \epsilon_{ik}) + \tau_{ij,kk}^{ik} - \tau_{ji,kk}^{jk} \right]
\end{aligned} \tag{11.15}$$

$$\begin{aligned}
&= \epsilon_{ij}^a - \epsilon_{ji}^a \\
&+ \sum_{k>l}^{all} U_{kl}^a \left[\delta_{li} (\zeta_{kj}^i - \epsilon_{jk}) - \delta_{lj} (\zeta_{ki}^j - \epsilon_{ik}) + \tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right. \\
&\quad \left. - \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) + \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) - \tau_{ij,lk}^{ik} + \tau_{ji,lk}^{jk} \right]
\end{aligned}$$

$$\begin{aligned}
& - \sum_{k>l}^{all} S_{kl}^a \left[\delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) + \tau_{ij,lk}^{ik} - \tau_{ji,lk}^{jk} \right] \\
& - \frac{1}{2} \sum_k^{all} S_{kk}^a \left[\tau_{ij,kk}^{ik} - \tau_{ji,kk}^{jk} \right] = 0
\end{aligned} \quad . \quad (11.16)$$

Rearranging equation (11.16), gives:

$$\begin{aligned}
& \sum_{k>l}^{all} U_{kl}^a \left[\tau_{ij,lk}^{ik} - \tau_{ji,lk}^{jk} - \tau_{ij,kl}^{il} + \tau_{ji,kl}^{jl} \right. \\
& \quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) - \delta_{li} (\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj} (\zeta_{ki}^j - \epsilon_{ik}) \right] \\
& = \epsilon_{ij}^a - \epsilon_{ji}^a \\
& - \sum_{k>l}^{all} S_{kl}^a \left[\tau_{ij,lk}^{ik} - \tau_{ji,lk}^{jk} + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\
& - \frac{1}{2} \sum_k^{all} S_{kk}^a \left[\tau_{ij,kk}^{ik} - \tau_{ji,kk}^{jk} \right]
\end{aligned} \quad . \quad (11.17)$$

Using the definition of the τ matrices in eq. (11.8), equation (11.17) may be formulated more explicitly as

$$\begin{aligned}
& \sum_{k>l}^{all} U_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \right. \\
& \quad \left. + (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl}) \{ (ik|jl) + (il|jk) \} \right. \\
& \quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) - \delta_{li} (\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj} (\zeta_{ki}^j - \epsilon_{ik}) \right] \\
& = \epsilon_{ij}^a - \epsilon_{ji}^a \\
& - \sum_{k>l}^{all} S_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\
& \quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\
& - \frac{1}{2} \sum_k^{all} S_{kk}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk}) \{ (ik|jk) + (ik|jk) \} \right]
\end{aligned} \quad . \quad (11.18)$$

In deriving eq. (11.18), the following equalities of the τ matrix elements,

$$\tau_{ij,kl}^{mn} = \tau_{ji,kl}^{mn} = \tau_{ij,lk}^{mn} = \tau_{ji,lk}^{mn} = \tau_{kl,ij}^{mn} = \tau_{lk,ij}^{mn} = \tau_{kl,ji}^{mn} = \tau_{lk,ji}^{mn} \quad (11.19)$$

were used. For the general restricted open-shell SCF wavefunction elements of the U^a matrix between the same shell (which share a common set of coupling constants; see Section 5.4)

are not determined uniquely. Such pairs of molecular orbitals are usually called “non-independent”. On the other hand, the MO pairs between different shells are uniquely determined and are termed “independent pairs”. These independent pairs for the three most common single-configuration SCF wavefunctions are illustrated by the shaded areas in Figure 11.1.

The two-electron coupling constants, α and β , are the same among the orbitals in the same shell and they are zero if the virtual orbitals are involved. Thus, eq. (11.18) may be rewritten for the independent pairs in the simpler form

$$\sum_{k>l}^{indep.\,pair} \mathbf{A}_{ij,kl} U_{kl}^a = B_{0,ij}^a , \quad (11.20)$$

where “*indep.pair*” denotes the independent pairs, and the \mathbf{A} and B_0^a matrices are defined by

$$\begin{aligned} \mathbf{A}_{ij,kl} &= 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\ &+ (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl})\{(ik|jl) + (il|jk)\} \\ &+ \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) - \delta_{li}(\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj}(\zeta_{ki}^j - \epsilon_{ik}) \end{aligned} \quad (11.21)$$

and

$$\begin{aligned} B_{0,ij}^a &= \epsilon_{ij}^a - \epsilon_{ji}^a \\ &- \sum_k^{all\ occ} S_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk})\{(ik|jl) + (il|jk)\} \right. \\ &\quad \left. + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) \right] \\ &- \sum_k^{occ} S_{kk}^a \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] . \end{aligned} \quad (11.22)$$

In the above summations, “*all*” implies a sum over both occupied and virtual (unoccupied) molecular orbitals, while “*occ*” denotes a sum over only occupied orbitals.

These simultaneous equations usually are large in dimension and are solved iteratively. When the dimension of the eq. (11.20) is not too large (less than ~ 1000), the equations can be solved using any of the standard methods for simultaneous equations.

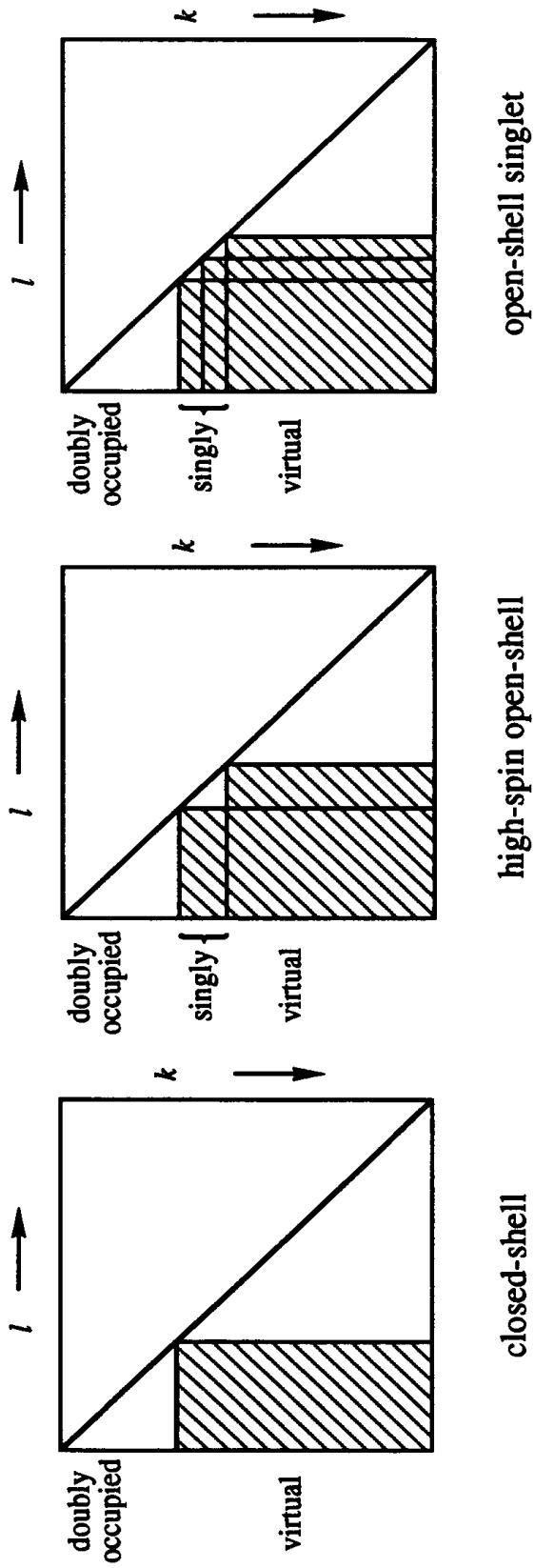


Figure 11.1 Independent pairs (*indep.pair*) of molecular orbitals in the coupled perturbed Hartree-Fock equations for GRSCF wavefunctions. Only the U^a matrix elements shown as shaded areas may be solved for uniquely.

11.2 The Averaged Fock Operator

In the general restricted open-shell SCF theory, a unitary transformation within unique shells, i.e., (doubly occupied-doubly occupied), (α spin- α spin), (β spin- β spin), and (virtual-virtual), does not change the total energy of the system. It is therefore advantageous to redefine these orbitals uniquely for use in a later process in which the entire U^a matrix is necessary. One of the most common procedures for this purpose is to employ the averaged Fock operator

$$\mathbf{F}^{av} = \mathbf{h} + \sum_k^{all} f_k (2\mathbf{J} - \mathbf{K}) , \quad (11.23)$$

where f_k is the occupation number of the k th molecular orbital. The elements of the averaged Fock matrix are given by

$$\epsilon'_{ij} = \langle \phi_i | \mathbf{F}^{av} | \phi_j \rangle = h_{ij} + \sum_k^{all} f_k \left\{ 2(ij|kk) - (ik|jk) \right\} . \quad (11.24)$$

After self-consistency is achieved, the molecular orbital coefficients and their “orbital energies”, ϵ' , are defined using the averaged Fock operator for each shell (e.g., closed-shell, α -spin shell, β -spin shell, and virtual shell). For each shell of non-independent pairs the following diagonality is established:

$$\epsilon'_{ij} = \delta_{ij} \epsilon'_i \quad (11.25)$$

where the indices i and j belong to the same shell.

The corresponding CPHF equations for the averaged Fock operator are derived in a similar manner to that described in Section 10.1. Differentiation of eq. (11.24) with respect to a cartesian coordinate “a”

$$\frac{\partial \epsilon'_{ij}}{\partial a} = \frac{\partial h_{ij}}{\partial a} + \sum_k^{all} f_k \left\{ 2 \frac{\partial (ij|kk)}{\partial a} - \frac{\partial (ik|jk)}{\partial a} \right\} \quad (11.26)$$

is required. Using the results presented in Sections 3.8 and 3.9, eq. (11.26) is expanded as

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= h_{ij}^a + \sum_m^{all} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \\ &+ \sum_k^{all} f_k \left[2(ij|kk)^a + 2 \sum_m^{all} \left\{ U_{mi}^a (mj|kk) + U_{mj}^a (im|kk) + 2U_{mk}^a (ij|mk) \right\} \right. \\ &\quad \left. - (ik|jk)^a - \sum_m^{all} \left\{ U_{mi}^a (mk|jk) + U_{mk}^a (im|jk) \right. \right. \\ &\quad \left. \left. + U_{mj}^a (ik|mk) + U_{mk}^a (ik|jm) \right\} \right] \\ &= h_{ij}^a + \sum_k^{all} f_k \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} \end{aligned} \quad (11.27)$$

$$\begin{aligned}
& + \sum_m^{all} U_{mi}^a \left[h_{mj} + \sum_k^{all} f_k \left\{ 2(mj|kk) - (mk|jk) \right\} \right] \\
& + \sum_m^{all} U_{mj}^a \left[h_{im} + \sum_k^{all} f_k \left\{ 2(im|kk) - (ik|mk) \right\} \right] \\
& + \sum_{mk}^{all} U_{mk}^a f_k \left\{ 4(ij|mk) - (im|jk) - (ik|jm) \right\} .
\end{aligned} \tag{11.28}$$

Using the definition of the averaged Fock matrix in eq. (11.24), this equation becomes

$$\begin{aligned}
\frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a + \sum_k^{all} U_{ki}^a \epsilon'_{kj} + \sum_k^{all} U_{kj}^a \epsilon'_{ik} \\
&+ \sum_{kl}^{all} U_{kl}^a f_l A_{ij,kl} .
\end{aligned} \tag{11.29}$$

The skeleton (core) first derivative averaged Fock matrix appearing in this equation is defined by

$$\epsilon'_{ij}^a = h_{ij}^a + \sum_k^{all} f_k \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} \tag{11.30}$$

and the A matrix by

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) . \tag{11.31}$$

Note that the A matrix in eq. (11.31) is a different quantity from the \mathbf{A} matrix in eq. (11.21). Using the diagonal nature of the averaged Fock matrix within the same shell, eq. (11.25), and the first derivative of the orthonormality condition of the molecular orbitals, eq. (11.13), equation (11.29) may be modified as

$$\begin{aligned}
\frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a + U_{ji}^a \epsilon'_{ij} + U_{ij}^a \epsilon'_{ii} + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\
&+ \sum_{kl}^{all} U_{kl}^a f_l A_{ij,kl}
\end{aligned} \tag{11.32}$$

$$\begin{aligned}
&= \epsilon'_{ij}^a - \left(U_{ij}^a + S_{ij}^a \right) \epsilon'_{ij} + U_{ij}^a \epsilon'_{ii} + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\
&+ \sum_{kl}^{all} U_{kl}^a f_l A_{ij,kl}
\end{aligned} \tag{11.33}$$

$$\begin{aligned}
&= \epsilon'_{ij}^a - \left(\epsilon'_{ij} - \epsilon'_{ii} \right) U_{ij}^a - S_{ij}^a \epsilon'_{ij} + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\
&+ \sum_{kl}^{all} U_{kl}^a f_l A_{ij,kl} .
\end{aligned} \tag{11.34}$$

Recalling again the relationship in eq. (11.13) the last term in eq. (11.34) may be manipulated in the following way:

$$\begin{aligned} \sum_{kl}^{all} U_{kl}^a f_l A_{ij,kl} &= \sum_{k>l}^{all} U_{kl}^a f_l A_{ij,kl} + \sum_{k>l}^{all} U_{lk}^a f_k A_{ij,lk} + \sum_k^{all} U_{kk}^a f_k A_{ij,kk} \\ &= \sum_{k>l}^{all} U_{kl}^a f_l A_{ij,kl} - \sum_{k>l}^{all} (U_{kl}^a + S_{kl}^a) f_k A_{ij,lk} \\ &\quad - \frac{1}{2} \sum_k^{all} S_{kk}^a f_k A_{ij,kk} \end{aligned} \quad (11.35)$$

$$\begin{aligned} &= \sum_{k>l}^{all} (f_l - f_k) U_{kl}^a A_{ij,kl} - \sum_{k>l}^{all} f_k S_{kl}^a A_{ij,kl} \\ &\quad - \frac{1}{2} \sum_k^{all} S_{kk}^a f_k A_{ij,kk} . \end{aligned} \quad (11.36)$$

It should be noted that the exchange of the k and l indices does not alter the value of the A matrix. The occupation number f_k is identical for all orbitals in the same shell and it is zero for the virtual orbitals. Thus, equation (11.36) is further reduced to

$$\begin{aligned} \sum_{kl}^{all} U_{kl}^a f_l A_{ij,kl} &= \sum_{k>l}^{indep.\,pair} (f_l - f_k) U_{kl}^a A_{ij,kl} - \sum_{k>l}^{occ} f_k S_{kl}^a A_{ij,kl} \\ &\quad - \sum_k^{occ} f_k S_{kk}^a \{ 2(ij|kk) - (ik|jk) \} . \end{aligned} \quad (11.37)$$

Combining eqs. (11.34) and (11.37) one obtains

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a - (\epsilon'_{ij} - \epsilon'_i) U_{ij}^a - S_{ij}^a \epsilon'_j + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\ &\quad + \sum_{k>l}^{indep.\,pair} (f_l - f_k) U_{kl}^a A_{ij,kl} - \sum_{k>l}^{occ} f_k S_{kl}^a A_{ij,kl} \\ &\quad - \sum_k^{occ} f_k S_{kk}^a \{ 2(ij|kk) - (ik|jk) \} . \end{aligned} \quad (11.38)$$

The final expression to evaluate elements of the U^a matrix for non-independent pairs is

$$\begin{aligned} U_{ij}^a &= \frac{1}{\epsilon'_j - \epsilon'_i} \left[\epsilon'_{ij}^a - S_{ij}^a \epsilon'_j + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \right. \\ &\quad + \sum_{k>l}^{indep.\,pair} (f_l - f_k) U_{kl}^a A_{ij,kl} - \sum_{k>l}^{occ} f_k S_{kl}^a A_{ij,kl} \\ &\quad \left. - \sum_k^{occ} f_k S_{kk}^a \{ 2(ij|kk) - (ik|jk) \} \right] . \end{aligned} \quad (11.39)$$

When the entire U^a matrix is required in the later process, the molecular orbitals must be subjected to a unitary transformation within unique shells using the averaged Fock operator in eq. (11.23) prior to solving the CPHF equations. Employing these redefined molecular orbitals, the elements of the U^a matrices for the independent pairs are then obtained by solution of the CPHF equations in eq. (11.20). Finally the elements for the non-independent pairs are determined in terms of the independent pair U^a elements from equation (11.39). An alternate approach to this subject has been discussed in References 4 and 5.

11.3 The Derivative of the ϵ^a Matrices

Before proceeding to the second-order CPHF equations it is useful to find derivative expressions for quantities involved in the second derivative of the Lagrangian matrix. Examining eq. (11.5) it is clear that those quantities include the ϵ^a , ζ^l , and τ matrices. This section and the next two sections are devoted to finding the derivative expressions of these quantities. The derivatives of the ϵ^a matrices are discussed here. Using the results from Sections 3.8 and 3.9, the derivative of eq. (11.6) with respect to a second variable "b" is written as:

$$\frac{\partial \epsilon_{ij}^a}{\partial b} = f_i \frac{\partial h_{ij}^a}{\partial b} + \sum_l^{all} \left\{ \alpha_{il} \frac{\partial (ij|ll)^a}{\partial b} + \beta_{il} \frac{\partial (il|jl)^a}{\partial b} \right\} \quad (11.40)$$

$$\begin{aligned} &= f_i \left[h_{ij}^{ab} + \sum_m^{all} \left(U_{mi}^b h_{mj}^a + U_{mj}^b h_{im}^a \right) \right] \\ &+ \sum_l^{all} \left[\alpha_{il} \left((ij|ll)^{ab} + \sum_m^{all} \left\{ U_{mi}^b (mj|ll)^a + U_{mj}^b (im|ll)^a + 2U_{ml}^b (ij|ml)^a \right\} \right) \right. \\ &\quad \left. + \beta_{il} \left((il|jl)^{ab} + \sum_m^{all} \left\{ U_{mi}^b (ml|jl)^a + U_{ml}^b (im|jl)^a + U_{mj}^b (il|ml)^a \right. \right. \right. \\ &\quad \left. \left. \left. + U_{ml}^b (il|jm)^a \right\} \right) \right] \end{aligned} \quad (11.41)$$

$$\begin{aligned} &= f_i h_{ij}^{ab} + \sum_l^{all} \left\{ \alpha_{il} (ij|ll)^{ab} + \beta_{il} (il|jl)^{ab} \right\} \\ &+ \sum_m^{all} U_{mi}^b \left[f_i h_{mj}^a + \sum_l^{all} \left\{ \alpha_{il} (mj|ll)^a + \beta_{il} (ml|jl)^a \right\} \right] \\ &+ \sum_m^{all} U_{mj}^b \left[f_i h_{im}^a + \sum_l^{all} \left\{ \alpha_{il} (im|ll)^a + \beta_{il} (il|ml)^a \right\} \right] \\ &+ \sum_{ml}^{all} U_{ml}^b \left[2\alpha_{il} (ij|ml)^a + \beta_{il} \left\{ (im|jl)^a + (il|jm)^a \right\} \right] \\ &= \epsilon_{ij}^{ab} + \sum_m^{all} U_{mi}^b \zeta_{mj}^{ia} + \sum_m^{all} U_{mj}^b \epsilon_{im}^a \end{aligned} \quad (11.42)$$

$$+ \sum_{ml}^{all} U_{ml}^b \left[2\alpha_{il}(ij|ml)^a + \beta_{il} \left\{ (im|jl)^a + (il|jm)^a \right\} \right] \quad (11.43)$$

$$= \epsilon_{ij}^{ab} + \sum_k^{all} \left(U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right) + \sum_{kl}^{all} U_{kl}^b \tau_{ij,kl}^{ila} . \quad (11.44)$$

The skeleton (core) second derivative Lagrangian matrices, ϵ^{ab} , the first derivative generalized Lagrangian matrices, ζ^{la} , and the first derivative τ matrices, τ^a , are

$$\epsilon_{ij}^{ab} = f_i h_{ij}^{ab} + \sum_l^{all} \left\{ \alpha_{il}(ij|ll)^{ab} + \beta_{il}(il|jl)^{ab} \right\} , \quad (11.45)$$

$$\zeta_{ij}^{la} = f_l h_{ij}^a + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk)^a + \beta_{lk}(ik|jk)^a \right\} , \quad (11.46)$$

and

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl)^a + \beta_{mn} \left\{ (ik|jl)^a + (il|jk)^a \right\} . \quad (11.47)$$

The derivative expression for the ϵ^a matrices in eq. (11.44) has a similar form to that of the ϵ matrix in eq. (11.5). Derivative expressions for the skeleton (core) higher derivative Lagrangian matrices are not worked out explicitly here, as they are found in a comparable manner to the derivatives of the ϵ^a matrices just discussed. These expressions are summarized in Appendix P.

11.4 The First Derivative of the Generalized Lagrangian Matrix

In this section, the first derivative of the generalized Lagrangian matrix, ζ^l , is obtained. Using the results from Sections 3.8 and 3.9, the derivative of eq. (11.7) with respect to the variable “ a ” is:

$$\frac{\partial \zeta_{ij}^l}{\partial a} = f_l \frac{\partial h_{ij}}{\partial a} + \sum_k^{all} \left\{ \alpha_{lk} \frac{\partial (ij|kk)}{\partial a} + \beta_{lk} \frac{\partial (ik|jk)}{\partial a} \right\} \quad (11.48)$$

$$\begin{aligned} &= f_l \left[h_{ij}^a + \sum_m^{all} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \right] \\ &+ \sum_k^{all} \left[\alpha_{lk} \left((ij|kk)^a + \sum_m^{all} \left\{ U_{mi}^a (mj|kk) + U_{mj}^a (im|kk) + 2U_{mk}^a (ij|mk) \right\} \right) \right. \\ &\quad \left. + \beta_{lk} \left((ik|jk)^a + \sum_m^{all} \left\{ U_{mi}^a (mk|jk) + U_{mk}^a (im|jk) \right. \right. \right. \\ &\quad \left. \left. \left. + U_{mj}^a (ik|mk) + U_{mk}^a (ik|jm) \right\} \right) \right] \end{aligned} \quad (11.49)$$

$$\begin{aligned}
&= f_l h_{ij}^a + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk)^a + \beta_{lk}(ik|jk)^a \right\} \\
&+ \sum_m^{all} U_{mi}^a \left[f_l h_{mj} + \sum_k^{all} \left\{ \alpha_{lk}(mj|kk) + \beta_{lk}(mk|jk) \right\} \right] \\
&+ \sum_m^{all} U_{mj}^a \left[f_l h_{im} + \sum_k^{all} \left\{ \alpha_{lk}(im|kk) + \beta_{lk}(ik|mk) \right\} \right] \\
&+ \sum_{mk}^{all} U_{mk}^a \left[2\alpha_{lk}(ij|mk) + \beta_{lk} \left\{ (im|jk) + (ik|jm) \right\} \right] . \tag{11.50}
\end{aligned}$$

Using the definitions of the ζ and τ matrices in eqs. (11.7) and (11.8) yields

$$\frac{\partial \zeta_{ij}^l}{\partial a} = \zeta_{ij}^{la} + \sum_m^{all} U_{mi}^a \zeta_{mj}^l + \sum_m^{all} U_{mj}^a \zeta_{im}^l + \sum_{mn}^{all} U_{mn}^a \tau_{ij,mn}^{ln} . \tag{11.51}$$

In eq. (11.51) the skeleton (core) derivative generalized Lagrangian matrices, ζ^{la} , were defined by eq. (11.46).

11.5 The First Derivative of the τ Matrices

In this section the derivative of the τ matrix appearing in eq. (11.5) is determined. Using results from Section 3.9, the derivative of the τ matrix, (11.8), is:

$$\frac{\partial \tau_{ij,kl}^{mn}}{\partial a} = 2\alpha_{mn} \frac{\partial (ij|kl)}{\partial a} + \beta_{mn} \left\{ \frac{\partial (ik|jl)}{\partial a} + \frac{\partial (il|jk)}{\partial a} \right\} \tag{11.52}$$

$$\begin{aligned}
&= 2\alpha_{mn} \left[(ij|kl)^a \right. \\
&\quad \left. + \sum_p^{all} \left\{ U_{pi}^a(pj|kl) + U_{pj}^a(ip|kl) + U_{pk}^a(ij|pl) + U_{pl}^a(ij|kp) \right\} \right] \\
&+ \beta_{mn} \left[(ik|jl)^a + \sum_p^{all} \left\{ U_{pi}^a(pk|jl) + U_{pk}^a(ip|jl) + U_{pj}^a(ik|pl) + U_{pl}^a(ik|jp) \right\} \right] \\
&+ \beta_{mn} \left[(il|jk)^a + \sum_p^{all} \left\{ U_{pi}^a(pl|jk) + U_{pl}^a(ip|jk) + U_{pj}^a(il|pk) + U_{pk}^a(il|jp) \right\} \right] \\
&\quad \tag{11.53}
\end{aligned}$$

$$\begin{aligned}
&= 2\alpha_{mn}(ij|kl)^a + \beta_{mn} \left\{ (ik|jl)^a + (il|jk)^a \right\} \\
&+ \sum_p^{all} U_{pi}^a \left[2\alpha_{mn}(pj|kl) + \beta_{mn} \left\{ (pk|jl) + (pl|jk) \right\} \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_m^{\text{all}} U_{pj}^a \left[2\alpha_{mn}(ip|kl) + \beta_{mn} \left\{ (ik|pl) + (il|pk) \right\} \right] \\
& + \sum_m^{\text{all}} U_{pk}^a \left[2\alpha_{mn}(ij|pl) + \beta_{mn} \left\{ (ip|jl) + (il|jp) \right\} \right] \\
& + \sum_m^{\text{all}} U_{pl}^a \left[2\alpha_{mn}(ij|kp) + \beta_{mn} \left\{ (ik|jp) + (ip|jk) \right\} \right] \quad . \tag{11.54}
\end{aligned}$$

The definition of the τ matrix, eq. (11.8), may be used to rewrite this equation in the simplified form

$$\begin{aligned}
\frac{\partial \tau_{ij,kl}^{mn}}{\partial a} &= \tau_{ij,kl}^{mn} \\
&+ \sum_p^{\text{all}} \left(U_{pi}^a \tau_{pj,kl}^{mn} + U_{pj}^a \tau_{ip,kl}^{mn} + U_{pk}^a \tau_{ij,pl}^{mn} + U_{pl}^a \tau_{ij,kp}^{mn} \right) \quad , \tag{11.55}
\end{aligned}$$

in which the τ^a matrices were defined by eq. (11.47).

11.6 The Second Derivative of the Lagrangian Matrix

The second derivative of the Lagrangian matrix is required for the derivation of the second-order CPHF equations and is obtained by differentiating eq. (11.5) with respect to a second variable “ b ”:

$$\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} = \frac{\partial}{\partial b} \left[\frac{\partial \epsilon_{ij}}{\partial a} \right] \tag{11.56}$$

$$= \frac{\partial}{\partial b} \left[\epsilon_{ij}^a + \sum_k^{\text{all}} U_{ki}^a \zeta_{kj}^i + \sum_k^{\text{all}} U_{kj}^a \epsilon_{ik} + \sum_{kl}^{\text{all}} U_{kl}^a \tau_{ij,kl}^{il} \right] \tag{11.57}$$

$$\begin{aligned}
&= \frac{\partial \epsilon_{ij}^a}{\partial b} + \sum_k^{\text{all}} \left[\frac{\partial U_{ki}^a}{\partial b} \zeta_{kj}^i + U_{ki}^a \frac{\partial \zeta_{kj}^i}{\partial b} \right] \\
&+ \sum_k^{\text{all}} \left[\frac{\partial U_{kj}^a}{\partial b} \epsilon_{ik} + U_{kj}^a \frac{\partial \epsilon_{ik}}{\partial b} \right] \\
&+ \sum_{kl}^{\text{all}} \left[\frac{\partial U_{kl}^a}{\partial b} \tau_{ij,kl}^{il} + U_{kl}^a \frac{\partial \tau_{ij,kl}^{il}}{\partial b} \right] \quad . \tag{11.58}
\end{aligned}$$

Results from Section 3.3 and the preceding sections allow eq. (11.58) to be rewritten as

$$\begin{aligned}
\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} &= \epsilon_{ij}^{ab} + \sum_k^{\text{all}} U_{ki}^b \zeta_{kj}^{ia} + \sum_k^{\text{all}} U_{kj}^b \epsilon_{ik}^a + \sum_{kl}^{\text{all}} U_{kl}^b \tau_{ij,kl}^{ila} \\
&+ \sum_k^{\text{all}} \left(U_{ki}^{ab} - \sum_m^{\text{all}} U_{km}^b U_{mi}^a \right) \zeta_{kj}^i
\end{aligned}$$

$$\begin{aligned}
& + \sum_k^{all} U_{ki}^a \left[\zeta_{kj}^{ib} + \sum_m^{all} U_{mk}^b \zeta_{mj}^i + \sum_m^{all} U_{mj}^b \zeta_{km}^i + \sum_{mn}^{all} U_{mn}^b \tau_{kj,mn}^{in} \right] \\
& + \sum_k^{all} \left(U_{kj}^{ab} - \sum_m^{all} U_{km}^b U_{mj}^a \right) \epsilon_{ik} \\
& + \sum_k^{all} U_{kj}^a \left[\epsilon_{ik}^b + \sum_m^{all} U_{mi}^b \zeta_{mk}^i + \sum_m^{all} U_{mk}^b \epsilon_{im} + \sum_{mn}^{all} U_{mn}^b \tau_{ik,mn}^{in} \right] \\
& + \sum_{kl}^{all} \left(U_{kl}^{ab} - \sum_m^{all} U_{km}^b U_{ml}^a \right) \tau_{ij,kl}^{il} \\
& + \sum_{kl}^{all} U_{kl}^a \left[\tau_{ij,kl}^{ilb} + \sum_m^{all} \left(U_{mi}^b \tau_{mj,kl}^{il} + U_{mj}^b \tau_{im,kl}^{il} \right. \right. \\
& \quad \left. \left. + U_{mk}^b \tau_{ij,ml}^{il} + U_{ml}^b \tau_{ij,km}^{il} \right) \right] \quad . \tag{11.59}
\end{aligned}$$

The expressions for the first derivative of the generalized Lagrangian matrix (11.51) and of the τ matrix (11.55) finally permit the reformulation of (11.59) as

$$\begin{aligned}
\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} & = \epsilon_{ij}^{ab} + \sum_k^{all} U_{ki}^{ab} \zeta_{kj}^i + \sum_k^{all} U_{kj}^{ab} \epsilon_{ik} \\
& + \sum_{kl}^{all} U_{kl}^{ab} \tau_{ij,kl}^{il} \\
& + \sum_{kl}^{all} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \zeta_{kl}^i \\
& + \sum_{klm}^{all} U_{km}^a U_{lm}^b \tau_{ij,kl}^{im} \\
& + \sum_{kmn}^{all} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \tau_{kj,mn}^{in} \\
& + \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ik,mn}^{in} \\
& + \sum_{kl}^{all} \left(U_{kl}^a \tau_{ij,kl}^{ilb} + U_{kl}^b \tau_{ij,kl}^{ila} \right) \\
& + \sum_k^{all} \left(U_{ki}^a \zeta_{kj}^{ib} + U_{kj}^a \epsilon_{ik}^b + U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right) \quad . \tag{11.60}
\end{aligned}$$

Note that the first four terms of the right hand side of eq. (11.60) have forms very similar to those of the first derivative of the ϵ matrix in eq. (11.5).

11.7 The Second-Order CPHF Equations

The second-order CPHF equations are derived by differentiating eq. (11.4) with respect to a cartesian coordinate “ b ”:

$$\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} - \frac{\partial^2 \epsilon_{ji}}{\partial a \partial b} = 0 \quad . \quad (11.61)$$

Substituting the Lagrangian second derivative eq. (11.60) into eq. (11.61) we have

$$\begin{aligned}
& \frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} - \frac{\partial^2 \epsilon_{ji}}{\partial a \partial b} \\
&= \epsilon_{ij}^{ab} + \sum_k^{all} \left(U_{ki}^{ab} \zeta_{kj}^i + U_{kj}^{ab} \epsilon_{ik} \right) + \sum_{kl}^{all} U_{kl}^{ab} \tau_{ij,kl}^{il} \\
&+ \sum_{kl}^{all} \left(U_{ki}^a U_{lj}^b + U_{kj}^b U_{li}^a \right) \zeta_{kl}^i \\
&+ \sum_{klm}^{all} U_{km}^a U_{lm}^b \tau_{ij,kl}^{im} \\
&+ \sum_{kmn}^{all} \left(U_{ki}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{kj,mn}^{in} + \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ik,mn}^{in} \\
&+ \sum_{kl}^{all} \left(U_{kl}^a \tau_{ij,kl}^{ilb} + U_{kl}^b \tau_{ij,kl}^{ila} \right) \\
&+ \sum_k^{all} \left(U_{ki}^a \zeta_{kj}^{ib} + U_{kj}^b \epsilon_{ik}^b + U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right) \\
&- \epsilon_{ji}^{ab} - \sum_k^{all} \left(U_{kj}^{ab} \zeta_{ki}^j + U_{ki}^{ab} \epsilon_{jk} \right) - \sum_{kl}^{all} U_{kl}^{ab} \tau_{ji,kl}^{jl} \\
&- \sum_{kl}^{all} \left(U_{kj}^a U_{li}^b + U_{kj}^b U_{li}^a \right) \zeta_{kl}^j \\
&- \sum_{klm}^{all} U_{km}^a U_{lm}^b \tau_{ji,kl}^{jm} \\
&- \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ki,mn}^{jn} - \sum_{kmn}^{all} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \tau_{jk,mn}^{jn} \\
&- \sum_{kl}^{all} \left(U_{kl}^a \tau_{ji,kl}^{jl^b} + U_{kl}^b \tau_{ji,kl}^{jl^a} \right) \\
&- \sum_k^{all} \left(U_{kj}^a \zeta_{ki}^{jb} + U_{ki}^a \epsilon_{jk}^b + U_{kj}^b \zeta_{ki}^{ja} + U_{ki}^b \epsilon_{jk}^a \right) \quad .
\end{aligned} \quad (11.62)$$

Rearrangement of terms gives

$$\begin{aligned}
 & \frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} - \frac{\partial^2 \epsilon_{ji}}{\partial a \partial b} \\
 &= \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
 &+ \sum_k^{\text{all}} \left[U_{ki}^{ab} \left(\zeta_{kj}^i - \epsilon_{jk} \right) - U_{kj}^{ab} \left(\zeta_{ki}^j - \epsilon_{ik} \right) \right] \\
 &+ \sum_{kl}^{\text{all}} U_{kl}^{ab} \left(\tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right) \\
 &+ \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
 &+ \sum_{klm}^{\text{all}} U_{km}^a U_{lm}^b \left(\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm} \right) \\
 &+ \sum_{kmn}^{\text{all}} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left(\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn} \right) \\
 &+ \sum_{kmn}^{\text{all}} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left(\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn} \right) \\
 &+ \sum_{kl}^{\text{all}} U_{kl}^a \left(\tau_{ij,kl}^{il^b} - \tau_{ji,kl}^{jl^b} \right) + \sum_{kl}^{\text{all}} U_{kl}^b \left(\tau_{ij,kl}^{il^a} - \tau_{ji,kl}^{jl^a} \right) \\
 &+ \sum_k^{\text{all}} \left[U_{ki}^a \left(\zeta_{kj}^{ib} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
 &\quad \left. - U_{kj}^a \left(\zeta_{ki}^{jb} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \quad . \tag{11.63}
 \end{aligned}$$

And finally we obtain

$$\begin{aligned}
 & \frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} - \frac{\partial^2 \epsilon_{ji}}{\partial a \partial b} \\
 &= \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
 &+ \sum_{kl}^{\text{all}} U_{kl}^{ab} \left[\delta_{li} \left(\zeta_{kj}^i - \epsilon_{jk} \right) - \delta_{lj} \left(\zeta_{ki}^j - \epsilon_{ik} \right) + \tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right] \\
 &+ \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
 &+ \sum_{klm}^{\text{all}} U_{km}^a U_{lm}^b \left(\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm} \right) \\
 &+ \sum_{kmn}^{\text{all}} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left(\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn} \right)
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left(\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn} \right) \\
& + \sum_{kl}^{all} U_{kl}^a \left(\tau_{ij,kl}^{ilb} - \tau_{ji,kl}^{jl^b} \right) + \sum_{kl}^{all} U_{kl}^b \left(\tau_{ij,kl}^{il^a} - \tau_{ji,kl}^{jl^a} \right) \\
& + \sum_k^{all} \left[U_{ki}^a \left(\zeta_{kj}^{ib} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
& \quad \left. - U_{kj}^a \left(\zeta_{ki}^{jb} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \quad . \quad (11.64)
\end{aligned}$$

In the above manipulations, the fact that the interchange of the indices k, l, m and n does not alter the equation was used. In eq. (11.64), the third term that involves U^{ab} has a form equivalent to eq. (11.11). Therefore, this equation is treated as in Section 11.1. Employing the second derivative orthonormality condition from Section 3.7

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad (11.65)$$

where

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) , \quad (11.66)$$

the second-order CPHF equations are given in familiar form (see Section 11.1):

$$\sum_{k>l}^{indep.\,pair} \mathbf{A}_{ij,kl} U_{kl}^{ab} = B_{0,ij}^{ab} . \quad (11.67)$$

The \mathbf{A} matrix appearing in the CPHF equations was defined in eq. (11.21) as

$$\begin{aligned}
\mathbf{A}_{ij,kl} &= 2 \left(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl} \right) (ij|kl) \\
&+ \left(\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl} \right) \left\{ (ik|jl) + (il|jk) \right\} \\
&+ \delta_{ki} \left(\zeta_{lj}^i - \epsilon_{jl} \right) - \delta_{kj} \left(\zeta_{li}^j - \epsilon_{il} \right) - \delta_{li} \left(\zeta_{kj}^i - \epsilon_{jk} \right) + \delta_{lj} \left(\zeta_{ki}^j - \epsilon_{ik} \right) \quad (11.68)
\end{aligned}$$

and

$$\begin{aligned}
B_{0,ij}^{ab} &= \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
&- \sum_{k>l}^{all\,occ} \xi_{kl}^{ab} \left[2 \left(\alpha_{ik} - \alpha_{jk} \right) (ij|kl) + \left(\beta_{ik} - \beta_{jk} \right) \left\{ (ik|jl) + (il|jk) \right\} \right. \\
&\quad \left. + \delta_{ki} \left(\zeta_{lj}^i - \epsilon_{jl} \right) - \delta_{kj} \left(\zeta_{li}^j - \epsilon_{il} \right) \right]
\end{aligned}$$

$$\begin{aligned}
& - \sum_k^{\text{occ}} \xi_{kk}^{ab} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\
& + \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
& + \sum_{klm}^{\text{all}} U_{km}^a U_{lm}^b \left(\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm} \right) \\
& + \sum_{kmn}^{\text{all}} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left(\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn} \right) \\
& + \sum_{kmn}^{\text{all}} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left(\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn} \right) \\
& + \sum_{kl}^{\text{all}} U_{kl}^a \left(\tau_{ij,kl}^{il^b} - \tau_{ji,kl}^{jl^b} \right) + \sum_{kl}^{\text{all}} U_{kl}^b \left(\tau_{ij,kl}^{il^a} - \tau_{ji,kl}^{jl^a} \right) \\
& + \sum_k^{\text{all}} \left[U_{ki}^a \left(\zeta_{kj}^{ib} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
& \quad \left. - U_{kj}^a \left(\zeta_{ki}^{jb} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \quad . \tag{11.69}
\end{aligned}$$

These B_0^{ab} matrices may be expressed in full detail by:

$$\begin{aligned}
B_{0,ij}^{ab} & = \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
& - \sum_{k>l}^{\text{all occ}} \xi_{kl}^{ab} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \left\{ (ik|jl) + (il|jk) \right\} \right. \\
& \quad \left. + \delta_{ki} \left(\zeta_{lj}^i - \epsilon_{jl} \right) - \delta_{kj} \left(\zeta_{li}^j - \epsilon_{il} \right) \right] \\
& - \sum_k^{\text{occ}} \xi_{kk}^{ab} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\
& + \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
& + \sum_{klm}^{\text{all}} U_{km}^a U_{lm}^b \left[2(\alpha_{im} - \alpha_{jm})(ij|kl) + (\beta_{im} - \beta_{jm}) \left\{ (ik|jl) + (il|jk) \right\} \right] \\
& + \sum_{kmn}^{\text{all}} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left[2(\alpha_{in} - \alpha_{jn})(kj|mn) \right. \\
& \quad \left. + (\beta_{in} - \beta_{jn}) \left\{ (km|jn) + (kn|jm) \right\} \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left[2(\alpha_{in} - \alpha_{jn})(ki|mn) \right. \\
& \quad \left. + (\beta_{in} - \beta_{jn}) \left\{ (km|in) + (kn|im) \right\} \right] \\
& + \sum_{kl}^{all} U_{kl}^a \left[2(\alpha_{il} - \alpha_{jl})(ij|kl)^b + (\beta_{il} - \beta_{jl}) \left\{ (ik|jl)^b + (il|jk)^b \right\} \right] \\
& + \sum_{kl}^{all} U_{kl}^b \left[2(\alpha_{il} - \alpha_{jl})(ij|kl)^a + (\beta_{il} - \beta_{jl}) \left\{ (ik|jl)^a + (il|jk)^a \right\} \right] \\
& + \sum_k^{all} \left[U_{ki}^a \left(\zeta_{kj}^{ib} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
& \quad \left. - U_{kj}^a \left(\zeta_{ki}^{jb} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \quad . \tag{11.70}
\end{aligned}$$

In deriving eq. (11.70), the equalities given in (11.19) were exploited. The first four terms of the right hand side of eq. (11.70) have similar forms to those for the first-order expression given by eq. (11.22).

11.8 An Alternative Derivation of the Second Derivative of the Lagrangian Matrix

Another expression for the second derivative of the Lagrangian matrix is obtained more laboriously by differentiating eq. (11.2) with respect to the two cartesian coordinates “a” and “b”,

$$\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} = f_i \frac{\partial^2 h_{ij}}{\partial a \partial b} + \sum_l^{all} \left\{ \alpha_{il} \frac{\partial^2 (ij|ll)}{\partial a \partial b} + \beta_{il} \frac{\partial^2 (il|jl)}{\partial a \partial b} \right\} \quad . \tag{11.71}$$

Using the results in Sections 3.8 and 3.9, this second derivative expression may be expanded to give:

$$\begin{aligned}
\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} & = f_i \left[h_{ij}^{ab} + \sum_m^{all} \left(U_{mi}^{ab} h_{mj} + U_{mj}^{ab} h_{im} \right) \right. \\
& \quad \left. + \sum_m^{all} \left(U_{mi}^a h_{mj}^b + U_{mi}^b h_{mj}^a + U_{mj}^a h_{im}^b + U_{mj}^b h_{im}^a \right) \right. \\
& \quad \left. + \sum_{mn}^{all} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) h_{mn} \right] \\
& + \sum_l^{all} \alpha_{il} \left[(ij|ll)^{ab} + \sum_m^{all} \left(U_{mi}^{ab} (mj|ll) + U_{mj}^{ab} (im|ll) + 2U_{ml}^{ab} (ij|ml) \right) \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_m^{all} \left(U_{mi}^a (mj|ll)^b + U_{mj}^a (im|ll)^b + 2U_{ml}^a (ij|ml)^b \right. \\
& + U_{mi}^b (mj|ll)^a + U_{mj}^b (im|ll)^a + 2U_{ml}^b (ij|ml)^a \Big) \\
& + \sum_{mn}^{all} \left\{ \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mn|ll) \right. \\
& + 2 \left(U_{mi}^a U_{nl}^b + U_{mi}^b U_{nl}^a \right) (mj|nl) + 2 \left(U_{mj}^a U_{nl}^b + U_{mj}^b U_{nl}^a \right) (im|nl) \\
& \left. + \left(U_{ml}^a U_{nl}^b + U_{ml}^b U_{nl}^a \right) (ij|mn) \right\} \\
& + \sum_l^{all} \beta_{il} \left[(il|jl)^{ab} \right. \\
& + \sum_m^{all} \left(U_{mi}^{ab} (ml|jl) + U_{ml}^{ab} (im|jl) + U_{mj}^{ab} (il|ml) + U_{ml}^{ab} (il|jm) \right) \\
& + \sum_m^{all} \left(U_{mi}^a (ml|jl)^b + U_{ml}^a (im|jl)^b + U_{mj}^a (il|ml)^b + U_{ml}^a (il|jm)^b \right. \\
& + U_{mi}^b (ml|jl)^a + U_{ml}^b (im|jl)^a + U_{mj}^b (il|ml)^a + U_{ml}^b (il|jm)^a \Big) \\
& + \sum_{mn}^{all} \left\{ \left(U_{mi}^a U_{nl}^b + U_{mi}^b U_{nl}^a \right) (mn|jl) + \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (ml|nl) \right. \\
& + \left(U_{mi}^a U_{nl}^b + U_{mi}^b U_{nl}^a \right) (ml|jn) + \left(U_{ml}^a U_{nj}^b + U_{ml}^b U_{nj}^a \right) (im|nl) \\
& \left. + \left(U_{ml}^a U_{nl}^b + U_{ml}^b U_{nl}^a \right) (im|jn) + \left(U_{mj}^a U_{nl}^b + U_{mj}^b U_{nl}^a \right) (il|mn) \right\} \tag{11.72}
\end{aligned}$$

Rearranging equation (11.72), gives:

$$\begin{aligned}
\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} &= f_i h_{ij}^{ab} + \sum_l^{all} \left\{ \alpha_{il} (ij|ll)^{ab} + \beta_{il} (il|jl)^{ab} \right\} \\
&+ \sum_m^{all} U_{mi}^{ab} \left[f_i h_{mj} + \sum_l^{all} \left\{ \alpha_{il} (mj|ll) + \beta_{il} (ml|jl) \right\} \right] \\
&+ \sum_m^{all} U_{mj}^{ab} \left[f_i h_{im} + \sum_l^{all} \left\{ \alpha_{il} (im|ll) + \beta_{il} (il|ml) \right\} \right] \\
&+ \sum_{ml}^{all} U_{ml}^{ab} \left[2\alpha_{il} (ij|ml) + \beta_{il} \{ (im|jl) + (il|jm) \} \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_{mn}^{all} U_{mi}^a U_{nj}^b \left[f_i h_{mn} + \sum_l^{all} \left\{ \alpha_{il}(mn|ll) + \beta_{il}(ml|nl) \right\} \right] \\
& + \sum_{mn}^{all} U_{mi}^b U_{nj}^a \left[f_i h_{mn} + \sum_l^{all} \left\{ \alpha_{il}(mn|ll) + \beta_{il}(ml|nl) \right\} \right] \\
& + \sum_{mnl}^{all} U_{ml}^a U_{nl}^b \left[2\alpha_{il}(ij|mn) + \beta_{il} \left\{ (im|jn) + (in|jm) \right\} \right] \\
& + \sum_{mnl}^{all} U_{mi}^a U_{nl}^b \left[2\alpha_{il}(mj|nl) + \beta_{il} \left\{ (mn|jl) + (ml|jn) \right\} \right] \\
& + \sum_{mnl}^{all} U_{mi}^b U_{nl}^a \left[2\alpha_{il}(mj|nl) + \beta_{il} \left\{ (mn|jl) + (ml|jn) \right\} \right] \\
& + \sum_{mnl}^{all} U_{mj}^a U_{nl}^b \left[2\alpha_{il}(im|nl) + \beta_{il} \left\{ (in|ml) + (il|mn) \right\} \right] \\
& + \sum_{mnl}^{all} U_{mj}^b U_{nl}^a \left[2\alpha_{il}(im|nl) + \beta_{il} \left\{ (in|ml) + (il|mn) \right\} \right] \\
& + \sum_{ml}^{all} U_{ml}^a \left[2\alpha_{il}(ij|ml)^b + \beta_{il} \left\{ (im|jl)^b + (il|jm)^b \right\} \right] \\
& + \sum_{ml}^{all} U_{ml}^b \left[2\alpha_{il}(ij|ml)^a + \beta_{il} \left\{ (im|jl)^a + (il|jm)^a \right\} \right] \\
& + \sum_m^{all} U_{mi}^a \left[f_i h_{mj}^b + \sum_l^{all} \left\{ \alpha_{il}(mj|ll)^b + \beta_{il}(ml|jl)^b \right\} \right] \\
& + \sum_m^{all} U_{mj}^a \left[f_i h_{im}^b + \sum_l^{all} \left\{ \alpha_{il}(im|ll)^b + \beta_{il}(il|ml)^b \right\} \right] \\
& + \sum_m^{all} U_{mi}^b \left[f_i h_{mj}^a + \sum_l^{all} \left\{ \alpha_{il}(mj|ll)^a + \beta_{il}(ml|jl)^a \right\} \right] \\
& + \sum_m^{all} U_{mj}^b \left[f_i h_{im}^a + \sum_l^{all} \left\{ \alpha_{il}(im|ll)^a + \beta_{il}(il|ml)^a \right\} \right]
\end{aligned} . \quad (11.73)$$

The definitions of ϵ , ϵ^a , ϵ^{ab} , ζ , ζ^a , τ and τ^a from eqs. (11.2), (11.6), (11.7), (11.8), (11.45), (11.46) and (11.47) are finally used to rewrite (11.73) as:

$$\begin{aligned}
\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} &= \epsilon_{ij}^{ab} + \sum_k^{all} U_{ki}^{ab} \zeta_{kj}^i + \sum_k^{all} U_{kj}^{ab} \epsilon_{ik} \\
&+ \sum_{kl}^{all} U_{kl}^{ab} \tau_{ij,kl}^{il}
\end{aligned}$$

$$\begin{aligned}
& + \sum_{kl}^{all} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \zeta_{kl}^i \\
& + \sum_{klm}^{all} U_{km}^a U_{lm}^b \tau_{ij,kl}^{im} \\
& + \sum_{kmn}^{all} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \tau_{kj,mn}^{in} \\
& + \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ik,mn}^{in} \\
& + \sum_{kl}^{all} \left(U_{kl}^a \tau_{ij,kl}^{ilb} + U_{kl}^b \tau_{ij,kl}^{ila} \right) \\
& + \sum_k^{all} \left(U_{ki}^a \zeta_{kj}^{ib} + U_{kj}^a \epsilon_{ik}^b + U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right) . \quad (11.74)
\end{aligned}$$

Equation (11.74) is seen to be equivalent to eq. (11.60).

References

1. C.C.J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).
2. F.W. Bobrowicz and W.A. Goddard, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.79 (1977).
3. R. Carbo and J.M. Riera, *A General SCF Theory*, Springer-Verlag, Berlin, 1978.
4. J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, and H.F. Schaefer, J. Chem. Phys. **85**, 963 (1986).
5. T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, J. Chem. Phys. **85**, 3930 (1986).

Suggested Reading

1. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, J. Chem. Phys. **77**, 383 (1982).
2. Y. Osamura, Y. Yamaguchi, P. Saxe, M.A. Vincent, J.F. Gaw, and H.F. Schaefer, Chem. Phys. **72**, 131 (1982).
3. Y. Osamura, Y. Yamaguchi, P. Saxe, D.J. Fox, M.A. Vincent, and H.F. Schaefer, J. Mol. Struct. **103**, 183 (1983).
4. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, Chem. Phys. **103**, 227 (1986).

Chapter 12

Coupled Perturbed Configuration Interaction Equations

The analytic evaluation of the second derivatives of the configuration interaction (CI) energy requires the solution of a very challenging set of equations. These coupled perturbed configuration interaction (CPCI) equations are those simultaneous equations which provide the derivatives of the CI coefficients with respect to perturbations. These CPCI equations are obtained by differentiating the variational condition on the CI space under the constraint of normalization on the CI coefficients. In this Chapter the first- and second-order CPCI equations are described.

12.1 The First-Order Coupled Perturbed Configuration Interaction Equations

The variational condition for the determination of the CI wavefunction is [1]

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad (12.1)$$

where the CI Hamiltonian matrix element was defined in Chapter 6 as

$$H_{IJ} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl) . \quad (12.2)$$

The CI coefficients are normalized according to the usual convention as

$$\sum_I^{CI} C_I^2 = 1 . \quad (12.3)$$

The one- and two-electron coupling constants, Q^{IJ} and G^{IJ} , appearing in eq. (12.2) are related to their "parent" quantities, the one- and two-electron reduced density matrices [2], through

$$Q_{ij} = \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} \quad (12.4)$$

$$G_{ijkl} = \sum_{IJ}^{CI} C_I C_J G_{ijkl}^{IJ} \quad . \quad (12.5)$$

The coupled perturbed configuration interaction (CPCI) equations may be obtained by directly differentiating the variational condition (12.1) under the constraint given by (12.3). Employing Lagrange's method of undetermined multipliers, the two equations are combined to give

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) + \theta \left(-1 + \sum_K^{CI} C_K^2 \right) = 0 \quad . \quad (12.6)$$

The factor θ may be chosen arbitrarily. It is convenient to set this factor to unity and thus

$$\sum_J^{CI} C_J \left\{ H_{IJ} - \delta_{IJ} \left(E_{elec} + 1 - \sum_K^{CI} C_K^2 \right) \right\} = 0 \quad . \quad (12.7)$$

The differentiation of eq. (12.7) with respect to a variable "a" leads to the CPCl equations,

$$\begin{aligned} & \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \left\{ H_{IJ} - \delta_{IJ} \left(E_{elec} + 1 - \sum_K^{CI} C_K^2 \right) \right\} \right. \\ & \left. + C_J \left\{ \frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \left(\frac{\partial E_{elec}}{\partial a} - 2 \sum_K^{CI} C_K \frac{\partial C_K}{\partial a} \right) \right\} \right] = 0 \quad . \quad (12.8) \end{aligned}$$

This equation is manipulated further to yield

$$\begin{aligned} & \sum_J^{CI} \frac{\partial C_J}{\partial a} \left[\left(H_{IJ} - \delta_{IJ} E_{elec} \right) - \delta_{IJ} \left(1 - \sum_K^{CI} C_K^2 \right) \right] \\ & + \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + \sum_J^{CI} C_J \delta_{IJ} \left(2 \sum_K^{CI} C_K \frac{\partial C_K}{\partial a} \right) = 0 \quad . \quad (12.9) \end{aligned}$$

The normalization condition and the interchangeability of the summations over J and K may be used to rewrite (12.9) as

$$\begin{aligned} & \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2 C_I C_J \right) \\ & + \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) = 0 \quad . \quad (12.10) \end{aligned}$$

Then equation (12.10) is rewritten as

$$\sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} = - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J . \quad (12.11)$$

The simultaneous equations given in eq. (12.11) are the first-order coupled perturbed configuration interaction (CPCI) equations, which involve the unknown variables $\partial C_J / \partial a$. The dimension of these CPCI equations is the same as that for the corresponding CI wavefunction. It should be noted that eq. (12.11) does not suffer from a singularity. The first derivative of the normalization condition (12.3)

$$\sum_I^{CI} C_I \frac{\partial C_I}{\partial a} = 0 \quad (12.12)$$

is explicitly included within it. The first derivative of the CI Hamiltonian matrix appearing in eq. (12.11) was derived in Section 6.4 and is

$$\frac{\partial H_{IJ}}{\partial a} = \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial h_{ij}}{\partial a} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial(ij|kl)}{\partial a} \quad (12.13)$$

$$= H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} . \quad (12.14)$$

The H_{IJ}^a and X^{IJ} matrices are defined by

$$H_{IJ}^a = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^a \quad (12.15)$$

and

$$X_{ij}^{IJ} = \sum_m^{MO} Q_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} G_{mkl}^{IJ} (im|kl) . \quad (12.16)$$

The “bare” Lagrangian matrices, X^{IJ} , are related to their “parents” through

$$X_{ij} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ} \quad (12.17)$$

$$= \sum_m^{MO} Q_{jm} h_{im} + 2 \sum_{mkl}^{MO} G_{mkl} (im|kl) . \quad (12.18)$$

The first derivative of the CI electronic energy, $\partial E_{elec} / \partial a$, and the U^a matrices must be obtained prior to solving the first-order CPCI equations. The evaluation of the CI energy first derivative was described in Chapter 6, and of the U^a matrices in Chapters 10 and 11 with more to come in Chapters 13 and 14.

12.2 The Second-Order Coupled Perturbed Configuration Interaction Equations

The second-order CPCI equations may be obtained by a further differentiation of eq. (12.11) with respect to a second variable “ b ”:

$$\begin{aligned}
 & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\
 & + \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + 2 \frac{\partial C_I}{\partial b} C_J + 2C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} \\
 & = - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\
 & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \frac{\partial C_J}{\partial b} .
 \end{aligned} \tag{12.19}$$

Rearranging both sides of this equation leads to

$$\begin{aligned}
 & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\
 & = - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\
 & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \frac{\partial C_J}{\partial b} - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \frac{\partial C_J}{\partial a} \\
 & - 2 \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \frac{\partial C_J}{\partial a} - 2C_I \sum_J^{CI} \frac{\partial C_J}{\partial b} \frac{\partial C_J}{\partial a} .
 \end{aligned} \tag{12.20}$$

Eq. (12.12), the first derivative of the normalization constraint, is used to rewrite (12.20) as

$$\begin{aligned}
 & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\
 & = - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\
 & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
 & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} .
 \end{aligned} \tag{12.21}$$

The simultaneous equations given in eq. (12.21) are the second-order CPCI equations, which involve the unknown variables, $\partial^2 C_J / \partial a \partial b$. The second derivative of the normalization

condition

$$\sum_I^{CI} \left(C_I \frac{\partial^2 C_I}{\partial a \partial b} + \frac{\partial C_I}{\partial a} \frac{\partial C_I}{\partial b} \right) = 0 \quad (12.22)$$

is explicitly included in the CPCI equation. The second derivative of the CI Hamiltonian matrix appearing in eq. (12.21) was derived in Section 6.6 and is

$$\frac{\partial^2 H_{IJ}}{\partial a \partial b} = \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial^2 h_{ij}}{\partial a \partial b} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial^2 (ij|kl)}{\partial a \partial b} \quad (12.23)$$

$$\begin{aligned} &= H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJ^a} + U_{ij}^a X_{ij}^{IJ^b} \right) \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} . \end{aligned} \quad (12.24)$$

The H_{IJ}^{ab} , $X_{ij}^{IJ^a}$, and Y_{ijkl}^{IJ} matrices are

$$H_{IJ}^{ab} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{ab} \quad (12.25)$$

$$X_{ij}^{IJ^a} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} G_{mkl}^{IJ} (im|kl)^a \quad (12.26)$$

and

$$Y_{ijkl}^{IJ} = Q_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ} (ik|mn) + 4 \sum_{mn}^{MO} G_{jmln}^{IJ} (im|kn) . \quad (12.27)$$

The “bare” quantities, $X_{ij}^{IJ^a}$ and Y_{ijkl}^{IJ} , are related to their “parents” through

$$X_{ij}^a = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ^a} \quad (12.28)$$

$$= \sum_m^{MO} Q_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} G_{mkl} (im|kl)^a \quad (12.29)$$

and

$$Y_{ijkl} = \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJ} \quad (12.30)$$

$$= Q_{jl} h_{ik} + 2 \sum_{mn}^{MO} G_{jlmn} (ik|mn) + 4 \sum_{mn}^{MO} G_{jmln} (im|kn) . \quad (12.31)$$

The first and second derivatives of the CI electronic energy, $\partial^2 E_{elec} / \partial a \partial b$, and the U^a and U^{ab} matrices must be evaluated before solving the second-order CPCI equations.

References

1. I. Shavitt, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.189 (1977).
2. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.

Suggested Reading

1. D.J. Fox, Y. Osamura, M.R. Hoffmann, J.F. Gaw, G. Fitzgerald, Y. Yamaguchi, and H.F. Schaefer, *Chem. Phys. Lett.* **102**, 17 (1983).
2. T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, *J. Chem. Phys.* **85**, 3930 (1986).
3. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *Theor. Chim. Acta*, **72**, 71 (1987).

Chapter 13

Coupled Perturbed Paired Excitation Multiconfiguration Hartree-Fock Equations

The coupled perturbed paired excitation multiconfiguration Hartree-Fock (CPPEMCHF) equations provide the derivatives of both the MO and CI coefficients with respect to perturbations. These CPPEMCHF equations are obtained by differentiating the variational conditions in both the MO and CI spaces subject to constraints. The equations consist of three parts: MO-MO, CI-CI, and CI-MO (or equivalently MO-CI) terms. Since the TC-SCF wavefunction described in Chapter 7 is a special (the simplest) case of the PEMCSCF wavefunction presented in Chapter 8, the coupled perturbed equations will be derived only for the more general PEMCSCF wavefunction in this chapter.

13.1 The First-Order CPPEMCHF Equations

13.1.1 The Molecular Orbital (MO) Part

For a PEMCSCF wavefunction described in Chapter 8 the generalized Fock operator is the same as for the GRSCF wavefunction [1,2]:

$$\mathbf{F}_i = f_i \mathbf{h} + \sum_l^{MO} \left(\alpha_{il} \mathbf{J}_l + \beta_{il} \mathbf{K}_l \right) . \quad (13.1)$$

The variational condition on the MO space is formally the same as for the GRSCF wavefunction, namely,

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad (13.2)$$

where the Lagrangian matrix is defined by

$$\epsilon_{ij} = \langle \phi_i | \mathbf{F}_i | \phi_j \rangle = f_i h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} . \quad (13.3)$$

The Lagrangian matrix is defined alternatively by an expression including the CI coefficients and the “bare” Lagrangian matrices:

$$\epsilon_{ij} = \sum_{IJ}^{CI} C_I C_J \epsilon_{ij}^{IJ} . \quad (13.4)$$

The “bare” Lagrangian matrices are

$$\epsilon_{ij}^{IJ} = f_i^{IJ} h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll) + \beta_{ij}^{IJ}(il|jl) \right\} . \quad (13.5)$$

The MO part of the first-order CPPEMCHF equations is obtained by differentiating eq. (13.2) with respect to the cartesian coordinate “ a ”:

$$\frac{\partial \epsilon_{ij}}{\partial a} - \frac{\partial \epsilon_{ji}}{\partial a} = 0 . \quad (13.6)$$

The required first derivative of the Lagrangian matrix is found by differentiating eq. (13.4) with respect to a cartesian coordinate “ a ”:

$$\frac{\partial \epsilon_{ij}}{\partial a} = \frac{\partial}{\partial a} \sum_{IJ}^{CI} C_I C_J \epsilon_{ij}^{IJ} \quad (13.7)$$

$$= \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} C_J \epsilon_{ij}^{IJ} + \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \epsilon_{ij}^{IJ} + \sum_{IJ}^{CI} C_I C_J \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} \quad (13.8)$$

$$= 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \epsilon_{ij}^{IJ} + \sum_{IJ}^{CI} C_I C_J \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} . \quad (13.9)$$

The first derivative of the “bare” Lagrangian matrices, ϵ^{IJ} , appearing in eq. (13.9), is derived in a similar manner to that of the Lagrangian matrix of the GRSCF wavefunction, since the coupling constants f^{IJ} , α^{IJ} and β^{IJ} are independent of the CI coefficients and nuclear coordinates. Differentiating eq. (13.5) with respect to the variable “ a ” gives

$$\frac{\partial \epsilon_{ij}^{IJ}}{\partial a} = f_i^{IJ} \frac{\partial h_{ij}}{\partial a} + \sum_l^{MO} \left\{ \alpha_{il}^{IJ} \frac{\partial (ij|ll)}{\partial a} + \beta_{il}^{IJ} \frac{\partial (il|jl)}{\partial a} \right\} \quad (13.10)$$

$$= \epsilon_{ij}^{IJ,a} + \sum_k^{MO} U_{ki}^a \zeta_{kj}^{ij,IJ} + \sum_k^{MO} U_{kj}^a \epsilon_{ik}^{IJ} \\ + \sum_{kl}^{MO} U_{kl}^a T_{ij,kl}^{il,IJ} . \quad (13.11)$$

The results of Section 5.5 were employed in this derivation. In eq. (13.11) elements of the skeleton (core) first derivative “bare” Lagrangian matrices ($\epsilon_{ij}^{IJ^a}$), the “bare” generalized Lagrangian matrices (ζ_{ij}^{IJ}), and the “bare” τ matrices (τ_{ij}^{IJ}) are defined by

$$\epsilon_{ij}^{IJ^a} = f_i^{IJ} h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll)^a + \beta_{il}^{IJ}(il|jl)^a \right\} , \quad (13.12)$$

$$\zeta_{ij}^{IJ} = f_l^{IJ} h_{ij} + \sum_k^{MO} \left\{ \alpha_{lk}^{IJ}(ij|kk) + \beta_{lk}^{IJ}(ik|jk) \right\} , \quad (13.13)$$

and

$$\tau_{ij,kl}^{mnIJ} = 2\alpha_{mn}^{IJ}(ij|kl) + \beta_{mn}^{IJ}\left\{(ik|jl) + (il|jk)\right\} . \quad (13.14)$$

These matrix elements are related to their “parent” quantities through

$$\epsilon_{ij}^a = \sum_{IJ}^{CI} C_I C_J \epsilon_{ij}^{IJ^a} \quad (13.15)$$

$$= f_i h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} , \quad (13.16)$$

$$\zeta_{ij}^l = \sum_{IJ}^{CI} C_I C_J \zeta_{ij}^{IJ} \quad (13.17)$$

$$= f_l h_{ij} + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk) + \beta_{lk}(ik|jk) \right\} , \quad (13.18)$$

and

$$\tau_{ij,kl}^{mn} = \sum_{IJ}^{CI} C_I C_J \tau_{ij,kl}^{mnIJ} \quad (13.19)$$

$$= 2\alpha_{mn}(ij|kl) + \beta_{mn}\left\{(ik|jl) + (il|jk)\right\} . \quad (13.20)$$

Combining eqs. (13.9) and (13.11), the first derivative of the Lagrangian matrix becomes

$$\begin{aligned} \frac{\partial \epsilon_{ij}}{\partial a} &= 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \epsilon_{ij}^{IJ} \\ &+ \epsilon_{ij}^a + \sum_k^{MO} \left(U_{ki}^a \zeta_{kj}^i + U_{kj}^a \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^a \tau_{ij,kl}^{il} . \end{aligned} \quad (13.21)$$

In deriving eq. (13.21), equations (13.4) and (13.15) to (13.20) were used. Note that the definition of the Lagrangian matrix in eq. (13.4) was employed as a starting equation to obtain eq. (13.21). Since the definition in eq. (13.3) contains the reduced density matrices

f , α , and β which are functions of the CI coefficients, the derivation starting from eq. (13.3) becomes much more complicated.

The MO part of the first-order CPPEMCHF equations is

$$\begin{aligned} \frac{\partial \epsilon_{ij}}{\partial a} - \frac{\partial \epsilon_{ji}}{\partial a} &= \epsilon_{ij}^a - \epsilon_{ji}^a \\ &+ \sum_{kl}^{MO} U_{kl}^a \left[\delta_{li} (\zeta_{kj}^i - \epsilon_{jk}) - \delta_{lj} (\zeta_{ki}^j - \epsilon_{ik}) + \tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right] \\ &+ 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial C_I}{\partial a} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) = 0 \quad . \end{aligned} \quad (13.22)$$

It is seen clearly in eq. (13.22) that the derivative of the variational condition in the MO space necessarily has a term due to the perturbation of the CI coefficients. For the PEMC-SCF wavefunction elements of the U^a matrix within the same shell (which share a common set of coupling constants; see Section 8.1) are not determined uniquely. Such pairs of molecular orbitals are called “non-independent”. On the other hand, MO pairs between different shells are determined uniquely and are termed “independent pairs”. These independent pairs for a high spin open-shell PEMCSCF wavefunction are illustrated by the shaded areas in Figure 13.1. In the figure the word “active” denotes paired excitation molecular orbitals, as described in Section 8.1.

Equation (13.22) may be manipulated in a similar manner as was done in Section 11.1 and then written as

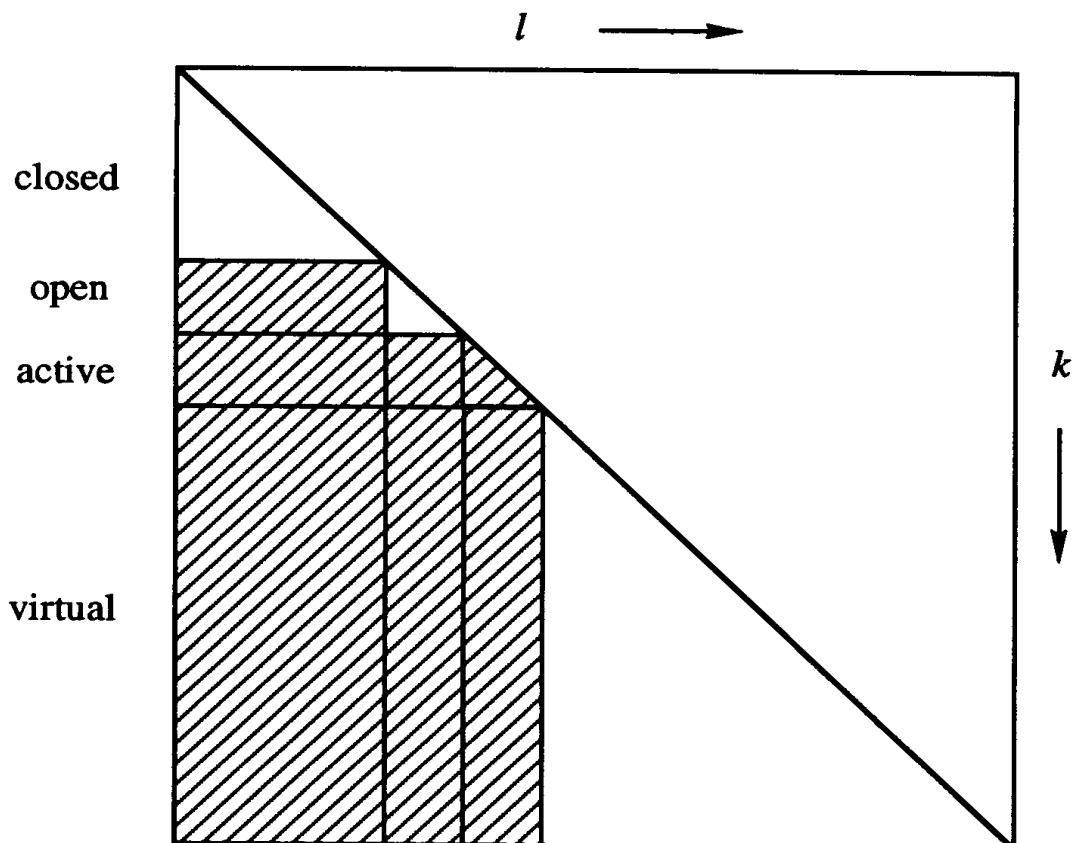
$$\begin{aligned} &\underset{\text{indep. pair}}{\sum_{k>l}} \mathbf{A}_{ij,kl} U_{kl}^a = \epsilon_{ij}^a - \epsilon_{ji}^a \\ &- \sum_{k>l}^{\text{all occ}} S_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\ &\quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\ &- \sum_k^{\text{occ}} S_{kk}^a \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\ &+ 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial C_I}{\partial a} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \end{aligned} \quad (13.23)$$

where “indep. pair” denotes the independent pairs, “all” implies a sum over both occupied and virtual (unoccupied) molecular orbitals, and “occ” means a sum over only occupied orbitals. The \mathbf{A} matrix in the above equation is defined by

$$\begin{aligned} \mathbf{A}_{ij,kl} &= 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\ &+ (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl}) \{ (ik|jl) + (il|jk) \} \end{aligned}$$

$$+ \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) - \delta_{li}(\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj}(\zeta_{ki}^j - \epsilon_{ik}) . \quad (13.24)$$

Equation (13.23) contains simultaneously the unknown variables U^a and $\partial C_I / \partial a$. Note that the last term in eq. (13.23) involves the CI-MO interactions.



PEMCSCF Wavefunction

Figure 13.1 Independent pairs (*indep.pair*) of molecular orbitals in the coupled perturbed Hartree-Fock equations for PEMCSCF wavefunctions. Only the U^a matrix elements shown as shaded areas may be solved for uniquely.

13.1.2 The Configuration Interaction (CI) Part

The variational condition in the CI space is given by

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 . \quad (13.25)$$

The CI Hamiltonian matrix elements were defined in Chapter 8 as

$$H_{IJ} = 2 \sum_i^{MO} f_i^{IJ} h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj) + \beta_{ij}^{IJ}(ij|ij) \right\} . \quad (13.26)$$

The following constraint exists on the CI coefficients, since the wavefunction is normalized:

$$\sum_I^{CI} C_I^2 = 1 . \quad (13.27)$$

The CI part of the first-order CPPEMCHF equations is derived by differentiating the variational condition (13.25) with respect to a variable “ a ” under the constraint of eq. (13.27):

$$\frac{\partial}{\partial a} \sum_J^{CI} \left[C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) + \theta \left(-1 + \sum_K^{CI} C_K^2 \right) \right] = 0 . \quad (13.28)$$

In the above expression, θ is a Lagrange undetermined multiplier. These differential equations were developed in detail in the preceding chapter and the result was

$$\sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} = - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J . \quad (13.29)$$

The first derivative of the Hamiltonian matrix from Chapter 8 is

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} . \quad (13.30)$$

The skeleton (core) first derivative Hamiltonian matrices, H_{IJ}^a , appearing in the above equation are

$$H_{IJ}^a = 2 \sum_i^{MO} f_i^{IJ} h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^a + \beta_{ij}^{IJ}(ij|ij)^a \right\} , \quad (13.31)$$

and the “bare” Lagrangian matrices, ϵ^{IJ} , were defined by eq. (13.5). Inserting eq. (13.30) into eq. (13.29) gives

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} \\ &= - \sum_J^{CI} \left[H_{IJ}^a + 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right] C_J \end{aligned} \quad (13.32)$$

$$= - \sum_J^{CI} C_J H_{IJ}^a - 4 \sum_J^{CI} C_J \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} + C_I \frac{\partial E_{elec}}{\partial a} . \quad (13.33)$$

There is a linear dependency among the elements of the U^a matrix appearing in the above equation since

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \quad . \quad (13.34)$$

In order to eliminate this linear dependency the second term in eq. (13.33) is modified as follows. The summation that involves the MOs is changed to

$$\sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} = \sum_{i>j}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} + \sum_{i>j}^{MO} U_{ji}^a \epsilon_{ij}^{IJ} + \sum_i^{MO} U_{ii}^a \epsilon_{ii}^{IJ} \quad (13.35)$$

$$= \sum_{i>j}^{MO} \left[U_{ij}^a \epsilon_{ji}^{IJ} - (U_{ij}^a + S_{ij}^a) \epsilon_{ij}^{IJ} \right] - \frac{1}{2} \sum_i^{MO} S_{ii}^a \epsilon_{ii}^{IJ} \quad (13.36)$$

$$= - \sum_{i>j}^{MO} U_{ij}^a (\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ}) - \sum_{i>j}^{MO} S_{ij}^a \epsilon_{ij}^{IJ} - \frac{1}{2} \sum_i^{MO} S_{ii}^a \epsilon_{ii}^{IJ} \quad . \quad (13.37)$$

The second term on the right hand side of eq. (13.33) is then rewritten as

$$\begin{aligned} & - 4 \sum_J^{CI} C_J \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} \\ & = 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^a (\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ}) \\ & + 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a \epsilon_{ij}^{IJ} + 2 \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a \epsilon_{ii}^{IJ} \quad . \end{aligned} \quad (13.38)$$

The CI part of the first-order CPPEMCHF equations is

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} \\ & = - \sum_J^{CI} C_J H_{IJ}^a + 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^a (\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ}) \\ & + 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a \epsilon_{ij}^{IJ} \\ & + 2 \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a \epsilon_{ii}^{IJ} + C_I \frac{\partial E_{elec}}{\partial a} \quad . \end{aligned} \quad (13.39)$$

Equation (13.39) simultaneously contains the unknown variables $\partial C_I / \partial a$ and U^a , as was the case for the MO part of these coupled perturbed equations in the previous section. It should be noted that the second term in eq. (13.39) involves the CI-MO interactions.

13.1.3 A Complete Expression for the First-Order CPPEMCHF Equations

In the preceding two subsections, the first derivatives of the variational conditions in both the MO and CI spaces were derived. Since the variational conditions in the two spaces interact, the simultaneous equations have the following general form:

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21^\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\mathbf{a}} \\ \partial \mathbf{C} / \partial \mathbf{a} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\mathbf{a}1} \\ \mathbf{B}_0^{\mathbf{a}2} \end{bmatrix} . \quad (13.40)$$

The \mathbf{A}^{11} expression in this equation is the MO term. Referring to eqs. (13.23) and (13.24), each element of this matrix is given by

$$\begin{aligned} \mathbf{A}_{ij,kl}^{11} = & 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\ & + (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl})\{(ik|jl) + (il|jk)\} \\ & + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) - \delta_{li}(\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj}(\zeta_{ki}^j - \epsilon_{ik}) . \end{aligned} \quad (13.41)$$

The \mathbf{A}^{22} term represents the CI part and its elements from the left hand side of eq. (13.39) are

$$\mathbf{A}_{I,J}^{22} = \frac{1}{2} (H_{IJ} - \delta_{IJ}E_{elec} + 2C_I C_J) . \quad (13.42)$$

Finally, the \mathbf{A}^{21} (or \mathbf{A}^{21^\dagger} , the transpose of the \mathbf{A}^{21} matrix) terms contain the CI-MO (or equivalently MO-CI) interactions. They correspond to the last term on the right hand side of eq. (13.23) and the second term on the rhs of eq. (13.39). Each element is given by

$$\mathbf{A}_{I,ij}^{21} = -2 \sum_J^{CI} C_J (\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ}) . \quad (13.43)$$

The perturbation term in the MO space from the MO part on the rhs of eq. (13.23) is

$$\begin{aligned} B_{0,ij}^{\mathbf{a}1} = & \epsilon_{ij}^a - \epsilon_{ji}^a \\ & - \sum_k^{\text{all occ}} S_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk})\{(ik|jl) + (il|jk)\} \right. \\ & \quad \left. + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) \right] \\ & - \sum_k^{\text{occ}} S_{kk}^a \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] . \end{aligned} \quad (13.44)$$

For the CI space, the perturbation terms from the CI part on the rhs of eq. (13.39) are

$$B_{0,I}^{\mathbf{a}2} = -\frac{1}{2} \sum_J^{CI} C_J H_{IJ}^a + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a \epsilon_{ij}^{IJ}$$

$$+ \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a \epsilon_{ii}^{IJ} + \frac{1}{2} C_I \frac{\partial E_{elec}}{\partial a} . \quad (13.45)$$

Note that the CI parts, \mathbf{A}^{22} in eq. (13.42) and $B_{0,I}^{a2}$ in eq. (13.45), were halved in order to adjust the coefficients of the CI-MO interactions, the last term of eq. (13.23) and the second term of eq. (13.39).

13.2 The Averaged Fock Operator

For the PEMCSCF wavefunction the elements of the U^a matrix for the independent pairs (MO pairs between different shells) may be determined uniquely by solving the CPHF equations in eq. (13.40). On the other hand a unitary transformation within unique shells does not alter the total energy of the system. Consequently the elements of the U^a matrix for the non-independent pairs (MO pairs within the same shell) are not evaluated uniquely. It is therefore advantageous to redefine these orbitals uniquely for use in a later process in which the entire U^a matrix is required. For this purpose the averaged Fock operator

$$\mathbf{F}^{av} = \mathbf{h} + \sum_k^{MO} f_k (2\mathbf{J} - \mathbf{K}) \quad (13.46)$$

usually is employed, where f_k is the occupation number of k th molecular orbital. The elements of the averaged Fock matrix are given by

$$\epsilon'_{ij} = \langle \phi_i | \mathbf{F}^{av} | \phi_j \rangle = h_{ij} + \sum_k^{MO} f_k \left\{ 2(ij|kk) - (ik|jk) \right\} . \quad (13.47)$$

After self-consistency is achieved, the molecular orbital coefficients and their “orbital energies”, ϵ' , are defined using the averaged Fock operator for each shell (e.g., closed-shell, α -spin shell, β -spin shell, paired excitation shell, and virtual shell). For each shell of non-independent pairs the following diagonality is established:

$$\epsilon'_{ij} = \delta_{ij} \epsilon'_i \quad (13.48)$$

where the indices i and j belong to the same shell.

The corresponding CPHF equations for the averaged Fock operator may be derived in a similar manner to that described in Section 10.1. Differentiation of eq. (13.47) with respect to a cartesian coordinate “a”:

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= \frac{\partial h_{ij}}{\partial a} + \sum_k^{MO} f_k \left\{ 2 \frac{\partial (ij|kk)}{\partial a} - \frac{\partial (ik|jk)}{\partial a} \right\} \\ &+ \sum_k^{MO} \frac{\partial f_k}{\partial a} \left\{ 2(ij|kk) - (ik|jk) \right\} . \end{aligned} \quad (13.49)$$

is required. Note that the derivative of the occupation number f_k does *not* vanish for the PEMCSCF wavefunction. In Section 8.1 the occupation number f_k was defined in CI form as

$$f_k = \sum_{IJ}^{CI} C_I C_J f_k^{IJ} . \quad (13.50)$$

The derivatives of the CI coefficients are, in general, not zero, although the coupling constants are independent of any real perturbations. Thus, the derivative of f_k becomes

$$\frac{\partial f_k}{\partial a} = \sum_{IJ}^{CI} \left\{ \frac{\partial C_I}{\partial a} C_J f_k^{IJ} + C_I \frac{\partial C_J}{\partial a} f_k^{IJ} \right\} \quad (13.51)$$

$$= 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} f_k^{IJ} . \quad (13.52)$$

The first two terms of eq. (13.49) may be manipulated in a similar way as was done in Section 11.2. Including the result in eq. (13.52), eq. (13.49) then becomes

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a + \sum_k^{MO} U_{ki}^a \epsilon'_{kj} + \sum_k^{MO} U_{kj}^a \epsilon'_{ik} \\ &+ \sum_{kl}^{MO} U_{kl}^a f_l A_{ij,kl} \\ &+ 2 \sum_k^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} f_k^{IJ} \left\{ 2(ij|kk) - (ik|jk) \right\} . \end{aligned} \quad (13.53)$$

The skeleton (core) first derivative averaged Fock matrix appearing in this equation is defined by

$$\epsilon'_{ij}^a = h_{ij}^a + \sum_k^{MO} f_k \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} \quad (13.54)$$

and the A matrix by

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) . \quad (13.55)$$

Note that the A matrix in eq. (13.55) is a different quantity from the \mathbf{A} matrix in eq. (13.24).

Recalling eq. (13.34) the first four terms of eq. (13.53) may be manipulated in the same manner as was done in Section 11.2 and the result is

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a - (\epsilon'_j - \epsilon'_i) U_{ij}^a - S_{ij}^a \epsilon'_j + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\ &+ \sum_{k>l}^{indep.\,pair} (f_l - f_k) U_{kl}^a A_{ij,kl} - \sum_{k>l}^{occ} f_k S_{kl}^a A_{ij,kl} \end{aligned}$$

$$- \sum_k^{\text{occ}} f_k S_{kk}^a \left\{ 2(ij|kk) - (ik|jk) \right\} \quad (13.56)$$

$$+ 2 \sum_k^{\text{occ}} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} f_k^{IJ} \left\{ 2(ij|kk) - (ik|jk) \right\} \quad . \quad (13.57)$$

The final expression to evaluate the elements of the U^a matrix for non-independent pairs is

$$\begin{aligned} U_{ij}^a = & \frac{1}{\epsilon_j' - \epsilon_i'} \left[\epsilon_{ij}' - S_{ij}^a \epsilon_j' + \sum_k^{\text{othershell}} U_{ki}^a \epsilon_{kj}' + \sum_k^{\text{othershell}} U_{kj}^a \epsilon_{ik}' \right. \\ & + \sum_{k>l}^{\text{indep. pair}} (f_l - f_k) U_{kl}^a A_{ij,kl} - \sum_{k>l}^{\text{occ}} f_k S_{kl}^a A_{ij,kl} \\ & - \sum_k^{\text{occ}} f_k S_{kk}^a \left\{ 2(ij|kk) - (ik|jk) \right\} \\ & \left. + 2 \sum_k^{\text{occ}} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} f_k^{IJ} \left\{ 2(ij|kk) - (ik|jk) \right\} \right] \quad . \quad (13.58) \end{aligned}$$

When the whole U^a matrix is required in the later process, the molecular orbitals must be transformed unitarily within unique shells using the averaged Fock operator in eq. (13.46) prior to solving the CPHF equations. Using these redefined molecular orbitals, the elements of the U^a matrices for the independent pairs are then obtained by solution of the CPHF equations in eq. (13.40). Finally the elements for the non-independent pairs are determined in terms of the U^a elements for the independent pairs from equation (13.58). An alternative approach to this subject has been discussed in References 3 and 4.

13.3 The Second-Order CPPEMCHF Equations

13.3.1 The Molecular Orbital (MO) Part

The MO part of the second-order CPPEMCHF equations is obtained by differentiating the variational condition in eq. (13.2) with respect to the cartesian coordinates “ a ” and “ b ”:

$$\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} - \frac{\partial^2 \epsilon_{ji}}{\partial a \partial b} = 0 \quad . \quad (13.59)$$

The second derivative of the Lagrangian matrix requires differentiating eq. (13.9) with respect to a second variable “ b ”:

$$\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial \epsilon_{ij}}{\partial a} \right) \quad (13.60)$$

$$= \frac{\partial}{\partial b} \left(2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \epsilon_{ij}^{IJ} + \sum_{IJ}^{CI} C_I C_J \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} \right) \quad (13.61)$$

$$\begin{aligned} &= 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} \frac{\partial C_J}{\partial a} \epsilon_{ij}^{IJ} + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} \epsilon_{ij}^{IJ} \\ &\quad + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \frac{\partial \epsilon_{ij}^{IJ}}{\partial b} \\ &\quad + \sum_{IJ}^{CI} \frac{\partial C_I}{\partial b} C_J \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} + \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial b} \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} \\ &\quad + \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 \epsilon_{ij}^{IJ}}{\partial a \partial b} \end{aligned} \quad (13.62)$$

$$\begin{aligned} &= 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \epsilon_{ij}^{IJ} + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} \epsilon_{ij}^{IJ} \\ &\quad + 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial \epsilon_{ij}^{IJ}}{\partial b} + \frac{\partial C_J}{\partial b} \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} \right) \\ &\quad + \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 \epsilon_{ij}^{IJ}}{\partial a \partial b} . \end{aligned} \quad (13.63)$$

The second derivative of the “bare” Lagrangian matrix is derived in a similar way to that of the GRSCF wavefunction, since the coupling constants f^{IJ} , α^{IJ} and β^{IJ} are independent of the CI coefficients and nuclear coordinates. After a similar derivation to that in Section 11.6, the second derivative of the ϵ^{IJ} matrix is

$$\frac{\partial^2 \epsilon_{ij}^{IJ}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial a} \right) \quad (13.64)$$

$$\begin{aligned} &= \epsilon_{ij}^{IJab} + \sum_k^{MO} U_{ki}^{ab} \zeta_{kj}^{ijIJ} + \sum_k^{MO} U_{kj}^{ab} \epsilon_{ik}^{IJ} + \sum_{kl}^{MO} U_{kl}^{ab} \tau_{ij,kl}^{ilIJ} \\ &\quad + \sum_{kl}^{MO} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \zeta_{kl}^{ijIJ} + \sum_{klm}^{MO} U_{km}^a U_{lm}^b \tau_{ij,kl}^{imIJ} \\ &\quad + \sum_{kmn}^{MO} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \tau_{kj,mn}^{inIJ} + \sum_{kmn}^{MO} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ik,mn}^{inIJ} \\ &\quad + \sum_{kl}^{MO} \left(U_{kl}^a \tau_{ij,kl}^{ilIJb} + U_{kl}^b \tau_{ij,kl}^{ilIJa} \right) \\ &\quad + \sum_k^{MO} \left(U_{ki}^a \zeta_{kj}^{ijIJb} + U_{kj}^a \epsilon_{ik}^{IJb} + U_{ki}^b \zeta_{kj}^{ijIJa} + U_{kj}^b \epsilon_{ik}^{IJa} \right) . \end{aligned} \quad (13.65)$$

The elements of the skeleton (core) second derivative “bare” Lagrangian matrices (ϵ^{IJab}), the first derivative “bare” generalized Lagrangian matrices (ζ^{IJa}), and the first derivative

“bare” τ matrices (τ^{IJ^a}) in the above equation are defined by

$$\epsilon_{ij}^{IJ^{ab}} = f_i^{IJ} h_{ij}^{ab} + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll)^{ab} + \beta_{il}^{IJ}(il|jl)^{ab} \right\} , \quad (13.66)$$

$$\zeta_{ij}^{IJ^a} = f_l^{IJ} h_{ij}^a + \sum_k^{MO} \left\{ \alpha_{lk}^{IJ}(ij|kk)^a + \beta_{lk}^{IJ}(ik|jk)^a \right\} , \quad (13.67)$$

and

$$\tau_{ij,kl}^{mnIJ^a} = 2\alpha_{mn}^{IJ}(ij|kl)^a + \beta_{mn}^{IJ} \left\{ (ik|jl)^a + (il|jk)^a \right\} . \quad (13.68)$$

These matrix elements are related to their “parent” quantities through

$$\epsilon_{ij}^{ab} = \sum_{IJ}^{CI} C_I C_J \epsilon_{ij}^{IJ^{ab}} \quad (13.69)$$

$$= f_i h_{ij}^{ab} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^{ab} + \beta_{il}(il|jl)^{ab} \right\} , \quad (13.70)$$

$$\zeta_{ij}^{l^a} = \sum_{IJ}^{CI} C_I C_J \zeta_{ij}^{IJ^a} \quad (13.71)$$

$$= f_l h_{ij}^a + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk)^a + \beta_{lk}(ik|jk)^a \right\} , \quad (13.72)$$

and

$$\tau_{ij,kl}^{mn^a} = \sum_{IJ}^{CI} C_I C_J \tau_{ij,kl}^{mnIJ^a} \quad (13.73)$$

$$= 2\alpha_{mn}(ij|kl)^a + \beta_{mn} \left\{ (ik|jl)^a + (il|jk)^a \right\} . \quad (13.74)$$

Combining eqs. (13.63) and (13.65), and using equations (13.4), (13.15) to (13.20) and (13.66) to (13.74), the second derivative of the Lagrangian matrix becomes:

$$\begin{aligned} \frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} &= 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \epsilon_{ij}^{IJ} + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} \epsilon_{ij}^{IJ} \\ &+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial \epsilon_{ij}^{IJ}}{\partial b} + \frac{\partial C_J}{\partial b} \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} \right) \\ &+ \epsilon_{ij}^{ab} + \sum_k^{MO} U_{ki}^{ab} \zeta_{kj}^i + \sum_k^{MO} U_{kj}^{ab} \epsilon_{ik} + \sum_{kl}^{MO} U_{kl}^{ab} \tau_{ij,kl}^{il} \\ &+ \sum_{kl}^{MO} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \zeta_{kl}^i + \sum_{klm}^{MO} U_{km}^a U_{lm}^b \tau_{ij,kl}^{im} \end{aligned}$$

$$\begin{aligned}
& + \sum_{kmn}^{MO} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \tau_{kj,mn}^{in} \\
& + \sum_{kmn}^{MO} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ik,mn}^{in} \\
& + \sum_{kl}^{MO} \left(U_{kl}^a \tau_{ij,kl}^{ilb} + U_{kl}^b \tau_{ij,kl}^{ila} \right) \\
& + \sum_k^{MO} \left(U_{ki}^a \zeta_{kj}^{ib} + U_{kj}^a \epsilon_{ik}^b + U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right) . \quad (13.75)
\end{aligned}$$

The MO part of the second-order CPPEMCHF equations is obtained by substituting eq. (13.75) into eq. (13.59):

$$\begin{aligned}
& \frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} - \frac{\partial^2 \epsilon_{ji}}{\partial a \partial b} = \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
& + \sum_{kl}^{MO} U_{kl}^{ab} \left[\delta_{li} \left(\zeta_{kj}^i - \epsilon_{jk} \right) - \delta_{lj} \left(\zeta_{ki}^j - \epsilon_{ik} \right) + \tau_{ij,kl}^{il} - \tau_{ji,kl}^{jl} \right] \\
& + \sum_{kl}^{MO} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
& + \sum_{klm}^{MO} U_{km}^a U_{lm}^b \left(\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm} \right) \\
& + \sum_{kmn}^{MO} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left(\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn} \right) \\
& + \sum_{kmn}^{MO} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left(\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn} \right) \\
& + \sum_{kl}^{MO} U_{kl}^a \left(\tau_{ij,kl}^{ilb} - \tau_{ji,kl}^{ilb} \right) + \sum_{kl}^{MO} U_{kl}^b \left(\tau_{ij,kl}^{ila} - \tau_{ji,kl}^{ila} \right) \\
& + \sum_k^{MO} \left[U_{ki}^a \left(\zeta_{kj}^{ib} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
& \quad \left. - U_{kj}^a \left(\zeta_{ki}^{jb} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \\
& + 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial^2 C_I}{\partial a \partial b} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial b} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial b} \right)
\end{aligned}$$

$$+ 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial b} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial a} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial a} \right) . \quad (13.76)$$

It is evident from this equation that the second derivative of the variational conditions in the MO space contains second-order terms due to the perturbations of the CI coefficients.

Equation (13.76) may be manipulated in a similar way to that in Section 11.7 and written as

$$\begin{aligned} & \sum_{k>l}^{indep.\,pair} \mathbf{A}_{ij,kl} U_{kl}^{ab} = \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\ & - \sum_{k>l}^{all\,occ} \xi_{kl}^{ab} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\ & \quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\ & - \sum_k^{occ} \xi_{kk}^{ab} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\ & + \sum_{kl}^{MO} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\ & + \sum_{klm}^{MO} U_{km}^a U_{lm}^b \left(\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm} \right) \\ & + \sum_{kmn}^{MO} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left(\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn} \right) \\ & + \sum_{kmn}^{MO} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left(\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn} \right) \\ & + \sum_{kl}^{MO} U_{kl}^a \left(\tau_{ij,kl}^{il^b} - \tau_{ji,kl}^{jl^b} \right) + \sum_{kl}^{MO} U_{kl}^b \left(\tau_{ij,kl}^{il^a} - \tau_{ji,kl}^{jl^a} \right) \\ & + \sum_k^{MO} \left[U_{ki}^a \left(\zeta_{kj}^{i^b} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{i^a} - \epsilon_{jk}^a \right) \right. \\ & \quad \left. - U_{kj}^a \left(\zeta_{ki}^{j^b} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{j^a} - \epsilon_{ik}^a \right) \right] \\ & + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \\ & + 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial^2 C_I}{\partial a \partial b} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial b} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial b} \right) \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial b} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial a} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial a} \right) .
\end{aligned} \quad (13.77)$$

The \mathbf{A} matrix was defined by eq. (13.24). Note that the third term from the last in eq. (13.77) contains the CI-MO interactions.

13.3.2 The Configuration Interaction (CI) Part

The CI part of the second-order CPPEMCHF equations is derived by differentiating the first-order equation (13.29) with respect to a second variable “ b ”:

$$\frac{\partial}{\partial b} \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} = - \frac{\partial}{\partial b} \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J . \quad (13.78)$$

These differential equations have been presented in Section 12.2 and were

$$\begin{aligned}
& \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\
& = - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} .
\end{aligned} \quad (13.79)$$

The second derivative of the Hamiltonian matrix element was shown in Chapter 8 to be

$$\begin{aligned}
\frac{\partial^2 H_{IJ}}{\partial a \partial b} & = H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji}^{IJ} \\
& + 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ a} + U_{ij}^a \epsilon_{ji}^{IJ b} \right) \\
& + 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{IJ} \\
& + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ijkl}^{JlIJ} .
\end{aligned} \quad (13.80)$$

The skeleton (core) second derivative Hamiltonian matrices, H_{IJ}^{ab} , appearing in the above equation are

$$H_{IJ}^{ab} = 2 \sum_i^{MO} f_i^{IJ} h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^{ab} + \beta_{ij}^{IJ}(ij|ij)^{ab} \right\} . \quad (13.81)$$

Using eq. (13.80), the first term on the rhs of eq. (13.79) may be rewritten as

$$\begin{aligned} & - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\ &= - \sum_J^{CI} \left[H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji}^{IJ} + 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \right. \\ & \quad \left. + 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{jIJ} + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlIJ} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right] C_J \end{aligned} \quad (13.82)$$

$$\begin{aligned} &= - \sum_J^{CI} C_J H_{IJ}^{ab} - 4 \sum_J^{CI} C_J \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji}^{IJ} \\ & \quad - 4 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\ & \quad - 4 \sum_J^{CI} C_J \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{jIJ} \\ & \quad - 4 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlIJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \end{aligned} \quad (13.83)$$

$$\begin{aligned} &= - \sum_J^{CI} C_J H_{IJ}^{ab} + 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^{ab} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \\ & \quad + 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} \epsilon_{ij}^{IJ} + 2 \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} \epsilon_{ii}^{IJ} \\ & \quad - 4 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\ & \quad - 4 \sum_J^{CI} C_J \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{jIJ} \\ & \quad - 4 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlIJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} . \end{aligned} \quad (13.84)$$

In the above equation ξ^{ab} was defined in Section 3.7

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \quad (13.85)$$

and satisfies the following equation:

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad . \quad (13.86)$$

In manipulating the second term in eq. (13.83), the techniques presented in the first two subsections of this chapter were used.

Combining eqs. (13.79) and (13.84) the CI part of the second-order CPPEMCHF equations is written finally as

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\ &= - \sum_J^{CI} C_J H_{IJ}^{ab} + 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^{ab} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \\ &+ 4 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} \epsilon_{ij}^{IJ} + 2 \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} \epsilon_{ii}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \\ &- 4 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ} + U_{ij}^a \epsilon_{ji}^{IJ} \right) \\ &- 4 \sum_J^{CI} C_J \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{ij} \\ &- 4 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ijkl}^{IJ} \\ &- \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\ &- \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} \quad . \end{aligned} \quad (13.87)$$

It should be noted that the second term in eq. (13.87) contains the CI-MO interactions.

13.3.3 A Complete Expression for the Second-Order CPPEMCHF Equations

In the preceding two subsections, the second derivatives of the variational conditions for both the MO and CI spaces were obtained. The second-order CPHF equations for the PEMCSCF wavefunctions are

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{ab} \\ \partial^2 \mathbf{C} / \partial \mathbf{a} \partial \mathbf{b} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{ab1} \\ \mathbf{B}_0^{ab2} \end{bmatrix} \quad . \quad (13.88)$$

The \mathbf{A}^{11} in this equation is the MO term. Each element of this matrix was given in eq. (13.24) as

$$\begin{aligned}\mathbf{A}_{ij,kl}^{11} = & 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\ & + (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl})\{(ik|jl) + (il|jk)\} \\ & + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) - \delta_{li}(\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj}(\zeta_{ki}^j - \epsilon_{ik}) .\end{aligned}\quad (13.89)$$

The \mathbf{A}^{22} term represents the CI part and its elements from eq. (13.87) are

$$\mathbf{A}_{I,J}^{22} = \frac{1}{2} (H_{IJ} - \delta_{IJ}E_{elec} + 2C_I C_J) .\quad (13.90)$$

Finally, the \mathbf{A}^{21} (or $\mathbf{A}^{21\dagger}$) terms contain the CI-MO (or MO-CI) interactions. Each element is given by

$$\mathbf{A}_{I,ij}^{21} = -2 \sum_J^{CI} C_J (\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ}) .\quad (13.91)$$

The perturbation term for the MO space comes from the MO part of the rhs of eq. (13.77):

$$\begin{aligned}B_{0,ij}^{ab1} = & \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\ & - \sum_{k>l}^{all\ occ} \xi_{ki}^{ab} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk})\{(ik|jl) + (il|jk)\} \right. \\ & \quad \left. + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) \right] \\ & - \sum_k^{occ} \xi_{kk}^{ab} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\ & + \sum_{kl}^{MO} (U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a) (\zeta_{kl}^i - \zeta_{kl}^j) \\ & + \sum_{klm}^{MO} U_{km}^a U_{lm}^b (\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm}) \\ & + \sum_{kmn}^{MO} (U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a) (\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn}) \\ & + \sum_{kmn}^{MO} (U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a) (\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn})\end{aligned}$$

$$\begin{aligned}
& + \sum_{kl}^{MO} U_{kl}^a \left(\tau_{ij,kl}^{i^b} - \tau_{ji,kl}^{j^b} \right) + \sum_{kl}^{MO} U_{kl}^b \left(\tau_{ij,kl}^{i^a} - \tau_{ji,kl}^{j^a} \right) \\
& + \sum_k^{MO} \left[U_{ki}^a \left(\zeta_{kj}^{i^b} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{i^a} - \epsilon_{jk}^a \right) \right. \\
& \quad \left. - U_{kj}^a \left(\zeta_{ki}^{j^b} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{j^a} - \epsilon_{ik}^a \right) \right] \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial a} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial b} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial b} \right) + \frac{\partial C_J}{\partial b} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial a} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial a} \right) \right\} \quad . \\
\end{aligned} \tag{13.92}$$

The perturbations in the CI space arise from the CI terms on the rhs of eq. (13.87):

$$\begin{aligned}
B_{0,I}^{ab2} &= -\frac{1}{2} \sum_J^{CI} C_J H_{IJ}^{ab} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} \epsilon_{ij}^{IJ} \\
&+ \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} \epsilon_{ii}^{IJ} + \frac{1}{2} C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \\
&- 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\
&- 2 \sum_J^{CI} C_J \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{j^I J} \\
&- 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl^I J} \\
&- \frac{1}{2} \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
&- \frac{1}{2} \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} \quad . \\
\end{aligned} \tag{13.93}$$

Note that the CI parts, the \mathbf{A}^{22} in eq. (13.90) and the $B_{0,I}^{ab2}$ in eq. (13.93), were halved in order to adjust the coefficients of the CI-MO interactions, i.e., the third term from the last in eq. (13.77) and the second term in eq. (13.87).

References

1. F.W. Bobrowicz and W.A. Goddard, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.79 (1977).

2. R. Carbo and J.M. Riera, *A General SCF Theory*, Springer-Verlag, Berlin, 1978.
3. J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, and H.F. Schaefer, *J. Chem. Phys.* **85**, 963 (1986).
4. T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, *J. Chem. Phys.* **85**, 3930 (1986).

Suggested Reading

1. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 383 (1982).
2. Y. Yamaguchi, Y. Osamura, and H.F. Schaefer, *J. Am. Chem. Soc.* **105**, 7506 (1983).
3. M. Duran, Y. Yamaguchi, and H.F. Schaefer, *J. Phys. Chem.* **92**, 3070 (1988).
4. M. Duran, Y. Yamaguchi, R.B. Remington, and H.F. Schaefer, *Chem. Phys.* **122**, 201 (1988).

Chapter 14

Coupled Perturbed Multiconfiguration Hartree-Fock Equations

We turn now to the case of the arbitrarily general MCSCF wavefunction. The analytic evaluation of the first derivatives of the MCSCF energy may be accomplished without consideration of the associated coupled perturbed equations. However, analytic MCSCF second derivatives do require the development and solution of this challenging set of equations. The coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) simultaneous equations provide the derivatives of both the MO and CI coefficients with respect to real perturbations. These CPMCHF equations are obtained by differentiating the variational conditions on both the MO and CI spaces. The equations consist of three parts: MO-MO, CI-CI, and CI-MO (or MO-CI) terms. In this chapter the first- and second-order CPMCHF equations for a general MCSCF wavefunction are derived.

Although we have attempted to define all terms as they appear for the first time in this text, this is a good place to review some terminology that is critical to our discussion but not yet part of the *lingua franca* of molecular quantum mechanics. For example, the word “bare” (as in “bare” Lagrangian matrices) is used for the quantity that does not include the CI coefficients in its definition, while the word “parent” is used for the corresponding quantity that explicitly involves the CI coefficients in its definition (as in Lagrangian matrix). These two words, “bare” and “parent”, are exploited in the derivative expressions only for correlated wavefunctions. The word “skeleton (or core)” (as in “skeleton” derivative Lagrangian matrices) indicates the derivative quantity that includes the AO (basis function and Hamiltonian operator) changes but does not involve the changes in the MO coefficients. This word “skeleton (or core)” is employed in the derivative expressions for all wavefunctions throughout this book.

14.1 The First-Order CPMCHF Equations

As mentioned in Chapter 9 an MCSCF wavefunction is constructed by optimizing simultaneously the MO and CI coefficients. Thus the derivatives of the MO and CI coefficients with respect to nuclear coordinates appearing in the energy derivative expressions may be obtained by solving the simultaneous equations which involve the derivatives of the variational conditions on the MO and CI spaces and the interacting term between the two spaces.

14.1.1 The Molecular Orbital (MO) Part

For an MCSCF wavefunction the variational conditions in the MO space require a symmetric Lagrangian matrix at convergence:

$$x_{ij} - x_{ji} = 0 \quad (14.1)$$

where the elements of the Lagrangian matrix are

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl) \quad . \quad (14.2)$$

The Lagrangian matrix also is defined by the CI expression

$$x_{ij} = \sum_{IJ}^{CI} C_I C_J x_{ij}^{IJ} \quad (14.3)$$

where the “bare” Lagrangian matrices are

$$x_{ij}^{IJ} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ}(im|kl) \quad . \quad (14.4)$$

The MO part of the first-order CPMCHF equations is obtained by differentiating eq. (14.1) with respect to the cartesian coordinate “ a ”:

$$\frac{\partial x_{ij}}{\partial a} - \frac{\partial x_{ji}}{\partial a} = 0 \quad . \quad (14.5)$$

The required first derivative of the Lagrangian matrix is obtained by differentiating eq. (14.3) with respect to a cartesian coordinate “ a ”:

$$\frac{\partial x_{ij}}{\partial a} = \frac{\partial}{\partial a} \sum_{IJ}^{CI} C_I C_J x_{ij}^{IJ} \quad (14.6)$$

$$= \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} C_J x_{ij}^{IJ} + \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} x_{ij}^{IJ} + \sum_{IJ}^{CI} C_I C_J \frac{\partial x_{ij}^{IJ}}{\partial a} \quad (14.7)$$

$$= 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} x_{ij}^{IJ} + \sum_{IJ}^{CI} C_I C_J \frac{\partial x_{ij}^{IJ}}{\partial a} \quad . \quad (14.8)$$

The first derivatives of the “bare” Lagrangian matrices, x^{IJ} , were derived in Section 6.5 and are

$$\frac{\partial x_{ij}^{IJ}}{\partial a} = \sum_m^{MO} \gamma_{jm}^{IJ} \frac{\partial h_{im}}{\partial a} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ} \frac{\partial(im|kl)}{\partial a} \quad (14.9)$$

$$= x_{ij}^{IJ^a} + \sum_k^{MO} U_{ki}^a x_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJ} . \quad (14.10)$$

The skeleton (core) first derivative “bare” Lagrangian matrices (x^{IJ^a}) and the “bare” y matrices (y^{IJ}) are defined by

$$x_{ij}^{IJ^a} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ} (im|kl)^a \quad (14.11)$$

and

$$y_{ijkl}^{IJ} = \gamma_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ} (ik|mn) + 4 \sum_{mn}^{MO} \Gamma_{jmkn}^{IJ} (im|kn) . \quad (14.12)$$

These matrix elements are related to their “parent” quantities through

$$x_{ij}^a = \sum_{IJ}^{CI} C_I C_J x_{ij}^{IJ^a} \quad (14.13)$$

$$= \sum_m^{MO} \gamma_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmkl} (im|kl)^a \quad (14.14)$$

and

$$y_{ijkl} = \sum_{IJ}^{CI} C_I C_J y_{ijkl}^{IJ} \quad (14.15)$$

$$= \gamma_{jl} h_{ik} + 2 \sum_{mn}^{MO} \Gamma_{jlmn} (ik|mn) + 4 \sum_{mn}^{MO} \Gamma_{jmkn} (im|kn) . \quad (14.16)$$

Combining eqs. (14.8) and (14.10), and noting the relationships in eq. (14.3) and eqs. (14.13) to (14.16), the first derivative of the Lagrangian matrix becomes

$$\begin{aligned} \frac{\partial x_{ij}}{\partial a} &= 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} x_{ij}^{IJ} \\ &+ x_{ij}^a + \sum_k^{MO} U_{ki}^a x_{kj} + \sum_{kl}^{MO} U_{kl}^a y_{ijkl} . \end{aligned} \quad (14.17)$$

The MO part of the first-order CPMCHF equations is now

$$\frac{\partial x_{ij}}{\partial a} - \frac{\partial x_{ji}}{\partial a} = x_{ij}^a - x_{ji}^a$$

$$\begin{aligned}
& + \sum_{kl}^{MO} U_{kl}^a \left(\delta_{li} x_{kj} - \delta_{lj} x_{ki} + y_{ijkl} - y_{jikl} \right) \\
& + 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial C_I}{\partial a} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) = 0
\end{aligned} \quad . \quad (14.18)$$

It is evident from this equation that the derivative of the variational condition in the MO space necessarily involves a term due to a perturbation of the CI coefficients. In order to eliminate linear dependencies among elements of the U^a matrix

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \quad (14.19)$$

the third term on the rhs of eq. (14.18) may be manipulated as follows:

$$\begin{aligned}
& \sum_{kl}^{MO} U_{kl}^a \left(\delta_{li} x_{kj} - \delta_{lj} x_{ki} + y_{ijkl} - y_{jikl} \right) \\
& = \sum_{k>l}^{MO} U_{kl}^a \left(\delta_{li} x_{kj} - \delta_{lj} x_{ki} + y_{ijkl} - y_{jikl} \right) \\
& + \sum_{k>l}^{MO} U_{lk}^a \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijlk} - y_{jilk} \right) \\
& + \sum_k^{MO} U_{kk}^a \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right)
\end{aligned} \quad . \quad (14.20)$$

Introducing the relationship eq. (14.19) into eq. (14.20) one obtains

$$\begin{aligned}
& \sum_{kl}^{MO} U_{kl}^a \left(\delta_{li} x_{kj} - \delta_{lj} x_{ki} + y_{ijkl} - y_{jikl} \right) \\
& = \sum_{k>l}^{MO} U_{kl}^a \left(\delta_{li} x_{kj} - \delta_{lj} x_{ki} + y_{ijkl} - y_{jikl} \right) \\
& - \sum_{k>l}^{MO} \left(U_{kl}^a + S_{kl}^a \right) \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijlk} - y_{jilk} \right) \\
& - \frac{1}{2} \sum_k^{MO} S_{kk}^a \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right)
\end{aligned} \quad (14.21)$$

$$\begin{aligned}
& = \sum_{k>l}^{MO} U_{kl}^a \left(\delta_{li} x_{kj} - \delta_{lj} x_{ki} - \delta_{ki} x_{lj} + \delta_{kj} x_{li} + y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} \right) \\
& - \sum_{k>l}^{MO} S_{kl}^a \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijlk} - y_{jilk} \right) \\
& - \frac{1}{2} \sum_k^{MO} S_{kk}^a \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right)
\end{aligned} \quad . \quad (14.22)$$

Combining eqs. (14.18) and (14.22), the MO part of the first-order CPMCHF equations becomes

$$\begin{aligned}
 \frac{\partial x_{ij}}{\partial a} - \frac{\partial x_{ji}}{\partial a} &= x_{ij}^a - x_{ji}^a \\
 &+ \sum_{k>l}^{MO} U_{kl}^a \left(\delta_{li}x_{kj} - \delta_{lj}x_{ki} - \delta_{ki}x_{lj} + \delta_{kj}x_{li} + y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} \right) \\
 &- \sum_{k>l}^{MO} S_{kl}^a \left(\delta_{ki}x_{lj} - \delta_{kj}x_{li} + y_{ijlk} - y_{jilk} \right) \\
 &- \frac{1}{2} \sum_k^{MO} S_{kk}^a \left(\delta_{ki}x_{kj} - \delta_{kj}x_{ki} + y_{ijkk} - y_{jikk} \right) \\
 &+ 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial C_I}{\partial a} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) = 0 \quad .
 \end{aligned} \tag{14.23}$$

This equation may be modified in a similar manner as was done in Section 11.1 and then written as

$$\sum_{k>l}^{MO} \mathbf{A}_{ij,kl} U_{kl}^a = B_{0,ij}^{a1} - 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial C_I}{\partial a} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \tag{14.24}$$

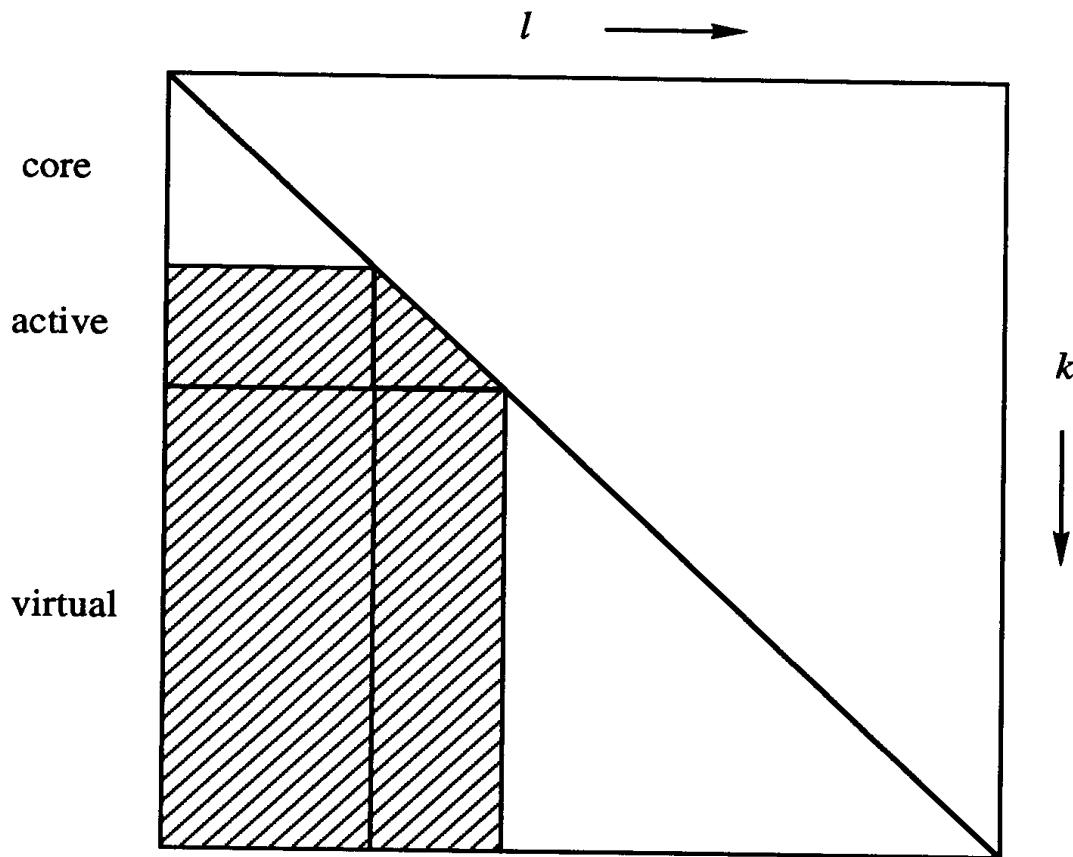
where

$$\begin{aligned}
 \mathbf{A}_{ij,kl} &= \delta_{li}x_{kj} - \delta_{lj}x_{ki} - \delta_{ki}x_{lj} + \delta_{kj}x_{li} \\
 &+ y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} \quad
 \end{aligned} \tag{14.25}$$

and

$$\begin{aligned}
 B_{0,ij}^{a1} &= -x_{ij}^a + x_{ji}^a \\
 &+ \sum_{k>l}^{MO} S_{kl}^a \left(\delta_{ki}x_{lj} - \delta_{kj}x_{li} + y_{ijlk} - y_{jilk} \right) \\
 &+ \frac{1}{2} \sum_k^{MO} S_{kk}^a (\delta_{ki}x_{kj} - \delta_{kj}x_{ki} + y_{ijkk} - y_{jikk}) \quad .
 \end{aligned} \tag{14.26}$$

Equation (14.24) simultaneously contains both the unknown variables U^a and the partial derivatives $\partial C_I / \partial a$. The second term on the rhs of eq. (14.24) represents the CI-MO interactions. These CPHF equations may be solved uniquely for the “independent pairs”; i.e., ($i = \text{active}$, $j = \text{core}$), ($i = \text{active}$, $j = \text{active}$), ($i = \text{virtual}$, $j = \text{core}$), and ($i = \text{virtual}$, $j = \text{active}$). The independent pairs for a MCSCF wavefunction are illustrated by the shaded areas in Figure 14.1. Determination of the “non-independent pairs” of the U^a matrices will be discussed in the following section.



MCSCF Wavefunction

Figure 14.1 Independent pairs (*indep.pair*) of molecular orbitals in the coupled perturbed Hartree-Fock equations for MCSCF wavefunctions. Only the U^a matrix elements shown as shaded areas may be solved for uniquely.

14.1.2 The Configuration Interaction (CI) Part

The variational condition on the CI space is

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad (14.27)$$

where the CI Hamiltonian matrix element was defined in Chapter 9 by

$$H_{IJ} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl) . \quad (14.28)$$

A constraint exists on the CI coefficients, since the wavefunction is normalized according to

$$\sum_I^{CI} C_I^2 = 1 . \quad (14.29)$$

The CI part of the first-order CPMCHF equations is derived by differentiating the variational condition (14.27) with respect to the variable “ a ” subject to the constraint in eq. (14.29):

$$\frac{\partial}{\partial a} \sum_J^{CI} \left[C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) + \theta \left(-1 + \sum_K^{CI} C_K^2 \right) \right] = 0 . \quad (14.30)$$

In this equation, θ is a Lagrange undetermined multiplier. These differential equations were developed further in Chapter 12 and the result was

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} \\ &= - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J . \end{aligned} \quad (14.31)$$

The first derivative of the Hamiltonian matrix was shown in Chapter 9 to be

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} . \quad (14.32)$$

The skeleton (core) first derivative Hamiltonian matrices (H_{IJ}^a) and the “bare” Lagrangian matrices (x^{IJ}) in this equation are

$$H_{IJ}^a = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ} (ij|kl)^a \quad (14.33)$$

$$x_{ij}^{IJ} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ} (im|kl) . \quad (14.34)$$

The “bare” and the “parent” Lagrangian matrices are related by

$$x_{ij} = \sum_{IJ}^{CI} C_I C_J x_{ij}^{IJ} \quad (14.35)$$

$$= \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl} (im|kl) . \quad (14.36)$$

The one- and two-electron reduced density matrices are defined by

$$\gamma_{ij} = \sum_{IJ}^{CI} C_I C_J \gamma_{ij}^{IJ} \quad (14.37)$$

and

$$\Gamma_{ijkl} = \sum_{IJ}^{CI} C_I C_J \Gamma_{ijkl}^{IJ} . \quad (14.38)$$

Inserting eq. (14.32) into eq. (14.31) results in

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} \\ &= - \sum_J^{CI} \left(H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J \end{aligned} \quad (14.39)$$

$$= - \sum_J^{CI} C_J H_{IJ}^a - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} + C_I \frac{\partial E_{elec}}{\partial a} . \quad (14.40)$$

There is a linear dependence among the elements of the U^a matrix appearing in eq. (14.40):

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 . \quad (14.41)$$

In order to eliminate this linear dependence the second term in eq. (14.40) is modified as follows. The summation over the MOs is rewritten as

$$\sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} = \sum_{i>j}^{MO} U_{ij}^a x_{ij}^{IJ} + \sum_{i>j}^{MO} U_{ji}^a x_{ji}^{IJ} + \sum_i^{MO} U_{ii}^a x_{ii}^{IJ} \quad (14.42)$$

$$= \sum_{i>j}^{MO} \left[U_{ij}^a x_{ij}^{IJ} - (U_{ij}^a + S_{ij}^a) x_{ji}^{IJ} \right] - \frac{1}{2} \sum_i^{MO} S_{ii}^a x_{ii}^{IJ} \quad (14.43)$$

$$= \sum_{i>j}^{MO} U_{ij}^a (x_{ij}^{IJ} - x_{ji}^{IJ}) - \sum_{i>j}^{MO} S_{ij}^a x_{ji}^{IJ} - \frac{1}{2} \sum_i^{MO} S_{ii}^a x_{ii}^{IJ} . \quad (14.44)$$

Using this equation, the second term on the rhs of eq. (14.40) becomes

$$\begin{aligned} & - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} \\ &= - 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^a (x_{ij}^{IJ} - x_{ji}^{IJ}) \\ &+ 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a x_{ii}^{IJ} . \end{aligned} \quad (14.45)$$

Thus, the CI part of the first-order CPMCHF equations is expressed as

$$\sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a}$$

$$\begin{aligned}
&= - \sum_J^{CI} C_J H_{IJ}^a - 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^a (x_{ij}^{IJ} - x_{ji}^{IJ}) \\
&\quad + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a x_{ii}^{IJ} + C_I \frac{\partial E_{elec}}{\partial a} .
\end{aligned} \quad (14.46)$$

This equation contains simultaneously the unknown variables $\partial C_I / \partial a$ and the U^a , as was the case for the MO part discussed in the preceding subsection. It should finally be noted that the second term on the rhs of eq. (14.46) contains the CI-MO interactions.

14.1.3 A Complete Expression for the First-Order CPMCHF Equations

In the preceding two subsections, the first derivatives of the variational conditions in both the MO and CI spaces were obtained. Since these two variational conditions interact, the simultaneous equations have the form

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21^\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^a \\ \partial C / \partial a \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{a1} \\ \mathbf{B}_0^{a2} \end{bmatrix} . \quad (14.47)$$

The \mathbf{A}^{11} term contains the MO part. Referring to eqs. (14.24) and (14.25) elements of this matrix are

$$\begin{aligned}
\mathbf{A}_{ij,kl}^{11} &= \delta_{li} x_{kj} - \delta_{lj} x_{ki} - \delta_{ki} x_{lj} + \delta_{kj} x_{li} \\
&\quad + y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} .
\end{aligned} \quad (14.48)$$

The \mathbf{A}^{22} term represents the CI part and each element, from the lhs of eq. (14.46), is of the form

$$\mathbf{A}_{I,J}^{22} = H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J . \quad (14.49)$$

Finally, the \mathbf{A}^{21} (\mathbf{A}^{21^\dagger}) term contains the CI-MO (or MO-CI) interaction. Referring to the second terms in eqs. (14.24) and (14.46), each element of this matrix is

$$\mathbf{A}_{I,ij}^{21} = 2 \sum_J^{CI} C_J (x_{ij}^{IJ} - x_{ji}^{IJ}) . \quad (14.50)$$

The perturbation term for the MO space, from the MO part of eq. (14.24), is

$$\begin{aligned}
B_{0,ij}^{a1} &= -x_{ij}^a + x_{ji}^a \\
&\quad + \sum_{k>l}^{MO} S_{kl}^a (\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijlk} - y_{jilk}) \\
&\quad + \frac{1}{2} \sum_k^{MO} S_{kk}^a (\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk}) ,
\end{aligned} \quad (14.51)$$

and that for the CI space from the CI part of eq. (14.46) is

$$\begin{aligned} B_{0,I}^{a2} = & - \sum_J^{CI} C_J H_{IJ}^a + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a x_{ji}^{IJ} \\ & + \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a x_{ii}^{IJ} + C_I \frac{\partial E_{elec}}{\partial a} . \end{aligned} \quad (14.52)$$

14.2 The Averaged Fock Operator

The two MCSCF conditions, eqs. (14.1) and (14.27), do not provide the unique variational criteria for the core and virtual orbitals as a unitary transformation among these orbitals does not change the electronic energy. Therefore, it is useful to redefine explicitly the core and virtual orbitals. One of the most common ways to define these orbitals is to use the averaged Fock operator

$$\mathbf{F}^{av} = \mathbf{h} + \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} (2\mathbf{J}_{kl} - \mathbf{K}_{kl}) , \quad (14.53)$$

where the elements of the averaged Fock matrix are given by

$$\epsilon'_{ij} = \langle \phi_i | \mathbf{F}^{av} | \phi_j \rangle = h_{ij} + \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} \left\{ 2(ij|kl) - (ik|jl) \right\} . \quad (14.54)$$

The two (core and virtual) parts of the Fock matrix are diagonalized and consequently the following diagonality is established for the core and virtual orbitals:

$$\epsilon'_{ij} = \delta_{ij} \epsilon'_i \quad (14.55)$$

where ϵ' are “orbital energies” and i and j belong to the same shell. The corresponding subsets of the original MCSCF molecular orbitals must be rotated using the resultant eigenvectors. This new set of molecular orbitals should be used for the CI procedure.

The corresponding CPHF equations for the averaged Fock operator may be derived in a manner similar to that described in Sections 11.2 and 13.2. Differentiation of eq. (14.54) with respect to a cartesian coordinate “a”

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} = & \frac{\partial h_{ij}}{\partial a} + \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} \left\{ 2 \frac{\partial (ij|kl)}{\partial a} - \frac{\partial (ik|jl)}{\partial a} \right\} \\ & + \frac{1}{2} \sum_{kl}^{MO} \frac{\partial \gamma_{kl}}{\partial a} \left\{ 2(ij|kl) - (ik|jl) \right\} \end{aligned} \quad (14.56)$$

is required. Note that the derivative of the one-electron reduced density matrix γ_{kl} does not vanish, since its definition, eq. (14.37), explicitly involves the CI coefficients. The derivative of γ_{kl} is obtained by differentiating eq. (14.37) with respect to the variable "a":

$$\frac{\partial \gamma_{kl}}{\partial a} = \frac{\partial}{\partial a} \left\{ \sum_{IJ}^{CI} C_I C_J \gamma_{kl}^{IJ} \right\} \quad (14.57)$$

$$= \sum_{IJ}^{CI} \left\{ \frac{\partial C_I}{\partial a} C_J \gamma_{kl}^{IJ} + C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} \right\} \quad (14.58)$$

$$= 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} . \quad (14.59)$$

Using the results from Sections 3.8 and 3.9 and eq. (14.59), eq. (14.56) may be expanded as

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= h_{ij}^a + \sum_m^{MO} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \\ &+ \sum_{kl}^{MO} \gamma_{kl} \left[(ij|kl)^a + \sum_m^{MO} U_{mi}^a (mj|kl) + \sum_m^{MO} U_{mj}^a (im|kl) \right. \\ &\quad \left. + \sum_m^{MO} U_{mk}^a (ij|ml) + \sum_m^{MO} U_{ml}^a (ij|km) \right] \\ &- \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} \left[(ik|jl)^a + \sum_m^{MO} U_{mi}^a (mk|jl) + \sum_m^{MO} U_{mk}^a (im|jl) \right. \\ &\quad \left. + \sum_m^{MO} U_{mj}^a (ik|ml) + \sum_m^{MO} U_{ml}^a (ik|jm) \right] \\ &+ \sum_{kl}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} \left\{ 2(ij|kl) - (ik|jl) \right\} . \end{aligned} \quad (14.60)$$

Rearranging terms in eq. (14.60) gives

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= h_{ij}^a + \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} \left\{ 2(ij|kl)^a - (ik|jl)^a \right\} \\ &+ \sum_m^{MO} U_{mi}^a \left[h_{mj} + \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} \left\{ 2(mj|kl) - (mk|jl) \right\} \right] \\ &+ \sum_m^{MO} U_{mj}^a \left[h_{im} + \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} \left\{ 2(im|kl) - (ik|ml) \right\} \right] \\ &+ \frac{1}{2} \sum_{mkl}^{MO} U_{mk}^a \gamma_{kl} \left\{ 2(ij|ml) - (im|jl) \right\} \\ &+ \frac{1}{2} \sum_{mkl}^{MO} U_{ml}^a \gamma_{kl} \left\{ 2(ij|km) - (ik|jm) \right\} \end{aligned}$$

$$+ \sum_{kl}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} \left\{ 2(ij|kl) - (ik|jl) \right\} . \quad (14.61)$$

Using the definition of the averaged Fock matrix in eq. (14.54), this equation may be rewritten as

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a + \sum_k^{MO} U_{ki}^a \epsilon'_{kj} + \sum_k^{MO} U_{kj}^a \epsilon'_{ik} \\ &+ \frac{1}{2} \sum_{kl}^{MO} U_{kl}^a \sum_m^{MO} \gamma_{lm} \left\{ 4(ij|km) - (ik|jm) - (im|jk) \right\} \\ &+ \sum_{kl}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} \left\{ 2(ij|kl) - (ik|jl) \right\} . \end{aligned} \quad (14.62)$$

In this equation the skeleton (core) first derivative averaged Fock matrices are defined by

$$\epsilon'_{ij}^a = h_{ij}^a + \frac{1}{2} \sum_{kl}^{MO} \gamma_{kl} \left\{ 2(ij|kl)^a - (ik|jl)^a \right\} . \quad (14.63)$$

Using the diagonal nature of the averaged Fock matrix for the core and virtual orbitals, eq. (14.55), and the first derivative of the orthonormality condition of the molecular orbitals, namely eq. (14.41), equation (14.62) may be modified as

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a + U_{ji}^a \epsilon'_{j} + U_{ij}^a \epsilon'_{i} + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\ &+ \frac{1}{2} \sum_{kl}^{MO} U_{kl}^a \sum_m^{MO} \gamma_{lm} \left\{ 4(ij|km) - (ik|jm) - (im|jk) \right\} \\ &+ \sum_{kl}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl} \left\{ 2(ij|kl) - (ik|jl) \right\} \end{aligned} \quad (14.64)$$

$$\begin{aligned} &= \epsilon'_{ij}^a - (\epsilon'_{j} - \epsilon'_{i}) U_{ij}^a - S_{ij}^a \epsilon'_{j} + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\ &+ \frac{1}{2} \sum_{kl}^{MO} U_{kl}^a \sum_m^{MO} \gamma_{lm} A_{ij,km} \\ &+ \sum_{kl}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} \left\{ 2(ij|kl) - (ik|jl) \right\} . \end{aligned} \quad (14.65)$$

The A matrix is defined by

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) . \quad (14.66)$$

Note that the A matrix in eq. (14.66) is a different quantity from the \mathbf{A} matrix in eq. (14.25).

Recalling again eq. (14.41), the second term from the last in eq. (14.65) may be manipulated in the following manner:

$$\begin{aligned} \sum_{kl}^{MO} U_{kl}^a \sum_m^{MO} \gamma_{lm} A_{ij,km} &= \sum_{k>l}^{MO} U_{kl}^a \sum_m^{MO} \gamma_{lm} A_{ij,km} + \sum_{k>l}^{MO} U_{lk}^a \sum_m^{MO} \gamma_{km} A_{ij,lm} \\ &+ \sum_k^{MO} U_{kk}^a \sum_m^{MO} \gamma_{km} A_{ij,km} \end{aligned} \quad (14.67)$$

$$\begin{aligned} &= \sum_{k>l}^{MO} U_{kl}^a \sum_m^{MO} \gamma_{lm} A_{ij,km} - \sum_{k>l}^{MO} (U_{kl}^a + S_{kl}^a) \sum_m^{MO} \gamma_{km} A_{ij,lm} \\ &- \frac{1}{2} \sum_k^{MO} S_{kk}^a \sum_m^{MO} \gamma_{km} A_{ij,km} \end{aligned} \quad (14.68)$$

$$\begin{aligned} &= \sum_{k>l}^{MO} U_{kl}^a \sum_m^{MO} (\gamma_{lm} A_{ij,km} - \gamma_{km} A_{ij,lm}) \\ &- \sum_{k>l}^{MO} S_{kl}^a \sum_m^{MO} \gamma_{km} A_{ij,lm} \\ &- \frac{1}{2} \sum_k^{MO} S_{kk}^a \sum_m^{MO} \gamma_{km} A_{ij,km} . \end{aligned} \quad (14.69)$$

Elements of the one-electron reduced density matrix involving the virtual orbitals vanish. Thus, equation (14.69) is further reduced to

$$\begin{aligned} \sum_{kl}^{MO} U_{kl}^a \sum_m^{MO} \gamma_{lm} A_{ij,km} &= \sum_{k>l}^{all\ occ} U_{kl}^a \sum_m^{occ} (\gamma_{lm} A_{ij,km} - \gamma_{km} A_{ij,lm}) \\ &- \sum_{k>l}^{occ} S_{kl}^a \sum_m^{occ} \gamma_{km} A_{ij,lm} \\ &- \frac{1}{2} \sum_k^{occ} S_{kk}^a \sum_m^{occ} \gamma_{km} A_{ij,km} . \end{aligned} \quad (14.70)$$

Combining eqs. (14.65) and (14.70) one obtains

$$\begin{aligned} \frac{\partial \epsilon'_{ij}}{\partial a} &= \epsilon'_{ij}^a - (\epsilon'_{ij} - \epsilon'_i) U_{ij}^a - S_{ij}^a \epsilon'_{ij} + \sum_k^{othershell} U_{ki}^a \epsilon'_{kj} + \sum_k^{othershell} U_{kj}^a \epsilon'_{ik} \\ &+ \frac{1}{2} \sum_{k>l}^{all\ occ} U_{kl}^a \sum_m^{occ} (\gamma_{lm} A_{ij,km} - \gamma_{km} A_{ij,lm}) \\ &- \frac{1}{2} \sum_{k>l}^{occ} S_{kl}^a \sum_m^{occ} \gamma_{km} A_{ij,lm} \\ &- \frac{1}{4} \sum_k^{occ} S_{kk}^a \sum_m^{occ} \gamma_{km} A_{ij,km} \end{aligned}$$

$$+ \sum_{kl}^{\text{occ}} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} \left\{ 2(ij|kl) - (ik|jl) \right\} . \quad (14.71)$$

The final equation for the non-independent pairs of the U^a matrices is

$$\begin{aligned} U_{ij}^a &= \frac{1}{\epsilon_j' - \epsilon_i'} \left[\epsilon_{ij}' - S_{ij}^a \epsilon_j' + \sum_k^{\text{othershell}} U_{ki}^a \epsilon_{kj}' + \sum_k^{\text{othershell}} U_{kj}^a \epsilon_{ik}' \right. \\ &+ \frac{1}{2} \sum_{k>l}^{\text{all occ}} U_{kl}^a \sum_m^{\text{occ}} \left(\gamma_{lm} A_{ij,km} - \gamma_{km} A_{ij,lm} \right) \\ &- \frac{1}{2} \sum_{k>l}^{\text{occ}} S_{kl}^a \sum_m^{\text{occ}} \gamma_{km} A_{ij,lm} \\ &- \frac{1}{4} \sum_k^{\text{occ}} S_{kk}^a \sum_m^{\text{occ}} \gamma_{km} A_{ij,km} \\ &\left. + \sum_{kl}^{\text{occ}} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{kl}^{IJ} \left\{ 2(ij|kl) - (ik|jl) \right\} \right] \end{aligned} \quad (14.72)$$

for ($i = \text{core}$, $j = \text{core}$) and ($i = \text{virtual}$, $j = \text{virtual}$). In the above formalism the molecular orbitals have to be first transformed unitarily using the averaged Fock operator in eq. (14.53) *prior* to solving the CPHF equations. Using these redefined molecular orbitals, the elements of the U^a matrices for the independent pairs are then obtained by solution of the CPHF equations in eq. (14.47). Finally the elements for the non-independent pairs are determined in terms of the U^a elements for the independent pairs from equation (14.72).

14.3 The First Derivative of the “Bare” y Matrix

It is necessary to derive the first derivative of the “bare” y matrix for later use. The first derivative of the “bare” y matrix is obtained by differentiating eq. (14.12) with respect to an arbitrary cartesian coordinate “ a ”:

$$\frac{\partial y_{ijkl}^{IJ}}{\partial a} = \gamma_{jl}^{IJ} \frac{\partial h_{ik}}{\partial a} + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ} \frac{\partial (ik|mn)}{\partial a} + 4 \sum_{mn}^{MO} \Gamma_{jmkn}^{IJ} \frac{\partial (im|kn)}{\partial a} . \quad (14.73)$$

Recall that the one- and two-electron coupling constants, γ^{IJ} and Γ^{IJ} , do not involve the CI coefficients. Therefore, the first derivative in eq. (14.73) is obtained easily using the results from Sections 3.8 and 3.9:

$$\begin{aligned} \frac{\partial y_{ijkl}^{IJ}}{\partial a} &= \gamma_{jl}^{IJ} \left\{ h_{ik}^a + \sum_p^{MO} (U_{pi}^a h_{pk} + U_{pk}^a h_{ip}) \right\} \\ &+ 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ} \left[(ik|mn)^a + \sum_p^{MO} \left\{ U_{pi}^a (pk|mn) + U_{pk}^a (ip|mn) \right. \right. \\ &\quad \left. \left. - (ip|kn)^a - (pk|in)^a \right\} \right] \end{aligned}$$

$$\begin{aligned}
& + U_{pm}^a(ik|pn) + U_{pn}^a(ik|mp) \Big\} \Big] \\
& + 4 \sum_{mn}^{MO} \Gamma_{jmln}^{IJ} \left[(im|kn)^a + \sum_p^{MO} \left\{ U_{pi}^a(pm|kn) + U_{pm}^a(ip|kn) \right. \right. \\
& \quad \left. \left. + U_{pk}^a(im|pn) + U_{pn}^a(im|kp) \right\} \right] . \tag{14.74}
\end{aligned}$$

The following relationships for the two-electron coupling constants

$$\Gamma_{ijkl}^{IJ} = \Gamma_{jikl}^{IJ} = \Gamma_{ijlk}^{IJ} = \Gamma_{jilk}^{IJ} = \Gamma_{klij}^{IJ} = \Gamma_{klji}^{IJ} = \Gamma_{lkij}^{IJ} = \Gamma_{lkji}^{IJ} \tag{14.75}$$

simplify equation (14.74). The resulting expression is

$$\begin{aligned}
\frac{\partial y_{ijkl}^{IJ}}{\partial a} &= \gamma_{jl}^{IJ} h_{ik}^a + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ}(ik|mn)^a + 4 \sum_{mn}^{MO} \Gamma_{jmln}^{IJ}(im|kn)^a \\
&+ \sum_p^{MO} U_{pi}^a \left\{ \gamma_{jl}^{IJ} h_{pk}^a + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ}(pk|mn)^a + 4 \sum_{mn}^{MO} \Gamma_{jmln}^{IJ}(pm|kn)^a \right\} \\
&+ \sum_p^{MO} U_{pk}^a \left\{ \gamma_{jl}^{IJ} h_{ip}^a + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ}(ip|mn)^a + 4 \sum_{mn}^{MO} \Gamma_{jmln}^{IJ}(im|pn)^a \right\} \\
&+ 2 \sum_{mnp}^{MO} U_{pm}^a \left\{ \Gamma_{jlmn}^{IJ}(ik|pn)^a + 2 \Gamma_{jmln}^{IJ}(ip|kn)^a \right\} \\
&+ 2 \sum_{mnp}^{MO} U_{pn}^a \left\{ \Gamma_{jlmn}^{IJ}(ik|mp)^a + 2 \Gamma_{jmln}^{IJ}(im|kp)^a \right\} \tag{14.76}
\end{aligned}$$

$$\begin{aligned}
&= y_{ijkl}^{IJ^a} + \sum_p^{MO} \left(U_{pi}^a y_{pjkl}^{IJ} + U_{pk}^a y_{ijpl}^{IJ} \right) \\
&+ 2 \sum_{mnp}^{MO} U_{pm}^a \left\{ \Gamma_{jlmn}^{IJ}(ik|pn)^a + 2 \Gamma_{jmln}^{IJ}(ip|kn)^a \right. \\
&\quad \left. + \Gamma_{jlnm}^{IJ}(ik|np)^a + 2 \Gamma_{jnlm}^{IJ}(in|kp)^a \right\} \tag{14.77}
\end{aligned}$$

$$\begin{aligned}
&= y_{ijkl}^{IJ^a} + \sum_p^{MO} \left(U_{pi}^a y_{pjkl}^{IJ} + U_{pk}^a y_{ijpl}^{IJ} \right) \\
&+ 4 \sum_{mnp}^{MO} U_{pm}^a \left\{ \Gamma_{jlmn}^{IJ}(ik|pn)^a + \Gamma_{jmln}^{IJ}(ip|kn)^a + \Gamma_{jnlm}^{IJ}(in|kp)^a \right\} . \tag{14.78}
\end{aligned}$$

In the above equation the skeleton (core) first derivative "bare" y matrix, y^{IJ^a} , is defined by

$$y_{ijkl}^{IJ^a} = \gamma_{jl}^{IJ} h_{ik}^a + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ}(ik|mn)^a + 4 \sum_{mn}^{MO} \Gamma_{jmln}^{IJ}(im|kn)^a . \tag{14.79}$$

14.4 The Second-Order CPMCHF Equations

14.4.1 The Molecular Orbital (MO) Part

The MO part of the second-order CPMCHF equations is obtained by differentiating the variational condition, eq. (14.1), with respect to the cartesian coordinates “*a*” and “*b*”:

$$\frac{\partial^2 x_{ij}}{\partial a \partial b} - \frac{\partial^2 x_{ji}}{\partial a \partial b} = 0 . \quad (14.80)$$

The required second derivative of the Lagrangian matrix is found by differentiating eq. (14.8) with respect to a second variable “*b*” in a way similar to that demonstrated in Section 13.3:

$$\frac{\partial^2 x_{ij}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial x_{ij}}{\partial a} \right) \quad (14.81)$$

$$= \frac{\partial}{\partial b} \left(2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} x_{ij}^{IJ} + \sum_{IJ}^{CI} C_I C_J \frac{\partial x_{ij}^{IJ}}{\partial a} \right) \quad (14.82)$$

$$\begin{aligned} &= 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} x_{ij}^{IJ} + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} x_{ij}^{IJ} \\ &+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial x_{ij}^{IJ}}{\partial b} + \frac{\partial C_J}{\partial b} \frac{\partial x_{ij}^{IJ}}{\partial a} \right] \\ &+ \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 x_{ij}^{IJ}}{\partial a \partial b} . \end{aligned} \quad (14.83)$$

The second derivative of the “bare” Lagrangian matrix is derived in a similar manner to that of the PEMCSCF wavefunction, since the coupling constants γ^{IJ} and Γ^{IJ} are independent of the CI coefficients. Using results from Section 14.1, the second derivative of the x^{IJ} matrix is expanded as

$$\frac{\partial^2 x_{ij}^{IJ}}{\partial a \partial b} = \frac{\partial}{\partial b} \left(\frac{\partial x_{ij}^{IJ}}{\partial a} \right) \quad (14.84)$$

$$= \frac{\partial}{\partial b} \left(x_{ij}^{IJ^a} + \sum_k^{MO} U_{ki}^a x_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJ} \right) \quad (14.85)$$

$$= \frac{\partial x_{ij}^{IJ^a}}{\partial b} + \frac{\partial}{\partial b} \sum_k^{MO} U_{ki}^a x_{kj}^{IJ} + \frac{\partial}{\partial b} \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJ} . \quad (14.86)$$

The first term on the rhs of eq. (14.86) is derived by the same sort of manipulation that led from eq. (14.9) to eq. (14.10):

$$\frac{\partial x_{ij}^{IJ^a}}{\partial b} = x_{ij}^{IJ^{ab}} + \sum_k^{MO} U_{ki}^b x_{kj}^{IJ^a} + \sum_{kl}^{MO} U_{kl}^b y_{ijkl}^{IJ^a} . \quad (14.87)$$

The skeleton (core) second derivative “bare” Lagrangian matrices (x^{IJab}) and the first derivative “bare” y matrices (y^{IJ^a}) are:

$$x_{ij}^{IJab} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im}^{ab} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ}(im|kl)^{ab} \quad (14.88)$$

and

$$y_{ijkl}^{IJ^a} = \gamma_{jl}^{IJ} h_{ik}^a + 2 \sum_{mn}^{MO} \Gamma_{jlmn}^{IJ}(ik|mn)^a + 4 \sum_{mn}^{MO} \Gamma_{jmkn}^{IJ}(im|kn)^a \quad . \quad (14.89)$$

These matrix elements are related to their “parent” quantities through the relationships

$$x_{ij}^{ab} = \sum_{IJ}^{CI} C_I C_J x_{ij}^{IJab} \quad (14.90)$$

$$= \sum_m^{MO} \gamma_{jm} h_{im}^{ab} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl)^{ab} \quad (14.91)$$

and

$$y_{ijkl}^a = \sum_{IJ}^{CI} C_I C_J y_{ijkl}^{IJ^a} \quad (14.92)$$

$$= \gamma_{jl} h_{ik}^a + 2 \sum_{mn}^{MO} \Gamma_{jlmn}(ik|mn)^a + 4 \sum_{mn}^{MO} \Gamma_{jmkn}(im|kn)^a \quad . \quad (14.93)$$

Employing the result in Section 3.3 and eq. (14.10), the second term of eq. (14.86) may be rewritten as

$$\frac{\partial}{\partial b} \sum_k^{MO} U_{ki}^a x_{kj}^{IJ} = \sum_k^{MO} \frac{\partial U_{ki}^a}{\partial b} x_{kj}^{IJ} + \sum_k^{MO} U_{ki}^a \frac{\partial x_{kj}^{IJ}}{\partial b} \quad (14.94)$$

$$= \sum_k^{MO} \left(U_{ki}^{ab} - \sum_m^{MO} U_{km}^b U_{mi}^a \right) x_{kj}^{IJ} \\ + \sum_k^{MO} U_{ki}^a \left(x_{kj}^{IJ^b} + \sum_m^{MO} U_{mk}^b x_{mj}^{IJ} + \sum_{mn}^{MO} U_{mn}^b y_{kjmn}^{IJ} \right) \quad (14.95)$$

$$= \sum_k^{MO} U_{ki}^{ab} x_{kj}^{IJ} + \sum_k^{MO} U_{ki}^a x_{kj}^{IJ^b} + \sum_{kmn}^{MO} U_{ki}^a U_{mn}^b y_{kjmn}^{IJ} \quad . \quad (14.96)$$

Using again the result in Section 3.3 and the results of Section 14.3, the third term of eq. (14.86) is manipulated to yield

$$\frac{\partial}{\partial b} \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJ} = \sum_{kl}^{MO} \frac{\partial U_{kl}^a}{\partial b} y_{ijkl}^{IJ} + \sum_{kl}^{MO} U_{kl}^a \frac{\partial y_{ijkl}^{IJ}}{\partial b} \quad (14.97)$$

$$\begin{aligned}
&= \sum_{kl}^{MO} \left(U_{kl}^{ab} - \sum_m^{MO} U_{km}^b U_{ml}^a \right) y_{ijkl}^{IJ} \\
&+ \sum_{kl}^{MO} U_{kl}^a \left\{ y_{ijkl}^{IJb} + \sum_p^{MO} \left(U_{pi}^b y_{pjkl}^{IJ} + U_{pk}^b y_{ijpl}^{IJ} \right) \right. \\
&\quad \left. + 4 \sum_{mnp}^{MO} U_{pm}^b \left(\Gamma_{jlmn}^{IJ}(ik|pn) + \Gamma_{jmkn}^{IJ}(ip|kn) + \Gamma_{jnkm}^{IJ}(in|kp) \right) \right\} \quad (14.98)
\end{aligned}$$

$$\begin{aligned}
&= \sum_{kl}^{MO} U_{kl}^{ab} y_{ijkl}^{IJ} + \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJb} + \sum_{klp}^{MO} U_{kl}^a U_{pi}^b y_{pjkl}^{IJ} \\
&+ 4 \sum_{klmnp}^{MO} U_{kl}^a U_{pm}^b \left\{ \Gamma_{jlmn}^{IJ}(ik|pn) + \Gamma_{jmkn}^{IJ}(ip|kn) + \Gamma_{jnkm}^{IJ}(in|kp) \right\} \quad . \quad (14.99)
\end{aligned}$$

Combining eqs. (14.86), (14.87), (14.96), and (14.99), the second derivative of the “bare” Lagrangian matrix is

$$\begin{aligned}
\frac{\partial^2 x_{ij}^{IJ}}{\partial a \partial b} &= x_{ij}^{IJab} + \sum_k^{MO} U_{ki}^b x_{kj}^{IJa} + \sum_{kl}^{MO} U_{kl}^b y_{ijkl}^{IJa} \\
&+ \sum_k^{MO} U_{ki}^{ab} x_{kj}^{IJ} + \sum_k^{MO} U_{ki}^a x_{kj}^{IJb} + \sum_{kmn}^{MO} U_{ki}^a U_{mn}^b y_{kjmn}^{IJ} \\
&+ \sum_{kl}^{MO} U_{kl}^{ab} y_{ijkl}^{IJ} + \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJb} + \sum_{klm}^{MO} U_{kl}^a U_{mi}^b y_{mjkl}^{IJ} \\
&+ 4 \sum_{klmnp}^{MO} U_{kl}^a U_{pm}^b \left\{ \Gamma_{jlmn}^{IJ}(ik|pn) + \Gamma_{jmkn}^{IJ}(ip|kn) + \Gamma_{jnkm}^{IJ}(in|kp) \right\} \quad (14.100)
\end{aligned}$$

$$\begin{aligned}
&= x_{ij}^{IJab} + \sum_k^{MO} U_{ki}^{ab} x_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^{ab} y_{ijkl}^{IJ} \\
&+ \sum_k^{MO} U_{ki}^a x_{kj}^{IJb} + \sum_k^{MO} U_{ki}^b x_{kj}^{IJa} \\
&+ \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJb} + \sum_{kl}^{MO} U_{kl}^b y_{ijkl}^{IJa} \\
&+ \sum_{kmn}^{MO} U_{ki}^a U_{mn}^b y_{kjmn}^{IJ} + \sum_{kmn}^{MO} U_{ki}^b U_{mn}^a y_{kjmn}^{IJ} \\
&+ 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{jlnp}^{IJ}(ik|mp) + \Gamma_{jnlp}^{IJ}(im|kp) + \Gamma_{jpln}^{IJ}(ip|km) \right\} \quad . \quad (14.101)
\end{aligned}$$

Inserting this equation into eq. (14.83), and noting the relationships in equations (14.3), (14.13), (14.15), (14.38), (14.90) and (14.92), the second derivative of the Lagrangian matrix is

$$\begin{aligned}
 \frac{\partial^2 x_{ij}}{\partial a \partial b} &= 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} x_{ij}^{IJ} + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} x_{ij}^{IJ} \\
 &+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial x_{ij}^{IJ}}{\partial b} + \frac{\partial C_J}{\partial b} \frac{\partial x_{ij}^{IJ}}{\partial a} \right] \\
 &+ x_{ij}^{ab} + \sum_k^{MO} U_{ki}^{ab} x_{kj} + \sum_{kl}^{MO} U_{kl}^{ab} y_{ijkl} \\
 &+ \sum_k^{MO} U_{ki}^a x_{kj}^b + \sum_k^{MO} U_{ki}^b x_{kj}^a \\
 &+ \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^b + \sum_{kl}^{MO} U_{kl}^b y_{ijkl}^a \\
 &+ \sum_{kmn}^{MO} U_{ki}^a U_{mn}^b y_{kjmn} + \sum_{kmn}^{MO} U_{ki}^b U_{mn}^a y_{kjmn} \\
 &+ 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right\} .
 \end{aligned} \tag{14.102}$$

The MO part of the second-order CPMCHF equations, eq. (14.80), is now

$$\begin{aligned}
 \frac{\partial^2 x_{ij}}{\partial a \partial b} - \frac{\partial^2 x_{ji}}{\partial a \partial b} &= x_{ij}^{ab} - x_{ji}^{ab} \\
 &+ \sum_{kl}^{MO} U_{kl}^{ab} \left(\delta_{li} x_{kj} - \delta_{lj} x_{ki} + y_{ijkl} - y_{jikl} \right) \\
 &+ \sum_k^{MO} \left(U_{ki}^a x_{kj}^b - U_{kj}^a x_{ki}^b \right) + \sum_k^{MO} \left(U_{ki}^b x_{kj}^a - U_{kj}^b x_{ki}^a \right) \\
 &+ \sum_{kl}^{MO} U_{kl}^a \left(y_{ijkl}^b - y_{jikl}^b \right) + \sum_{kl}^{MO} U_{kl}^b \left(y_{ijkl}^a - y_{jikl}^a \right) \\
 &+ \sum_{kmn}^{MO} U_{mn}^b \left(U_{ki}^a y_{kjmn} - U_{kj}^a y_{kimn} \right) + \sum_{kmn}^{MO} U_{mn}^a \left(U_{ki}^b y_{kjmn} - U_{kj}^b y_{kimn} \right) \\
 &+ 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\
 &\quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\}
 \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\
& + 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial^2 C_I}{\partial a \partial b} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(\frac{\partial x_{ij}^{IJ}}{\partial b} - \frac{\partial x_{ji}^{IJ}}{\partial b} \right) \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial b} \left(\frac{\partial x_{ij}^{IJ}}{\partial a} - \frac{\partial x_{ji}^{IJ}}{\partial a} \right) = 0
\end{aligned} \quad (14.103)$$

This equation shows clearly that the second derivative of the variational conditions in the MO space contains second-order terms due to perturbations by the CI coefficients.

Equation (14.103) may be manipulated as was done in Section 14.1 and eventually written in a familiar form as

$$\begin{aligned}
& \sum_{k>l}^{MO} \mathbf{A}_{ij,kl} U_{kl}^{ab} = -x_{ij}^{ab} + x_{ji}^{ab} \\
& + \sum_{k>l}^{MO} \xi_{kl}^{ab} \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijkl} - y_{jilk} \right) \\
& + \frac{1}{2} \sum_k^{MO} \xi_{kk}^{ab} \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right) \\
& - \sum_k^{MO} \left(U_{ki}^a x_{kj}^b - U_{kj}^a x_{ki}^b \right) - \sum_k^{MO} \left(U_{ki}^b x_{kj}^a - U_{kj}^b x_{ki}^a \right) \\
& - \sum_{kl}^{MO} U_{kl}^a \left(y_{ijkl}^b - y_{jikl}^b \right) - \sum_{kl}^{MO} U_{kl}^b \left(y_{ijkl}^a - y_{jikl}^a \right) \\
& - \sum_{kmn}^{MO} U_{mn}^b \left(U_{ki}^a y_{kjmn} - U_{kj}^a y_{kimn} \right) - \sum_{kmn}^{MO} U_{mn}^a \left(U_{ki}^b y_{kjmn} - U_{kj}^b y_{kimn} \right) \\
& - 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{ilnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\
& \quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\} \\
& - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\
& - 2 \sum_J^{CI} C_J \sum_I^{CI} \frac{\partial^2 C_I}{\partial a \partial b} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right)
\end{aligned}$$

$$- 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial a} \left(\frac{\partial x_{ij}^{IJ}}{\partial b} - \frac{\partial x_{ji}^{IJ}}{\partial b} \right) + \frac{\partial C_J}{\partial b} \left(\frac{\partial x_{ij}^{IJ}}{\partial a} - \frac{\partial x_{ji}^{IJ}}{\partial a} \right) \right\} \quad (14.104)$$

The \mathbf{A} matrix was defined by eq. (14.25) and the ξ^{ab} matrices were developed in Section 3.7 and satisfy

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad . \quad (14.105)$$

Note that the second term from the last in eq. (14.104) contains the CI-MO interactions.

14.4.2 The Configuration Interaction (CI) Part

The CI part of the second-order CPMCHF equations is derived by differentiating the first-order equation (14.31) with respect to a second variable “ b ”:

$$\frac{\partial}{\partial b} \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} = - \frac{\partial}{\partial b} \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J \quad . \quad (14.106)$$

These differential equations were developed in Section 12.2 and the result was

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\ &= - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} \quad . \end{aligned} \quad (14.107)$$

The second derivative of the Hamiltonian matrix element from Chapter 9 is

$$\begin{aligned} \frac{\partial^2 H_{IJ}}{\partial a \partial b} &= H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} x_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \quad . \end{aligned} \quad (14.108)$$

The skeleton (core) second derivative Hamiltonian matrices, H_{IJ}^{ab} , in this equation are of the form

$$H_{IJ}^{ab} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ} (ij|kl)^{ab} . \quad (14.109)$$

Using eq. (14.108), the first term on the rhs of eq. (14.107) is rewritten as

$$\begin{aligned} & - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\ &= - \sum_J^{CI} \left[H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} x_{ij}^{IJ} + 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \right. \\ & \quad \left. + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \right] C_J + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \end{aligned} \quad (14.110)$$

$$\begin{aligned} &= - \sum_J^{CI} C_J H_{IJ}^{ab} - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} U_{ij}^{ab} x_{ij}^{IJ} \\ & \quad - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\ & \quad - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \end{aligned} \quad (14.111)$$

$$\begin{aligned} &= - \sum_J^{CI} C_J H_{IJ}^{ab} - 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^{ab} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\ & \quad + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} x_{ii}^{IJ} \\ & \quad - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\ & \quad - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} . \end{aligned} \quad (14.112)$$

In manipulating the second term of eq. (14.111), the technique used in Section 14.1 (see eqs. (14.42) through eq. (14.45)) was employed.

Combining eqs. (14.107) and (14.112) the CI part of the second-order CPMCHF equations is now

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\ &= - \sum_J^{CI} C_J H_{IJ}^{ab} - 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} U_{ij}^{ab} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} x_{ii}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \\
& - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\
& - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} . \quad (14.113)
\end{aligned}$$

It should be noted that the second term of eq. (14.113) represents the CI-MO interactions.

14.4.3 A Complete Expression for the Second-Order CPMCHF Equations

In the preceding two subsections, the second derivatives of the variational conditions on both the MO and CI spaces were derived. The second-order CPHF equations for the MCSCF wavefunctions are

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21^\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{ab} \\ \partial^2 \mathbf{C} / \partial \mathbf{a} \partial \mathbf{b} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{ab1} \\ \mathbf{B}_0^{ab2} \end{bmatrix} . \quad (14.114)$$

The \mathbf{A}^{11} term contains the MO part. Elements of this matrix were given in eq. (14.25) as

$$\begin{aligned}
\mathbf{A}_{ij,kl}^{11} = & \delta_{li} x_{kj} - \delta_{lj} x_{ki} - \delta_{ki} x_{lj} + \delta_{kj} x_{li} \\
& + y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} . \quad (14.115)
\end{aligned}$$

The \mathbf{A}^{22} term represents the CI part and each element was defined in eq. (14.113):

$$\mathbf{A}_{I,J}^{22} = H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J . \quad (14.116)$$

The \mathbf{A}^{21} (\mathbf{A}^{21^\dagger}) term contains the CI-MO (or MO-CI) interaction. Referring to the second term from the last in eq. (14.104) and the second term in (14.113), each element of this matrix is

$$\mathbf{A}_{I,ij}^{21} = 2 \sum_J^{CI} C_J \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) . \quad (14.117)$$

The perturbation term for the MO space, from the MO part of eq. (14.104), is

$$B_{0,ij}^{ab1} = -x_{ij}^{ab} + x_{ji}^{ab}$$

$$\begin{aligned}
& + \sum_{k>l}^{MO} \xi_{kl}^{ab} (\delta_{ki}x_{lj} - \delta_{kj}x_{li} + y_{ijlk} - y_{jilk}) \\
& + \frac{1}{2} \sum_k^{MO} \xi_{kk}^{ab} (\delta_{ki}x_{kj} - \delta_{kj}x_{ki} + y_{ijkk} - y_{jikk}) \\
& - \sum_k^{MO} (U_{ki}^a x_{kj}^b - U_{kj}^a x_{ki}^b) - \sum_k^{MO} (U_{ki}^b x_{kj}^a - U_{kj}^b x_{ki}^a) \\
& - \sum_{kl}^{MO} U_{kl}^a (y_{ijkl}^b - y_{jikl}^b) - \sum_{kl}^{MO} U_{kl}^b (y_{ijkl}^a - y_{jikl}^a) \\
& - \sum_{kmn}^{MO} U_{mn}^b (U_{ki}^a y_{kjmn} - U_{kj}^a y_{kimn}) - \sum_{kmn}^{MO} U_{mn}^a (U_{ki}^b y_{kjmn} - U_{kj}^b y_{kimn}) \\
& - 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\
& \quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\} \\
& - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (x_{ij}^{IJ} - x_{ji}^{IJ}) \\
& - 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial a} \left(\frac{\partial x_{ij}^{IJ}}{\partial b} - \frac{\partial x_{ji}^{IJ}}{\partial b} \right) + \frac{\partial C_J}{\partial b} \left(\frac{\partial x_{ij}^{IJ}}{\partial a} - \frac{\partial x_{ji}^{IJ}}{\partial a} \right) \right\} .
\end{aligned} \tag{14.118}$$

Referring to the rhs of eq. (14.113), the perturbation term for the CI space is given by

$$\begin{aligned}
B_{0,I}^{ab2} & = - \sum_J^{CI} C_J H_{IJ}^{ab} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} x_{ii}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \\
& - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} (U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b}) \\
& - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} .
\end{aligned} \tag{14.119}$$

The solutions to the first-order CPMCHF equations are required in order to construct these second-order CPMCHF equations.

References

1. H.-J. Werner, in *Advances in Chemical Physics : Ab Initio Methods in Quantum Chemistry Part II.*, K.P. Lawley editor, John Wiley & Sons, New York, vol. 69, p.1 (1987).
2. R. Shepard, *ibid.*, p.63 (1987).
3. B.O. Roos, *ibid.*, p.399 (1987).
4. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.

Suggested Reading

1. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 383 (1982).
2. P. Pulay, *J. Chem. Phys.* **78**, 5043 (1983).
3. R.N. Camp, H.F. King, J.W. McIver, Jr., and D. Mullally, *J. Chem. Phys.* **79**, 1088 (1983).
4. M.R. Hoffmann, D.J. Fox, J.F. Gaw, Y. Osamura, Y. Yamaguchi, R.S. Grev, G. Fitzgerald, H.F. Schaefer, P.J. Knowles, and N.C. Handy, *J. Chem. Phys.* **80**, 2660 (1984).
5. M. Page, P. Saxe, G.F. Adams, and B.H. Lengsfeld, *J. Chem. Phys.* **81**, 434 (1984).
6. T.U. Helgaker, J. Almlöf, H. J. Aa. Jensen, and P. Jørgensen, *J. Chem. Phys.* **84**, 6266 (1986).
7. R. Shepard, *Int. J. Quantum Chem.* **31**, 33 (1987).

Chapter 15

Third and Fourth Energy Derivatives for Configuration Interaction Wavefunctions

An energy expression that explicitly includes the orthonormality condition for the configuration interaction (CI) wavefunction is presented in this chapter. First this equation is used to derive the first and second derivatives of the electronic energy. Then the technique is extended to third and fourth derivatives. Such third and fourth derivatives of reliable correlated wavefunctions could add much detail to our knowledge of anharmonic effects in the rotational and vibrational spectra of polyatomic molecules. Anharmonicity is clearly one of the important frontiers of modern physical chemistry and chemical physics. It is demonstrated that these third and fourth derivative expressions are symmetric with respect to the interchange of differential variables (nuclear coordinates). Formulae for the energy derivatives of the CI wavefunction up to fourth-order are presented in full detail to encourage the computational implementation of these methods.

Once the derivative expressions for CI wavefunctions are obtained, it is relatively easy to find the corresponding derivative expressions for other variational wavefunctions, such as multiconfiguration self-consistent-field (MCSCF) and restricted self-consistent-field (SCF), by using the relationships for the density matrices among various types of wavefunctions and imposing constraints on the molecular orbital space. This subject will be discussed in detail in Chapter 16.

15.1 The First and Second Derivatives of the Electronic Energy for a CI Wavefunction

The first and second derivatives of the electronic energy for a CI wavefunction have been described in Chapter 6. In this section a new derivation of these derivatives is presented in order to demonstrate the power of the new method, which will be extended to the higher-order derivatives in the following sections. The electronic energy of the CI wavefunction is usually expressed by [1]

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (15.1)$$

where the CI Hamiltonian matrix is defined by

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (15.2)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl) . \quad (15.3)$$

Q^{IJ} and G^{IJ} are the one- and two-electron coupling constant matrices and they are related to the one- and two-electron reduced density matrices Q and G through [2]

$$Q_{ij} = \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} \quad (15.4)$$

and

$$G_{ijkl} = \sum_{IJ}^{CI} C_I C_J G_{ijkl}^{IJ} . \quad (15.5)$$

Using these quantities the electronic energy of the CI wavefunction is given in MO form by

$$E_{elec} = \sum_{ij}^{MO} Q_{ij} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl) . \quad (15.6)$$

The variational conditions for the determination of the CI wavefunction are

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad (15.7)$$

and the wavefunction is normalized, giving the condition

$$\sum_I^{CI} C_I^2 = 1 . \quad (15.8)$$

While the electronic energy in CI form is usually given by eq. (15.1), the following alternative form will be used in this chapter:

$$\sum_{IJ}^{CI} C_I C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad (15.9)$$

so that the equation explicitly includes the normalization condition (15.8).

The first derivative of the CI electronic energy may be obtained by differentiation of eq. (15.9) with respect to a nuclear coordinate “ a ”:

$$\sum_{IJ}^{CI} C_I C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad . \quad (15.10)$$

The second term of eq. (15.10) vanishes due to the variational conditions (15.7), and thus,

$$\frac{\partial}{\partial a} \left[\sum_{IJ}^{CI} C_I C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \right] = \sum_{IJ}^{CI} C_I C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) = 0 \quad . \quad (15.11)$$

Using the normalization condition, eq. (15.8), an expression for the first derivative of the CI electronic energy is

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad (15.12)$$

which is identical to the result presented in Section 6.2. The first derivative of the Hamiltonian matrix was found in Section 6.4 to be

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \quad . \quad (15.13)$$

The second derivative of the CI electronic energy may be obtained by further differentiation of eq. (15.11) with respect to a second nuclear coordinate “ b ”:

$$\begin{aligned} & \frac{\partial^2}{\partial a \partial b} \left[\sum_{IJ}^{CI} C_I C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \right] \\ &= \frac{\partial}{\partial b} \left[\sum_{IJ}^{CI} C_I C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \right] \end{aligned} \quad (15.14)$$

$$\begin{aligned} &= \sum_{IJ}^{CI} C_I C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \\ &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) = 0 \quad . \end{aligned} \quad (15.15)$$

Note that eq. (15.15) is not symmetric with respect to the differential variables a and b .

The differentiation of the variational condition (15.7) gives relationships between the derivatives of the CI coefficients and those of the Hamiltonian matrix elements

$$\sum_J^{CI} \frac{\partial C_J}{\partial a} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) + \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) = 0 \quad . \quad (15.16)$$

These conditions are equivalent to the first-order coupled perturbed configuration interaction (CPCI) equations which were discussed in Chapter 12. Substituting eq. (15.16) into the second term of eq. (15.15), one obtains

$$\begin{aligned} & \frac{\partial^2}{\partial a \partial b} \left[\sum_{IJ}^{CI} C_I C_J (H_{IJ} - \delta_{IJ} E_{elec}) \right] \\ &= \sum_{IJ}^{CI} C_I C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \\ &\quad - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) = 0 \quad . \end{aligned} \quad (15.17)$$

Using the normalization condition in eq. (15.8), the second derivative becomes

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) \quad (15.18)$$

which is identical to the result given in Section 6.7. The second derivative of the Hamiltonian matrix was found in Section 6.6 as

$$\begin{aligned} \frac{\partial^2 H_{IJ}}{\partial a \partial b} &= H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \\ &\quad + 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJ^a} + U_{ij}^a X_{ij}^{IJ^b} \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} \quad . \end{aligned} \quad (15.19)$$

The “bare” quantities such as X^{IJ} used in the above equations were also explicitly defined in Chapter 6.

At this point the second derivatives of the variational conditions, eq. (15.7), are introduced for future use. They are easily obtained by differentiating eq. (15.16) with respect to a second variable “ b ”:

$$\begin{aligned} & \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} (H_{IJ} - \delta_{IJ} E_{elec}) + \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \\ &+ \sum_J^{CI} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) = 0 \quad . \end{aligned} \quad (15.20)$$

These conditions are equivalent to the second-order CPCI equations described in Chapter 12. The first derivative of the normalization condition, eq. (15.8), is also presented here:

$$\sum_I^{CI} C_I \frac{\partial C_I}{\partial a} = 0 \quad . \quad (15.21)$$

15.2 The Third Derivative of the Electronic Energy for a CI Wavefunction

The third derivative of the electronic energy is obtained by further differentiating eq. (15.17) with respect to a third variable “ c ”:

$$\begin{aligned}
 & \frac{\partial^3}{\partial a \partial b \partial c} \left[\sum_{IJ}^{CI} C_I C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \right] \\
 &= \sum_{IJ}^{CI} C_I C_J \left(\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial c} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \\
 &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \\
 &- 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} \frac{\partial^2 C_J}{\partial b \partial c} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \\
 &- 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} \frac{\partial^2 C_J}{\partial c \partial a} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad .
 \end{aligned} \tag{15.22}$$

Using eq. (15.20), the last two terms in eq. (15.22) may be rewritten as

$$\begin{aligned}
 & - 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} \frac{\partial^2 C_J}{\partial b \partial c} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \\
 & - 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} \frac{\partial^2 C_J}{\partial c \partial a} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \\
 &= 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \left[\sum_J^{CI} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) + \sum_J^{CI} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \right. \\
 & \quad \left. + \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \right] \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \left[\sum_J^{CI} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + \sum_J^{CI} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right. \\
 & \quad \left. + \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial c \partial a} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial a} \right) \right] \\
 &= 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \right]
 \end{aligned} \tag{15.23}$$

$$\begin{aligned}
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right] \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial c \partial a} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial a} \right) \quad . \tag{15.24}
\end{aligned}$$

Inserting eq. (15.24) into eq. (15.22), one obtains

$$\begin{aligned}
& \frac{\partial^3}{\partial a \partial b \partial c} \left[\sum_{IJ}^{CI} C_I C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \right] \\
& = \sum_I^{CI} C_I C_J \left(\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial c \partial a} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial a} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial c} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) = 0 \quad . \tag{15.25}
\end{aligned}$$

The terms including the second derivatives of the CI energy, such as $\delta_{IJ} \partial^2 E_{elec} / \partial a \partial b$, may be eliminated using a condition in eq. (15.21). Thus the final expression for the energy third derivative becomes

$$\begin{aligned}
\frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} & = \sum_{IJ}^{CI} C_I C_J \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H_{IJ}}{\partial b \partial c} + \frac{\partial C_J}{\partial b} \frac{\partial^2 H_{IJ}}{\partial c \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^2 H_{IJ}}{\partial a \partial b} \right) \\
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \right] \quad . \tag{15.26}
\end{aligned}$$

Note that this derivative expression is symmetric with respect to the interchange of differential variables (nuclear coordinates).

15.3 The Fourth Derivative of the Electronic Energy for the CI Wavefunction

The fourth derivative expression arises from differentiating eq. (15.25) with respect to another nuclear coordinate “ d ”:

$$\begin{aligned}
 & \frac{\partial^4}{\partial a \partial b \partial c \partial d} \left[\sum_{IJ}^{CI} C_I C_J (H_{IJ} - \delta_{IJ} E_{elec}) \right] \\
 &= \sum_{IJ}^{CI} C_I C_J \left(\frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} - \delta_{IJ} \frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial d} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial b \partial c \partial d} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial b \partial c \partial d} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial^2 C_I}{\partial a \partial d} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial c \partial a \partial d} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial c \partial a \partial d} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial a} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial a} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial^2 C_I}{\partial b \partial d} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial c \partial a} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial a} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial c} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial d} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial d} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial C_I}{\partial c} \sum_J^{CI} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \\
 &+ 2 \sum_I^{CI} \frac{\partial^2 C_I}{\partial c \partial d} \sum_J^{CI} C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \\
 &+ 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right)
 \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial^2 C_J}{\partial b \partial d} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial^2 C_I}{\partial a \partial d} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial b} \frac{\partial^2 C_J}{\partial c \partial d} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial^2 C_I}{\partial b \partial d} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial c} \frac{\partial^2 C_J}{\partial a \partial d} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \\
& + 2 \sum_{IJ}^{CI} \frac{\partial^2 C_I}{\partial c \partial d} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right)
\end{aligned} \quad . \quad (15.27)$$

Collecting terms in this equation, the expression may be rewritten as

$$\begin{aligned}
& \frac{\partial^4}{\partial a \partial b \partial c \partial d} \left[\sum_{IJ}^{CI} C_I C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \right] \\
& = \sum_{IJ}^{CI} C_I C_J \left(\frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} - \delta_{IJ} \frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial b \partial c \partial d} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial b \partial c \partial d} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial c \partial d \partial a} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial c \partial d \partial a} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial c} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial d \partial a \partial b} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial d \partial a \partial b} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial d} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} \right) \\
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
& + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \\
& + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \\
& + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \Big] \\
& + 2 \sum_I^{CI} \frac{\partial^2 C_I}{\partial c \partial d} \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \right. \\
& \quad \left. + \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \right] \\
& + 2 \sum_I^{CI} \frac{\partial^2 C_I}{\partial b \partial d} \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right. \\
& \quad \left. + \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) + C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \right] \\
& + 2 \sum_I^{CI} \frac{\partial^2 C_I}{\partial a \partial d} \sum_J^{CI} \left[\frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right. \\
& \quad \left. + \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) + C_J \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \right] . \\
\end{aligned} \tag{15.28}$$

Using eq. (15.20), the last three terms are simplified to yield

$$\begin{aligned}
& \frac{\partial^4}{\partial a \partial b \partial c \partial d} \left[\sum_{IJ}^{CI} C_I C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \right] \\
& = \sum_{IJ}^{CI} C_I C_J \left(\frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} - \delta_{IJ} \frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial b \partial c \partial d} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial b \partial c \partial d} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial c \partial d \partial a} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial c \partial d \partial a} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial c} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial d \partial a \partial b} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial d \partial a \partial b} \right) \\
& + 2 \sum_I^{CI} \frac{\partial C_I}{\partial d} \sum_J^{CI} C_J \left(\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} - \delta_{IJ} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} \right)
\end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right) \right. \\
& + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \\
& + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
& + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \\
& + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \\
& \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \right] \\
& - 2 \sum_{IJ}^{CI} \left[\frac{\partial^2 C_I}{\partial a \partial b} \frac{\partial^2 C_J}{\partial c \partial d} + \frac{\partial^2 C_I}{\partial a \partial c} \frac{\partial^2 C_J}{\partial b \partial d} + \frac{\partial^2 C_I}{\partial a \partial d} \frac{\partial^2 C_J}{\partial b \partial c} \right] \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad . \tag{15.29}
\end{aligned}$$

In the sequence of differentiation, each term contains the Hamiltonian matrix and energy in the form of $(H_{IJ} - \delta_{IJ} E_{elec})$ and their derivatives. This structure has the advantage of being able to obtain the higher energy derivatives by differentiating eq. (15.9) instead of eq. (15.1). In eq. (15.29), the terms involving the third derivatives of the CI energy, such as $\delta_{IJ} \partial^3 E_{elec} / \partial a \partial b \partial c$, are eliminated using the derivative of the normalization condition, eq. (15.21). Thus a complete expression for the fourth derivative is

$$\begin{aligned}
\frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} &= \sum_{IJ}^{CI} C_I C_J \frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} \\
&+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial^3 H_{IJ}}{\partial b \partial c \partial d} + \frac{\partial C_J}{\partial b} \frac{\partial^3 H_{IJ}}{\partial c \partial d \partial a} \right. \\
&\quad \left. + \frac{\partial C_J}{\partial c} \frac{\partial^3 H_{IJ}}{\partial d \partial a \partial b} + \frac{\partial C_J}{\partial d} \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \right] \\
&+ 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right) \right. \\
&\quad \left. + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \right. \\
&\quad \left. + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \right. \\
&\quad \left. + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \\
& + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \Big] \\
- 2 \sum_{IJ}^{CI} & \left[\frac{\partial^2 C_I}{\partial a \partial b} \frac{\partial^2 C_J}{\partial c \partial d} + \frac{\partial^2 C_I}{\partial a \partial c} \frac{\partial^2 C_J}{\partial b \partial d} + \frac{\partial^2 C_I}{\partial a \partial d} \frac{\partial^2 C_J}{\partial b \partial c} \right] \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \\
& .
\end{aligned} \tag{15.30}$$

Note that this derivative expression is symmetric with respect to the interchange of differential variables (nuclear coordinates). Several of the terms appearing in eqs. (15.26) and (15.30) have not yet been elaborated and this is the task for the remainder of Chapter 15.

15.4 The Third Derivative of the Hamiltonian Matrix

The third derivative expression for the Hamiltonian matrix appears in eqs. (15.26) and (15.30) in the previous two sections. This third derivative expression comes from differentiating eq. (15.19) with respect to the variable “c”:

$$\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} = \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial^3 h_{ij}}{\partial a \partial b \partial c} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial^3 (ij|kl)}{\partial a \partial b \partial c} \tag{15.31}$$

$$= \frac{\partial}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} \right) \tag{15.32}$$

$$\begin{aligned}
= \frac{\partial}{\partial c} & \left[H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \right. \\
& \left. + 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJ^a} + U_{ij}^a X_{ij}^{IJ^b} \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} \right] \tag{15.33}
\end{aligned}$$

$$\begin{aligned}
= \frac{\partial H_{IJ}^{ab}}{\partial c} & + 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^{ab}}{\partial c} X_{ij}^{IJ} + U_{ij}^{ab} \frac{\partial X_{ij}^{IJ}}{\partial c} \right) \\
& + 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^b}{\partial c} X_{ij}^{IJ^a} + U_{ij}^b \frac{\partial X_{ij}^{IJ^a}}{\partial c} + \frac{\partial U_{ij}^a}{\partial c} X_{ij}^{IJ^b} + U_{ij}^a \frac{\partial X_{ij}^{IJ^b}}{\partial c} \right) \\
& + 2 \sum_{ijkl}^{MO} \left(\frac{\partial U_{ij}^a}{\partial c} U_{kl}^b Y_{ijkl}^{IJ} + U_{ij}^a \frac{\partial U_{kl}^b}{\partial c} Y_{ijkl}^{IJ} + U_{ij}^a U_{kl}^b \frac{\partial Y_{ijkl}^{IJ}}{\partial c} \right) . \tag{15.34}
\end{aligned}$$

The four terms in this equation are now considered separately. The first term in the above equation is manipulated as was done in Section 6.6, to yield

$$\frac{\partial H_{IJ}^{ab}}{\partial c} = \frac{\partial}{\partial c} \left[\sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{ab} \right] \tag{15.35}$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial h_{ij}^{ab}}{\partial c} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial (ij|kl)^{ab}}{\partial c} \quad (15.36)$$

$$= H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^c X_{ij}^{IJab} . \quad (15.37)$$

The skeleton (core) third derivative Hamiltonian matrices H_{IJ}^{abc} and the skeleton (core) second derivative “bare” Lagrangian matrices X^{IJab} are defined by

$$H_{IJ}^{abc} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{abc} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{abc} \quad (15.38)$$

and

$$X_{ij}^{IJab} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^{ab} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (im|kl)^{ab} . \quad (15.39)$$

The skeleton (core) second derivative Lagrangian and the derivative “bare” Lagrangian matrices are related by

$$X_{ij}^{ab} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJab} . \quad (15.40)$$

Using the results in Sections 3.3 and 6.5, the second term in eq. (15.34) may be rewritten as

$$\begin{aligned} & 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^{ab}}{\partial c} X_{ij}^{IJ} + U_{ij}^{ab} \frac{\partial X_{ij}^{IJ}}{\partial c} \right) \\ &= 2 \sum_{ij}^{MO} \left(U_{ij}^{abc} - \sum_k^{MO} U_{ik}^c U_{kj}^{ab} \right) X_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^{ab} \left(X_{ij}^{IJc} + \sum_k^{MO} U_{ki}^c X_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^c Y_{ijkl}^{IJ} \right) \end{aligned} \quad (15.41)$$

$$\begin{aligned} &= 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ} - 2 \sum_{ijk}^{MO} U_{ik}^c U_{kj}^{ab} X_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJc} + 2 \sum_{ijk}^{MO} U_{ij}^{ab} U_{ki}^c X_{kj}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^{ab} U_{kl}^c Y_{ijkl}^{IJ} \end{aligned} \quad (15.42)$$

$$= 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJc} + 2 \sum_{ijkl}^{MO} U_{ij}^{ab} U_{kl}^c Y_{ijkl}^{IJ} . \quad (15.43)$$

The third term in eq. (15.34) is manipulated to give

$$2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^b}{\partial c} X_{ij}^{IJa} + U_{ij}^b \frac{\partial X_{ij}^{IJa}}{\partial c} + \frac{\partial U_{ij}^a}{\partial c} X_{ij}^{IJb} + U_{ij}^a \frac{\partial X_{ij}^{IJb}}{\partial c} \right)$$

$$\begin{aligned}
&= 2 \sum_{ij}^{MO} \left[\left(U_{ij}^{bc} - \sum_k^{MO} U_{ik}^c U_{kj}^b \right) X_{ij}^{IJ^a} \right. \\
&\quad + U_{ij}^b \left(X_{ij}^{IJ^{ac}} + \sum_k^{MO} U_{ki}^c X_{kj}^{IJ^a} + \sum_{kl}^{MO} U_{kl}^c Y_{ijkl}^{IJ^a} \right) \\
&\quad + \left(U_{ij}^{ac} - \sum_k^{MO} U_{ik}^c U_{kj}^a \right) X_{ij}^{IJ^b} \\
&\quad \left. + U_{ij}^a \left(X_{ij}^{IJ^{bc}} + \sum_k^{MO} U_{ki}^c X_{kj}^{IJ^b} + \sum_{kl}^{MO} U_{kl}^c Y_{ijkl}^{IJ^b} \right) \right] \quad (15.44)
\end{aligned}$$

$$\begin{aligned}
&= 2 \sum_{ij}^{MO} U_{ij}^{bc} X_{ij}^{IJ^a} - 2 \sum_{ijk}^{MO} U_{ik}^c U_{kj}^b X_{ij}^{IJ^a} \\
&\quad + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJ^{ac}} + 2 \sum_{ijk}^{MO} U_{ij}^b U_{ki}^c X_{kj}^{IJ^a} + 2 \sum_{ijkl}^{MO} U_{ij}^b U_{kl}^c Y_{ijkl}^{IJ^a} \\
&\quad + 2 \sum_{ij}^{MO} U_{ij}^{ac} X_{ij}^{IJ^b} - 2 \sum_{ijk}^{MO} U_{ik}^c U_{kj}^a X_{ij}^{IJ^b} \\
&\quad + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ^{bc}} + 2 \sum_{ijk}^{MO} U_{ij}^a U_{ki}^c X_{kj}^{IJ^b} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^c Y_{ijkl}^{IJ^b} \quad (15.45)
\end{aligned}$$

$$\begin{aligned}
&= 2 \sum_{ij}^{MO} U_{ij}^{bc} X_{ij}^{IJ^a} + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJ^{ac}} + 2 \sum_{ijkl}^{MO} U_{ij}^b U_{kl}^c Y_{ijkl}^{IJ^a} \\
&\quad + 2 \sum_{ij}^{MO} U_{ij}^{ac} X_{ij}^{IJ^b} + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ^{bc}} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^c Y_{ijkl}^{IJ^b} \quad . \quad (15.46)
\end{aligned}$$

Using the results in Sections 3.3 and 14.3, the last term in eq. (15.34) is rearranged to yield

$$\begin{aligned}
&2 \sum_{ijkl}^{MO} \left(\frac{\partial U_{ij}^a}{\partial c} U_{kl}^b Y_{ijkl}^{IJ} + U_{ij}^a \frac{\partial U_{kl}^b}{\partial c} Y_{ijkl}^{IJ} + U_{ij}^a U_{kl}^b \frac{\partial Y_{ijkl}^{IJ}}{\partial c} \right) \\
&= 2 \sum_{ijkl}^{MO} \left[\left(U_{ij}^{ac} - \sum_m^{MO} U_{im}^c U_{mj}^a \right) U_{kl}^b Y_{ijkl}^{IJ} \right. \\
&\quad + U_{ij}^a \left(U_{kl}^{bc} - \sum_m^{MO} U_{km}^c U_{ml}^b \right) Y_{ijkl}^{IJ} \\
&\quad + U_{ij}^a U_{kl}^b \left(Y_{ijkl}^{IJ^c} + \sum_p^{MO} U_{pi}^c Y_{pjkl}^{IJ} + \sum_{\hat{p}}^{MO} U_{pk}^c Y_{ijpl}^{IJ} \right. \\
&\quad \left. \left. + 4 \sum_{mnp}^{MO} U_{pm}^c \left\{ G_{jlmn}^{IJ}(ik|pn) + G_{jmkn}^{IJ}(ip|kn) + G_{jnkm}^{IJ}(in|kp) \right\} \right) \right] \quad (15.47)
\end{aligned}$$

$$\begin{aligned}
&= 2 \sum_{ijkl}^{MO} U_{ij}^{ac} U_{kl}^b Y_{ijkl}^{IJ} - 2 \sum_{ijklm}^{MO} U_{im}^c U_{mj}^a U_{kl}^b Y_{ijkl}^{IJ} \\
&+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^{bc} Y_{ijkl}^{IJ} - 2 \sum_{ijklm}^{MO} U_{ij}^a U_{km}^c U_{ml}^b Y_{ijkl}^{IJ} \\
&+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJc} + 2 \sum_{ijklp}^{MO} U_{ij}^a U_{kl}^b U_{pi}^c Y_{pjkl}^{IJ} + 2 \sum_{ijklp}^{MO} U_{ij}^a U_{kl}^b U_{pk}^c Y_{ijpl}^{IJ} \\
&+ 8 \sum_{ijklmnp}^{MO} U_{ij}^a U_{kl}^b U_{pm}^c \left\{ G_{jlmn}^{IJ}(ik|pn) + G_{jmln}^{IJ}(ip|kn) + G_{jnlm}^{IJ}(in|kp) \right\} \\
\end{aligned} \tag{15.48}$$

$$\begin{aligned}
&= 2 \sum_{ijkl}^{MO} U_{ij}^{ac} U_{kl}^b Y_{ijkl}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^{bc} Y_{ijkl}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJc} \\
&+ 8 \sum_{ijklmnp}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \left\{ G_{jlnp}^{IJ}(ik|mp) + G_{jnlp}^{IJ}(im|kp) + G_{jpln}^{IJ}(ip|km) \right\} \\
\end{aligned} \tag{15.49}$$

$$\begin{aligned}
&= 2 \sum_{ijkl}^{MO} U_{ij}^{ac} U_{kl}^b Y_{ijkl}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^{bc} Y_{ijkl}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJc} \\
&+ 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJ} .
\end{aligned} \tag{15.50}$$

The “bare” Z matrices Z^{IJ} introduced in this equation are defined by

$$Z_{ijklmn}^{IJ} = 4 \sum_p^{MO} \left\{ G_{jlnp}^{IJ}(ik|mp) + G_{jnlp}^{IJ}(im|kp) + G_{jpln}^{IJ}(ip|km) \right\} \tag{15.51}$$

and are related to their “parents” by

$$Z_{ijklmn} = \sum_{IJ}^{CI} C_I C_J Z_{ijklmn}^{IJ} \tag{15.52}$$

$$= 4 \sum_p^{MO} \left\{ G_{jlnp}^{IJ}(ik|mp) + G_{jnlp}^{IJ}(im|kp) + G_{jpln}^{IJ}(ip|km) \right\} . \tag{15.53}$$

Thus, the last term of eq. (15.50) may be rewritten as

$$\begin{aligned}
&2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJ} \\
&= 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} G_{jlnp}^{IJ}(ik|mp) \\
\end{aligned} \tag{15.54}$$

Combining eqs. (15.37), (15.43), (15.46) and (15.50), the following third derivative expression is obtained:

$$\begin{aligned}
 \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} = & H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^c X_{ij}^{IJab} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJc} + 2 \sum_{ijkl}^{MO} U_{ij}^{ab} U_{kl}^c Y_{ijkl}^{IJ} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{bc} X_{ij}^{IJ^a} + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJ^{ac}} + 2 \sum_{ijkl}^{MO} U_{ij}^b U_{kl}^c Y_{ijkl}^{IJ^a} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{ac} X_{ij}^{IJ^b} + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ^{bc}} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^c Y_{ijkl}^{IJ^b} \\
 & + 2 \sum_{ijkl}^{MO} U_{ij}^{ac} U_{kl}^b Y_{ijkl}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^{bc} Y_{ijkl}^{IJ} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ^c} \\
 & + 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJ} .
 \end{aligned} \tag{15.55}$$

This expression is rewritten in a simpler final form as

$$\begin{aligned}
 \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} = & H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ} \\
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{IJ^c} + U_{ij}^{bc} X_{ij}^{IJ^a} + U_{ij}^{ca} X_{ij}^{IJ^b} \right) \\
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{IJ^{bc}} + U_{ij}^b X_{ij}^{IJ^{ca}} + U_{ij}^c X_{ij}^{IJ^{ab}} \right) \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJ} \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ^c} + U_{ij}^b U_{kl}^c Y_{ijkl}^{IJ^a} + U_{ij}^c U_{kl}^a Y_{ijkl}^{IJ^b} \right) \\
 & + 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} G_{jlnp}^{IJ}(ik|mp)
 \end{aligned} \tag{15.56}$$

Note that interchange of the i, j, k, l, m, n , and p indices does not alter the equation as the summations run over all molecular orbitals.

15.5 An Explicit Expression for the Third Derivative of the Electronic Energy

An explicit expression for the third derivative of the electronic energy is provided by combining eq. (15.26) for the energy third derivative and eq. (15.56) for the Hamiltonian third derivative:

$$\begin{aligned}
 \frac{\partial^3 E}{\partial a \partial b \partial c} = & \sum_{ij}^{MO} Q_{ij} h_{ij}^{abc} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{abc} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij} \\
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^c + U_{ij}^{bc} X_{ij}^a + U_{ij}^{ca} X_{ij}^b \right) \\
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{bc} + U_{ij}^b X_{ij}^{ca} + U_{ij}^c X_{ij}^{ab} \right) \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl} \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^c + U_{ij}^b U_{kl}^c Y_{ijkl}^a + U_{ij}^c U_{kl}^a Y_{ijkl}^b \right) \\
 & + 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} G_{jlnp}(ik|mp) \\
 & + 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H_{IJ}}{\partial b \partial c} + \frac{\partial C_J}{\partial b} \frac{\partial^2 H_{IJ}}{\partial c \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^2 H_{IJ}}{\partial a \partial b} \right) \\
 & + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right. \\
 & \quad \left. + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \right. \\
 & \quad \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \right] . \tag{15.57}
 \end{aligned}$$

The first and second derivatives of the Hamiltonian matrices in this equation were defined explicitly by eqs. (15.13) and (15.19). The skeleton (core) derivative Lagrangian and Y matrices are

$$X_{ij}^a = \sum_m^{MO} Q_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^a , \tag{15.58}$$

$$X_{ij}^{ab} = \sum_m^{MO} Q_{jm} h_{im}^{ab} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^{ab} , \tag{15.59}$$

and

$$Y_{ijkl}^a = Q_{jil} h_{ik}^a + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn)^a + 4 \sum_{mn}^{MO} G_{jmkn}(im|kn)^a . \quad (15.60)$$

15.6 The First Derivative Expression for the “Bare” Z Matrix

It is convenient to find the first derivative expression for the “bare” Z matrix before proceeding to the section on fourth derivatives. This derivative is obtained by differentiating eq. (15.51) with respect to a variable “ a ”:

$$\frac{\partial Z_{ijklmn}^{IJ}}{\partial a} = 4 \sum_p^{MO} \frac{\partial}{\partial a} \left(G_{jlnp}^{IJ}(ik|mp) + G_{jnlp}^{IJ}(im|kp) + G_{jpln}^{IJ}(ip|km) \right) \quad (15.61)$$

$$= 4 \sum_p^{MO} \left(G_{jlnp}^{IJ} \frac{\partial(ik|mp)}{\partial a} + G_{jnlp}^{IJ} \frac{\partial(im|kp)}{\partial a} + G_{jpln}^{IJ} \frac{\partial(ip|km)}{\partial a} \right) \quad (15.62)$$

$$\begin{aligned} &= 4 \sum_p^{MO} G_{jlnp}^{IJ} \left[(ik|mp)^a + \sum_r^{MO} \left\{ U_{ri}^a(rk|mp) + U_{rk}^a(ir|mp) \right. \right. \\ &\quad \left. \left. + U_{rm}^a(ik|rp) + U_{rp}^a(ik|mr) \right\} \right] \\ &+ 4 \sum_p^{MO} G_{jnlp}^{IJ} \left[(im|kp)^a + \sum_r^{MO} \left\{ U_{ri}^a(rm|kp) + U_{rm}^a(ir|kp) \right. \right. \\ &\quad \left. \left. + U_{rk}^a(im|rp) + U_{rp}^a(im|kr) \right\} \right] \\ &+ 4 \sum_p^{MO} G_{jpln}^{IJ} \left[(ip|km)^a + \sum_r^{MO} \left\{ U_{ri}^a(rp|km) + U_{rp}^a(ir|km) \right. \right. \\ &\quad \left. \left. + U_{rk}^a(ip|rm) + U_{rm}^a(ip|kr) \right\} \right] \end{aligned} \quad (15.63)$$

$$\begin{aligned} &= 4 \sum_p^{MO} \left(G_{jlnp}^{IJ}(ik|mp)^a + G_{jnlp}^{IJ}(im|kp)^a + G_{jpln}^{IJ}(ip|km)^a \right) \\ &+ 4 \sum_{pr}^{MO} U_{ri}^a \left\{ G_{jlnp}^{IJ}(rk|mp) + G_{jnlp}^{IJ}(rm|kp) + G_{jpln}^{IJ}(rp|km) \right\} \\ &+ 4 \sum_{pr}^{MO} U_{rk}^a \left\{ G_{jlnp}^{IJ}(ir|mp) + G_{jnlp}^{IJ}(im|rp) + G_{jpln}^{IJ}(ip|rm) \right\} \\ &+ 4 \sum_{pr}^{MO} U_{rm}^a \left\{ G_{jlnp}^{IJ}(ik|rp) + G_{jnlp}^{IJ}(ir|kp) + G_{jpln}^{IJ}(ip|kr) \right\} \end{aligned}$$

$$+ 4 \sum_{pr}^{MO} U_{rp}^a \left\{ G_{jlnp}^{IJ}(ik|mr) + G_{jnlp}^{IJ}(im|kr) + G_{jpln}^{IJ}(ir|km) \right\} . \quad (15.64)$$

The skeleton (core) first derivative “bare” Z matrices are defined by

$$Z_{ijklmn}^{IJ^a} = 4 \sum_p^{MO} \left\{ G_{jlnp}^{IJ}(ik|mp)^a + G_{jnlp}^{IJ}(im|kp)^a + G_{jpln}^{IJ}(ip|km)^a \right\} . \quad (15.65)$$

Using this definition, the following considerably more compact expression is possible:

$$\begin{aligned} \frac{\partial Z_{ijklmn}^{IJ}}{\partial a} &= Z_{ijklmn}^{IJ^a} \\ &+ \sum_r^{MO} \left(U_{ri}^a Z_{rjklmn}^{IJ} + U_{rk}^a Z_{ijrlmn}^{IJ} + U_{rm}^a Z_{ijklrn}^{IJ} \right) \\ &+ 4 \sum_{pr}^{MO} U_{rp}^a \left\{ G_{jlnp}^{IJ}(ik|mr) + G_{jnlp}^{IJ}(im|kr) + G_{jpln}^{IJ}(ir|km) \right\} . \end{aligned} \quad (15.66)$$

15.7 The Fourth Derivative of the Hamiltonian Matrix

The fourth derivative expression for the Hamiltonian matrix is critical for obtaining CI energy fourth derivatives and follows from differentiating either eq. (15.55) or eq. (15.56) with respect to the variable “ d ”:

$$\frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} = \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial^4 h_{ij}}{\partial a \partial b \partial c \partial d} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial^4 (ij|kl)}{\partial a \partial b \partial c \partial d} \quad (15.67)$$

$$= \frac{\partial}{\partial d} \left(\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \right) \quad (15.68)$$

$$\begin{aligned} &= \frac{\partial}{\partial d} \left[H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ} \right. \\ &\quad \left. + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{IJ^c} + U_{ij}^{bc} X_{ij}^{IJ^a} + U_{ij}^{ca} X_{ij}^{IJ^b} \right) \right. \\ &\quad \left. + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{IJ^{bc}} + U_{ij}^b X_{ij}^{IJ^{ca}} + U_{ij}^c X_{ij}^{IJ^{ab}} \right) \right. \\ &\quad \left. + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJ} \right] \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{IJc} + U_{ij}^b U_{kl}^c Y_{ijkl}^{IJa} + U_{ij}^c U_{kl}^a Y_{ijkl}^{IJb} \right) \\
& + 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJ} \quad (15.69) \\
= & \frac{\partial H_{IJ}^{abc}}{\partial d} + 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^{abc}}{\partial d} X_{ij}^{IJ} + U_{ij}^{abc} \frac{\partial X_{ij}^{IJ}}{\partial d} \right) \\
+ & 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^{ab}}{\partial d} X_{ij}^{IJc} + U_{ij}^{ab} \frac{\partial X_{ij}^{IJc}}{\partial d} + \frac{\partial U_{ij}^{bc}}{\partial d} X_{ij}^{IJa} + U_{ij}^{bc} \frac{\partial X_{ij}^{IJa}}{\partial d} \right. \\
& \left. + \frac{\partial U_{ij}^{ca}}{\partial d} X_{ij}^{IJb} + U_{ij}^{ca} \frac{\partial X_{ij}^{IJb}}{\partial d} \right) \\
+ & 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^a}{\partial d} X_{ij}^{IJbc} + U_{ij}^a \frac{\partial X_{ij}^{IJbc}}{\partial d} + \frac{\partial U_{ij}^b}{\partial d} X_{ij}^{IJca} + U_{ij}^b \frac{\partial X_{ij}^{IJca}}{\partial d} \right. \\
& \left. + \frac{\partial U_{ij}^c}{\partial d} X_{ij}^{IJab} + U_{ij}^c \frac{\partial X_{ij}^{IJab}}{\partial d} \right) \\
+ & 2 \sum_{ijkl}^{MO} \left(\frac{\partial U_{ij}^{ab}}{\partial d} U_{kl}^c + U_{ij}^{ab} \frac{\partial U_{kl}^c}{\partial d} + \frac{\partial U_{ij}^{bc}}{\partial d} U_{kl}^a + U_{ij}^{bc} \frac{\partial U_{kl}^a}{\partial d} \right. \\
& \left. + \frac{\partial U_{ij}^{ca}}{\partial d} U_{kl}^b + U_{ij}^{ca} \frac{\partial U_{kl}^b}{\partial d} \right) Y_{ijkl}^{IJ} \\
+ & 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) \frac{\partial Y_{ijkl}^{IJ}}{\partial d} \\
+ & 2 \sum_{ijkl}^{MO} \left(\frac{\partial U_{ij}^a}{\partial d} U_{kl}^b Y_{ijkl}^{IJc} + U_{ij}^a \frac{\partial U_{kl}^b}{\partial d} Y_{ijkl}^{IJc} + U_{ij}^a U_{kl}^b \frac{\partial Y_{ijkl}^{IJc}}{\partial d} \right. \\
& \left. + \frac{\partial U_{ij}^b}{\partial d} U_{kl}^c Y_{ijkl}^{IJa} + U_{ij}^b \frac{\partial U_{kl}^c}{\partial d} Y_{ijkl}^{IJa} + U_{ij}^b U_{kl}^c \frac{\partial Y_{ijkl}^{IJa}}{\partial d} \right. \\
& \left. + \frac{\partial U_{ij}^c}{\partial d} U_{kl}^a Y_{ijkl}^{IJb} + U_{ij}^c \frac{\partial U_{kl}^a}{\partial d} Y_{ijkl}^{IJb} + U_{ij}^c U_{kl}^a \frac{\partial Y_{ijkl}^{IJb}}{\partial d} \right) \\
+ & 2 \sum_{ijklmn}^{MO} \left(\frac{\partial U_{ij}^a}{\partial d} U_{kl}^b U_{mn}^c + U_{ij}^a \frac{\partial U_{kl}^b}{\partial d} U_{mn}^c + U_{ij}^a U_{kl}^b \frac{\partial U_{mn}^c}{\partial d} \right) Z_{ijklmn}^{IJ} \\
+ & 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \frac{\partial Z_{ijklmn}^{IJ}}{\partial d} \quad . \quad (15.70)
\end{aligned}$$

Each of the nine terms in eq. (15.70) will be rewritten separately and then reassembled into the final full equation for the fourth derivative. The first term in this equation is treated

in a manner similar to that used in Section 6.6:

$$\frac{\partial H_{IJ}^{abc}}{\partial d} = \frac{\partial}{\partial d} \left[\sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{abc} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{abc} \right] \quad (15.71)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} \frac{\partial h_{ij}^{abc}}{\partial d} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} \frac{\partial (ij|kl)^{abc}}{\partial d} \quad (15.72)$$

$$= H_{IJ}^{abcd} + 2 \sum_{ij}^{MO} U_{ij}^d X_{ij}^{IJ^{abc}} . \quad (15.73)$$

The skeleton (core) fourth derivative Hamiltonian matrices H_{IJ}^{abcd} are

$$H_{IJ}^{abcd} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{abcd} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{abcd} \quad (15.74)$$

and the skeleton (core) third derivative “bare” Lagrangian matrices are

$$X_{ij}^{IJ^{abc}} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^{abc} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (im|kl)^{abc} . \quad (15.75)$$

The skeleton (core) third derivative Lagrangian and derivative “bare” Lagrangian matrices are connected by

$$X_{ij}^{abc} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ^{abc}} . \quad (15.76)$$

The second term of eq. (15.70) is rearranged to

$$\begin{aligned} & 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^{abc}}{\partial d} X_{ij}^{IJ} + U_{ij}^{abc} \frac{\partial X_{ij}^{IJ}}{\partial d} \right) \\ &= 2 \sum_{ij}^{MO} \left(U_{ij}^{abcd} - \sum_k^{MO} U_{ik}^d U_{kj}^{abc} \right) X_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^{abc} \left(X_{ij}^{IJ^d} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ} \right) \end{aligned} \quad (15.77)$$

$$= 2 \sum_{ij}^{MO} U_{ij}^{abcd} X_{ij}^{IJ} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ^d} + 2 \sum_{ijkl}^{MO} U_{ij}^{abc} U_{kl}^d Y_{ijkl}^{IJ} . \quad (15.78)$$

The third term of eq. (15.70) may be treated as

$$\begin{aligned} & 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^{ab}}{\partial d} X_{ij}^{IJ^c} + U_{ij}^{ab} \frac{\partial X_{ij}^{IJ^c}}{\partial d} + \frac{\partial U_{ij}^{bc}}{\partial d} X_{ij}^{IJ^a} + U_{ij}^{bc} \frac{\partial X_{ij}^{IJ^a}}{\partial d} \right. \\ & \quad \left. + \frac{\partial U_{ij}^{ca}}{\partial d} X_{ij}^{IJ^b} + U_{ij}^{ca} \frac{\partial X_{ij}^{IJ^b}}{\partial d} \right) \end{aligned}$$

$$\begin{aligned}
&= 2 \sum_{ij}^{MO} \left[\left(U_{ij}^{abd} - \sum_k^{MO} U_{ik}^d U_{kj}^{ab} \right) X_{ij}^{IJ^c} \right. \\
&\quad + U_{ij}^{ab} \left(X_{ij}^{IJ^{cd}} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ^c} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ^c} \right) \\
&\quad + \left(U_{ij}^{bcd} - \sum_k^{MO} U_{ik}^d U_{kj}^{bc} \right) X_{ij}^{IJ^a} \\
&\quad + U_{ij}^{bc} \left(X_{ij}^{IJ^{ad}} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ^a} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ^a} \right) \\
&\quad + \left(U_{ij}^{cad} - \sum_k^{MO} U_{ik}^d U_{kj}^{ca} \right) X_{ij}^{IJ^b} \\
&\quad \left. + U_{ij}^{ca} \left(X_{ij}^{IJ^{bd}} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ^b} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ^b} \right) \right] \tag{15.79}
\end{aligned}$$

$$\begin{aligned}
&= 2 \sum_{ij}^{MO} U_{ij}^{abd} X_{ij}^{IJ^c} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ^{cd}} + 2 \sum_{ijkl}^{MO} U_{ij}^{ab} U_{kl}^d Y_{ijkl}^{IJ^c} \\
&\quad + 2 \sum_{ij}^{MO} U_{ij}^{bcd} X_{ij}^{IJ^a} + 2 \sum_{ij}^{MO} U_{ij}^{bc} X_{ij}^{IJ^{ad}} + 2 \sum_{ijkl}^{MO} U_{ij}^{bc} U_{kl}^d Y_{ijkl}^{IJ^a} \\
&\quad + 2 \sum_{ij}^{MO} U_{ij}^{cad} X_{ij}^{IJ^b} + 2 \sum_{ij}^{MO} U_{ij}^{ca} X_{ij}^{IJ^{bd}} + 2 \sum_{ijkl}^{MO} U_{ij}^{ca} U_{kl}^d Y_{ijkl}^{IJ^b} \quad . \tag{15.80}
\end{aligned}$$

The fourth term of eq. (15.70) may be manipulated as

$$\begin{aligned}
&2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^a}{\partial d} X_{ij}^{IJ^{bc}} + U_{ij}^a \frac{\partial X_{ij}^{IJ^{bc}}}{\partial d} + \frac{\partial U_{ij}^b}{\partial d} X_{ij}^{IJ^{ca}} + U_{ij}^b \frac{\partial X_{ij}^{IJ^{ca}}}{\partial d} \right. \\
&\quad \left. + \frac{\partial U_{ij}^c}{\partial d} X_{ij}^{IJ^{ab}} + U_{ij}^c \frac{\partial X_{ij}^{IJ^{ab}}}{\partial d} \right) \\
&= 2 \sum_{ij}^{MO} \left[\left(U_{ij}^{ad} - \sum_k^{MO} U_{ik}^d U_{kj}^a \right) X_{ij}^{IJ^{bc}} \right. \\
&\quad + U_{ij}^a \left(X_{ij}^{IJ^{bcd}} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ^{bc}} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ^{bc}} \right) \\
&\quad + \left(U_{ij}^{bd} - \sum_k^{MO} U_{ik}^d U_{kj}^b \right) X_{ij}^{IJ^{ca}} \\
&\quad \left. + U_{ij}^b \left(X_{ij}^{IJ^{cad}} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ^{ca}} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ^{ca}} \right) \right]
\end{aligned}$$

$$\begin{aligned}
& + \left(U_{ij}^{cd} - \sum_k^{MO} U_{ik}^d U_{kj}^c \right) X_{ij}^{IJ^{ab}} \\
& + U_{ij}^c \left(X_{ij}^{IJ^{abd}} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ^{ab}} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ^{ab}} \right) \Big] \quad (15.81) \\
= & 2 \sum_{ij}^{MO} U_{ij}^{ad} X_{ij}^{IJ^{bc}} + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ^{bcd}} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^d Y_{ijkl}^{IJ^{bc}} \\
+ & 2 \sum_{ij}^{MO} U_{ij}^{bd} X_{ij}^{IJ^{ca}} + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJ^{cad}} + 2 \sum_{ijkl}^{MO} U_{ij}^b U_{kl}^d Y_{ijkl}^{IJ^{ca}} \\
+ & 2 \sum_{ij}^{MO} U_{ij}^{cd} X_{ij}^{IJ^{ab}} + 2 \sum_{ij}^{MO} U_{ij}^c X_{ij}^{IJ^{abd}} + 2 \sum_{ijkl}^{MO} U_{ij}^c U_{kl}^d Y_{ijkl}^{IJ^{ab}} \quad . \quad (15.82)
\end{aligned}$$

The fifth term of eq. (15.70) is treated as

$$\begin{aligned}
& 2 \sum_{ijkl}^{MO} \left(\frac{\partial U_{ij}^{ab}}{\partial d} U_{kl}^c + U_{ij}^{ab} \frac{\partial U_{kl}^c}{\partial d} + \frac{\partial U_{ij}^{bc}}{\partial d} U_{kl}^a + U_{ij}^{bc} \frac{\partial U_{kl}^a}{\partial d} \right. \\
& \quad \left. + \frac{\partial U_{ij}^{ca}}{\partial d} U_{kl}^b + U_{ij}^{ca} \frac{\partial U_{kl}^b}{\partial d} \right) Y_{ijkl}^{IJ} \\
= & 2 \sum_{ijkl}^{MO} \left[\left(U_{ij}^{abd} - \sum_m^{MO} U_{im}^d U_{mj}^{ab} \right) U_{kl}^c + U_{ij}^{ab} \left(U_{kl}^{cd} - \sum_m^{MO} U_{km}^d U_{ml}^c \right) \right. \\
& \quad + \left(U_{ij}^{bcd} - \sum_m^{MO} U_{im}^d U_{mj}^{bc} \right) U_{kl}^a + U_{ij}^{bc} \left(U_{kl}^{ad} - \sum_m^{MO} U_{km}^d U_{ml}^a \right) \\
& \quad \left. + \left(U_{ij}^{cad} - \sum_m^{MO} U_{im}^d U_{mj}^{ca} \right) U_{kl}^b + U_{ij}^{ca} \left(U_{kl}^{bd} - \sum_m^{MO} U_{km}^d U_{ml}^b \right) \right] Y_{ijkl}^{IJ} \tag{15.83} \\
= & 2 \sum_{ijkl}^{MO} \left(U_{ij}^{abd} U_{kl}^c - \sum_m^{MO} U_{im}^d U_{mj}^{ab} U_{kl}^c + U_{ij}^{ab} U_{kl}^{cd} - \sum_m^{MO} U_{ij}^{ab} U_{km}^d U_{ml}^c \right. \\
& \quad + U_{ij}^{bcd} U_{kl}^a - \sum_m^{MO} U_{im}^d U_{mj}^{bc} U_{kl}^a + U_{ij}^{bc} U_{kl}^{ad} - \sum_m^{MO} U_{ij}^{bc} U_{km}^d U_{ml}^a \\
& \quad \left. + U_{ij}^{cad} U_{kl}^b - \sum_m^{MO} U_{im}^d U_{mj}^{ca} U_{kl}^b + U_{ij}^{ca} U_{kl}^{bd} - \sum_m^{MO} U_{ij}^{ca} U_{km}^d U_{ml}^b \right) Y_{ijkl}^{IJ} \tag{15.84}
\end{aligned}$$

$$= 2 \sum_{ijkl}^{MO} \left(U_{ij}^{abd} U_{kl}^c + U_{ij}^{bcd} U_{kl}^a + U_{ij}^{cad} U_{kl}^b \right) Y_{ijkl}^{IJ} \\ + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{bc} U_{kl}^{ad} + U_{ij}^{ca} U_{kl}^{bd} \right) Y_{ijkl}^{IJ}$$

$$\begin{aligned}
& - 2 \sum_{ijklm}^{MO} \left(U_{im}^d U_{mj}^{ab} U_{kl}^c + U_{ij}^{ab} U_{km}^d U_{ml}^c + U_{im}^d U_{mj}^{bc} U_{kl}^a + U_{ij}^{bc} U_{km}^d U_{ml}^a \right. \\
& \quad \left. + U_{im}^d U_{mj}^{ca} U_{kl}^b + U_{ij}^{ca} U_{km}^d U_{ml}^b \right) Y_{ijkl}^{IJ} \quad .
\end{aligned} \tag{15.85}$$

Using the result in Section 14.3 the sixth term of eq. (15.70) may be handled as

$$\begin{aligned}
& 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) \frac{\partial Y_{ijkl}^{IJ}}{\partial d} \\
& = 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) \left[Y_{ijkl}^{IJd} + \sum_p^{MO} \left(U_{pi}^d Y_{pjkl}^{IJ} + U_{pk}^d Y_{ijpl}^{IJ} \right) \right. \\
& \quad \left. + 4 \sum_{mnp}^{MO} U_{pm}^d \left\{ G_{jlmn}^{IJ}(ik|pn) + G_{jmtn}^{IJ}(ip|kn) + G_{jnlm}^{IJ}(in|kp) \right\} \right] \quad (15.86)
\end{aligned}$$

$$\begin{aligned}
& = 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJd} \\
& + 2 \sum_{ijklp}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{pi}^d + U_{ij}^{bc} U_{kl}^a U_{pi}^d + U_{ij}^{ca} U_{kl}^b U_{pi}^d \right) Y_{pjkl}^{IJ} \\
& + 2 \sum_{ijklp}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{pk}^d + U_{ij}^{bc} U_{kl}^a U_{pk}^d + U_{ij}^{ca} U_{kl}^b U_{pk}^d \right) Y_{ijpl}^{IJ} \\
& + 8 \sum_{ijklmnp}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{pm}^d + U_{ij}^{bc} U_{kl}^a U_{pm}^d + U_{ij}^{ca} U_{kl}^b U_{pm}^d \right) \\
& \quad \times \left\{ G_{jlmn}^{IJ}(ik|pn) + G_{jmtn}^{IJ}(ip|kn) + G_{jnlm}^{IJ}(in|kp) \right\} \quad (15.87)
\end{aligned}$$

$$\begin{aligned}
& = 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJd} \\
& + 2 \sum_{ijklp}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{pi}^d + U_{ij}^{bc} U_{kl}^a U_{pi}^d + U_{ij}^{ca} U_{kl}^b U_{pi}^d \right) Y_{pjkl}^{IJ} \\
& + 2 \sum_{ijklp}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{pk}^d + U_{ij}^{bc} U_{kl}^a U_{pk}^d + U_{ij}^{ca} U_{kl}^b U_{pk}^d \right) Y_{ijpl}^{IJ} \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{mn}^d + U_{ij}^{bc} U_{kl}^a U_{mn}^d + U_{ij}^{ca} U_{kl}^b U_{mn}^d \right) Z_{ijklmn}^{IJ} \quad .
\end{aligned} \tag{15.88}$$

The seventh term of eq. (15.70) may be processed as

$$2 \sum_{ijkl}^{MO} \left[\frac{\partial U_{ij}^a}{\partial d} U_{kl}^b Y_{ijkl}^{IJc} + U_{ij}^a \frac{\partial U_{kl}^b}{\partial d} Y_{ijkl}^{IJc} + U_{ij}^a U_{kl}^b \frac{\partial Y_{ijkl}^{IJc}}{\partial d} \right]$$

$$\begin{aligned}
& + \frac{\partial U_{ij}^b}{\partial d} U_{kl}^c Y_{ijkl}^{IJ^a} + U_{ij}^b \frac{\partial U_{kl}^c}{\partial d} Y_{ijkl}^{IJ^a} + U_{ij}^b U_{kl}^c \frac{\partial Y_{ijkl}^{IJ^a}}{\partial d} \\
& + \frac{\partial U_{ij}^c}{\partial d} U_{kl}^a Y_{ijkl}^{IJ^b} + U_{ij}^c \frac{\partial U_{kl}^a}{\partial d} Y_{ijkl}^{IJ^b} + U_{ij}^c U_{kl}^a \frac{\partial Y_{ijkl}^{IJ^b}}{\partial d} \Big] \\
= & 2 \sum_{ijkl}^{MO} \left[\left(U_{ij}^{ad} - \sum_m^{MO} U_{im}^d U_{mj}^a \right) U_{kl}^b Y_{ijkl}^{IJ^c} + U_{ij}^a \left(U_{kl}^{bd} - \sum_m^{MO} U_{km}^d U_{ml}^b \right) Y_{ijkl}^{IJ^c} \right. \\
& + U_{ij}^a U_{kl}^b \left(Y_{ijkl}^{IJ^{cd}} + \sum_p^{MO} U_{pi}^d Y_{pjkl}^{IJ^c} + \sum_p^{MO} U_{pk}^d Y_{ijpl}^{IJ^c} \right. \\
& + 4 \sum_{mnp}^{MO} U_{pm}^d \left\{ G_{jlmn}^{IJ}(ik|pn)^c + G_{jmln}^{IJ}(ip|kn)^c + G_{jnlm}^{IJ}(in|kp)^c \right\} \Big) \\
& + \left(U_{ij}^{bd} - \sum_m^{MO} U_{im}^d U_{mj}^b \right) U_{kl}^c Y_{ijkl}^{IJ^a} + U_{ij}^b \left(U_{kl}^{cd} - \sum_m^{MO} U_{km}^d U_{ml}^c \right) Y_{ijkl}^{IJ^a} \\
& + U_{ij}^b U_{kl}^c \left(Y_{ijkl}^{IJ^{ad}} + \sum_p^{MO} U_{pi}^d Y_{pjkl}^{IJ^a} + \sum_p^{MO} U_{pk}^d Y_{ijpl}^{IJ^a} \right. \\
& + 4 \sum_{mnp}^{MO} U_{pm}^d \left\{ G_{jlmn}^{IJ}(ik|pn)^a + G_{jmln}^{IJ}(ip|kn)^a + G_{jnlm}^{IJ}(in|kp)^a \right\} \Big) \\
& + \left(U_{ij}^{cd} - \sum_m^{MO} U_{im}^d U_{mj}^c \right) U_{kl}^a Y_{ijkl}^{IJ^b} + U_{ij}^c \left(U_{kl}^{ad} - \sum_m^{MO} U_{km}^d U_{ml}^a \right) Y_{ijkl}^{IJ^b} \\
& + U_{ij}^c U_{kl}^a \left(Y_{ijkl}^{IJ^{bd}} + \sum_p^{MO} U_{pi}^d Y_{pjkl}^{IJ^b} + \sum_p^{MO} U_{pk}^d Y_{ijpl}^{IJ^b} \right. \\
& + 4 \sum_{mnp}^{MO} U_{pm}^d \left\{ G_{jlmn}^{IJ}(ik|pn)^b + G_{jmln}^{IJ}(ip|kn)^b + G_{jnlm}^{IJ}(in|kp)^b \right\} \Big) \Big] \quad (15.90) \\
= & 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ad} U_{kl}^b + U_{ij}^a U_{kl}^{bd} \right) Y_{ijkl}^{IJ^c} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ^{cd}} \\
& + 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^d Z_{ijklmn}^{IJ^c} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{bd} U_{kl}^c + U_{ij}^b U_{kl}^{cd} \right) Y_{ijkl}^{IJ^a} + 2 \sum_{ijkl}^{MO} U_{ij}^b U_{kl}^c Y_{ijkl}^{IJ^{ad}} \\
& + 2 \sum_{ijklmn}^{MO} U_{ij}^b U_{kl}^c U_{mn}^d Z_{ijklmn}^{IJ^a} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^a + U_{ij}^c U_{kl}^{ad} \right) Y_{ijkl}^{IJ^b} + 2 \sum_{ijkl}^{MO} U_{ij}^c U_{kl}^a Y_{ijkl}^{IJ^{bd}}
\end{aligned}$$

$$+ 2 \sum_{ijklmn}^{MO} U_{ij}^c U_{kl}^a U_{mn}^d Z_{ijklmn}^{IJb} . \quad (15.91)$$

The eighth term of eq. (15.70) may be treated as

$$\begin{aligned} & 2 \sum_{ijklmn}^{MO} \left(\frac{\partial U_{ij}^a}{\partial d} U_{kl}^b U_{mn}^c + U_{ij}^a \frac{\partial U_{kl}^b}{\partial d} U_{mn}^c + U_{ij}^a U_{kl}^b \frac{\partial U_{mn}^c}{\partial d} \right) Z_{ijklmn}^{IJ} \\ &= 2 \sum_{ijklmn}^{MO} \left[\left(U_{ij}^{ad} - \sum_r^{MO} U_{ir}^d U_{rj}^a \right) U_{kl}^b U_{mn}^c + U_{ij}^a \left(U_{kl}^{bd} - \sum_r^{MO} U_{kr}^d U_{rl}^b \right) U_{mn}^c \right. \\ &\quad \left. + U_{ij}^a U_{kl}^b \left(U_{mn}^{cd} - \sum_r^{MO} U_{mr}^d U_{rn}^c \right) \right] Z_{ijklmn}^{IJ} \end{aligned} \quad (15.92)$$

$$\begin{aligned} &= 2 \sum_{ijklmn}^{MO} \left(U_{ij}^{ad} U_{kl}^b U_{mn}^c + U_{ij}^a U_{kl}^{bd} U_{mn}^c + U_{ij}^a U_{kl}^b U_{mn}^{cd} \right) Z_{ijklmn}^{IJ} \\ &- 2 \sum_{ijklmn, r}^{MO} \left(U_{ir}^d U_{rj}^a U_{kl}^b U_{mn}^c + U_{ij}^a U_{kr}^d U_{rl}^b U_{mn}^c + U_{ij}^a U_{kl}^b U_{mr}^d U_{rn}^c \right) Z_{ijklmn}^{IJ} . \end{aligned} \quad (15.93)$$

Employing the result in Section 15.6 the ninth and final term of eq. (15.70) becomes

$$\begin{aligned} & 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \frac{\partial Z_{ijklmn}^{IJ}}{\partial d} \\ &= 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \left[Z_{ijklmn}^{IJd} + \sum_r^{MO} \left(U_{ri}^d Z_{rjklmn}^{IJ} + U_{rk}^d Z_{ijrlmn}^{IJ} + U_{rm}^d Z_{ijklrn}^{IJ} \right) \right. \\ &\quad \left. + 4 \sum_{pr}^{MO} U_{rp}^d \left\{ G_{jlnp}^{IJ}(ik|mr) + G_{jnlp}^{IJ}(im|kr) + G_{jpln}^{IJ}(ir|km) \right\} \right] \end{aligned} \quad (15.94)$$

$$\begin{aligned} &= 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJd} \\ &+ 2 \sum_{ijklmn, r}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{ri}^d Z_{rjklmn}^{IJ} + U_{ij}^a U_{kl}^b U_{mn}^c U_{rk}^d Z_{ijrlmn}^{IJ} \right. \\ &\quad \left. + U_{ij}^a U_{kl}^b U_{mn}^c U_{rm}^d Z_{ijklrn}^{IJ} \right) \\ &+ 8 \sum_{ijklmn, p}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c U_{rp}^d \left\{ G_{jlnp}^{IJ}(ik|mr) + G_{jnlp}^{IJ}(im|kr) + G_{jpln}^{IJ}(ir|km) \right\} . \end{aligned} \quad (15.95)$$

Combining eqs. (15.73), (15.78), (15.80), (15.82), (15.85), (15.88), (15.91), (15.93) and

(15.95), yields the following equation involving 44 terms:

$$\begin{aligned}
 \frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} = & H_{IJ}^{abcd} + 2 \sum_{ij}^{MO} U_{ij}^d X_{ij}^{IJ^{abc}} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{abcd} X_{ij}^{IJ} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ^d} + 2 \sum_{ijkl}^{MO} U_{ij}^{abc} U_{kl}^d Y_{ijkl}^{IJ} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{abd} X_{ij}^{IJ^c} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ^{cd}} + 2 \sum_{ijkl}^{MO} U_{ij}^{ab} U_{kl}^d Y_{ijkl}^{IJ^c} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{bcd} X_{ij}^{IJ^a} + 2 \sum_{ij}^{MO} U_{ij}^{bc} X_{ij}^{IJ^{ad}} + 2 \sum_{ijkl}^{MO} U_{ij}^{bc} U_{kl}^d Y_{ijkl}^{IJ^a} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{cad} X_{ij}^{IJ^b} + 2 \sum_{ij}^{MO} U_{ij}^{ca} X_{ij}^{IJ^{bd}} + 2 \sum_{ijkl}^{MO} U_{ij}^{ca} U_{kl}^d Y_{ijkl}^{IJ^b} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{ad} X_{ij}^{IJ^{bc}} + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ^{bcd}} + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^d Y_{ijkl}^{IJ^{bc}} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{bd} X_{ij}^{IJ^{ca}} + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJ^{cad}} + 2 \sum_{ijkl}^{MO} U_{ij}^b U_{kl}^d Y_{ijkl}^{IJ^{ca}} \\
 & + 2 \sum_{ij}^{MO} U_{ij}^{cd} X_{ij}^{IJ^{ab}} + 2 \sum_{ij}^{MO} U_{ij}^c X_{ij}^{IJ^{abd}} + 2 \sum_{ijkl}^{MO} U_{ij}^c U_{kl}^d Y_{ijkl}^{IJ^{ab}} \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{abd} U_{kl}^c + U_{ij}^{bcd} U_{kl}^a + U_{ij}^{cad} U_{kl}^b \right) Y_{ijkl}^{IJ} \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{bc} U_{kl}^{ad} + U_{ij}^{ca} U_{kl}^{bd} \right) Y_{ijkl}^{IJ} \\
 & - 2 \sum_{ijklm}^{MO} \left(U_{im}^d U_{mj}^{ab} U_{kl}^c + U_{ij}^{ab} U_{km}^d U_{ml}^c + U_{im}^d U_{mj}^{bc} U_{kl}^a \right. \\
 & \quad \left. + U_{ij}^{bc} U_{km}^d U_{ml}^a + U_{im}^d U_{mj}^{ca} U_{kl}^b + U_{ij}^{ca} U_{km}^d U_{ml}^b \right) Y_{ijklm}^{IJ} \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJ^d} \\
 & + 2 \sum_{ijklp}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{pi}^d + U_{ij}^{bc} U_{kl}^a U_{pi}^d + U_{ij}^{ca} U_{kl}^b U_{pi}^d \right) Y_{ijkpl}^{IJ} \\
 & + 2 \sum_{ijklp}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{pk}^d + U_{ij}^{bc} U_{kl}^a U_{pk}^d + U_{ij}^{ca} U_{kl}^b U_{pk}^d \right) Y_{ijklp}^{IJ}
 \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{mn}^d + U_{ij}^{bc} U_{kl}^a U_{mn}^d + U_{ij}^{ca} U_{kl}^b U_{mn}^d \right) Z_{ijklmn}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ad} U_{kl}^b + U_{ij}^a U_{kl}^{bd} \right) Y_{ijkl}^{IJ^c} \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ^{cd}} + 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^d Z_{ijklmn}^{IJ^c} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{bd} U_{kl}^c + U_{ij}^b U_{kl}^{cd} \right) Y_{ijkl}^{IJ^a} \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^b U_{kl}^c Y_{ijkl}^{IJ^{ad}} + 2 \sum_{ijklmn}^{MO} U_{ij}^b U_{kl}^c U_{mn}^d Z_{ijklmn}^{IJ^a} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^a + U_{ij}^c U_{kl}^{ad} \right) Y_{ijkl}^{IJ^b} \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^c U_{kl}^a Y_{ijkl}^{IJ^{bd}} + 2 \sum_{ijklmn}^{MO} U_{ij}^c U_{kl}^a U_{mn}^d Z_{ijklmn}^{IJ^b} \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^{ad} U_{kl}^b U_{mn}^c + U_{ij}^a U_{kl}^{bd} U_{mn}^c + U_{ij}^a U_{kl}^b U_{mn}^{cd} \right) Z_{ijklmn}^{IJ} \\
& - 2 \sum_{ijklmnqr}^{MO} \left(U_{ir}^d U_{rj}^a U_{kl}^b U_{mn}^c + U_{ij}^a U_{kr}^d U_{rl}^b U_{mn}^c + U_{ij}^a U_{kl}^b U_{mr}^d U_{rn}^c \right) Z_{ijklmn}^{IJ} \\
& + 2 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJ^d} \\
& + 2 \sum_{ijklmnqr}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{ri}^d Z_{rjklmn}^{IJ} + U_{ij}^a U_{kl}^b U_{mn}^c U_{rk}^d Z_{ijrlmn}^{IJ} \right. \\
& \quad \left. + U_{ij}^a U_{kl}^b U_{mn}^c U_{rm}^d Z_{ijkln}^{IJ} \right) \\
& + 8 \sum_{ijklmnpr}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c U_{rp}^d \left(G_{jlnp}^{IJ}(ik|mr) + G_{jnlp}^{IJ}(im|kr) \right. \\
& \quad \left. + G_{jpln}^{IJ}(ir|km) \right) . \tag{15.96}
\end{aligned}$$

Collecting terms within (15.96) reduces the expression to 15 terms:

$$\begin{aligned}
\frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} & = H_{IJ}^{abcd} + 2 \sum_{ij}^{MO} U_{ij}^{abcd} X_{ij}^{IJ} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{abc} X_{ij}^{IJ^d} + U_{ij}^{abd} X_{ij}^{IJ^c} + U_{ij}^{acd} X_{ij}^{IJ^b} + U_{ij}^{bcd} X_{ij}^{IJ^a} \right)
\end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{IJ^{cd}} + U_{ij}^{ac} X_{ij}^{IJ^{bd}} + U_{ij}^{ad} X_{ij}^{IJ^{bc}} \right. \\
& \quad \left. + U_{ij}^{bc} X_{ij}^{IJ^{ad}} + U_{ij}^{bd} X_{ij}^{IJ^{ac}} + U_{ij}^{cd} X_{ij}^{IJ^{ab}} \right) \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{IJ^{bcd}} + U_{ij}^b X_{ij}^{IJ^{cad}} + U_{ij}^c X_{ij}^{IJ^{dab}} + U_{ij}^d X_{ij}^{IJ^{abc}} \right) \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{abc} U_{kl}^d + U_{ij}^{abd} U_{kl}^c + U_{ij}^{acd} U_{kl}^b + U_{ij}^{bcd} U_{kl}^a \right) Y_{ijkl}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) Y_{ijkl}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJ^d} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^d + U_{ij}^{bd} U_{kl}^a + U_{ij}^{ad} U_{kl}^b \right) Y_{ijkl}^{IJ^c} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^a + U_{ij}^{ac} U_{kl}^d + U_{ij}^{ad} U_{kl}^c \right) Y_{ijkl}^{IJ^b} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^b + U_{ij}^{bd} U_{kl}^c + U_{ij}^{bc} U_{kl}^d \right) Y_{ijkl}^{IJ^a} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ^{cd}} + U_{ij}^a U_{kl}^c Y_{ijkl}^{IJ^{bd}} + U_{ij}^a U_{kl}^d Y_{ijkl}^{IJ^{bc}} \right. \\
& \quad \left. + U_{ij}^c U_{kl}^d Y_{ijkl}^{IJ^{ab}} + U_{ij}^b U_{kl}^d Y_{ijkl}^{IJ^{ca}} + U_{ij}^b U_{kl}^c Y_{ijkl}^{IJ^{ad}} \right) \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{mn}^d + U_{ij}^{ac} U_{kl}^b U_{mn}^d + U_{ij}^{ad} U_{kl}^b U_{mn}^c \right. \\
& \quad \left. + U_{ij}^{bc} U_{kl}^a U_{mn}^d + U_{ij}^{bd} U_{kl}^a U_{mn}^c + U_{ij}^{cd} U_{kl}^a U_{mn}^b \right) Z_{ijklmn}^{IJ} \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJ^d} + U_{ij}^a U_{kl}^b U_{mn}^d Z_{ijklmn}^{IJ^c} \right. \\
& \quad \left. + U_{ij}^a U_{kl}^c U_{mn}^d Z_{ijklmn}^{IJ^b} + U_{ij}^b U_{kl}^c U_{mn}^d Z_{ijklmn}^{IJ^a} \right) \\
& + 8 \sum_{ijklmno}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d \right. \\
& \quad \left. + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) G_{jlinp}^{IJ}(ik|mo) \quad . \tag{15.97}
\end{aligned}$$

Substitution of this equation into eq. (15.30) will give the desired result in the next section.

15.8 An Explicit Expression for the Fourth Derivative of the Electronic Energy

By combining eq. (15.30) for the fourth energy derivative and eq. (15.97), which contains the fourth derivative of the Hamiltonian matrix element, an explicit expression for the fourth derivative of the electronic energy is straightforwardly but laboriously obtained:

$$\begin{aligned}
 \frac{\partial^4 E_{CI}}{\partial a \partial b \partial c \partial d} = & \sum_{ij}^{MO} Q_{ij} h_{ij}^{abcd} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{abcd} + 2 \sum_{ij}^{MO} U_{ij}^{abcd} X_{ij} \\
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^{abc} X_{ij}^d + U_{ij}^{abd} X_{ij}^c + U_{ij}^{acd} X_{ij}^b + U_{ij}^{bcd} X_{ij}^a \right) \\
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{cd} + U_{ij}^{ac} X_{ij}^{bd} + U_{ij}^{ad} X_{ij}^{bc} \right. \\
 & \quad \left. + U_{ij}^{bc} X_{ij}^{ad} + U_{ij}^{bd} X_{ij}^{ac} + U_{ij}^{cd} X_{ij}^{ab} \right) \\
 & + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{bcd} + U_{ij}^b X_{ij}^{cad} + U_{ij}^c X_{ij}^{dab} + U_{ij}^d X_{ij}^{abc} \right) \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{abc} U_{kl}^d + U_{ij}^{abd} U_{kl}^c + U_{ij}^{acd} U_{kl}^b + U_{ij}^{bcd} U_{kl}^a \right) Y_{ijkl} \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) Y_{ijkl} \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^d \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^d + U_{ij}^{bd} U_{kl}^a + U_{ij}^{ad} U_{kl}^b \right) Y_{ijkl}^c \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^a + U_{ij}^{ac} U_{kl}^d + U_{ij}^{ad} U_{kl}^c \right) Y_{ijkl}^b \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^b + U_{ij}^{bd} U_{kl}^c + U_{ij}^{bc} U_{kl}^d \right) Y_{ijkl}^a \\
 & + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{cd} + U_{ij}^a U_{kl}^c Y_{ijkl}^{bd} + U_{ij}^a U_{kl}^d Y_{ijkl}^{bc} \right. \\
 & \quad \left. + U_{ij}^c U_{kl}^d Y_{ijkl}^{ab} + U_{ij}^b U_{kl}^d Y_{ijkl}^{ca} + U_{ij}^b U_{kl}^c Y_{ijkl}^{ad} \right)
 \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{mn}^d + U_{ij}^{ac} U_{kl}^b U_{mn}^d + U_{ij}^{ad} U_{kl}^b U_{mn}^c \right. \\
& \quad \left. + U_{ij}^{bc} U_{kl}^a U_{mn}^d + U_{ij}^{bd} U_{kl}^a U_{mn}^c + U_{ij}^{cd} U_{kl}^a U_{mn}^b \right) Z_{ijklmn} \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^d + U_{ij}^a U_{kl}^b U_{mn}^d Z_{ijklmn}^c \right. \\
& \quad \left. + U_{ij}^a U_{kl}^c U_{mn}^d Z_{ijklmn}^b + U_{ij}^b U_{kl}^c U_{mn}^d Z_{ijklmn}^a \right) \\
& + 8 \sum_{ijklmno}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d \right. \\
& \quad \left. + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) G_{jlnp}(ik|mo) \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial^3 H_{IJ}}{\partial b \partial c \partial d} + \frac{\partial C_J}{\partial b} \frac{\partial^3 H_{IJ}}{\partial c \partial d \partial a} \right. \\
& \quad \left. + \frac{\partial C_J}{\partial c} \frac{\partial^3 H_{IJ}}{\partial d \partial a \partial b} + \frac{\partial C_J}{\partial d} \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \right] \\
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \right] \\
& - 2 \sum_{IJ}^{CI} \left[\frac{\partial^2 C_I}{\partial a \partial b} \frac{\partial^2 C_J}{\partial c \partial d} + \frac{\partial^2 C_I}{\partial a \partial c} \frac{\partial^2 C_J}{\partial b \partial d} + \frac{\partial^2 C_I}{\partial a \partial d} \frac{\partial^2 C_J}{\partial b \partial c} \right] \left(H_{IJ} - \delta_{IJ} E_{elec} \right)
\end{aligned} \tag{15.98}$$

The second and third derivatives of the Hamiltonian matrices appearing in eq. (15.98) were defined explicitly by eqs. (15.19) and (15.56). The skeleton (core) derivative Lagrangian, Y , and Z matrices are

$$X_{ij}^{abc} = \sum_m^{MO} Q_{jm} h_{im}^{abc} + 2 \sum_{mkl}^{MO} G_{jmkl} (im|kl)^{abc}, \tag{15.99}$$

$$Y_{ijkl}^{ab} = Q_{jl} h_{ik}^{ab} + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn)^{ab} + 4 \sum_{mn}^{MO} G_{jmfn}(im|kn)^{ab} , \quad (15.100)$$

and

$$Z_{ijklmn}^a = 4 \sum_p^{MO} \left\{ G_{jlnp}(ik|mp)^a + G_{jnlp}(im|kp)^a + G_{jpln}(ip|km)^a \right\} . \quad (15.101)$$

It is seen clearly that the solutions of the first- (U^a), second- (U^{ab}), third- (U^{abc}) and fourth-order (U^{abcd}) CPHF equations and the first- ($\partial C_I / \partial a$) and second-order ($\partial^2 C_I / \partial a \partial b$) CPCI equations are required to evaluate the fourth derivative of the electronic energy for the CI wavefunction. Needless to say, this will be a formidable computational task.

References

1. I. Shavitt, in *Modern Theoretical Chemistry*, H.F. Schaefer editor, Plenum, New York, Vol. 3, p.189 (1977).
2. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.

Suggested Reading

1. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *Theor. Chim. Acta* **72**, 71 (1987).

Chapter 16

Correspondence Between Correlated and Restricted Hartree-Fock Wavefunctions

In terms of the complexity of the analytic derivative expressions, the configuration interaction (CI) case, for which the molecular orbitals are not determined variationally, is by far the most difficult of those considered explicitly in this text. Analytic higher derivative expressions for CI wavefunctions can be used to obtain the corresponding energy derivative formula for multiconfiguration self-consistent-field (MCSCF), paired excitation (PE) MCSCF, general restricted open-shell (GR) SCF, and closed-shell (CL) SCF wavefunctions by explicitly imposing variational and orthonormality conditions on the molecular orbital (MO) space. The reduction procedure used follows the steps

$$\text{CI} \longrightarrow \text{MCSCF} \longrightarrow \text{PEMCSCF} \longrightarrow \text{GRSCF} \longrightarrow \text{CLSFC} \quad .$$

The equations expressing the correspondence between correlated and RHF wavefunctions are presented in this chapter to interrelate explicitly the conditions and definitions involved in various energy derivative expressions.

16.1 Configuration Interaction (CI) Wavefunctions

16.1.1 Electronic Energy and the Variational Condition

The electronic energy of a CI wavefunction is given by

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (16.1)$$

$$= \sum_{ij}^{MO} Q_{ij} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl) . \quad (16.2)$$

The Hamiltonian matrix element H_{IJ} between configurations I and J is

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (16.3)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl) . \quad (16.4)$$

The one- and two-electron reduced density matrices, Q and G , are related to their “bare” quantities, the one- and two-electron coupling constant matrices, Q^{IJ} and G^{IJ} , through

$$Q_{ij} = \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} \quad (16.5)$$

and

$$G_{ijkl} = \sum_{IJ}^{CI} C_I C_J G_{ijkl}^{IJ} . \quad (16.6)$$

The variational condition in the CI space is

$$\sum_J^{CI} C_J (H_{IJ} - \delta_{IJ} E_{elec}) = 0 \quad (16.7)$$

and the CI coefficients are normalized in the conventional manner:

$$\sum_I^{CI} C_I^2 = 1 . \quad (16.8)$$

16.1.2 First Derivative

The first derivative of the electronic energy expression was derived in Chapter 6 and is

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad (16.9)$$

$$= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a \\ + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij} . \quad (16.10)$$

The Lagrangian matrix X in this equation is defined by

$$X_{ij} = \sum_m^{MO} Q_{jm} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl) . \quad (16.11)$$

Note that the first derivative expression (16.10) requires the solution of the first-order CPHF equations for U^a .

16.1.3 Second Derivative

The second derivative of the electronic energy expression was derived in Chapter 6 and is

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) \quad (16.12)$$

where the first term in eq. (16.12) may be expressed as

$$\begin{aligned} \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{ab} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} \\ &+ 2 \sum_{ij}^{MO} (U_{ij}^b X_{ij}^a + U_{ij}^a X_{ij}^b) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl} . \end{aligned} \quad (16.13)$$

The skeleton (core) first derivative Lagrangian matrices in this equation are

$$X_{ij}^a = \sum_m^{MO} Q_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^a , \quad (16.14)$$

and the Y matrix is given by

$$Y_{ijkl} = Q_{jl} h_{ik} + 2 \sum_{mn}^{MO} \left\{ G_{jlmn}(ik|mn) + 2G_{jmkn}(im|kn) \right\} . \quad (16.15)$$

It should be noted that the second derivative equation (16.12) requires the solution of both the first- and second-order CPHF equations (for U^a and U^{ab}) and the first-order CPCI equations (for $\partial C_I / \partial a$).

16.1.4 Third Derivative

The third derivative of electronic energy expression derived in Chapter 15 is

$$\begin{aligned} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} &= \sum_{IJ}^{CI} C_I C_J \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \\ &+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H_{IJ}}{\partial b \partial c} + \frac{\partial C_J}{\partial b} \frac{\partial^2 H_{IJ}}{\partial c \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^2 H_{IJ}}{\partial a \partial b} \right) \\ &+ 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right] \end{aligned}$$

$$+ \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \\ + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \] . \quad (16.16)$$

The first derivative of the CI Hamiltonian matrix was developed in Section 6.4 as

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} , \quad (16.17)$$

where the H^a and X^{IJ} matrices are

$$H_{IJ}^a = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^a , \quad (16.18)$$

$$X_{ij}^{IJ} = \sum_m^{MO} Q_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (im|kl) . \quad (16.19)$$

The second derivative expression for the Hamiltonian matrix was derived in Section 6.6 as

$$\frac{\partial^2 H_{IJ}}{\partial a \partial b} = H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \\ + 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJ^a} + U_{ij}^a X_{ij}^{IJ^b} \right) \\ + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} \quad (16.20)$$

where

$$H_{IJ}^{ab} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ} (ij|kl)^{ab} , \quad (16.21)$$

$$X_{ij}^{IJ^a} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ} (im|kl)^a , \quad (16.22)$$

$$Y_{ijkl}^{IJ} = Q_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} \left\{ G_{jlmn}^{IJ} (ik|mn) + 2G_{jmkn}^{IJ} (im|kn) \right\} . \quad (16.23)$$

It is useful to define the modified first derivative Lagrangian matrices as

$$X_{ij}^{[a]} = X_{ij}^a + \sum_{kl}^{MO} U_{kl}^a Y_{ijkl} . \quad (16.24)$$

Using these quantities and the result from Section 15.4 the first term in eq. (16.16) is explicitly given as

$$\begin{aligned}
 \sum_{IJ}^{CI} C_I C_J \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^{abc} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{abc} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij} \\
 &+ 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{[c]} + U_{ij}^{bc} X_{ij}^{[a]} + U_{ij}^{ca} X_{ij}^{[b]} \right) \\
 &+ 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{bc} + U_{ij}^b X_{ij}^{ca} + U_{ij}^c X_{ij}^{ab} \right) \\
 &+ 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^c + U_{ij}^b U_{kl}^c Y_{ijkl}^a + U_{ij}^c U_{kl}^a Y_{ijkl}^b \right) \\
 &+ 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \\
 &\times \sum_p^{MO} G_{jlnp}(ik|mp) . \tag{16.25}
 \end{aligned}$$

The skeleton (core) second derivative Lagrangian matrices in this equation are defined by

$$X_{ij}^{ab} = \sum_m^{MO} Q_{jm} h_{im}^{ab} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^{ab} , \tag{16.26}$$

and the skeleton (core) first derivative Y matrices are given by

$$Y_{ijkl}^a = Q_{jl} h_{ik}^a + 2 \sum_{mn}^{MO} \left\{ G_{jlmn}(ik|mn)^a + 2G_{jmln}(im|kn)^a \right\} . \tag{16.27}$$

Note that the third derivative equation as formulated above requires the solutions of the first- (U^a), second- (U^{ab}) and third-order (U^{abc}) CPHF equations *and* the first-order ($\partial C_I / \partial a$) CPCI equations.

16.1.5 Fourth Derivative

The fourth derivative of the electronic energy found in Chapter 15 is

$$\begin{aligned}
 \frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} &= \sum_{IJ}^{CI} C_I C_J \frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} \\
 &+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial^3 H_{IJ}}{\partial b \partial c \partial d} + \frac{\partial C_J}{\partial b} \frac{\partial^3 H_{IJ}}{\partial c \partial d \partial a} \right]
 \end{aligned}$$

$$\begin{aligned}
& + \frac{\partial C_J}{\partial c} \frac{\partial^3 H_{IJ}}{\partial d \partial a \partial b} + \frac{\partial C_J}{\partial d} \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \Big] \\
+ & 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right) \right. \\
& + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \\
& + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
& + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \\
& + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \\
& \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \right] \\
- & 2 \sum_{IJ}^{CI} \left[\frac{\partial^2 C_I}{\partial a \partial b} \frac{\partial^2 C_J}{\partial c \partial d} + \frac{\partial^2 C_I}{\partial a \partial c} \frac{\partial^2 C_J}{\partial b \partial d} + \frac{\partial^2 C_I}{\partial a \partial d} \frac{\partial^2 C_J}{\partial b \partial c} \right] \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \\
& .
\end{aligned} \tag{16.28}$$

The third derivative expression of the Hamiltonian matrix was developed in Section 15.4 as

$$\begin{aligned}
\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} = & H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{IJc} + U_{ij}^{bc} X_{ij}^{IJa} + U_{ij}^{ca} X_{ij}^{IJb} \right) \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{IJbc} + U_{ij}^b X_{ij}^{IJca} + U_{ij}^c X_{ij}^{IJab} \right) \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{IJc} + U_{ij}^b U_{kl}^c Y_{ijkl}^{IJa} + U_{ij}^c U_{kl}^a Y_{ijkl}^{IJb} \right) \\
& + 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} G_{jlnp}^{IJ}(ik|mp)
\end{aligned} \tag{16.29}$$

where the H_{IJ}^{abc} , X^{IJab} , and Y^{IJa} matrices are defined by

$$H_{IJ}^{abc} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{abc} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^{abc}, \tag{16.30}$$

$$X_{ij}^{IJab} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^{ab} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl)^{ab} , \quad (16.31)$$

and

$$Y_{ijkl}^{IJ^a} = Q_{jl}^{IJ} h_{ik}^a + 2 \sum_{mn}^{MO} \left\{ G_{jlmn}^{IJ}(ik|mn)^a + 2G_{jmln}^{IJ}(im|kn)^a \right\} . \quad (16.32)$$

It is then useful to introduce the modified second derivative Lagrangian matrices as

$$X_{ij}^{[ab]} = X_{ij}^{ab} + \sum_{kl}^{MO} \left(U_{kl}^b Y_{ijkl}^a + U_{kl}^a Y_{ijkl}^b \right) + \sum_{klmn}^{MO} U_{kl}^a U_{mn}^b Z_{ijklmn} \quad (16.33)$$

where the Z matrix is defined by

$$Z_{ijklmn} = 4 \sum_p^{MO} \left\{ G_{jlnp}(ik|mp) + G_{jnlp}(im|kp) + G_{jpln}(ip|km) \right\} . \quad (16.34)$$

Using eqs. (16.24) and (16.33) and the result from Section 15.7, the first term of eq. (16.28) is explicitly written as

$$\begin{aligned} \sum_{IJ}^{CI} C_I C_J \frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^{abcd} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{abcd} + 2 \sum_{ij}^{MO} U_{ij}^{abcd} X_{ij} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^{abc} X_{ij}^{[d]} + U_{ij}^{bcd} X_{ij}^{[a]} + U_{ij}^{cda} X_{ij}^{[b]} + U_{ij}^{dab} X_{ij}^{[c]} \right) \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{[cd]} + U_{ij}^{ac} X_{ij}^{[bd]} + U_{ij}^{ad} X_{ij}^{[bc]} \right. \\ &\quad \left. + U_{ij}^{bc} X_{ij}^{[ad]} + U_{ij}^{bd} X_{ij}^{[ac]} + U_{ij}^{cd} X_{ij}^{[ab]} \right) \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{bcd} + U_{ij}^b X_{ij}^{cda} + U_{ij}^c X_{ij}^{dab} + U_{ij}^d X_{ij}^{abc} \right) \\ &+ 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) Y_{ijkl} \\ &+ 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{cd} + U_{ij}^a U_{kl}^c Y_{ijkl}^{bd} + U_{ij}^a U_{kl}^d Y_{ijkl}^{bc} \right. \\ &\quad \left. + U_{ij}^b U_{kl}^c Y_{ijkl}^{ad} + U_{ij}^b U_{kl}^d Y_{ijkl}^{ac} + U_{ij}^c U_{kl}^d Y_{ijkl}^{ab} \right) \\ &+ 2 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^d + U_{ij}^b U_{kl}^c U_{mn}^d Z_{ijklmn}^a \right) \end{aligned}$$

$$\begin{aligned}
& + U_{ij}^c U_{kl}^d U_{mn}^a Z_{ijklmn}^b + U_{ij}^d U_{kl}^a U_{mn}^b Z_{ijklmn}^c \Big) \\
+ & 8 \sum_{ijklmno}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d \right. \\
& \left. + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) G_{jlnp}(ik|mo) . \quad (16.35)
\end{aligned}$$

The skeleton (core) derivative Lagrangian, Y , and Z matrices in this equation are defined by

$$X_{ij}^{abc} = \sum_m^{MO} Q_{jm} h_{im}^{abc} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^{abc} , \quad (16.36)$$

$$Y_{ijkl}^{ab} = Q_{jl} h_{ik}^{ab} + 2 \sum_{mn}^{MO} \left\{ G_{jlmn}(ik|mn)^{ab} + 2G_{jmln}(im|kn)^{ab} \right\} , \quad (16.37)$$

and

$$Z_{ijklmn}^a = 4 \sum_p^{MO} \left\{ G_{jlnp}(ik|mp)^a + G_{jnlp}(im|kp)^a + G_{jpln}(ip|km)^a \right\} . \quad (16.38)$$

Note that the solutions of the first- (U^a), second- (U^{ab}), third- (U^{abc}) and fourth-order (U^{abcd}) CPHF equations *and* the first- ($\partial C_I / \partial a$) and second-order ($\partial^2 C_I / \partial a \partial b$) CPCI equations are required in the above formulation to evaluate the fourth derivative of the electronic energy of the CI wavefunction.

16.2 Correspondence Equations

Higher energy derivative expressions for configuration interaction (CI) wavefunctions described in the preceding section can be used to obtain the corresponding energy derivative formula for multiconfiguration (MC) SCF, paired excitation (PE) MCSCF, general restricted open-shell (GR) SCF, and closed-shell (CL) SCF restricted Hartree-Fock (RHF) wavefunctions by explicitly imposing variational and orthonormality conditions on the MO space. The general structure of the reduction procedure used in the following sections is

$$\text{CI} \longrightarrow \text{MCSCF} \longrightarrow \text{PEMCSCF} \longrightarrow \text{GRSCF} \longrightarrow \text{CLSCF} .$$

The equations expressing the correspondence between correlated and RHF wavefunctions are presented in detail in each section to interrelate the various conditions and definitions involved in energy derivative expressions. Table 16.1 on the next page summarizes the *correspondence equations* for some basic quantities.

Table 16.1 Correspondence Equations for Basic Quantities

Wavefunction Matrices	CI	MCSCF	PEMCSCF	GRSCF	CLSCF
one-electron density	Q_{ij}	γ_{ij}	$2\delta_{ij}f_i$	$2\delta_{ij}f_i$	$2\delta_{ij}$
two-electron density	G_{ijkl}	Γ_{ijkl}	$\delta_{ij}\delta_{kl}\alpha_{ik}$ $+ \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\beta_{ij}$	$\delta_{ij}\delta_{kl}\alpha_{ik}$ $+ \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\beta_{ij}$	$2\delta_{ij}\delta_{kl}$ $- \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$
Lagrangian	X_{ij}	x_{ij}	$2\epsilon_{ji}$	$2\epsilon_{ji}$	$2F_{ij}$
Derivative Lagrangian	X_{ij}^a	x_{ij}^a	$2\epsilon_{ji}^a$	$2\epsilon_{ji}^a$	$2F_{ij}^a$
Y	Y_{ijkl}	y_{ijkl}	$2\delta_{jl}\zeta_{ik}^j + 2\tau_{ijkl}^{jl}$	$2\delta_{jl}\zeta_{ik}^j + 2\tau_{ijkl}^{jl}$	$2\delta_{jk}F_{ik} + 2A_{ijkl}$
Derivative Y	Y_{ijkl}^a	y_{ijkl}^a	$2\delta_{jl}\zeta_{ik}^{ja} + 2\tau_{ijkl}^{jal}$	$2\delta_{jl}\zeta_{ik}^{ja} + 2\tau_{ijkl}^{jal}$	$2\delta_{jk}F_{ik}^a + 2A_{ijkl}^a$

16.3 Multiconfiguration Self-Consistent-Field (MCSCF) Wavefunctions

16.3.1 Electronic Energy and the Variational Condition

The electronic energy for an MCSCF wavefunction is given by

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (16.39)$$

$$= \sum_{ij}^{MO} \gamma_{ij} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl) \quad (16.40)$$

where the Hamiltonian matrix element H_{IJ} between configurations I and J is defined by

$$H_{IJ} = \langle \Phi_I | \mathbf{H}_{elec} | \Phi_J \rangle \quad (16.41)$$

$$= \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl) \quad . \quad (16.42)$$

The one- and two-electron reduced density matrices, γ and Γ , are related to their “bare” quantities, the one- and two-electron coupling constants, γ^{IJ} and Γ^{IJ} , through

$$\gamma_{ij} = \sum_{IJ}^{CI} C_I C_J \gamma_{ij}^{IJ} \quad (16.43)$$

and

$$\Gamma_{ijkl} = \sum_{IJ}^{CI} C_I C_J \Gamma_{ijkl}^{IJ} \quad . \quad (16.44)$$

All the equations in Section 16.1 are applicable formally to an MCSCF wavefunction. However, two additional conditions in the MO space must be satisfied for this type of wavefunction. First, the variational condition

$$x_{ij} - x_{ji} = 0 \quad (16.45)$$

with the Lagrangian matrix x defined by

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl) \quad (16.46)$$

must be met. Secondly, the orthonormality condition on the molecular orbitals

$$S_{ij} = \delta_{ij} \quad . \quad (16.47)$$

must be imposed. Here δ is the usual Kronecker delta function.

16.3.2 First Derivative

The first derivative form of the orthonormality condition for the molecular orbitals was obtained in Chapter 3 as

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \quad . \quad (16.48)$$

Using eqs. (16.45) and (16.48), the first derivative expression for a CI wavefunction, eq. (16.9), may be specialized to that for a MCSCF wavefunction as follows:

$$\frac{\partial E_{elec}}{\partial a} = \sum_{IJ}^{CI} C_I C_J \frac{\partial H_{IJ}}{\partial a} \quad (16.49)$$

$$\begin{aligned} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a \\ &+ 2 \sum_{ij}^{MO} U_{ij}^a x_{ij} \end{aligned} \quad (16.50)$$

$$\begin{aligned} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a \\ &+ \sum_{ij}^{MO} \left(U_{ij}^a + U_{ji}^a \right) x_{ij} \end{aligned} \quad (16.51)$$

$$\begin{aligned} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a \\ &- \sum_{ij}^{MO} S_{ij}^a x_{ij} \end{aligned} \quad . \quad (16.52)$$

Equation (16.52) shows that the first derivative methods for an MCSCF wavefunction do *not* require solution of the coupled perturbed MCHF (CPMCHF) equations. The variational parameters (C_μ and C_I) are optimized simultaneously for the MCSCF wavefunctions as stated clearly in eqs. (16.7) and (16.45). Thus, the MCSCF analytic derivative evaluation is much simpler than the CI case with the same set of configurations.

16.3.3 Second Derivative

The second derivative form of the normalization condition of the molecular orbitals was found in Chapter 3 as

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad . \quad (16.53)$$

The augmented S matrix, ξ^{ab} , in the above equation is defined by

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \quad . \quad (16.54)$$

The second derivative of the MCSCF energy is obtained from eqs. (16.12) and (16.13) as

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = \sum_{IJ}^{CI} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a \partial b} - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) . \quad (16.55)$$

The term involving U^{ab} in eq. (16.13) may be rewritten in terms of ξ^{ab} using eqs. (16.45) and (16.53) as

$$2 \sum_{ij}^{MO} U_{ij}^{ab} x_{ij} = \sum_{ij}^{MO} (U_{ij}^a + U_{ji}^a) x_{ij} \quad (16.56)$$

$$= - \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij} . \quad (16.57)$$

Combining eqs. (16.13), (16.55), and (16.57), the second derivative of the MCSCF energy is given by

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{ab} \\ &- \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij} \\ &+ 2 \sum_{ij}^{MO} (U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E_{elec}) . \end{aligned} \quad (16.58)$$

The skeleton (core) first derivative Lagrangian matrix, x^a , appearing in eq. (16.58) is defined by

$$x_{ij}^a = \sum_m^{MO} \gamma_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl)^a , \quad (16.59)$$

and the y matrix by

$$y_{ijkl} = \gamma_{jl} h_{ik} + 2 \sum_{mn}^{MO} \left\{ \Gamma_{jlmn}(ik|mn) + 2\Gamma_{jmln}(im|kn) \right\} . \quad (16.60)$$

Note that the second derivative of the MCSCF energy requires the solution of the first-order CPMCHF equations. These equations provide the derivative information for both the MO coefficients (U^a) and the CI coefficients ($\partial C_I / \partial a$).

16.3.4 Third Derivative

The third derivative of the electronic energy may be obtained from the CI third derivative expression presented in Section 16.1. For this purpose it is necessary to introduce the third

derivative form of the orthonormality condition on the molecular orbitals as

$$U_{ij}^{abc} + U_{ji}^{abc} + \xi_{ij}^{abc} = 0 \quad (16.61)$$

where the augmented S matrix, ξ^{abc} , is defined by

$$\begin{aligned} \xi_{ij}^{abc} &= S_{ij}^{abc} \\ &+ \sum_m^{MO} \left(U_{im}^{ab} U_{jm}^c + U_{jm}^{ab} U_{im}^c + U_{im}^{bc} U_{jm}^a + U_{jm}^{bc} U_{im}^a + U_{im}^{ca} U_{jm}^b + U_{jm}^{ca} U_{im}^b \right) \\ &- \sum_m^{MO} \left(S_{im}^{ab} S_{jm}^c + S_{jm}^{ab} S_{im}^c + S_{im}^{bc} S_{jm}^a + S_{jm}^{bc} S_{im}^a + S_{im}^{ca} S_{jm}^b + S_{jm}^{ca} S_{im}^b \right) \\ &+ \sum_{mn}^{MO} \left(S_{im}^a S_{jn}^b S_{mn}^c + S_{jm}^a S_{in}^b S_{mn}^c + S_{im}^b S_{jn}^c S_{mn}^a + S_{jm}^b S_{in}^c S_{mn}^a \right. \\ &\quad \left. + S_{im}^c S_{jn}^a S_{mn}^b + S_{jm}^c S_{in}^a S_{mn}^b \right) \quad . \end{aligned} \quad (16.62)$$

It is further required to introduce the first derivative form of the variational condition on the MO space:

$$\frac{\partial x_{ij}}{\partial a} - \frac{\partial x_{ji}}{\partial a} = 0 \quad . \quad (16.63)$$

It is useful to introduce the modified first derivative Lagrangian matrices as

$$x_{ij}^{[a]} = x_{ij}^a + \sum_{kl}^{MO} U_{kl}^a y_{ijkl} \quad . \quad (16.64)$$

The first derivative of the Lagrangian matrix in eq. (16.63) may be expressed using the result in Section 14.1 and eq. (16.64) as

$$\frac{\partial x_{ij}}{\partial a} = x_{ij}^{[a]} + \sum_k^{MO} U_{ki}^a x_{kj} + 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} x_{ij}^{IJ} \quad (16.65)$$

with the “bare” Lagrangian matrices x^{IJ}

$$x_{ij}^{IJ} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ}(im|kl) \quad . \quad (16.66)$$

In eqs. (16.16) and (16.25), those terms potentially including the second and third derivatives of the MO coefficients are

$$\begin{aligned} &2 \sum_{ij}^{MO} U_{ij}^{abc} x_{ij} + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} x_{ij}^{[c]} + U_{ij}^{bc} x_{ij}^{[a]} + U_{ij}^{ca} x_{ij}^{[b]} \right) \\ &+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H_{IJ}}{\partial b \partial c} + \frac{\partial C_J}{\partial b} \frac{\partial^2 H_{IJ}}{\partial c \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^2 H_{IJ}}{\partial a \partial b} \right) \quad . \end{aligned} \quad (16.67)$$

The third derivative of the MO coefficients in the first term of eq. (16.67) may be eliminated using eqs. (16.45), (16.61) and (16.62) as

$$2 \sum_{ij}^{MO} U_{ij}^{abc} x_{ij} = \sum_{ij}^{MO} \left(U_{ij}^{abc} + U_{ji}^{abc} \right) x_{ij} \quad (16.68)$$

$$= - \sum_{ij}^{MO} \xi_{ij}^{abc} x_{ij} \quad (16.69)$$

$$= - \sum_{ij}^{MO} S_{ij}^{abc} x_{ij}$$

$$- 2 \sum_{ijk}^{MO} \left(U_{ik}^{ab} U_{jk}^c + U_{ik}^{bc} U_{jk}^a + U_{ik}^{ca} U_{jk}^b \right) x_{ij}$$

$$+ 2 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^c + S_{ik}^{bc} S_{jk}^a + S_{ik}^{ca} S_{jk}^b \right) x_{ij}$$

$$- 2 \sum_{ijkl}^{MO} \left(S_{ik}^a S_{jl}^b S_{kl}^c + S_{ik}^b S_{jl}^c S_{kl}^a + S_{ik}^c S_{jl}^a S_{kl}^b \right) x_{ij} \quad . \quad (16.70)$$

Referring to eq. (16.20), the last term of eq. (16.67) involving U^{ab} elements is explicitly written as

$$\begin{aligned} & 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial c} \frac{\partial^2 H_{IJ}}{\partial a \partial b} \\ &= 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial c} \left[H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} x_{ij}^{IJ} + 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \right. \\ & \quad \left. + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \right] \end{aligned} \quad (16.71)$$

where the H^{ab} , x^{IJ^a} , and y^{IJ} matrices are

$$H_{IJ}^{ab} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ} (ij|kl)^{ab} \quad (16.72)$$

$$x_{ij}^{IJ^a} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ} (im|kl)^a \quad (16.73)$$

$$y_{ijkl}^{IJ} = \gamma_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} \left\{ \Gamma_{jlmn}^{IJ} (ik|mn) + 2 \Gamma_{jmln}^{IJ} (im|kn) \right\} \quad . \quad (16.74)$$

Combining eqs. (16.70) and (16.71) with eq. (16.67), the terms involving the second-order U matrices are manipulated as follows:

$$2 \sum_{ij}^{MO} U_{ij}^{ab} \left[x_{ij}^{[c]} - \sum_k^{MO} U_{kj}^c x_{ki} + 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial c} x_{ij}^{IJ} \right] \quad (16.75)$$

$$= 2 \sum_{ij}^{MO} U_{ij}^{ab} \left[\frac{\partial x_{ij}}{\partial c} - \sum_k^{MO} (U_{ki}^c x_{kj} + U_{kj}^c x_{ki}) \right] \quad (16.76)$$

$$= - \sum_{ij}^{MO} \xi_{ij}^{ab} \left[\frac{\partial x_{ij}}{\partial c} - \sum_k^{MO} (U_{ki}^c x_{kj} + U_{kj}^c x_{ki}) \right] \quad (16.77)$$

$$= - \sum_{ij}^{MO} \xi_{ij}^{ab} \left[x_{ij}^{[c]} - \sum_k^{MO} U_{kj}^c x_{ki} + 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial c} x_{ij}^{IJ} \right] . \quad (16.78)$$

The definition (16.65) was used for the first equality from eq. (16.75) to eq. (16.76) and the relationships (16.53) and (16.63) were introduced to obtain eq. (16.78). The skeleton (core) second derivative Lagrangian matrices are defined by

$$x_{ij}^{ab} = \sum_m^{MO} \gamma_{jm} h_{im}^{ab} + 2 \sum_{mkl}^{MO} \Gamma_{jml}(im|kl)^{ab} \quad (16.79)$$

and the skeleton (core) first derivative y matrices by

$$y_{ijkl}^a = \gamma_{jl} h_{ik}^a + 2 \sum_{mn}^{MO} \left\{ \Gamma_{jlmn}(ik|mn)^a + 2\Gamma_{jmln}(im|kn)^a \right\} . \quad (16.80)$$

Using the result in eq. (16.78) and definitions in eqs. (16.79) and (16.80), the third derivative expression for the MCSCF energy is found from eqs. (16.16) and (16.25) to be

$$\begin{aligned} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{abc} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{abc} - \sum_{ij}^{MO} S_{ij}^{abc} x_{ij} \\ &+ 2 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^c + S_{ik}^{bc} S_{jk}^a + S_{ik}^{ca} S_{jk}^b \right) x_{ij} \\ &- 2 \sum_{ijkl}^{MO} \left(S_{ik}^a S_{jl}^b S_{kl}^c + S_{ik}^b S_{jl}^c S_{kl}^a + S_{ik}^c S_{jl}^a S_{kl}^b \right) x_{ij} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^a x_{ij}^{bc} + U_{ij}^b x_{ij}^{ca} + U_{ij}^c x_{ij}^{ab} \right) \\ &+ 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b y_{ijkl}^c + U_{ij}^b U_{kl}^c y_{ijkl}^a + U_{ij}^c U_{kl}^a y_{ijkl}^b \right) \\ &+ 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} \Gamma_{jlnp}(ik|mp) \\ &- \sum_{ij}^{MO} \left[\xi_{ij}^{ab} \left(x_{ij}^{[c]} - \sum_k^{MO} U_{kj}^c x_{ki} \right) + \xi_{ij}^{bc} \left(x_{ij}^{[a]} - \sum_k^{MO} U_{kj}^a x_{ki} \right) \right. \\ &\quad \left. + \xi_{ij}^{ca} \left(x_{ij}^{[b]} - \sum_k^{MO} U_{kj}^b x_{ki} \right) \right] \end{aligned}$$

$$\begin{aligned}
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H'_{IJ}}{\partial b \partial c} + \frac{\partial C_J}{\partial b} \frac{\partial^2 H'_{IJ}}{\partial c \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^2 H'_{IJ}}{\partial a \partial b} \right) \\
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right. \\
& \quad + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \\
& \quad \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \right] \tag{16.81}
\end{aligned}$$

where

$$\frac{\partial^2 H'_{IJ}}{\partial a \partial b} = H_{IJ}^{ab} - \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij}^{IJ} + 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} . \tag{16.82}$$

Note that the third derivative of an MCSCF wavefunction requires *only* the solution of the first-order CPMCHF equations.

16.3.5 Fourth Derivative

The fourth derivative of the electronic energy may be obtained by manipulating the CI fourth derivative expression presented in Section 16.1. For this purpose it is necessary to introduce the fourth derivative form of the orthonormality condition of the molecular orbitals as

$$U_{ij}^{abcd} + U_{ji}^{abcd} + \xi_{ij}^{abcd} = 0 \tag{16.83}$$

where the augmented S matrix, ξ^{abcd} , is defined by

$$\begin{aligned}
\xi_{ij}^{abcd} &= S_{ij}^{abcd} \\
&+ \sum_m^{MO} \left(U_{im}^{abc} U_{jm}^d + U_{jm}^{abc} U_{im}^d + U_{im}^{bcd} U_{jm}^a + U_{jm}^{bcd} U_{im}^a \right. \\
&\quad \left. + U_{im}^{cda} U_{jm}^b + U_{jm}^{cda} U_{im}^b + U_{im}^{dab} U_{jm}^c + U_{jm}^{dab} U_{im}^c \right) \\
&+ \sum_m^{MO} \left(U_{im}^{ab} U_{jm}^{cd} + U_{jm}^{ab} U_{im}^{cd} + U_{im}^{ac} U_{jm}^{bd} + U_{jm}^{ac} U_{im}^{bd} + U_{im}^{ad} U_{jm}^{bc} + U_{jm}^{ad} U_{im}^{bc} \right) \\
&- \sum_m^{MO} \left(S_{im}^{abc} S_{jm}^d + S_{jm}^{abc} S_{im}^d + S_{im}^{bcd} S_{jm}^a + S_{jm}^{bcd} S_{im}^a \right. \\
&\quad \left. + S_{im}^{cda} S_{jm}^b + S_{jm}^{cda} S_{im}^b + S_{im}^{dab} S_{jm}^c + S_{jm}^{dab} S_{im}^c \right) \\
&- \sum_m^{MO} \left(S_{im}^{ab} S_{jm}^{cd} + S_{jm}^{ab} S_{im}^{cd} + S_{im}^{ac} S_{jm}^{bd} + S_{jm}^{ac} S_{im}^{bd} + S_{im}^{ad} S_{jm}^{bc} + S_{jm}^{ad} S_{im}^{bc} \right) \\
&+ \omega_{ij}^{abcd} . \tag{16.84}
\end{aligned}$$

The ω matrices in eq. (16.84) are defined by

$$\begin{aligned}
 \omega_{ij}^{abcd} = & \sum_m^{MO} \left(S_{im}^{ab} \pi_{jm}^{cd} + S_{jm}^{ab} \pi_{im}^{cd} + S_{im}^{ac} \pi_{jm}^{bd} + S_{jm}^{ac} \pi_{im}^{bd} + S_{im}^{ad} \pi_{jm}^{bc} + S_{jm}^{ad} \pi_{im}^{bc} \right. \\
 & + S_{im}^{bc} \pi_{jm}^{ad} + S_{jm}^{bc} \pi_{im}^{ad} + S_{im}^{bd} \pi_{jm}^{ac} + S_{jm}^{bd} \pi_{im}^{ac} + S_{im}^{cd} \pi_{jm}^{ab} + S_{jm}^{cd} \pi_{im}^{ab} \Big) \\
 & + \sum_{mn}^{MO} \left[\left(S_{mn}^{ab} - \pi_{mn}^{ab} \right) \left(S_{im}^c S_{jn}^d + S_{jm}^c S_{in}^d \right) \right. \\
 & + \left(S_{mn}^{ac} - \pi_{mn}^{ac} \right) \left(S_{im}^b S_{jn}^d + S_{jm}^b S_{in}^d \right) \\
 & + \left(S_{mn}^{ad} - \pi_{mn}^{ad} \right) \left(S_{im}^b S_{jn}^c + S_{jm}^b S_{in}^c \right) \\
 & + \left(S_{mn}^{bc} - \pi_{mn}^{bc} \right) \left(S_{im}^a S_{jn}^d + S_{jm}^a S_{in}^d \right) \\
 & + \left(S_{mn}^{bd} - \pi_{mn}^{bd} \right) \left(S_{im}^a S_{jn}^c + S_{jm}^a S_{in}^c \right) \\
 & \left. \left. + \left(S_{mn}^{cd} - \pi_{mn}^{cd} \right) \left(S_{im}^a S_{jn}^b + S_{jm}^a S_{in}^b \right) \right] \right] \tag{16.85}
 \end{aligned}$$

where

$$\pi_{mn}^{ab} = \sum_k^{MO} \left(S_{mk}^a S_{nk}^b + S_{mk}^b S_{nk}^a \right) . \tag{16.86}$$

In eqs. (16.28) and (16.35), those terms that potentially include the third and fourth derivatives of the MO coefficients are

$$\begin{aligned}
 & 2 \sum_{ij}^{MO} U_{ij}^{abcd} x_{ij} + 2 \sum_{ij}^{MO} \left(U_{ij}^{abc} x_{ij}^{[d]} + U_{ij}^{bcd} x_{ij}^{[a]} + U_{ij}^{cda} x_{ij}^{[b]} + U_{ij}^{dab} x_{ij}^{[c]} \right) \\
 & + 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial^3 H_{IJ}}{\partial b \partial c \partial d} + \frac{\partial C_J}{\partial b} \frac{\partial^3 H_{IJ}}{\partial c \partial d \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^3 H_{IJ}}{\partial d \partial a \partial b} + \frac{\partial C_J}{\partial d} \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \right) \\
 & . \tag{16.87}
 \end{aligned}$$

The fourth derivatives of the MO coefficients in the first term of eq. (16.87) may be removed using eqs. (16.45), (16.83) and (16.84) as

$$2 \sum_{ij}^{MO} U_{ij}^{abcd} x_{ij} = \sum_{ij}^{MO} \left(U_{ij}^{abcd} + U_{ji}^{abcd} \right) x_{ij} \tag{16.88}$$

$$= - \sum_{ij}^{MO} \xi_{ij}^{abcd} x_{ij} \tag{16.89}$$

$$= - \sum_{ij}^{MO} S_{ij}^{abcd} x_{ij}$$

$$\begin{aligned}
& - 2 \sum_{ijk}^{MO} \left(U_{ik}^{abc} U_{jk}^d + U_{ik}^{bcd} U_{jk}^a + U_{ik}^{cda} U_{jk}^b + U_{ik}^{dab} U_{jk}^c \right) x_{ij} \\
& - 2 \sum_{ijk}^{MO} \left(U_{ik}^{ab} U_{jk}^{cd} + U_{ik}^{ac} U_{jk}^{bd} + U_{ik}^{ad} U_{jk}^{bc} \right) x_{ij} \\
& + 2 \sum_{ijk}^{MO} \left(S_{ik}^{abc} S_{jk}^d + S_{ik}^{bcd} S_{jk}^a + S_{ik}^{cda} S_{jk}^b + S_{ik}^{dab} S_{jk}^c \right) x_{ij} \\
& + 2 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^{cd} + S_{ik}^{ac} S_{jk}^{bd} + S_{ik}^{ad} S_{jk}^{bc} \right) x_{ij} \\
& - \sum_{ij}^{MO} \omega_{ij}^{abcd} x_{ij} . \tag{16.90}
\end{aligned}$$

Referring to eq. (16.29), the last term of eq. (16.87) involving U^{abc} elements is explicitly written as

$$\begin{aligned}
& 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial d} \frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} \\
& = 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial d} \left[H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^{abc} x_{ij}^{IJ} \right. \\
& \quad + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} x_{ij}^{IJ^c} + U_{ij}^{bc} x_{ij}^{IJ^a} + U_{ij}^{ca} x_{ij}^{IJ^b} \right) \\
& \quad + 2 \sum_{ij}^{MO} \left(U_{ij}^a x_{ij}^{IJ^{bc}} + U_{ij}^b x_{ij}^{IJ^{ca}} + U_{ij}^c x_{ij}^{IJ^{ab}} \right) \\
& \quad + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) y_{ijkl}^{IJ} \\
& \quad + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b y_{ijkl}^{IJ^c} + U_{ij}^b U_{kl}^c y_{ijkl}^{IJ^a} + U_{ij}^c U_{kl}^a y_{ijkl}^{IJ^b} \right) \\
& \quad \left. + 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} \Gamma_{jlnp}^{IJ}(ik|mp) \right] \tag{16.91}
\end{aligned}$$

where the H_{IJ}^{abc} , $x_{ij}^{IJ^{ab}}$, and $y_{ijkl}^{IJ^a}$ matrices are

$$H_{IJ}^{abc} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{abc} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl)^{abc} , \tag{16.92}$$

$$x_{ij}^{IJ^{ab}} = \sum_{jm}^{MO} \gamma_{jm}^{IJ} h_{im}^{ab} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ}(im|kl)^{ab} , \tag{16.93}$$

and

$$y_{ijkl}^{IJ^a} = \gamma_{jl}^{IJ} h_{ik}^a + 2 \sum_{mn}^{MO} \left\{ \Gamma_{jlmn}^{IJ}(ik|mn)^a + 2\Gamma_{jmln}^{IJ}(im|kn)^a \right\} . \quad (16.94)$$

Combining eqs. (16.90) and (16.91) with eq. (16.87), the terms involving the third derivative U matrices are treated in a similar manner as for the second derivative U matrices in the preceding subsection:

$$2 \sum_{ij}^{MO} U_{ij}^{abc} \left[x_{ij}^{[d]} - \sum_k^{MO} U_{kj}^d x_{ki} + 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial d} x_{ij}^{IJ} \right] \quad (16.95)$$

$$= 2 \sum_{ij}^{MO} U_{ij}^{abc} \left[\frac{\partial x_{ij}}{\partial d} - \sum_k^{MO} (U_{ki}^d x_{kj} + U_{kj}^d x_{ki}) \right] \quad (16.96)$$

$$= - \sum_{ij}^{MO} \xi_{ij}^{abc} \left[\frac{\partial x_{ij}}{\partial d} - \sum_k^{MO} (U_{ki}^d x_{kj} + U_{kj}^d x_{ki}) \right] \quad (16.97)$$

$$= - \sum_{ij}^{MO} \xi_{ij}^{abc} \left[x_{ij}^{[d]} - \sum_k^{MO} U_{kj}^d x_{ki} + 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial d} x_{ij}^{IJ} \right] . \quad (16.98)$$

The definition (16.65) was used for the first equality from eq. (16.95) to eq. (16.96) and the relationships (16.63) and (16.83) were employed to obtain eq. (16.98). It is useful to define the modified second derivative Lagrangian matrices as

$$x_{ij}^{[ab]} = x_{ij}^{ab} + \sum_{kl}^{MO} (U_{kl}^b y_{ijkl}^a + U_{kl}^a y_{ijkl}^b) + \sum_{klmn}^{MO} U_{kl}^a U_{mn}^b z_{ijklmn} \quad (16.99)$$

where the z matrix is given by

$$z_{ijklmn} = 4 \sum_p^{MO} \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right\} . \quad (16.100)$$

The skeleton (core) third derivative Lagrangian matrices are defined by

$$x_{ij}^{abc} = \sum_m^{MO} \gamma_{jm} h_{im}^{abc} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl)^{abc} , \quad (16.101)$$

the skeleton (core) second derivative y matrices by

$$y_{ijkl}^{ab} = \gamma_{jl} h_{ik}^{ab} + 2 \sum_{mn}^{MO} \left\{ \Gamma_{jlmn}(ik|mn)^{ab} + 2\Gamma_{jmln}(im|kn)^{ab} \right\} , \quad (16.102)$$

and the skeleton (core) first derivative z matrices by

$$z_{ijklmn}^a = 4 \sum_p^{MO} \left\{ \Gamma_{jlnp}(ik|mp)^a + \Gamma_{jnlp}(im|kp)^a + \Gamma_{jpln}(ip|km)^a \right\} . \quad (16.103)$$

Using the result in eq. (16.98) and definitions from eqs. (16.99) to (16.103), the fourth derivative expression for the MCSCF energy is found from eqs. (16.28) and (16.35) to be

$$\begin{aligned}
\frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} = & \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{abcd} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{abcd} - \sum_{ij}^{MO} S_{ij}^{abcd} x_{ij} \\
& - 2 \sum_{ijk}^{MO} \left(U_{ik}^{ab} U_{jk}^{cd} + U_{ik}^{ac} U_{jk}^{bd} + U_{ik}^{ad} U_{jk}^{bc} \right) x_{ij} \\
& + 2 \sum_{ijk}^{MO} \left(S_{ik}^{abc} S_{jk}^d + S_{ik}^{bcd} S_{jk}^a + S_{ik}^{cda} S_{jk}^b + S_{ik}^{dab} S_{jk}^c \right) x_{ij} \\
& + 2 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^{cd} + S_{ik}^{ac} S_{jk}^{bd} + S_{ik}^{ad} S_{jk}^{bc} \right) x_{ij} \\
& - \sum_{ij}^{MO} \omega_{ij}^{abcd} x_{ij} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} x_{ij}^{[cd]} + U_{ij}^{ac} x_{ij}^{[bd]} + U_{ij}^{ad} x_{ij}^{[bc]} \right. \\
& \quad \left. + U_{ij}^{bc} x_{ij}^{[ad]} + U_{ij}^{bd} x_{ij}^{[ac]} + U_{ij}^{cd} x_{ij}^{[ab]} \right) \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^a x_{ij}^{bcd} + U_{ij}^b x_{ij}^{cda} + U_{ij}^c x_{ij}^{dab} + U_{ij}^d x_{ij}^{abc} \right) \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) y_{ijkl} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b y_{ijkl}^{cd} + U_{ij}^a U_{kl}^c y_{ijkl}^{bd} + U_{ij}^a U_{kl}^d y_{ijkl}^{bc} \right. \\
& \quad \left. + U_{ij}^b U_{kl}^c y_{ijkl}^{ad} + U_{ij}^b U_{kl}^d y_{ijkl}^{ac} + U_{ij}^c U_{kl}^d y_{ijkl}^{ab} \right) \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c z_{ijklmn}^d + U_{ij}^b U_{kl}^c U_{mn}^d z_{ijklmn}^a \right. \\
& \quad \left. + U_{ij}^c U_{kl}^d U_{mn}^a z_{ijklmn}^b + U_{ij}^d U_{kl}^a U_{mn}^b z_{ijklmn}^c \right) \\
& + 8 \sum_{ijklmno}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) \\
& \quad \times \Gamma_{jlnp}(ik|mo) \\
& - \sum_{ij}^{MO} \left[\xi_{ij}^{abc} \left(x_{ij}^{[d]} - \sum_k^{MO} U_{kj}^d x_{ki} \right) + \xi_{ij}^{bcd} \left(x_{ij}^{[a]} - \sum_k^{MO} U_{kj}^a x_{ki} \right) \right]
\end{aligned}$$

$$\begin{aligned}
& + \xi_{ij}^{eda} \left(x_{ij}^{[b]} - \sum_k^{MO} U_{kj}^b x_{ki} \right) + \xi_{ij}^{dab} \left(x_{ij}^{[c]} - \sum_k^{MO} U_{kj}^c x_{ki} \right) \Big] \\
+ & 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial^3 H'_{IJ}}{\partial b \partial c \partial d} + \frac{\partial C_J}{\partial b} \frac{\partial^3 H'_{IJ}}{\partial c \partial d \partial a} \right. \\
& \quad \left. + \frac{\partial C_J}{\partial c} \frac{\partial^3 H'_{IJ}}{\partial d \partial a \partial b} + \frac{\partial C_J}{\partial d} \frac{\partial^3 H'_{IJ}}{\partial a \partial b \partial c} \right] \\
+ & 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right) \right. \\
& \quad + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \\
& \quad + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
& \quad + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \\
& \quad + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \\
& \quad \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \right] \\
- & 2 \sum_{IJ}^{CI} \left[\frac{\partial^2 C_I}{\partial a \partial b} \frac{\partial^2 C_J}{\partial c \partial d} + \frac{\partial^2 C_I}{\partial a \partial c} \frac{\partial^2 C_J}{\partial b \partial d} + \frac{\partial^2 C_I}{\partial a \partial d} \frac{\partial^2 C_J}{\partial b \partial c} \right] \left(H_{IJ} - \delta_{IJ} E_{elec} \right)
\end{aligned} \tag{16.104}$$

where

$$\begin{aligned}
\frac{\partial^3 H'_{IJ}}{\partial a \partial b \partial c} = & H_{IJ}^{abc} - \sum_{ij}^{MO} \xi_{ij}^{abc} x_{ij}^{IJ} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} x_{ij}^{IJc} + U_{ij}^{bc} x_{ij}^{IJa} + U_{ij}^{ca} x_{ij}^{IJb} \right) \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^a x_{ij}^{IJbc} + U_{ij}^b x_{ij}^{IJca} + U_{ij}^c x_{ij}^{IJab} \right) \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) y_{ijkl}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b y_{ijkl}^{IJc} + U_{ij}^b U_{kl}^c y_{ijkl}^{IJa} + U_{ij}^c U_{kl}^a y_{ijkl}^{IJb} \right) \\
& + 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} \Gamma_{jlnp}^{IJ}(ik|mp) \\
& .
\end{aligned} \tag{16.105}$$

Note that the fourth derivative of an MCSCF wavefunction requires the solutions of both the first- *and* second-order CPMCHF equations.

16.4 Paired Excitation Multiconfiguration Self-Consistent-Field (PEMCSCF) Wavefunctions

16.4.1 Electronic Energy and the Variational Condition

The electronic energy of a PEMCSCF wavefunction is given by the much less intricate (compared to general MCSCF) expression

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (16.106)$$

$$= 2 \sum_i^{MO} f_i h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} . \quad (16.107)$$

Two-configuration self-consistent-field (TCSCF) and generalized valence bond (GVB) wavefunctions are in turn special cases of PEMCSCF wavefunctions. While the equations from the previous section for an MCSCF wavefunction formally are applicable to a PEMCSCF wavefunction, the following *correspondence* relationships are introduced to further simplify the energy and derivative expressions.

For the one-electron reduced density and coupling constant matrices the relations

$$\gamma_{ij} = 2\delta_{ij}f_i \quad (16.108)$$

and

$$\gamma_{ij}^{IJ} = 2\delta_{ij}f_i^{IJ} \quad (16.109)$$

hold. For the two-electron reduced density and coupling constant matrices,

$$\Gamma_{ijkl} = \delta_{ij}\delta_{kl}\alpha_{ik} + \frac{1}{2} \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} \right) \beta_{ij} \quad (16.110)$$

and

$$\Gamma_{ijkl}^{IJ} = \delta_{ij}\delta_{kl}\alpha_{ik}^{IJ} + \frac{1}{2} \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} \right) \beta_{ij}^{IJ} . \quad (16.111)$$

These equations clearly show the one-dimensionality of the one-electron reduced density matrix and the two-dimensionality of the two-electron reduced density matrix for a PEMCSCF wavefunction as was described in Chapter 8.

Using eqs. (16.108) and (16.110), the expression for the electronic energy, eq. (16.107), is derived from eq. (16.40) as follows :

$$E_{elec} = \sum_{ij}^{MO} \gamma_{ij} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl) \quad (16.112)$$

$$\begin{aligned}
&= \sum_{ij}^{MO} (2\delta_{ij}f_i)h_{ij} \\
&+ \sum_{ijkl}^{MO} \left\{ \delta_{ij}\delta_{kl}\alpha_{ik} + \frac{1}{2} (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\beta_{ij} \right\} (ij|kl) \quad (16.113)
\end{aligned}$$

$$\begin{aligned}
&= 2 \sum_i^{MO} f_i h_{ii} + \sum_{ik}^{MO} \alpha_{ik}(ii|kk) + \frac{1}{2} \sum_{ij}^{MO} \beta_{ij} \left\{ (ij|ij) + (ij|ji) \right\} \\
&\quad . \quad (16.114)
\end{aligned}$$

$$\begin{aligned}
&= 2 \sum_i^{MO} f_i h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} . \quad (16.115)
\end{aligned}$$

After similar manipulations, the CI Hamiltonian matrix for the PEMCSCF wavefunction becomes

$$H_{IJ} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ} (ij|kl) \quad (16.116)$$

$$= 2 \sum_i^{MO} f_i^{IJ} h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj) + \beta_{ij}^{IJ}(ij|ij) \right\} . \quad (16.117)$$

The variational condition in the MO space for the PEMCSCF wavefunction is given by

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad (16.118)$$

where the Lagrangian matrix ϵ is

$$\epsilon_{ij} = f_i h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} . \quad (16.119)$$

Using the *correspondence* equations (16.108) and (16.110), eqs. (16.46) and (16.119) are related as follows:

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl} (im|kl) \quad (16.120)$$

$$\begin{aligned}
&= \sum_m^{MO} (2\delta_{jm}f_j)h_{im} \\
&+ 2 \sum_{mkl}^{MO} \left\{ \delta_{jm}\delta_{kl}\alpha_{jk} + \frac{1}{2} (\delta_{jk}\delta_{ml} + \delta_{jl}\delta_{mk})\beta_{jm} \right\} (im|kl) \quad (16.121)
\end{aligned}$$

$$\begin{aligned}
&= 2f_j h_{ij} \\
&+ 2 \sum_k^{MO} \alpha_{jk}(ij|kk) + \sum_l^{MO} \beta_{jl}(il|jl) + \sum_k^{MO} \beta_{jk}(ik|kj) \quad (16.122)
\end{aligned}$$

$$= 2f_j h_{ij} + 2 \sum_l^{MO} \left\{ \alpha_{jl}(ij|ll) + \beta_{jl}(il|jl) \right\} \quad (16.123)$$

$$= 2\epsilon_{ji} . \quad (16.124)$$

16.4.2 First Derivative

The first derivative of the electronic energy is obtained from eq. (16.52) using the *correspondence* equations, eqs. (16.108), (16.110) and (16.124):

$$\frac{\partial E_{elec}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a - \sum_{ij}^{MO} S_{ij}^a x_{ij} \quad (16.125)$$

$$\begin{aligned} &= \sum_{ij}^{MO} (2\delta_{ij} f_i) h_{ij}^a \\ &+ \sum_{ijkl}^{MO} \left\{ \delta_{ij} \delta_{kl} \alpha_{ik} + \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \beta_{ij} \right\} (ij|kl)^a \\ &- \sum_{ij}^{MO} S_{ij}^a (2\epsilon_{ji}) \end{aligned} \quad (16.126)$$

$$\begin{aligned} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{MO} S_{ij}^a \epsilon_{ij} . \end{aligned} \quad (16.127)$$

Equation (16.127) shows that, as with any other MCSCF wavefunction, the first derivative of a PEMCSCF wavefunction does *not* require solution of the coupled perturbed PEMCHF (CPPEMCHF) equations.

16.4.3 Second Derivative

Before continuing on to the second derivative expression, it is necessary to define one more *correspondence* equation for the y matrix:

$$y_{ijkl} = 2\delta_{jl}\zeta_{ik}^j + 2\tau_{ij,kl}^{jl} . \quad (16.128)$$

The generalized Lagrangian ζ^l and τ matrices in this equation are

$$\zeta_{ij}^l = f_l h_{ij} + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk) + \beta_{lk}(ik|jk) \right\} \quad (16.129)$$

and

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl) + \beta_{mn}\left\{(ik|jl) + (il|jk)\right\} . \quad (16.130)$$

Given these *correspondence* equations, the second derivative of the electronic energy for the PEMCSCF wavefunction is derived from eq. (16.58) as

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{ab} \\ &- \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (16.131)$$

An obvious relationship for the skeleton (core) first derivative Lagrangian matrices is

$$x_{ij}^a = 2\epsilon_{ji}^a \quad (16.132)$$

which with

$$\epsilon_{ij}^a = f_i h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} \quad (16.133)$$

can be used to rewrite eq. (16.131) above as

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} (2\delta_{ij} f_i) h_{ij}^{ab} \\ &+ \sum_{ijkl}^{MO} \left\{ \delta_{ij} \delta_{kl} \alpha_{ik} + \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \beta_{ij} \right\} (ij|kl)^{ab} \\ &- \sum_{ij}^{MO} \xi_{ij}^{ab} (2\epsilon_{ji}^a) \\ &+ 2 \sum_{ij}^{MO} \left\{ U_{ij}^b (2\epsilon_{ji}^a) + U_{ij}^a (2\epsilon_{ji}^b) \right\} \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \left(2\delta_{jl} \zeta_{ik}^j + 2\tau_{ij,kl}^{jl} \right) \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \end{aligned} \quad (16.134)$$

$$\begin{aligned}
&= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
&- 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \epsilon_{ij} \\
&+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\
&+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \\
&- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) .
\end{aligned} \tag{16.135}$$

The ξ^{ab} matrices were defined by eq. (16.54) and H_{IJ} by eq. (16.117). Note that the second derivative of the PEMCSCF energy requires the solution of the first-order CPPEMCHF equations.

16.4.4 Third Derivative

The third derivative of the electronic energy may be obtained from the MCSCF third derivative expression presented in Section 16.3. For this purpose the following correspondence relationships are employed:

$$x_{ij}^{ab} = 2\epsilon_{ji}^{ab} \tag{16.136}$$

with

$$\epsilon_{ij}^{ab} = f_i h_{ij}^{ab} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^{ab} + \beta_{il}(il|jl)^{ab} \right\} , \tag{16.137}$$

$$y_{ijkl}^a = 2\delta_{jl}\zeta_{ik}^{ja} + 2\tau_{ij,kl}^{jl} \tag{16.138}$$

with

$$\zeta_{ij}^{la} = f_l h_{ij}^a + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk)^a + \beta_{lk}(ik|jk)^a \right\} \tag{16.139}$$

and

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl)^a + \beta_{mn} \left\{ (ik|jl)^a + (il|jk)^a \right\} , \tag{16.140}$$

$$x_{ij}^{IJ} = 2\epsilon_{ji}^{IJ} \tag{16.141}$$

with

$$\epsilon_{ij}^{IJ} = f_i^{IJ} h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll) + \beta_{il}^{IJ}(il|jl) \right\} , \tag{16.142}$$

$$y_{ijkl}^{IJ} = 2\delta_{jl}\zeta_{ik}^{IJ} + 2\tau_{ij,kl}^{jlIJ} \tag{16.143}$$

with

$$\zeta_{ij}^{IJ} = f_l^{IJ} h_{ij} + \sum_k^{MO} \left\{ \alpha_{lk}^{IJ}(ij|kk) + \beta_{lk}^{IJ}(ik|jk) \right\} \quad (16.144)$$

and

$$\tau_{ij,kl}^{mnIJ} = 2\alpha_{mn}^{IJ}(ij|kl) + \beta_{mn}^{IJ}\left\{ (ik|jl) + (il|jk) \right\} \quad , \quad (16.145)$$

$$x_{ij}^{IJ^a} = 2\epsilon_{ji}^{IJ^a} \quad (16.146)$$

with

$$\epsilon_{ij}^{IJ^a} = f_i^{IJ} h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll)^a + \beta_{il}^{IJ}(il|jl)^a \right\} \quad . \quad (16.147)$$

In eq. (16.81) one of the terms involving a product of U^a , U^b , and U^c may be simplified in the following manner:

$$\begin{aligned} & 8 \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \sum_p^{MO} \Gamma_{jlnp}(ik|mp) \\ &= 8 \sum_{ijklmnp}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \left[\delta_{jl} \delta_{np} \alpha_{jn} + \frac{1}{2} \left(\delta_{jn} \delta_{lp} + \delta_{jp} \delta_{ln} \right) \beta_{jl} \right] (ik|mp) \end{aligned} \quad (16.148)$$

$$\begin{aligned} &= 8 \sum_{ijklm}^{MO} U_{im}^a U_{jm}^b U_{kl}^c \alpha_{ml}(ij|kl) \\ &+ 4 \sum_{ijklm}^{MO} U_{jm}^a U_{kl}^b U_{im}^c \beta_{ml}(il|jk) + 4 \sum_{ijklm}^{MO} U_{kl}^a U_{im}^b U_{jm}^c \beta_{ml}(ik|jl) \quad . \quad (16.149) \end{aligned}$$

Using this result, the three terms involving products of U^a , U^b , and U^c in eq. (16.81) are manipulated as

$$\begin{aligned} & 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} \Gamma_{jlnp}(ik|mp) \\ &= 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \\ &\quad \times \left[2\alpha_{ml}(ij|kl) + \beta_{ml}(ik|jl) + \beta_{ml}(il|jk) \right] \quad (16.150) \end{aligned}$$

$$= 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml} \quad . \quad (16.151)$$

The first derivative form of the variational condition on the MO space is related to

$$\frac{\partial x_{ij}}{\partial a} - \frac{\partial x_{ji}}{\partial a} = 2\frac{\partial \epsilon_{ji}}{\partial a} - 2\frac{\partial \epsilon_{ij}}{\partial a} = 0 \quad . \quad (16.152)$$

The modified first derivative Lagrangian matrices in eq. (16.64) are related to the corresponding quantities as

$$x_{ij}^{[a]} = 2\epsilon_{ji}^{[a]} = x_{ij}^a + \sum_{kl}^{MO} U_{kl}^a y_{ijkl} \quad (16.153)$$

$$= 2\epsilon_{ji}^a + \sum_{kl}^{MO} U_{kl}^a (2\delta_{jl}\zeta_{ik}^j + 2\tau_{ij,kl}^{jl}) \quad . \quad (16.154)$$

Using eqs. (16.124) and (16.154), the term involving $x^{[c]}$ in eq. (16.81) may be rewritten as

$$\begin{aligned} & \sum_{ij}^{MO} \xi_{ij}^{ab} \left[x_{ij}^{[c]} - \sum_k^{MO} U_{kj}^c x_{ki} \right] \\ &= \sum_{ij}^{MO} \xi_{ij}^{ab} \left[2\epsilon_{ji}^c + \sum_{kl}^{MO} U_{kl}^c (2\delta_{jl}\zeta_{ik}^j + 2\tau_{ij,kl}^{jl}) - \sum_k^{MO} U_{kj}^c (2\epsilon_{ik}) \right] \end{aligned} \quad (16.155)$$

$$= 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \left[\epsilon_{ji}^c + \sum_k^{MO} U_{kj}^c (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^c \tau_{ij,kl}^{jl} \right] \quad . \quad (16.156)$$

The skeleton (core) first and second derivative Hamiltonian matrices are related to

$$H_{IJ}^a = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl)^a \quad (16.157)$$

$$= 2 \sum_i^{MO} f_i^{IJ} h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^a + \beta_{ij}^{IJ}(ij|ij)^a \right\} \quad (16.158)$$

and

$$H_{IJ}^{ab} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl)^{ab} \quad (16.159)$$

$$= 2 \sum_i^{MO} f_i^{IJ} h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^{ab} + \beta_{ij}^{IJ}(ij|ij)^{ab} \right\} \quad . \quad (16.160)$$

The first derivative of the Hamiltonian matrix element is rewritten as

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} \quad (16.161)$$

$$= H_{IJ}^a + 4 \sum_{ij}^{MO} U_{ij}^a \epsilon_{ji}^{IJ} \quad . \quad (16.162)$$

Using the corresponding equations given above, the third derivative in eq. (16.81) is reexpressed for the PEMCSCF wavefunction as

$$\frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} = 2 \sum_i^{MO} f_i h_{ii}^{abc} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{abc} + \beta_{ij}(ij|ij)^{abc} \right\} - 2 \sum_{ij}^{MO} S_{ij}^{abc} \epsilon_{ij} \quad$$

$$\begin{aligned}
& + 4 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^c + S_{ik}^{bc} S_{jk}^a + S_{ik}^{ca} S_{jk}^b \right) \epsilon_{ij} \\
& - 4 \sum_{ijkl}^{MO} \left(S_{ik}^a S_{jl}^b S_{kl}^c + S_{ik}^b S_{jl}^c S_{kl}^a + S_{ik}^c S_{jl}^a S_{kl}^b \right) \epsilon_{ij} \\
& + 4 \sum_{ij}^{MO} \left(U_{ij}^a \epsilon_{ji}^{bc} + U_{ij}^b \epsilon_{ji}^{ca} + U_{ij}^c \epsilon_{ji}^{ab} \right) \\
& + 4 \sum_{ijk}^{MO} \left(U_{ij}^a U_{kj}^b \zeta_{ik}^{jc} + U_{ij}^b U_{kj}^c \zeta_{ik}^{ja} + U_{ij}^c U_{kj}^a \zeta_{ik}^{jb} \right) \\
& + 4 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} + U_{ij}^b U_{kl}^c \tau_{ij,kl}^{jl} + U_{ij}^c U_{kl}^a \tau_{ij,kl}^{jl} \right) \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml} \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \left[\epsilon_{ji}^c + \sum_k^{MO} U_{kj}^c (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^c \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{bc} \left[\epsilon_{ji}^a + \sum_k^{MO} U_{kj}^a (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^a \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{ca} \left[\epsilon_{ji}^b + \sum_k^{MO} U_{kj}^b (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^b \tau_{ij,kl}^{jl} \right] \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H'_{IJ}}{\partial b \partial c} + \frac{\partial C_J}{\partial b} \frac{\partial^2 H'_{IJ}}{\partial c \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^2 H'_{IJ}}{\partial a \partial b} \right) \\
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ} \frac{\partial E_{elec}}{\partial c} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \right. \\
& \quad \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \frac{\partial E_{elec}}{\partial b} \right) \right]
\end{aligned} \tag{16.163}$$

where

$$\begin{aligned}
\frac{\partial^2 H'_{IJ}}{\partial a \partial b} & = H_{IJ}^{ab} - \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij}^{IJ} + 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ} + U_{ij}^a x_{ij}^{IJ} \right) \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \\
& = 2 \sum_i^{MO} f_i^{IJ} h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ} (ii|jj)^{ab} + \beta_{ij}^{IJ} (ij|ij)^{ab} \right\} - 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \epsilon_{ji}^{IJ}
\end{aligned} \tag{16.164}$$

$$\begin{aligned}
& + 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\
& + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \left(\delta_{jl} \zeta_{ik}^{jIJ} + \tau_{ij,kl}^{jIJ} \right) .
\end{aligned} \tag{16.165}$$

Equations (16.163) and (16.165) show that the third derivative of a PEMCSCF wavefunction requires *only* the solution of the first-order CPPEMCHF equations.

16.4.5 Fourth Derivative

The fourth derivative of the electronic energy may be obtained from the fourth derivative expression for the MCSCF wavefunction discussed in the preceding section. For this purpose the following correspondence relationships are used:

$$x_{ij}^{abc} = 2\epsilon_{ji}^{abc} \tag{16.166}$$

with

$$\epsilon_{ij}^{abc} = f_i h_{ij}^{abc} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^{abc} + \beta_{il}(il|jl)^{abc} \right\} , \tag{16.167}$$

$$y_{ijkl}^{ab} = 2\delta_{jl} \zeta_{ik}^{jab} + 2\tau_{ij,kl}^{jab} \tag{16.168}$$

with

$$\zeta_{ij}^{ab} = f_l h_{ij}^{ab} + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk)^{ab} + \beta_{lk}(ik|jk)^{ab} \right\} \tag{16.169}$$

and

$$\tau_{ij,kl}^{mnab} = 2\alpha_{mn}(ij|kl)^{ab} + \beta_{mn} \left\{ (ik|jl)^{ab} + (il|jk)^{ab} \right\} , \tag{16.170}$$

$$y_{ijkl}^{IJ^a} = 2\delta_{jl} \zeta_{ik}^{IJ^a} + 2\tau_{ij,kl}^{IJ^a} \tag{16.171}$$

with

$$\zeta_{ij}^{IJ^a} = f_l^{IJ} h_{ij}^a + \sum_k^{MO} \left\{ \alpha_{lk}^{IJ}(ij|kk)^a + \beta_{lk}^{IJ}(ik|jk)^a \right\} \tag{16.172}$$

and

$$\tau_{ij,kl}^{mnIJ^a} = 2\alpha_{mn}^{IJ}(ij|kl)^a + \beta_{mn}^{IJ} \left\{ (ik|jl)^a + (il|jk)^a \right\} , \tag{16.173}$$

$$x_{ij}^{IJab} = 2\epsilon_{ji}^{IJab} \tag{16.174}$$

with

$$\epsilon_{ij}^{IJab} = f_i^{IJ} h_{ij}^{ab} + \sum_l^{MO} \left\{ \alpha_{il}^{IJ}(ij|ll)^{ab} + \beta_{il}^{IJ}(il|jl)^{ab} \right\} . \tag{16.175}$$

The modified second derivative Lagrangian matrices in eq. (16.99) are manipulated as follows:

$$x_{ij}^{[ab]} = x_{ij}^{ab} + \sum_{kl}^{MO} \left(U_{kl}^b y_{ijkl}^a + U_{kl}^a y_{ijkl}^b \right) + \sum_{klmn}^{MO} U_{kl}^a U_{mn}^b z_{ijklmn} \quad (16.176)$$

$$= 2\epsilon_{ji}^{ab} + \sum_{kl}^{MO} U_{kl}^b \left(2\delta_{jl}\zeta_{ik}^{ja} + 2\tau_{ij,kl}^{jl^a} \right) + \sum_{kl}^{MO} U_{kl}^a \left(2\delta_{jl}\zeta_{ik}^{jb} + 2\tau_{ij,kl}^{jl^b} \right) \\ + \sum_{klmn}^{MO} U_{kl}^a U_{mn}^b z_{ijklmn} . \quad (16.177)$$

The last term of eq. (16.176) may then be simplified as

$$\sum_{klmn}^{MO} U_{kl}^a U_{mn}^b z_{ijklmn} \\ = 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right\} \quad (16.178)$$

$$= 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left[\left\{ \delta_{jl}\delta_{np}\alpha_{jn} + \frac{1}{2} (\delta_{jn}\delta_{lp} + \delta_{jp}\delta_{ln})\beta_{jl} \right\} (ik|mp) \right. \\ \left. + \left\{ \delta_{jn}\delta_{lp}\alpha_{jl} + \frac{1}{2} (\delta_{jl}\delta_{np} + \delta_{jp}\delta_{nl})\beta_{jn} \right\} (im|kp) \right. \\ \left. + \left\{ \delta_{jp}\delta_{ln}\alpha_{jl} + \frac{1}{2} (\delta_{jl}\delta_{pn} + \delta_{jn}\delta_{pl})\beta_{jp} \right\} (ip|km) \right] \quad (16.179)$$

$$= 2 \sum_{klm}^{MO} \left[\left(2U_{kj}^a U_{lm}^b \alpha_{jm}(ik|lm) + U_{km}^a U_{lj}^b \beta_{jm}(ik|lm) + U_{km}^a U_{lm}^b \beta_{jm}(ik|jl) \right) \right. \\ \left. + \left(2U_{km}^a U_{lj}^b \alpha_{jm}(il|km) + U_{kj}^a U_{lm}^b \beta_{jm}(il|km) + U_{km}^a U_{lm}^b \beta_{jm}(il|jk) \right) \right. \\ \left. + \left(2U_{km}^a U_{lm}^b \alpha_{jm}(ij|kl) + U_{kj}^a U_{lm}^b \beta_{jm}(im|kl) + U_{km}^a U_{lj}^b \beta_{jm}(im|kl) \right) \right] \quad (16.180)$$

$$= 2 \sum_{klm}^{MO} \left(U_{kj}^a U_{lm}^b \tau_{ik,lm}^{jm} + U_{km}^a U_{lj}^b \tau_{il,km}^{jm} + U_{km}^a U_{lm}^b \tau_{ij,kl}^{jm} \right) . \quad (16.181)$$

Thus, equation (16.176) is given in the following final form:

$$x_{ij}^{[ab]} = 2\epsilon_{ji}^{[ab]} \quad (16.182)$$

$$= 2\epsilon_{ji}^{ab} + 2 \sum_k^{MO} \left(U_{kj}^b \zeta_{ik}^{ja} + U_{kj}^a \zeta_{ik}^{jb} \right) + 2 \sum_{kl}^{MO} \left(U_{kl}^b \tau_{ij,kl}^{jl^a} + U_{kl}^a \tau_{ij,kl}^{jl^b} \right) \\ + 2 \sum_{klm}^{MO} \left(U_{kj}^a U_{lm}^b \tau_{ik,lm}^{jm} + U_{km}^a U_{lj}^b \tau_{il,km}^{jm} + U_{km}^a U_{lm}^b \tau_{ij,kl}^{jm} \right) . \quad (16.183)$$

In eq. (16.104) one of the terms involving the z^a matrices is reformulated as

$$\begin{aligned} & \sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c z_{ijklmn}^d \\ &= 4 \sum_{ijklmnp}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \left\{ \Gamma_{jlnp}(ik|mp)^d + \Gamma_{jnlp}(im|kp)^d + \Gamma_{jpln}(ip|km)^d \right\} \end{aligned} \quad (16.184)$$

$$\begin{aligned} &= 4 \sum_{ijklmn}^{MO} \left[U_{ij}^a U_{kl}^b U_{mn}^c \left\{ \delta_{jl} \delta_{np} \alpha_{jn} + \frac{1}{2} (\delta_{jn} \delta_{lp} + \delta_{jp} \delta_{ln}) \beta_{jl} \right\} (ik|mp)^d \right. \\ &\quad + U_{ij}^a U_{kl}^b U_{mn}^c \left\{ \delta_{jn} \delta_{lp} \alpha_{jl} + \frac{1}{2} (\delta_{jl} \delta_{np} + \delta_{jp} \delta_{nl}) \beta_{jn} \right\} (im|kp)^d \\ &\quad \left. + U_{ij}^a U_{kl}^b U_{mn}^c \left\{ \delta_{jp} \delta_{ln} \alpha_{jl} + \frac{1}{2} (\delta_{jl} \delta_{pn} + \delta_{jn} \delta_{pl}) \beta_{jp} \right\} (ip|km)^d \right] \end{aligned} \quad (16.185)$$

$$\begin{aligned} &= 2 \sum_{ijklm}^{MO} \left[\left(2U_{im}^a U_{jm}^b U_{kl}^c \alpha_{ml} (ij|kl)^d + U_{im}^c U_{jm}^a U_{kl}^b \beta_{ml} (il|jk)^d \right. \right. \\ &\quad + U_{im}^b U_{jm}^c U_{kl}^a \beta_{ml} (ik|jl)^d \Big) \\ &\quad + \left(2U_{im}^c U_{jm}^a U_{kl}^b \alpha_{ml} (ij|kl)^d + U_{im}^a U_{jm}^b U_{kl}^c \beta_{ml} (ik|jl)^d \right. \\ &\quad + U_{im}^b U_{jm}^c U_{kl}^a \beta_{ml} (il|jk)^d \Big) \\ &\quad \left. \left. + \left(2U_{im}^b U_{jm}^c U_{kl}^a \alpha_{ml} (ij|kl)^d + U_{im}^a U_{jm}^b U_{kl}^c \beta_{ml} (il|jk)^d \right. \right. \right. \\ &\quad \left. \left. \left. + U_{im}^c U_{jm}^a U_{kl}^b \beta_{ml} (ik|jl)^d \right) \right] \end{aligned} \quad (16.186)$$

$$= 2 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml^d}. \quad (16.187)$$

In eq. (16.104) one of the terms involving a product of U^a , U^b , U^c and U^d may be simplified in the following manner:

$$\begin{aligned} & 8 \sum_{ijklmno}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d \Gamma_{jlnp}(ik|mo) \\ &= 8 \sum_{ijklmno}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d \left[\delta_{jl} \delta_{np} \alpha_{jn} + \frac{1}{2} (\delta_{jn} \delta_{lp} + \delta_{jp} \delta_{ln}) \beta_{jl} \right] (ik|mo) \\ &= 8 \sum_{ijklmn}^{MO} U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d \alpha_{mn} (ij|kl) \end{aligned} \quad (16.188)$$

$$\begin{aligned}
& + 4 \sum_{ijklmn}^{MO} U_{im}^a U_{kn}^b U_{jm}^c U_{ln}^d \beta_{mn}(ik|jl) \\
& + 4 \sum_{ijklmn}^{MO} U_{im}^a U_{kn}^b U_{ln}^c U_{jm}^d \beta_{mn}(ik|jl) \quad . \tag{16.189}
\end{aligned}$$

Using this result the three terms involving products of U^a , U^b , U^c and U^d in eq. (16.104) are manipulated as

$$\begin{aligned}
& 8 \sum_{ijklmnp}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) \Gamma_{jlnp}(ik|mo) \\
& = 4 \sum_{ijklmn}^{MO} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) \\
& \quad \times \left[2\alpha_{mn}(ij|kl) + \beta_{mn}(ik|jl) + \beta_{mn}(il|jk) \right] \tag{16.190}
\end{aligned}$$

$$= 4 \sum_{ijklmn}^{MO} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) \tau_{ij,kl}^{mn} \quad . \tag{16.191}$$

The skeleton (core) third derivative Hamiltonian matrices are related to

$$H_{IJ}^{abc} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{abc} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl)^{abc} \tag{16.192}$$

$$= 2 \sum_i^{MO} f_i^{IJ} h_{ii}^{abc} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj)^{abc} + \beta_{ij}^{IJ}(ij|ij)^{abc} \right\} \quad . \tag{16.193}$$

The second derivative of the Hamiltonian matrix element is reformulated as

$$\begin{aligned}
\frac{\partial^2 H_{IJ}}{\partial a \partial b} & = H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} x_{ij}^{IJ} + 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\
& + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \tag{16.194}
\end{aligned}$$

$$\begin{aligned}
& = H_{IJ}^{ab} + 4 \sum_{ij}^{MO} U_{ij}^{ab} \epsilon_{ji}^{IJ} + 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\
& + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \left(\delta_{jl} \zeta_{ik}^{jIJ} + \tau_{ij,kl}^{jIJ} \right) \quad . \tag{16.195}
\end{aligned}$$

Using the correspondence equations given above, the fourth derivative in eq. (16.104) is reformulated for the PEMCSCF wavefunction as

$$\frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} = 2 \sum_i^{MO} f_i h_{ii}^{abcd} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{abcd} + \beta_{ij}(ij|ij)^{abcd} \right\} \quad$$

$$\begin{aligned}
& - 2 \sum_{ij}^{MO} S_{ij}^{abcd} \epsilon_{ij} \\
& - 4 \sum_{ijk}^{MO} \left(U_{ik}^{ab} U_{jk}^{cd} + U_{ik}^{ac} U_{jk}^{bd} + U_{ik}^{ad} U_{jk}^{bc} \right) \epsilon_{ij} \\
& + 4 \sum_{ijk}^{MO} \left(S_{ik}^{abc} S_{jk}^d + S_{ik}^{bcd} S_{jk}^a + S_{ik}^{cda} S_{jk}^b + S_{ik}^{dab} S_{jk}^c \right) \epsilon_{ij} \\
& + 4 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^{cd} + S_{ik}^{ac} S_{jk}^{bd} + S_{ik}^{ad} S_{jk}^{bc} \right) \epsilon_{ij} \\
& - 2 \sum_{ij}^{MO} \omega_{ij}^{abcd} \epsilon_{ij} \\
& + 4 \sum_{ij}^{MO} \left(U_{ij}^{ab} \epsilon_{ji}^{[cd]} + U_{ij}^{ac} \epsilon_{ji}^{[bd]} + U_{ij}^{ad} \epsilon_{ji}^{[bc]} \right. \\
& \quad \left. + U_{ij}^{bc} \epsilon_{ji}^{[ad]} + U_{ij}^{bd} \epsilon_{ji}^{[ac]} + U_{ij}^{cd} \epsilon_{ji}^{[ab]} \right) \\
& + 4 \sum_{ij}^{MO} \left(U_{ij}^a \epsilon_{ji}^{bcd} + U_{ij}^b \epsilon_{ji}^{cda} + U_{ij}^c \epsilon_{ji}^{dab} + U_{ij}^d \epsilon_{ji}^{abc} \right) \\
& + 4 \sum_{ijk}^{MO} \left(U_{ij}^{ab} U_{kj}^{cd} + U_{ij}^{ac} U_{kj}^{bd} + U_{ij}^{ad} U_{kj}^{bc} \right) \zeta_{ik}^j \\
& + 4 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) \tau_{ij,kl}^{jl} \\
& + 4 \sum_{ijk}^{MO} \left(U_{ij}^a U_{kj}^b \zeta_{ik}^{jcd} + U_{ij}^a U_{kj}^c \zeta_{ik}^{jbd} + U_{ij}^a U_{kj}^d \zeta_{ik}^{jbc} \right. \\
& \quad \left. + U_{ij}^b U_{kj}^c \zeta_{ik}^{jad} + U_{ij}^b U_{kj}^d \zeta_{ik}^{jac} + U_{ij}^c U_{kj}^d \zeta_{ik}^{jab} \right) \\
& + 4 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jcd} + U_{ij}^a U_{kl}^c \tau_{ij,kl}^{jbd} + U_{ij}^a U_{kl}^d \tau_{ij,kl}^{jbc} \right. \\
& \quad \left. + U_{ij}^b U_{kl}^c \tau_{ij,kl}^{jad} + U_{ij}^b U_{kl}^d \tau_{ij,kl}^{jac} + U_{ij}^c U_{kl}^d \tau_{ij,kl}^{jab} \right) \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml^d} \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^b U_{jm}^c U_{kl}^d + U_{im}^c U_{jm}^d U_{kl}^b + U_{im}^d U_{jm}^b U_{kl}^c \right) \tau_{ij,kl}^{ml^a}
\end{aligned}$$

$$\begin{aligned}
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^c U_{jm}^d U_{kl}^a + U_{im}^d U_{jm}^a U_{kl}^c + U_{im}^a U_{jm}^c U_{kl}^d \right) \tau_{ij,kl}^{mlb} \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^d U_{jm}^a U_{kl}^b + U_{im}^a U_{jm}^b U_{kl}^d + U_{im}^b U_{jm}^d U_{kl}^a \right) \tau_{ij,kl}^{mlc} \\
& + 4 \sum_{ijklmn}^{MO} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) \tau_{ij,kl}^{mn} \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{abc} \left[\epsilon_{ji}^d + \sum_k^{MO} U_{kj}^d \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^d \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{bcd} \left[\epsilon_{ji}^a + \sum_k^{MO} U_{kj}^a \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^a \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{cda} \left[\epsilon_{ji}^b + \sum_k^{MO} U_{kj}^b \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^b \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{dab} \left[\epsilon_{ji}^c + \sum_k^{MO} U_{kj}^c \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^c \tau_{ij,kl}^{jl} \right] \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial^3 H'_{IJ}}{\partial b \partial c \partial d} + \frac{\partial C_J}{\partial b} \frac{\partial^3 H'_{IJ}}{\partial c \partial d \partial a} \right. \\
& \quad \left. + \frac{\partial C_J}{\partial c} \frac{\partial^3 H'_{IJ}}{\partial d \partial a \partial b} + \frac{\partial C_J}{\partial d} \frac{\partial^3 H'_{IJ}}{\partial a \partial b \partial c} \right] \\
& + 2 \sum_{IJ}^{CI} \left[\frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\frac{\partial^2 H_{IJ}}{\partial c \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial c \partial d} \right) \right. \\
& \quad + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial d} \right) \\
& \quad + \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial b \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial b \partial c} \right) \\
& \quad + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial c} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial d} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial d} \right) \\
& \quad + \frac{\partial C_I}{\partial b} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial c} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial c} \right) \\
& \quad \left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial d} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) \right] \\
& - 2 \sum_{IJ}^{CI} \left[\frac{\partial^2 C_I}{\partial a \partial b} \frac{\partial^2 C_J}{\partial c \partial d} + \frac{\partial^2 C_I}{\partial a \partial c} \frac{\partial^2 C_J}{\partial b \partial d} + \frac{\partial^2 C_I}{\partial a \partial d} \frac{\partial^2 C_J}{\partial b \partial c} \right] \left(H_{IJ} - \delta_{IJ} E_{elec} \right)
\end{aligned} \tag{16.196}$$

where

$$\begin{aligned}
 \frac{\partial^3 H'_{IJ}}{\partial a \partial b \partial c} &= H_{IJ}^{abc} - \sum_{ij}^{MO} \xi_{ij}^{abc} x_{ij}^{IJ} \\
 &+ 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} x_{ij}^{IJc} + U_{ij}^{bc} x_{ij}^{IJa} + U_{ij}^{ca} x_{ij}^{IJb} \right) \\
 &+ 2 \sum_{ij}^{MO} \left(U_{ij}^a x_{ij}^{IJbc} + U_{ij}^b x_{ij}^{IJca} + U_{ij}^c x_{ij}^{IJab} \right) \\
 &+ 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) y_{ijkl}^{IJ} \\
 &+ 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b y_{ijkl}^{IJc} + U_{ij}^b U_{kl}^c y_{ijkl}^{IJa} + U_{ij}^c U_{kl}^a y_{ijkl}^{IJb} \right) \\
 &+ 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} \Gamma_{jlnp}^{IJ}(ik|mp) \\
 &\quad (16.197)
 \end{aligned}$$

$$\begin{aligned}
 &= H_{IJ}^{abc} - 2 \sum_{ij}^{MO} \xi_{ij}^{abc} \epsilon_{ji}^{IJ} \\
 &+ 4 \sum_{ij}^{MO} \left(U_{ij}^{ab} \epsilon_{ji}^{IJc} + U_{ij}^{bc} \epsilon_{ji}^{IJa} + U_{ij}^{ca} \epsilon_{ji}^{IJb} \right) \\
 &+ 4 \sum_{ij}^{MO} \left(U_{ij}^a \epsilon_{ji}^{IJbc} + U_{ij}^b \epsilon_{ji}^{IJca} + U_{ij}^c \epsilon_{ji}^{IJab} \right) \\
 &+ 4 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) \left(\delta_{jl} \zeta_{ik}^{IJ} + \tau_{ij,kl}^{IJ} \right) \\
 &+ 4 \sum_{ijkl}^{MO} \left[U_{ij}^a U_{kl}^b \left(\delta_{jl} \zeta_{ik}^{IJc} + \tau_{ij,kl}^{IJc} \right) + U_{ij}^b U_{kl}^c \left(\delta_{jl} \zeta_{ik}^{IJa} + \tau_{ij,kl}^{IJa} \right) \right. \\
 &\quad \left. + U_{ij}^c U_{kl}^a \left(\delta_{jl} \zeta_{ik}^{IJb} + \tau_{ij,kl}^{IJb} \right) \right] \\
 &+ 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{IJ} . \quad (16.198)
 \end{aligned}$$

For the last term of eq. (16.198) a correspondence equation similar to eq. (16.151) was used. Equations (16.196) and (16.198) indicate that evaluation of a PEMCSCF wavefunction requires the solution of both the first- and second-order CPPEMCHF equations.

16.5 General Restricted Open-Shell Self-Consistent-Field (GRSCF) Wavefunctions

16.5.1 Electronic Energy and the Variational Condition

The GRSCF wavefunction described in this section represents a further simplification of the PEMCSCF approach. The electronic energy for the GRSCF wavefunction is given by

$$E_{elec} = 2 \sum_i^{MO} f_i h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad (16.199)$$

where the summations run over all orbitals.

In principle, all the equations from the preceding two sections are applicable to a GRSCF wavefunction when appropriate restrictions specific to the single-configuration open-shell wavefunction are applied. The *correspondence* equations for the one- and two-electron density matrices formally are the same as for the PEMCSCF wavefunction of Section 16.4:

$$\gamma_{ij} = 2\delta_{ij}f_i \quad (16.200)$$

and

$$\Gamma_{ijkl} = \delta_{ij}\delta_{kl}\alpha_{ik} + \frac{1}{2} \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} \right) \beta_{ij} \quad . \quad (16.201)$$

In fact, the f 's, α 's, and β 's are much simpler for the single-configuration open-shell case than for the more complicated PEMCSCF case. In a very similar manner as was presented in Section 16.4, the energy expression (16.199) is derived from that for a MCSCF wavefunction, eq. (16.40):

$$E_{elec} = \sum_{ij}^{MO} \gamma_{ij} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl) \quad (16.202)$$

$$= \sum_{ij}^{MO} \left(2\delta_{ij}f_i \right) h_{ij} \\ + \sum_{ijkl}^{MO} \left\{ \delta_{ij}\delta_{kl}\alpha_{ik} + \frac{1}{2} \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} \right) \beta_{ij} \right\} (ij|kl) \quad (16.203)$$

$$= 2 \sum_i^{MO} f_i h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad . \quad (16.204)$$

The variational condition for this GRSCF wavefunction is

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad (16.205)$$

where the Lagrangian matrix ϵ is defined by

$$\epsilon_{ij} = f_i h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} \quad . \quad (16.206)$$

Using the *correspondence* equations (16.200) and (16.201), the relationship between eqs. (16.46) and (16.206) is obtained in the same way as was presented in Section 16.4:

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl) \quad (16.207)$$

$$\begin{aligned} &= \sum_m^{MO} (2\delta_{jm} f_j) h_{im} \\ &+ 2 \sum_{mkl}^{MO} \left\{ \delta_{jm} \delta_{kl} \alpha_{jk} + \frac{1}{2} (\delta_{jk} \delta_{ml} + \delta_{jl} \delta_{mk}) \beta_{jm} \right\} (im|kl) \end{aligned} \quad (16.208)$$

$$= 2f_j h_{ij} + 2 \sum_l^{MO} \left\{ \alpha_{jl}(ij|ll) + \beta_{jl}(il|jl) \right\} \quad (16.209)$$

$$= 2\epsilon_{ji} . \quad (16.210)$$

16.5.2 First Derivative

The first derivative of the electronic energy follows from eq. (16.52) and the *correspondence* equations, (16.200), (16.201) and (16.210):

$$\frac{\partial E_{elec}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a - \sum_{ij}^{MO} S_{ij}^a x_{ij} \quad (16.211)$$

$$\begin{aligned} &= \sum_{ij}^{MO} (2\delta_{ij} f_i) h_{ij}^a \\ &+ \sum_{ijkl}^{MO} \left\{ \delta_{ij} \delta_{kl} \alpha_{ik} + \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \beta_{ij} \right\} (ij|kl)^a \\ &- \sum_{ij}^{MO} S_{ij}^a (2\epsilon_{ji}) \end{aligned} \quad (16.212)$$

$$\begin{aligned} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{MO} S_{ij}^a \epsilon_{ij} . \end{aligned} \quad (16.213)$$

16.5.3 Second Derivative

In order to derive the second derivative expression for a GRSCF property from that for a MCSCF wavefunction, the following additional *correspondence* equation is necessary:

$$y_{ijkl} = 2\delta_{jl}\zeta_{ik}^j + 2\tau_{ij,kl}^{jl} . \quad (16.214)$$

The generalized Lagrangian ζ^l and τ matrices in this equation are defined by

$$\zeta_{ij}^l = f_l h_{ij} + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk) + \beta_{lk}(ik|jk) \right\} \quad (16.215)$$

and

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl) + \beta_{mn} \left\{ (ik|jl) + (il|jk) \right\} . \quad (16.216)$$

The second derivative expression for the MCSCF, eq. (16.58), is written without the CI contribution as

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{ab} \\ &- \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} . \end{aligned} \quad (16.217)$$

The following relationship may be derived in a manner similar to that of the Lagrangian matrix, eq. (16.207),

$$x_{ij}^a = 2\epsilon_{ji}^a \quad (16.218)$$

with

$$\epsilon_{ij}^a = f_i h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} \quad (16.219)$$

is also required to complete the derivation.

Using the correspondence equations described above, the energy second derivative expression for a GRSCF wavefunction is manipulated as

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \left(2\delta_{ij} f_i \right) h_{ij}^{ab} \\ &+ \sum_{ijkl}^{MO} \left\{ \delta_{ij} \delta_{kl} \alpha_{ik} + \frac{1}{2} \left(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right) \beta_{ij} \right\} (ij|kl)^{ab} \\ &- \sum_{ij}^{MO} \xi_{ij}^{ab} (2\epsilon_{ji}) \\ &+ 2 \sum_{ij}^{MO} \left\{ U_{ij}^b (2\epsilon_{ji}^a) + U_{ij}^a (2\epsilon_{ji}^b) \right\} \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \left\{ 2\delta_{jl} \zeta_{ik}^j + 2\tau_{ij,kl}^{jl} \right\} \end{aligned} \quad (16.220)$$

$$\begin{aligned}
&= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\
&- 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \epsilon_{ij} \\
&+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\
&+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} .
\end{aligned} \tag{16.221}$$

Equation (16.221) is equivalent to the MO part of eq. (16.135) for a PEMCSCF wavefunction.

16.5.4 Third Derivative

The third derivative of the electronic energy may be obtained from the MCSCF third derivative expression presented in Section 16.3 without the CI contributions. The following correspondence relationships are employed:

$$x_{ij}^{ab} = 2\epsilon_{ji}^{ab} \tag{16.222}$$

with

$$\epsilon_{ij}^{ab} = f_i h_{ij}^{ab} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^{ab} + \beta_{il}(il|jl)^{ab} \right\} , \tag{16.223}$$

$$y_{ijkl}^a = 2\delta_{jl}\zeta_{ik}^{ja} + 2\tau_{ij,kl}^{jl} \tag{16.224}$$

with

$$\zeta_{ij}^{la} = f_l h_{ij}^a + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk)^a + \beta_{lk}(ik|jk)^a \right\} \tag{16.225}$$

and

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl)^a + \beta_{mn} \left\{ (ik|jl)^a + (il|jk)^a \right\} , \tag{16.226}$$

$$\begin{aligned}
&8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} \Gamma_{jlnp}(ik|mp) \\
&= 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml} .
\end{aligned} \tag{16.227}$$

The first derivative form of the variational condition on the MO space is related to

$$\frac{\partial x_{ij}}{\partial a} - \frac{\partial x_{ji}}{\partial a} = 2\frac{\partial \epsilon_{ji}}{\partial a} - 2\frac{\partial \epsilon_{ij}}{\partial a} = 0 . \tag{16.228}$$

The modified first derivative Lagrangian matrices in eq. (16.64) are related to the corresponding quantities as

$$x_{ij}^{[a]} = 2\epsilon_{ji}^{[a]} = x_{ij}^a + \sum_{kl}^{MO} U_{kl}^a y_{ijkl} \quad (16.229)$$

$$= 2\epsilon_{ji}^a + \sum_{kl}^{MO} U_{kl}^a (2\delta_{jl}\zeta_{ik}^j + 2\tau_{ij,kl}^{jl}) \quad . \quad (16.230)$$

Using eqs. (16.210) and (16.230), the term involving $x^{[c]}$ in eq. (16.81) may be rewritten as

$$\begin{aligned} & \sum_{ij}^{MO} \xi_{ij}^{ab} \left[x_{ij}^{[c]} - \sum_k^{MO} U_{kj}^c x_{ki} \right] \\ &= 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \left[\epsilon_{ji}^c + \sum_k^{MO} U_{kj}^c (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^c \tau_{ij,kl}^{jl} \right] \quad . \quad (16.231) \end{aligned}$$

Using the corresponding equations given above, the third derivative in eq. (16.81) is reexpressed for the GRSCF wavefunction as

$$\begin{aligned} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} &= 2 \sum_i^{MO} f_i h_{ii}^{abc} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{abc} + \beta_{ij}(ij|ij)^{abc} \right\} - 2 \sum_{ij}^{MO} S_{ij}^{abc} \epsilon_{ij} \\ &+ 4 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^c + S_{ik}^{bc} S_{jk}^a + S_{ik}^{ca} S_{jk}^b \right) \epsilon_{ij} \\ &- 4 \sum_{ijkl}^{MO} \left(S_{ik}^a S_{jl}^b S_{kl}^c + S_{ik}^b S_{jl}^c S_{kl}^a + S_{ik}^c S_{jl}^a S_{kl}^b \right) \epsilon_{ij} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^a \epsilon_{ji}^{bc} + U_{ij}^b \epsilon_{ji}^{ca} + U_{ij}^c \epsilon_{ji}^{ab} \right) \\ &+ 4 \sum_{ijk}^{MO} \left(U_{ij}^a U_{kj}^b \zeta_{ik}^{jc} + U_{ij}^b U_{kj}^c \zeta_{ik}^{ja} + U_{ij}^c U_{kj}^a \zeta_{ik}^{jb} \right) \\ &+ 4 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} + U_{ij}^b U_{kl}^c \tau_{ij,kl}^{jl} + U_{ij}^c U_{kl}^a \tau_{ij,kl}^{jl} \right) \\ &+ 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml} \\ &- 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \left[\epsilon_{ji}^c + \sum_k^{MO} U_{kj}^c (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^c \tau_{ij,kl}^{jl} \right] \\ &- 2 \sum_{ij}^{MO} \xi_{ij}^{bc} \left[\epsilon_{ji}^a + \sum_k^{MO} U_{kj}^a (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^a \tau_{ij,kl}^{jl} \right] \end{aligned}$$

$$- 2 \sum_{ij}^{MO} \xi_{ij}^{ca} \left[\epsilon_{ji}^b + \sum_k^{MO} U_{kj}^b (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^b \tau_{ij,kl}^{jl} \right] . \quad (16.232)$$

Equation (16.232) is formally equivalent to the MO part of eq. (16.163) for a PEMCSCF wavefunction. This equation shows that a third derivative property for a GRSCF wavefunction requires *only* the solution of the first-order CPHF equations.

16.5.5 Fourth Derivative

The fourth derivative of the electronic energy may be obtained from the fourth derivative expression for the MCSCF wavefunction discussed in Section 16.3. For this purpose the following correspondence relationships are used:

$$x_{ij}^{abc} = 2\epsilon_{ji}^{abc} \quad (16.233)$$

with

$$\epsilon_{ij}^{abc} = f_i h_{ij}^{abc} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^{abc} + \beta_{il}(il|jl)^{abc} \right\} , \quad (16.234)$$

$$y_{ijkl}^{ab} = 2\delta_{jl}\zeta_{ik}^{jab} + 2\tau_{ij,kl}^{jab} \quad (16.235)$$

with

$$\zeta_{ij}^{lab} = f_l h_{ij}^{ab} + \sum_k^{MO} \left\{ \alpha_{lk}(ij|kk)^{ab} + \beta_{lk}(ik|jk)^{ab} \right\} \quad (16.236)$$

and

$$\tau_{ij,kl}^{mnab} = 2\alpha_{mn}(ij|kl)^{ab} + \beta_{mn} \left\{ (ik|jl)^{ab} + (il|jk)^{ab} \right\} , \quad (16.237)$$

The modified second derivative Lagrangian matrices in eq. (16.99) are related to

$$x_{ij}^{[ab]} = x_{ij}^{ab} + \sum_{kl}^{MO} \left(U_{kl}^b y_{ijkl}^a + U_{kl}^a y_{ijkl}^b \right) + \sum_{klmn}^{MO} U_{kl}^a U_{mn}^b z_{ijklmn} \quad (16.238)$$

$$= 2\epsilon_{ji}^{[ab]} \quad (16.239)$$

$$= 2\epsilon_{ji}^{ab} + 2 \sum_k^{MO} \left(U_{kj}^b \zeta_{ik}^{ja} + U_{kj}^a \zeta_{ik}^{jb} \right) + 2 \sum_{kl}^{MO} \left(U_{kl}^b \tau_{ij,kl}^{jal} + U_{kl}^a \tau_{ij,kl}^{jal} \right) \\ + 2 \sum_{klm}^{MO} \left(U_{kj}^a U_{lm}^b \tau_{ik,lm}^{jm} + U_{km}^a U_{lj}^b \tau_{il,km}^{jm} + U_{km}^a U_{lm}^b \tau_{ij,kl}^{jm} \right) . \quad (16.240)$$

In eq. (16.104) one of the terms involving the z^a matrices is reformulated for the GRSCF wavefunction as

$$\sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c z_{ijklmn}^d$$

$$= 4 \sum_{ijklmnp}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \left\{ \Gamma_{jlnp}(ik|mp)^d + \Gamma_{jnlp}(im|kp)^d + \Gamma_{jpln}(ip|km)^d \right\} \quad (16.241)$$

$$= 2 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml^d} \quad . \quad (16.242)$$

The terms involving a product of U^a , U^b , U^c and U^d in eq. (16.104) may be rewritten in a simple manner:

$$\begin{aligned} & 8 \sum_{ijklmno}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) \Gamma_{jlnp}(ik|mo) \\ & = 4 \sum_{ijklmn}^{MO} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) \tau_{ij,kl}^{mn} \quad . \end{aligned} \quad (16.243)$$

Using the correspondence equations given above, the fourth derivative in eq. (16.104) is finally reformulated for the GRSCF wavefunction as

$$\begin{aligned} \frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} & = 2 \sum_i^{MO} f_i h_{ii}^{abcd} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{abcd} + \beta_{ij}(ij|ij)^{abcd} \right\} \\ & - 2 \sum_{ij}^{MO} S_{ij}^{abcd} \epsilon_{ij} \\ & - 4 \sum_{ijk}^{MO} \left(U_{ik}^{ab} U_{jk}^{cd} + U_{ik}^{ac} U_{jk}^{bd} + U_{ik}^{ad} U_{jk}^{bc} \right) \epsilon_{ij} \\ & + 4 \sum_{ijk}^{MO} \left(S_{ik}^{abc} S_{jk}^d + S_{ik}^{bcd} S_{jk}^a + S_{ik}^{cda} S_{jk}^b + S_{ik}^{dab} S_{jk}^c \right) \epsilon_{ij} \\ & + 4 \sum_{ijk}^{MO} \left(S_{ik}^{ab} S_{jk}^{cd} + S_{ik}^{ac} S_{jk}^{bd} + S_{ik}^{ad} S_{jk}^{bc} \right) \epsilon_{ij} \\ & - 2 \sum_{ij}^{MO} \omega_{ij}^{abcd} \epsilon_{ij} \\ & + 4 \sum_{ij}^{MO} \left(U_{ij}^{ab} \epsilon_{ji}^{[cd]} + U_{ij}^{ac} \epsilon_{ji}^{[bd]} + U_{ij}^{ad} \epsilon_{ji}^{[bc]} \right. \\ & \quad \left. + U_{ij}^{bc} \epsilon_{ji}^{[ad]} + U_{ij}^{bd} \epsilon_{ji}^{[ac]} + U_{ij}^{cd} \epsilon_{ji}^{[ab]} \right) \\ & + 4 \sum_{ij}^{MO} \left(U_{ij}^a \epsilon_{ji}^{bcd} + U_{ij}^b \epsilon_{ji}^{cda} + U_{ij}^c \epsilon_{ji}^{dab} + U_{ij}^d \epsilon_{ji}^{abc} \right) \end{aligned}$$

$$\begin{aligned}
& + 4 \sum_{ijk}^{MO} \left(U_{ij}^{ab} U_{kj}^{cd} + U_{ij}^{ac} U_{kj}^{bd} + U_{ij}^{ad} U_{kj}^{bc} \right) \zeta_{ik}^j \\
& + 4 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) \tau_{ij,kl}^{jl} \\
& + 4 \sum_{ijk}^{MO} \left(U_{ij}^a U_{kj}^b \zeta_{ik}^{jcd} + U_{ij}^a U_{kj}^c \zeta_{ik}^{jbd} + U_{ij}^a U_{kj}^d \zeta_{ik}^{jbc} \right. \\
& \quad \left. + U_{ij}^b U_{kj}^c \zeta_{ik}^{jad} + U_{ij}^b U_{kj}^d \zeta_{ik}^{jac} + U_{ij}^c U_{kj}^d \zeta_{ik}^{jab} \right) \\
& + 4 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlc} + U_{ij}^a U_{kl}^c \tau_{ij,kl}^{jld} + U_{ij}^a U_{kl}^d \tau_{ij,kl}^{jlb} \right. \\
& \quad \left. + U_{ij}^b U_{kl}^c \tau_{ij,kl}^{jla} + U_{ij}^b U_{kl}^d \tau_{ij,kl}^{jla} + U_{ij}^c U_{kl}^d \tau_{ij,kl}^{jlb} \right) \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) \tau_{ij,kl}^{ml} \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^b U_{jm}^c U_{kl}^d + U_{im}^c U_{jm}^d U_{kl}^b + U_{im}^d U_{jm}^b U_{kl}^c \right) \tau_{ij,kl}^{ml} \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^c U_{jm}^d U_{kl}^a + U_{im}^d U_{jm}^a U_{kl}^c + U_{im}^a U_{jm}^c U_{kl}^d \right) \tau_{ij,kl}^{ml} \\
& + 4 \sum_{ijklm}^{MO} \left(U_{im}^d U_{jm}^a U_{kl}^b + U_{im}^a U_{jm}^b U_{kl}^d + U_{im}^b U_{jm}^d U_{kl}^a \right) \tau_{ij,kl}^{ml} \\
& + 4 \sum_{ijklmn}^{MO} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) \tau_{ij,kl}^{mn} \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{abc} \left[\epsilon_{ji}^d + \sum_k^{MO} U_{kj}^d \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^d \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{bcd} \left[\epsilon_{ji}^a + \sum_k^{MO} U_{kj}^a \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^a \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{cda} \left[\epsilon_{ji}^b + \sum_k^{MO} U_{kj}^b \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^b \tau_{ij,kl}^{jl} \right] \\
& - 2 \sum_{ij}^{MO} \xi_{ij}^{dab} \left[\epsilon_{ji}^c + \sum_k^{MO} U_{kj}^c \left(\zeta_{ik}^j - \epsilon_{ik} \right) + \sum_{kl}^{MO} U_{kl}^c \tau_{ij,kl}^{jl} \right] \quad . \quad (16.244)
\end{aligned}$$

Equation (16.244) is equivalent to the MO part of eq. (16.196) for a PEMCSCF wavefunction. This equation indicates that evaluation of a fourth-order property of a GRSCF wavefunction requires the solutions of both the first- and second-order CPHF equations.

16.6 Closed-Shell Self-Consistent-Field (CLSCF) Wavefunctions

16.6.1 Electronic Energy and the Variational Condition

Finally, we turn to the simplest type of wavefunction considered here. The electronic energy for the CLSCF wavefunction is

$$E_{elec} = 2 \sum_i^{d.o.} h_{ii} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj) - (ij|ij) \right\} \quad (16.245)$$

where the summations run over doubly occupied (*d.o.*) orbitals.

Since the closed-shell SCF wavefunction is a special case of GRSCF and/or MCSCF wavefunctions, the energy and derivative expressions may be derived from either starting point. The *correspondence* equations between GRSCF and CLSCF wavefunctions for the one- and two-electron coupling constants are

$$f_i = \begin{cases} 1 & \text{for } i = \text{doubly occupied} \\ 0 & \text{for } i = \text{virtual} \end{cases} \quad (16.246)$$

$$\alpha_{ij} = \begin{cases} 2 & \text{for } i, j = \text{doubly occupied} \\ 0 & \text{otherwise} \end{cases} \quad (16.247)$$

$$\beta_{ij} = \begin{cases} -1 & \text{for } i, j = \text{doubly occupied} \\ 0 & \text{otherwise} \end{cases} \quad (16.248)$$

The electronic energy expression in eq. (16.245) is derived directly from eq. (16.199) using the equations (16.246) through (16.248).

The variational condition for a CLSCF wavefunction is given by

$$F_{ij} = 0 \quad \text{for } i = \text{doubly occupied and for } j = \text{virtual} \quad (16.249)$$

where the Fock matrix is defined by

$$F_{ij} = h_{ij} + \sum_k^{d.o.} \left\{ 2(ij|kk) - (ik|jk) \right\} = F_{ji} \quad . \quad (16.250)$$

The Lagrangian matrix for the GRSCF wavefunction in eq. (16.206) is related to the Fock matrix for the CLSCF wavefunction:

$$\epsilon_{ij} = f_i h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} \quad (16.251)$$

$$= h_{ij} + \sum_k^{d.o.} \left\{ 2(ij|kk) - (ik|jk) \right\} \quad (16.252)$$

$$= F_{ij} \quad \text{for } i = \text{doubly occupied} \quad . \quad (16.253)$$

Since the SCF energy is invariant under a unitary transformation within the occupied space, the diagonality of the Fock matrix is ordinarily used to define the canonical SCF molecular orbitals. In this section, however, in order to maintain generality, the derivative expressions for the CLSCF energy are derived without introducing the diagonality condition of the Fock matrix.

The *correspondence* equations between MCSCF and CLSCF wavefunctions for the one- and two-electron density matrices are

$$\gamma_{ij} = \begin{cases} 2\delta_{ij} & \text{for } i, j = \text{doubly occupied} \\ 0 & \text{otherwise} \end{cases} \quad (16.254)$$

and

$$\Gamma_{ijkl} = \begin{cases} 2\delta_{ij}\delta_{kl} - \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) & \text{for } i, j, k, l = \text{doubly occupied} \\ 0 & \text{otherwise} \end{cases} \quad (16.255)$$

The energy expression (16.245) may be derived from eq. (16.40) using eqs. (16.254) and (16.255):

$$E_{elec} = \sum_{ij}^{MO} \gamma_{ij} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl) \quad (16.256)$$

$$= \sum_{ij}^{\text{d.o.}} (2\delta_{ij}) h_{ij} + \sum_{ijkl}^{\text{d.o.}} \left\{ 2\delta_{ij}\delta_{kl} - \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \right\} (ij|kl) \quad (16.257)$$

$$= 2 \sum_i^{\text{d.o.}} h_{ii} + 2 \sum_{ik}^{\text{d.o.}} (ii|kk) - \frac{1}{2} \sum_{ij}^{\text{d.o.}} \left\{ (ij|ij) + (ij|ji) \right\} \quad (16.258)$$

$$= 2 \sum_i^{\text{d.o.}} h_{ii} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj) - (ij|ij) \right\} \quad . \quad (16.259)$$

Using the *correspondence* equations (16.254) and (16.255), the relationship between the Lagrangian matrix in eq. (16.46) and the Fock matrix in (16.250) is demonstrated as follows:

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl) \quad (16.260)$$

$$= \sum_m^{\text{d.o.}} (2\delta_{jm}) h_{im} + 2 \sum_{mkl}^{\text{d.o.}} \left\{ 2\delta_{jm}\delta_{kl} - \frac{1}{2}(\delta_{jk}\delta_{ml} + \delta_{jl}\delta_{mk}) \right\} (im|kl) \quad (16.261)$$

$$= 2h_{ij} + 2 \sum_k^{d.o.} 2(ij|kk) - \sum_l^{d.o.} (il|jl) - \sum_k^{d.o.} (ik|kj) \quad (16.262)$$

$$= 2h_{ij} + 2 \sum_k^{d.o.} \left\{ 2(ij|kk) - (ik|jk) \right\} \quad (16.263)$$

$$= 2F_{ij} \quad \text{for } i = \text{all and } j = \text{doubly occupied} \quad . \quad (16.264)$$

It should be noted that the CLSCF condition (16.249) is included in the variational condition for the MCSCF wavefunction:

$$x_{ij} - x_{ji} = 0 \quad . \quad (16.265)$$

16.6.2 First Derivative

Using the correspondence equations and the variational condition described in the preceding subsection, the first derivative expression for the CLSCF energy may be derived straightforwardly from eq. (16.213) for the GRSCF wavefunction as

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{MO} S_{ij}^a \epsilon_{ij} \end{aligned} \quad (16.266)$$

$$\begin{aligned} &= 2 \sum_i^{d.o.} h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{d.o.} S_{ij}^a F_{ij} \end{aligned} \quad . \quad (16.267)$$

Note that the summations run over only doubly occupied (*d.o.*) molecular orbitals.

Alternatively the first derivative of the electronic energy is obtained from the expression for the MCSCF wavefunction, eq. (16.52), using the relationships eqs. (16.254), (16.255) and (16.264) as

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a - \sum_{ij}^{MO} S_{ij}^a x_{ij} \\ &= \sum_{ij}^{d.o.} (2\delta_{ij}) h_{ij}^a \\ &+ \sum_{ijkl}^{d.o.} \left\{ 2\delta_{ij}\delta_{kl} - \frac{1}{2} (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \right\} (ij|kl)^a \end{aligned} \quad (16.268)$$

$$- \sum_{ij}^{d.o.} S_{ij}^a (2F_{ij}) \quad (16.269)$$

$$\begin{aligned} &= 2 \sum_i h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{d.o.} S_{ij}^a F_{ij} . \end{aligned} \quad (16.270)$$

Equations (16.267) and (16.270) are seen to be identical.

16.6.3 Second Derivative

An expression for the second derivative for the CLSCF energy may be derived from the equation for the GRSCF wavefunction. For this purpose three more correspondence equations must be introduced:

$$\epsilon_{ij}^a = F_{ij}^a \quad \text{for } i = \text{doubly occupied} \quad (16.271)$$

with

$$F_{ij}^a = h_{ij}^a + \sum_k^{d.o.} \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} , \quad (16.272)$$

$$\zeta_{ij}^l = F_{ij} \quad \text{for } l = \text{doubly occupied} , \quad (16.273)$$

and

$$\tau_{ij,kl}^{mn} = A_{ij,kl} \quad \text{for } m,n = \text{doubly occupied} \quad (16.274)$$

where the A matrix is defined by

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) . \quad (16.275)$$

Using the relationships given above, the second derivative expression (16.221) for the GRSCF may be reformulated for the CLSCF wavefunction as

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &- 2 \sum_{ij}^{MO} \xi_{ij}^{ab} \epsilon_{ij} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \end{aligned} \quad (16.276)$$

$$\begin{aligned}
&= 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
&- 2 \sum_{ij}^{d.o.} \xi_{ij}^{ab} F_{ij} \\
&+ 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
&+ 4 \sum_i^{all} \sum_j^{all} \sum_k^{d.o.} U_{ik}^a U_{jk}^b F_{ij} \\
&+ 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} U_{ij}^a U_{kl}^b A_{ij,kl} . \tag{16.277}
\end{aligned}$$

The ξ^{ab} matrices were defined in eq. (16.54). It should be noted that the F^a matrices are symmetric, i.e.,

$$F_{ij}^a = F_{ji}^a \tag{16.278}$$

since there is only one Fock operator for a CLSCF wavefunction.

In order to derive the second derivative expression for the CLSCF wavefunction from that for the MCSCF wavefunction two additional *correspondence* equations are necessary:

$$y_{ijkl} = 2\delta_{jl}F_{ik} + 2A_{ij,kl} \quad \text{for } i, k = \text{all and } j, l = \text{doubly occupied} , \tag{16.279}$$

and

$$x_{ij}^a = 2F_{ij}^a \quad \text{for } i = \text{all and } j = \text{doubly occupied} . \tag{16.280}$$

The second derivative expression for the MCSCF energy without the CI contributions is

$$\begin{aligned}
\frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl} (ij|kl)^{ab} \\
&- \sum_{ij}^{MO} \xi_{ij}^{ab} x_{ij} \\
&+ 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} . \tag{16.281}
\end{aligned}$$

Equation (16.281) may be reformulated for the CLSCF wavefunction as follows:

$$\begin{aligned}
\frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{d.o.} (2\delta_{ij}) h_{ij}^{ab} + \sum_{ijkl}^{d.o.} \left\{ 2\delta_{ij}\delta_{kl} - \frac{1}{2} (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \right\} (ij|kl)^{ab} \\
&- \sum_{ij}^{d.o.} \xi_{ij}^{ab} (2F_{ij})
\end{aligned}$$

$$\begin{aligned}
& + 2 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} 2 \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
& + 2 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} 2 U_{ij}^a U_{kl}^b \left(\delta_{jl} F_{ik} + A_{ij,kl} \right)
\end{aligned} \tag{16.282}$$

$$\begin{aligned}
& = 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\
& - 2 \sum_{ij}^{\text{d.o.}} \xi_{ij}^{ab} F_{ij} \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{all d.o.}} \sum_k^{\text{d.o.}} U_{ik}^a U_{jk}^b F_{ij} \\
& + 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{all d.o.}} \sum_k^{\text{d.o.}} \sum_l^{\text{d.o.}} U_{ij}^a U_{kl}^b A_{ij,kl} .
\end{aligned} \tag{16.283}$$

Equations (16.277) and (16.283) are naturally identical.

16.6.4 Third Derivative

The third derivative of the electronic energy may be obtained from the GRSCF third derivative expression presented in Section 16.5. The following correspondence relationships are employed:

$$\epsilon_{ij}^{ab} = F_{ij}^{ab} \quad \text{for } i = \text{doubly occupied} \tag{16.284}$$

with

$$F_{ij}^{ab} = h_{ij}^{ab} + \sum_k^{\text{d.o.}} \left\{ 2(ij|kk)^{ab} - (ik|jk)^{ab} \right\} , \tag{16.285}$$

$$\zeta_{ij}^{la} = F_{ij}^a \quad \text{for } l = \text{doubly occupied} , \tag{16.286}$$

and

$$\tau_{ij,kl}^{mn} = A_{ij,kl}^a \quad \text{for } m, n = \text{doubly occupied} \tag{16.287}$$

with

$$A_{ij,kl}^a = 4(ij|kl)^a - (ik|jl)^a - (il|jk)^a . \tag{16.288}$$

In Section 4.5 the first derivative of the Fock matrix was derived as

$$\frac{\partial F_{ij}}{\partial a} = F_{ij}^a + \sum_k^{\text{all}} U_{ki}^a F_{kj} + \sum_k^{\text{all}} U_{kj}^a F_{ik} + \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^a A_{ij,kl} . \tag{16.289}$$

Utilizing this expression one of the last three terms in eq. (16.232) may be manipulated as follows

$$\sum_{ij}^{MO} \xi_{ij}^{ab} \left[\epsilon_{ji}^c + \sum_k^{MO} U_{kj}^c (\zeta_{ik}^j - \epsilon_{ik}) + \sum_{kl}^{MO} U_{kl}^c \tau_{ij,kl}^{jl} \right] \quad (16.290)$$

$$= \sum_i^{all d.o.} \sum_j^{d.o.} \xi_{ij}^{ab} \left[F_{ij}^c + \sum_k^{all} U_{kj}^c F_{ik} - \sum_k^{all} U_{ki}^c F_{jk} + \sum_k^{all} \sum_l^{d.o.} U_{kl}^c A_{ij,kl} \right] \quad (16.291)$$

$$= \sum_i^{all d.o.} \sum_j^{d.o.} \xi_{ij}^{ab} \left[\frac{\partial F_{ij}}{\partial c} - 2 \sum_k^{all} U_{ki}^c F_{kj} \right] \quad . \quad (16.292)$$

In the above manipulation note the difference in the summation limit for each index.

Using the corresponding equations given above, the third derivative for the GRSCF energy in eq. (16.232) is reexpressed for the CLSCF wavefunction as

$$\begin{aligned} \frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} &= 2 \sum_i^{d.o.} h_{ii}^{abc} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{abc} - (ij|ij)^{abc} \right\} - 2 \sum_{ij}^{d.o.} S_{ij}^{abc} F_{ij} \\ &+ 4 \sum_{ij}^{d.o.} \sum_k^{all} \left(S_{ik}^{ab} S_{jk}^c + S_{ik}^{bc} S_{jk}^a + S_{ik}^{ca} S_{jk}^b \right) F_{ij} \\ &- 4 \sum_{ij}^{d.o.} \sum_{kl}^{all} \left(S_{ik}^a S_{jl}^b S_{kl}^c + S_{ik}^b S_{jl}^c S_{kl}^a + S_{ik}^c S_{jl}^a S_{kl}^b \right) F_{ij} \\ &+ 4 \sum_i^{all d.o.} \sum_j \left(U_{ij}^a F_{ij}^{bc} + U_{ij}^b F_{ij}^{ca} + U_{ij}^c F_{ij}^{ab} \right) \\ &+ 4 \sum_{ij}^{all d.o.} \sum_k \left(U_{ik}^a U_{jk}^b F_{ij}^c + U_{ik}^b U_{jk}^c F_{ij}^a + U_{ik}^c U_{jk}^a F_{ij}^b \right) \\ &+ 4 \sum_i^{all d.o.} \sum_j^{all d.o.} \sum_k^{all d.o.} \left(U_{ij}^a U_{kl}^b A_{ij,kl}^c + U_{ij}^b U_{kl}^c A_{ij,kl}^a + U_{ij}^c U_{kl}^a A_{ij,kl}^b \right) \\ &+ 4 \sum_{ijk}^{all d.o.} \sum_{lm}^{all d.o.} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) A_{ij,kl} \\ &- 2 \sum_i^{all d.o.} \sum_j^{d.o.} \xi_{ij}^{ab} \left[\frac{\partial F_{ij}}{\partial c} - 2 \sum_k^{all} U_{ki}^c F_{kj} \right] \\ &- 2 \sum_i^{all d.o.} \sum_j^{d.o.} \xi_{ij}^{bc} \left[\frac{\partial F_{ij}}{\partial a} - 2 \sum_k^{all} U_{ki}^a F_{kj} \right] \\ &- 2 \sum_i^{all d.o.} \sum_j^{d.o.} \xi_{ij}^{ca} \left[\frac{\partial F_{ij}}{\partial b} - 2 \sum_k^{all} U_{ki}^b F_{kj} \right] \quad . \quad (16.293) \end{aligned}$$

This equation shows that the third derivative of a CLSCF wavefunction requires *only* the solution of the first-order CPHF equations.

Alternatively the third derivative of the CLSCF energy may be obtained from the MCSCF third derivative expression presented in Section 16.3 without the CI contributions. For this purpose the following correspondence relationships are utilized:

$$y_{ijkl}^a = 2\delta_{jl}F_{ik}^a + 2A_{ij,kl}^a \quad \text{for } i, k = \text{all and } j, l = \text{doubly occupied} \quad , \quad (16.294)$$

$$x_{ij}^{ab} = 2F_{ij}^{ab} \quad \text{for } i = \text{all and } j = \text{doubly occupied} \quad , \quad (16.295)$$

and

$$\begin{aligned} 8 \sum_{ijklmn}^{MO} & \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} \Gamma_{jlnp}(ik|mp) \\ & = 4 \sum_{ijk}^{all} \sum_{lm}^{d.o.} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) A_{ij,kl} \quad . \end{aligned} \quad (16.296)$$

The modified first derivative Lagrangian matrices in eq. (16.64) are related to the corresponding quantities in the following manner:

$$x_{ij}^{[a]} = 2F_{ij}^{[a]} = x_{ij}^a + \sum_{kl}^{MO} U_{kl}^a y_{ijkl} \quad (16.297)$$

$$= 2F_{ij}^a + \sum_k^{all} \sum_l^{d.o.} U_{kl}^a \left(2\delta_{jl}F_{ik} + 2A_{ij,kl} \right) \quad . \quad (16.298)$$

Utilizing this relationship and eq. (16.289), the term involving $x^{[c]}$ in eq. (16.81) may be rewritten as

$$\sum_{ij}^{MO} \xi_{ij}^{ab} \left[x_{ij}^{[c]} - \sum_k^{MO} U_{kj}^c x_{ki} \right] \quad (16.299)$$

$$= 2 \sum_i^{all} \sum_j^{d.o.} \xi_{ij}^{ab} \left[F_{ij}^c + \sum_k^{all} U_{kj}^c F_{ik} + \sum_k^{all} \sum_l^{d.o.} U_{kl}^c A_{ij,kl} - \sum_k^{all} U_{ki}^c F_{kj} \right] \quad (16.300)$$

$$= 2 \sum_i^{all} \sum_j^{d.o.} \xi_{ij}^{ab} \left[\frac{\partial F_{ij}}{\partial c} - 2 \sum_k^{all} U_{ki}^c F_{kj} \right] \quad . \quad (16.301)$$

Applying the corresponding equations given above in the third derivative expression for the MCSCF energy in eq. (16.81) produces the identical formula for the CLSCF energy third derivative presented in eq. (16.293).

16.6.5 Fourth Derivative

The fourth derivative of the electronic energy may be obtained from the fourth derivative expression for the GRSCF wavefunction discussed in Section 16.5. For this purpose the

following correspondence relationships are used:

$$\epsilon_{ij}^{abc} = F_{ij}^{abc} \quad \text{for } i = \text{doubly occupied} \quad (16.302)$$

with

$$F_{ij}^{abc} = h_{ij}^{abc} + \sum_k^{d.o.} \left\{ 2(ij|kk)^{abc} - (ik|jk)^{abc} \right\}, \quad (16.303)$$

$$\zeta_{ij}^{lab} = F_{ij}^{ab} \quad \text{for } l = \text{doubly occupied}, \quad (16.304)$$

and

$$\tau_{ij,kl}^{mnab} = A_{ij,kl}^{ab} \quad \text{for } m, n = \text{doubly occupied} \quad (16.305)$$

with

$$A_{ij,kl}^{ab} = 4(ij|kl)^{ab} - (ik|jl)^{ab} - (il|jk)^{ab}. \quad (16.306)$$

The modified second derivative Lagrangian matrices are then given by

$$\begin{aligned} \epsilon_{ij}^{[ab]} &= \epsilon_{ij}^{ab} + \sum_k^{MO} \left(U_{ki}^b \zeta_{jk}^{ia} + U_{ki}^a \zeta_{jk}^{ib} \right) + \sum_{kl}^{MO} \left(U_{kl}^b \tau_{ij,kl}^{il,a} + U_{kl}^a \tau_{ij,kl}^{il,b} \right) \\ &+ \sum_{klm}^{MO} \left(U_{ki}^a U_{lm}^b \tau_{jk,lm}^{im} + U_{km}^a U_{li}^b \tau_{jl,km}^{im} + U_{km}^a U_{lm}^b \tau_{ij,kl}^{im} \right) \end{aligned} \quad (16.307)$$

$$= F_{ij}^{[ab]} \quad (16.308)$$

$$\begin{aligned} &= F_{ij}^{ab} + \sum_k^{all} \left(U_{ki}^b F_{jk}^a + U_{ki}^a F_{jk}^b \right) + \sum_k^{all} \sum_l^{d.o.} \left(U_{kl}^b A_{ij,kl}^a + U_{kl}^a A_{ij,kl}^b \right) \\ &+ \sum_{kl}^{all} \sum_m^{d.o.} \left(U_{ki}^a U_{lm}^b A_{jk,lm} + U_{km}^a U_{li}^b A_{jl,km} + U_{km}^a U_{lm}^b A_{ij,kl} \right). \end{aligned} \quad (16.309)$$

Using the correspondence equations given above, the GRSCF energy fourth derivative in eq. (16.244) may be reformulated for the CLSCF wavefunction as

$$\begin{aligned} \frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} &= 2 \sum_i^{d.o.} h_{ii}^{abcd} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{abcd} - (ij|ij)^{abcd} \right\} \\ &- 2 \sum_{ij}^{d.o.} S_{ij}^{abcd} F_{ij} \\ &- 4 \sum_{ij}^{d.o.} \sum_k^{all} \left(U_{ik}^{ab} U_{jk}^{cd} + U_{ik}^{ac} U_{jk}^{bd} + U_{ik}^{ad} U_{jk}^{bc} \right) F_{ij} \\ &+ 4 \sum_{ij}^{d.o.} \sum_k^{all} \left(S_{ik}^{abc} S_{jk}^d + S_{ik}^{bcd} S_{jk}^a + S_{ik}^{cda} S_{jk}^b + S_{ik}^{dab} S_{jk}^c \right) F_{ij} \\ &+ 4 \sum_{ij}^{d.o.} \sum_k^{all} \left(S_{ik}^{ab} S_{jk}^{cd} + S_{ik}^{ac} S_{jk}^{bd} + S_{ik}^{ad} S_{jk}^{bc} \right) F_{ij} \end{aligned}$$

$$\begin{aligned}
& - 2 \sum_{ij}^{d.o.} \omega_{ij}^{abcd} F_{ij} \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^{ab} F_{ij}^{[cd]} + U_{ij}^{ac} F_{ij}^{[bd]} + U_{ij}^{ad} F_{ij}^{[bc]} \right. \\
& \quad \left. + U_{ij}^{bc} F_{ij}^{[ad]} + U_{ij}^{bd} F_{ij}^{[ac]} + U_{ij}^{cd} F_{ij}^{[ab]} \right) \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^a F_{ij}^{bcd} + U_{ij}^b F_{ij}^{cda} + U_{ij}^c F_{ij}^{dab} + U_{ij}^d F_{ij}^{abc} \right) \\
& + 4 \sum_{ij}^{all} \sum_k^{d.o.} \left(U_{ik}^{ab} U_{jk}^{cd} + U_{ik}^{ac} U_{jk}^{bd} + U_{ik}^{ad} U_{jk}^{bc} \right) F_{ij} \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) A_{ij,kl} \\
& + 4 \sum_{ij}^{all} \sum_k^{d.o.} \left(U_{ik}^a U_{jk}^b F_{ij}^{cd} + U_{ik}^a U_{jk}^c F_{ij}^{bd} + U_{ik}^a U_{jk}^d F_{ij}^{bc} \right. \\
& \quad \left. + U_{ik}^b U_{jk}^c F_{ij}^{ad} + U_{ik}^b U_{jk}^d F_{ij}^{ac} + U_{ik}^c U_{jk}^d F_{ij}^{ab} \right) \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} \left(U_{ij}^a U_{kl}^b A_{ij,kl}^{cd} + U_{ij}^a U_{kl}^c A_{ij,kl}^{bd} + U_{ij}^a U_{kl}^d A_{ij,kl}^{bc} \right. \\
& \quad \left. + U_{ij}^b U_{kl}^c A_{ij,kl}^{ad} + U_{ij}^b U_{kl}^d A_{ij,kl}^{ac} + U_{ij}^c U_{kl}^d A_{ij,kl}^{ab} \right) \\
& + 4 \sum_{ijk}^{all} \sum_{lm}^{d.o.} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) A_{ij,kl}^d \\
& + 4 \sum_{ijk}^{all} \sum_{lm}^{d.o.} \left(U_{im}^b U_{jm}^c U_{kl}^d + U_{im}^c U_{jm}^d U_{kl}^b + U_{im}^d U_{jm}^b U_{kl}^c \right) A_{ij,kl}^a \\
& + 4 \sum_{ijk}^{all} \sum_{lm}^{d.o.} \left(U_{im}^c U_{jm}^d U_{kl}^a + U_{im}^d U_{jm}^a U_{kl}^c + U_{im}^a U_{jm}^c U_{kl}^d \right) A_{ij,kl}^b \\
& + 4 \sum_{ijk}^{all} \sum_{lm}^{d.o.} \left(U_{im}^d U_{jm}^a U_{kl}^b + U_{im}^a U_{jm}^b U_{kl}^d + U_{im}^b U_{jm}^d U_{kl}^a \right) A_{ij,kl}^c \\
& + 4 \sum_{ijkl}^{all} \sum_{mn}^{d.o.} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) A_{ij,kl} \\
& - 2 \sum_i^{all} \sum_j^{d.o.} \xi_{ij}^{abc} \left[\frac{\partial F_{ij}}{\partial d} - 2 \sum_k^{all} U_{ki}^d F_{kj} \right]
\end{aligned}$$

$$\begin{aligned}
& - 2 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \xi_{ij}^{bcd} \left[\frac{\partial F_{ij}}{\partial a} - 2 \sum_k^{\text{all}} U_{ki}^a F_{kj} \right] \\
& - 2 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \xi_{ij}^{cda} \left[\frac{\partial F_{ij}}{\partial b} - 2 \sum_k^{\text{all}} U_{ki}^b F_{kj} \right] \\
& - 2 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} \xi_{ij}^{dab} \left[\frac{\partial F_{ij}}{\partial c} - 2 \sum_k^{\text{all}} U_{ki}^c F_{kj} \right]
\end{aligned} \quad . \quad (16.310)$$

Equation (16.310) indicates that evaluation of fourth derivatives for a CLSCF wavefunction requires the solution of both the first- and second-order CPHF equations.

Alternatively the fourth derivative of the CLSCF electronic energy may be obtained from the expression for the MCSCF wavefunction discussed in Section 16.3 without the CI contributions. For this purpose the following correspondence relationships are used:

$$y_{ijkl}^{ab} = 2\delta_{jl}F_{ik}^{ab} + 2A_{ij,kl}^{ab} \quad \text{for } i, k = \text{all and } j, l = \text{doubly occupied} \quad , \quad (16.311)$$

$$x_{ij}^{abc} = 2F_{ij}^{abc} \quad \text{for } i = \text{all and } j = \text{doubly occupied} \quad , \quad (16.312)$$

$$\begin{aligned}
z_{ijklmn} &= 2\delta_{jl}A_{ik,mn} + 2\delta_{jn}A_{im,kl} + 2\delta_{ln}A_{ij,km} \\
&\quad \text{for } i, k, m = \text{all and } j, l, n = \text{doubly occupied} \quad ,
\end{aligned} \quad (16.313)$$

and

$$\begin{aligned}
z_{ijklmn}^a &= 2\delta_{jl}A_{ik,mn}^a + 2\delta_{jn}A_{im,kl}^a + 2\delta_{ln}A_{ij,km}^a \\
&\quad \text{for } i, k, m = \text{all and } j, l, n = \text{doubly occupied} \quad .
\end{aligned} \quad (16.314)$$

The modified second derivative Lagrangian matrices in eq. (16.99) are then of the form

$$x_{ij}^{[ab]} = x_{ij}^{ab} + \sum_{kl}^{MO} (U_{kl}^b y_{ijkl}^a + U_{kl}^a y_{ijkl}^b) + \sum_{klmn}^{MO} U_{kl}^a U_{mn}^b z_{ijklmn} \quad (16.315)$$

$$= 2F_{ij}^{[ab]} \quad (16.316)$$

$$\begin{aligned}
&= 2F_{ij}^{ab} + 2 \sum_k^{\text{all}} (U_{kj}^b F_{ik}^a + U_{kj}^a F_{ik}^b) + 2 \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} (U_{kl}^b A_{ij,kl}^a + U_{kl}^a A_{ij,kl}^b) \\
&+ 2 \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} (U_{kj}^a U_{lm}^b A_{ik,lm} + U_{km}^a U_{lj}^b A_{il,km} + U_{km}^a U_{lm}^b A_{ij,kl}) \quad .
\end{aligned} \quad (16.317)$$

In eq. (16.104) one of the terms involving the z^a matrices is reformulated for a CLSCF wavefunction as

$$\sum_{ijklmn}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c z_{ijklmn}^d$$

$$= 4 \sum_{ijklmnp}^{MO} U_{ij}^a U_{kl}^b U_{mn}^c \left\{ \Gamma_{jlnp}(ik|mp)^d + \Gamma_{jnlp}(im|kp)^d + \Gamma_{jpln}(ip|km)^d \right\} \quad (16.318)$$

$$= 2 \sum_{ijk}^{\text{all d.o.}} \sum_{lm} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) A_{ij,kl}^d \quad . \quad (16.319)$$

The terms involving a product of U^a , U^b , U^c and U^d in eq. (16.104) may be rewritten in the following simple manner:

$$\begin{aligned} & 8 \sum_{ijklmno}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) \Gamma_{jlnp}(ik|mo) \\ & = 4 \sum_{ijkl}^{\text{all d.o.}} \sum_{mn} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) A_{ij,kl} \quad . \end{aligned} \quad (16.320)$$

Using relationships given above, the MCSCF energy fourth derivative in eq. (16.104) is reformulated for the CLSCF wavefunction to produce the identical formula presented in eq. (16.310).

16.7 Energy Derivative Expressions Using Orbital Energies

When the SCF molecular orbitals are determined in the conventional manner so that the Fock matrix is diagonal, the SCF condition is given by

$$F_{ij} = \delta_{ij}\epsilon_i \quad (16.321)$$

where the quantity ϵ having a single suffix is specifically called an orbital energy. Then eq. (16.321) is one of the expressions for the variational condition for the CLSCF wavefunction. It should be noted that eq. (16.321) defines orbital energies for virtual orbitals as well as for doubly occupied orbitals. If the condition (16.321) is used, the formulae for the energy derivatives become somewhat simpler. Since the double sum over the terms involving the overlap derivatives may be replaced by a single sum, the first derivative expression for the CLSCF energy, eq. (16.267), becomes

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{\text{d.o.}} h_{ii}^a + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &\quad - 2 \sum_i^{\text{d.o.}} S_{ii}^a \epsilon_i \quad . \end{aligned} \quad (16.322)$$

Similarly, the second derivative in eq. (16.277) may be written as

$$\frac{\partial^2 E_{elec}}{\partial a \partial b} = 2 \sum_i^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\}$$

$$\begin{aligned}
& - 2 \sum_i^{d.o.} \xi_{ii}^{ab} \epsilon_i \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\
& + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^a U_{ij}^b \epsilon_i \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} U_{ij}^a U_{kl}^b A_{ij,kl} \quad . \tag{16.323}
\end{aligned}$$

If the diagonality condition in eq. (16.321) is used to determine a CLSCF wavefunction, then the diagonality in the derivatives of the Fock matrix also has to be satisfied:

$$\frac{\partial F_{ij}}{\partial a} = \delta_{ij} \frac{\partial \epsilon_i}{\partial a} \quad . \tag{16.324}$$

The first derivative of the orbital energy appearing in this equation is given by

$$\frac{\partial \epsilon_i}{\partial a} = \frac{\partial F_{ii}}{\partial a} \tag{16.325}$$

$$= F_{ii}^a - S_{ii}^a \epsilon_i + \sum_k^{all} \sum_l^{d.o.} U_{kl}^a A_{ii,kl} \quad . \tag{16.326}$$

Enforcing the diagonal nature of the Fock matrix, the third derivative expression for the CLSCF wavefunction in eq. (16.293) is reformulated as

$$\begin{aligned}
\frac{\partial^3 E_{elec}}{\partial a \partial b \partial c} & = 2 \sum_i^{d.o.} h_{ii}^{abc} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{abc} - (ij|ij)^{abc} \right\} \\
& - 2 \sum_i^{d.o.} S_{ii}^{abc} \epsilon_i \\
& + 4 \sum_i^{d.o.} \sum_j^{all} \left(S_{ij}^{ab} S_{ij}^c + S_{ij}^{bc} S_{ij}^a + S_{ij}^{ca} S_{ij}^b \right) \epsilon_i \\
& - 4 \sum_i^{d.o.} \sum_{jk}^{all} \left(S_{ij}^a S_{ik}^b S_{jk}^c + S_{ij}^b S_{ik}^c S_{jk}^a + S_{ij}^c S_{ik}^a S_{jk}^b \right) \epsilon_i \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^a F_{ij}^{bc} + U_{ij}^b F_{ij}^{ca} + U_{ij}^c F_{ij}^{ab} \right) \\
& + 4 \sum_{ij}^{all} \sum_k^{d.o.} \left(U_{ik}^a U_{jk}^b F_{ij}^c + U_{ik}^b U_{jk}^c F_{ij}^a + U_{ik}^c U_{jk}^a F_{ij}^b \right) \\
& + 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} \left(U_{ij}^a U_{kl}^b A_{ij,kl}^c + U_{ij}^b U_{kl}^c A_{ij,kl}^a + U_{ij}^c U_{kl}^a A_{ij,kl}^b \right)
\end{aligned}$$

$$\begin{aligned}
& + 4 \sum_{ijk}^{\text{all}} \sum_{lm}^{\text{d.o.}} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) A_{ij,kl} \\
& - 2 \sum_i^{\text{d.o.}} \left[\xi_{ii}^{ab} \frac{\partial \epsilon_i}{\partial c} + \xi_{ii}^{bc} \frac{\partial \epsilon_i}{\partial a} + \xi_{ii}^{ca} \frac{\partial \epsilon_i}{\partial b} \right] \\
& + 4 \sum_i^{\text{d.o.}} \sum_j^{\text{all}} \left[\xi_{ij}^{ab} U_{ij}^c + \xi_{ij}^{bc} U_{ij}^a + \xi_{ij}^{ca} U_{ij}^b \right] \epsilon_i \quad . \tag{16.327}
\end{aligned}$$

The fourth derivative of the electronic energy in eq. (16.310) may be reformulated using the diagonality of the Fock matrix as

$$\begin{aligned}
\frac{\partial^4 E_{elec}}{\partial a \partial b \partial c \partial d} & = 2 \sum_i^{\text{d.o.}} h_{ii}^{abcd} + \sum_{ij}^{\text{d.o.}} \left\{ 2(ii|jj)^{abcd} - (ij|ij)^{abcd} \right\} \\
& - 2 \sum_i^{\text{d.o.}} S_{ii}^{abcd} \epsilon_i \\
& - 4 \sum_i^{\text{d.o.}} \sum_j^{\text{all}} \left(U_{ij}^{ab} U_{ij}^{cd} + U_{ij}^{ac} U_{ij}^{bd} + U_{ij}^{ad} U_{ij}^{bc} \right) \epsilon_i \\
& + 4 \sum_i^{\text{d.o.}} \sum_j^{\text{all}} \left(S_{ij}^{abc} S_{ij}^d + S_{ij}^{bcd} S_{ij}^a + S_{ij}^{cda} S_{ij}^b + S_{ij}^{dab} S_{ij}^c \right) \epsilon_i \\
& + 4 \sum_i^{\text{d.o.}} \sum_j^{\text{all}} \left(S_{ij}^{ab} S_{ij}^{cd} + S_{ij}^{ac} S_{ij}^{bd} + S_{ij}^{ad} S_{ij}^{bc} \right) \epsilon_i \\
& - 2 \sum_i^{\text{d.o.}} \omega_{ii}^{abcd} \epsilon_i \\
& + 4 \sum_i^{\text{all}} \sum_j^{\text{d.o.}} \left(U_{ij}^{ab} F_{ij}^{[cd]} + U_{ij}^{ac} F_{ij}^{[bd]} + U_{ij}^{ad} F_{ij}^{[bc]} \right. \\
& \quad \left. + U_{ij}^{bc} F_{ij}^{[ad]} + U_{ij}^{bd} F_{ij}^{[ac]} + U_{ij}^{cd} F_{ij}^{[ab]} \right) \\
& + 4 \sum_i^{\text{all}} \sum_j^{\text{d.o.}} \left(U_{ij}^a F_{ij}^{bcd} + U_{ij}^b F_{ij}^{cda} + U_{ij}^c F_{ij}^{dab} + U_{ij}^d F_{ij}^{abc} \right) \\
& + 4 \sum_i^{\text{all}} \sum_j^{\text{d.o.}} \left(U_{ij}^{ab} U_{ij}^{cd} + U_{ij}^{ac} U_{ij}^{bd} + U_{ij}^{ad} U_{ij}^{bc} \right) \epsilon_i \\
& + 4 \sum_i^{\text{all}} \sum_j^{\text{d.o.}} \sum_k^{\text{all}} \sum_l^{\text{d.o.}} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) A_{ij,kl} \\
& + 4 \sum_{ij}^{\text{all}} \sum_k^{\text{d.o.}} \left(U_{ik}^a U_{jk}^b F_{ij}^{cd} + U_{ik}^a U_{jk}^c F_{ij}^{bd} + U_{ik}^a U_{jk}^d F_{ij}^{bc} \right)
\end{aligned}$$

$$\begin{aligned}
& + U_{ik}^b U_{jk}^c F_{ij}^{ad} + U_{ik}^b U_{jk}^d F_{ij}^{ac} + U_{ik}^c U_{jk}^d F_{ij}^{ab} \Big) \\
+ & 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{all d.o.}} \sum_k^{\text{all d.o.}} \sum_l^{\text{all d.o.}} \left(U_{ij}^a U_{kl}^b A_{ij,kl}^{cd} + U_{ij}^a U_{kl}^c A_{ij,kl}^{bd} + U_{ij}^a U_{kl}^d A_{ij,kl}^{bc} \right. \\
& \quad \left. + U_{ij}^b U_{kl}^c A_{ij,kl}^{ad} + U_{ij}^b U_{kl}^d A_{ij,kl}^{ac} + U_{ij}^c U_{kl}^d A_{ij,kl}^{ab} \right) \\
+ & 4 \sum_{ijk}^{\text{all d.o.}} \sum_{lm}^{\text{all d.o.}} \left(U_{im}^a U_{jm}^b U_{kl}^c + U_{im}^b U_{jm}^c U_{kl}^a + U_{im}^c U_{jm}^a U_{kl}^b \right) A_{ij,kl}^d \\
+ & 4 \sum_{ijk}^{\text{all d.o.}} \sum_{lm}^{\text{all d.o.}} \left(U_{im}^b U_{jm}^c U_{kl}^d + U_{im}^c U_{jm}^d U_{kl}^b + U_{im}^d U_{jm}^b U_{kl}^c \right) A_{ij,kl}^a \\
+ & 4 \sum_{ijk}^{\text{all d.o.}} \sum_{lm}^{\text{all d.o.}} \left(U_{im}^c U_{jm}^d U_{kl}^a + U_{im}^d U_{jm}^a U_{kl}^c + U_{im}^a U_{jm}^c U_{kl}^d \right) A_{ij,kl}^b \\
+ & 4 \sum_{ijk}^{\text{all d.o.}} \sum_{lm}^{\text{all d.o.}} \left(U_{im}^d U_{jm}^a U_{kl}^b + U_{im}^a U_{jm}^b U_{kl}^d + U_{im}^b U_{jm}^d U_{kl}^a \right) A_{ij,kl}^c \\
+ & 4 \sum_{ijkl}^{\text{all d.o.}} \sum_{mn}^{\text{all d.o.}} \left(U_{im}^a U_{jm}^b U_{kn}^c U_{ln}^d + U_{im}^a U_{jm}^c U_{kn}^b U_{ln}^d + U_{im}^a U_{jm}^d U_{kn}^b U_{ln}^c \right) A_{ij,kl} \\
- & 2 \sum_i^{\text{d.o.}} \left[\xi_{ii}^{abc} \frac{\partial \epsilon_i}{\partial d} + \xi_{ii}^{bcd} \frac{\partial \epsilon_i}{\partial a} + \xi_{ii}^{cda} \frac{\partial \epsilon_i}{\partial b} + \xi_{ii}^{dab} \frac{\partial \epsilon_i}{\partial c} \right] \\
+ & 4 \sum_i^{\text{d.o.}} \sum_j^{\text{all}} \left[\xi_{ij}^{abc} U_{ij}^d + \xi_{ij}^{bcd} U_{ij}^a + \xi_{ij}^{cda} U_{ij}^b + \xi_{ij}^{dab} U_{ij}^c \right] \epsilon_i \quad . \quad (16.328)
\end{aligned}$$

The equations given in this section are presented in symmetric form to aid the evaluation of the higher energy derivatives of the CLSCF wavefunction.

Suggested Reading

1. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *Theor. Chim. Acta* **72**, 71 (1987).
2. Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *Theor. Chim. Acta* **72**, 93 (1987).

Chapter 17

Analytic Derivatives Involving Electric Field Perturbations

All of the derivative expressions described thus far are applicable to any *real* perturbations, including the nuclear perturbations that were emphasized. Obviously, most of the motivation for the rapid development of analytic derivative methods has come from the use of energy gradients and energy second derivatives for the optimization of stationary point geometries and the evaluation of vibrational frequencies. In this chapter, however, analytic derivative expressions specifically involving electric field perturbations are discussed. Relevant topics include the electric dipole moment, electric polarizability, and the dipole moment derivatives with respect to nuclear coordinates. This mixed (cross) perturbation method easily can be extended to other types of real variables and higher-order properties. Analytic energy derivative expressions involving electric field perturbations are greatly simplified, since standard atomic orbital basis sets depend only on the nuclear coordinates and not on the electric field.

17.1 The Electric Field Perturbation

17.1.1 The Hamiltonian Operator with Mixed Perturbations

Let us consider mixed (cross) perturbation terms in the following Hamiltonian operator \mathbf{H} , appearing in standard perturbation theory:

$$\mathbf{H} = \mathbf{H}_0 + \lambda_a \mathbf{H}'_a + \lambda_f \mathbf{H}'_f + \lambda_a \lambda_f \mathbf{H}''_{af} + \dots . \quad (17.1)$$

In eq. (17.1) \mathbf{H}_0 is the Hamiltonian operator without perturbations, \mathbf{H}'_a is the first-order change in the Hamiltonian operator due to a nuclear perturbation, and \mathbf{H}'_f is the first-order change in the Hamiltonian operator due to an electronic field. λ_a is a nuclear coordinate (*a*) perturbation and λ_f is an electric field (*F*) perturbation. It should be noted that standard

atomic orbital (AO) basis sets depend only on the nuclear coordinates and not on the electric field. For such standard basis sets, \mathbf{H}'_a affects the one-electron, two-electron, and overlap integrals as was shown in Chapter 3. However, \mathbf{H}'_f affects only the one-electron integrals.

17.1.2 The Derivative of the Molecular Orbital Coefficients

Using the notation of Chapter 3, the molecular orbital (MO) coefficient changes with respect to electric fields and nuclear coordinates are

$$\frac{\partial C_\mu^i}{\partial F} = \sum_m^{MO} U_{mi}^f C_\mu^m , \quad (17.2)$$

$$\frac{\partial^2 C_\mu^i}{\partial F \partial G} = \sum_m^{MO} U_{mi}^{fg} C_\mu^m , \quad (17.3)$$

and

$$\frac{\partial^2 C_\mu^i}{\partial a \partial F} = \sum_m^{MO} U_{mi}^{af} C_\mu^m \quad (17.4)$$

where “ a ” is a nuclear coordinate and F and G are electric field perturbations. The relationship between the first- and second-order U matrices including nuclear perturbations was presented in Section 3.3:

$$\frac{\partial U_{ij}^a}{\partial b} = U_{ij}^{ab} - \sum_m^{MO} U_{im}^b U_{mj}^a . \quad (17.5)$$

The corresponding relationships involving electric field perturbations are

$$\frac{\partial U_{ij}^f}{\partial G} = U_{ij}^{fg} - \sum_m^{MO} U_{im}^g U_{mj}^f , \quad (17.6)$$

and

$$\frac{\partial U_{ij}^f}{\partial a} = U_{ij}^{af} - \sum_m^{MO} U_{im}^a U_{mj}^f . \quad (17.7)$$

17.1.3 The Derivative One-Electron AO Integrals

As mentioned above, the electric field does not affect the overlap and two-electron integrals for standard AO basis sets. The relevant non-vanishing one-electron derivative AO integrals that involve electric field perturbations are dipole moment integrals and their nuclear derivatives. A first-order change in the one-electron integral with respect to an electric field

has been related to a position operator (see, for example, [1,2]) and the negative of this integral is termed a dipole moment integral:

$$\frac{\partial h_{\mu\nu}}{\partial F} = \left\langle \chi_\mu \left| \frac{\partial \mathbf{H}}{\partial F} \right| \chi_\nu \right\rangle = \left\langle \chi_\mu \left| \mathbf{H}'_f \right| \chi_\nu \right\rangle \quad (17.8)$$

$$= -e \left\langle \chi_\mu \left| r_f \right| \chi_\nu \right\rangle = -d_{\mu\nu}^f \quad (17.9)$$

where e stands for the electronic charge. The derivative of this integral with respect to a nuclear coordinate “ a ” is

$$\frac{\partial^2 h_{\mu\nu}}{\partial a \partial F} = \frac{\partial}{\partial a} \left(\frac{\partial h_{\mu\nu}}{\partial F} \right) \quad (17.10)$$

$$= -e \frac{\partial}{\partial a} \left\langle \chi_\mu \left| r_f \right| \chi_\nu \right\rangle \quad (17.11)$$

$$= -e \left\langle \frac{\partial \chi_\mu}{\partial a} \left| r_f \right| \chi_\nu \right\rangle - e \left\langle \chi_\mu \left| r_f \right| \frac{\partial \chi_\nu}{\partial a} \right\rangle \quad (17.12)$$

$$= h_{\mu\nu}^{af}. \quad (17.13)$$

Derivative one-electron integrals involving second- or higher-order electric perturbations are unimportant and thus are usually neglected (see, for example, [1-7]).

17.1.4 The Derivative One-Electron MO Integrals

The non-vanishing derivative AO integrals described above may be transformed into the MO basis as

$$h_{ij}^f = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial F} \quad (17.14)$$

$$= - \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j d_{\mu\nu}^f = -d_{ij}^f \quad (17.15)$$

and

$$h_{ij}^{af} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial^2 h_{\mu\nu}}{\partial a \partial F} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j h_{\mu\nu}^{af}. \quad (17.16)$$

The general form for the derivatives of the skeleton (core) derivative integrals is given by (see Chapter 3 or Appendix K)

$$\frac{\partial h_{ij}^a}{\partial b} = \sum_m^{MO} \left(U_{mi}^b h_{mj}^a + U_{mj}^b h_{im}^a \right) + h_{ij}^{ab}. \quad (17.17)$$

Thus, the derivatives of the one-electron integral, h_{ij}^f in eq. (17.14), with respect to a second electric field G and a nuclear coordinate “ a ”, are:

$$\frac{\partial h_{ij}^f}{\partial G} = \sum_m^{MO} \left(U_{mi}^g h_{mj}^f + U_{mj}^g h_{im}^f \right) \quad (17.18)$$

and

$$\frac{\partial h_{ij}^f}{\partial a} = \sum_m^{MO} \left(U_{mi}^a h_{mj}^f + U_{mj}^a h_{im}^f \right) + h_{ij}^{af} . \quad (17.19)$$

Note that derivative one-electron integrals involving second-order electric field perturbations were neglected.

17.1.5 Constraints on the Molecular Orbitals

The set of molecular orbitals is orthonormal, and in the MO basis this condition is

$$S_{ij} = \delta_{ij} \quad (17.20)$$

where δ is the Kronecker delta function. The general form of the first derivative of these conditions including nuclear perturbations is (see Chapter 3 or Appendix J)

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 . \quad (17.21)$$

The first derivative form of the orthonormality condition with respect to an electric field perturbation is given by

$$U_{ij}^f + U_{ji}^f = 0 , \quad (17.22)$$

since the overlap integral in the AO basis is not affected by an electric field perturbation.

The general form of the second derivative of the orthonormality condition including nuclear perturbations is (see Chapter 3 or Appendix L)

$$U_{ij}^{ab} + U_{ji}^{ab} + \xi_{ij}^{ab} = 0 \quad (17.23)$$

with

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) . \quad (17.24)$$

There are two forms of second derivatives of the normalization conditions when electric field perturbations are involved. For pure electric field perturbations,

$$U_{ij}^{fg} + U_{ji}^{gf} + \xi_{ij}^{fg} = 0 \quad (17.25)$$

with

$$\xi_{ij}^{fg} = \sum_m^{MO} \left(U_{im}^f U_{jm}^g + U_{im}^g U_{jm}^f \right) . \quad (17.26)$$

For mixed perturbations, incorporating one electric field and one nuclear perturbation,

$$U_{ij}^{af} + U_{ji}^{af} + \xi_{ij}^{af} = 0 \quad (17.27)$$

with

$$\xi_{ij}^{af} = \sum_m^{MO} \left(U_{im}^a U_{jm}^f + U_{im}^f U_{jm}^a \right) . \quad (17.28)$$

17.2 The Electric Dipole Moment

The electric dipole moment is defined by (see, for example, [1-7])

$$\mu_f = - \frac{\partial E_{total}}{\partial F} \quad (17.29)$$

$$= - \frac{\partial E_{nuc}}{\partial F} - \frac{\partial E_{elec}}{\partial F} \quad (17.30)$$

$$= \mu_f^{nuc} + \mu_f^{elec} \quad (17.31)$$

where F stands for the electric field along the f axis. The nuclear part of the dipole moment for a molecule with N nuclei is given by

$$\mu_f^{nuc} = e \sum_A^N Z_A R_A^f \quad . \quad (17.32)$$

In this equation Z_A is the atomic number of nucleus A and R_A^f is the distance along the f direction between the A th nucleus and the reference position (usually the center of mass of the molecule). The electronic part of the dipole moment is expressed as

$$\mu_f^{elec} = - \frac{\partial E_{elec}}{\partial F} \quad . \quad (17.33)$$

For the *exact* wavefunction this equation is equivalent to the expectation value of the dipole moment operator [1-7]:

$$\mu_f^{elec} = - \left\langle \Psi \left| \frac{\partial \mathbf{H}}{\partial F} \right| \Psi \right\rangle \quad (17.34)$$

$$= - \left\langle \Psi \left| \mathbf{H}'_f \right| \Psi \right\rangle \quad (17.35)$$

$$= - e \left\langle \Psi \left| r_f \right| \Psi \right\rangle \quad . \quad (17.36)$$

Equation (17.34) represents one statement of the well-known Hellmann-Feynman theorem [8,9]. However, the results from eqs. (17.33) and (17.34) need not agree for *approximate* wavefunctions.

17.2.1 The Closed-Shell SCF Wavefunction

The general equation for the energy first derivative of a closed-shell SCF wavefunction including a nuclear perturbation was given in Chapter 4 as

$$\frac{\partial E_{elec}}{\partial a} = 2 \sum_i^{d.o.} h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} - 2 \sum_i^{d.o.} S_{ii}^a \epsilon_i \quad (17.37)$$

where *d.o.* denotes the doubly occupied orbitals and ϵ_i orbital energies. As mentioned in the preceding section, the second and third terms of eq. (17.37) vanish for an electric field

perturbation. Therefore

$$\mu_f^{elec} = - \frac{\partial E_{elec}}{\partial F} = - 2 \sum_i^{d.o.} h_{ii}^f = 2 \sum_i^{d.o.} d_{ii}^f . \quad (17.38)$$

From the definition of the dipole moment integral in eqs. (17.9) and (17.14), it is evident that equation (17.38) is equal to an expectation value of the dipole moment operator. In the closed-shell SCF case, the two expressions, the energy derivative from eq. (17.33) and the expectation value from eq. (17.34), give identical results.

17.2.2 The General Restricted Open-Shell SCF Wavefunction

The general equation for the energy first derivative of a general restricted open-shell SCF wavefunction including a nuclear perturbation was given in Chapter 5 as

$$\frac{\partial E_{elec}}{\partial a} = 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} - 2 \sum_{ij}^{MO} S_{ij}^a \epsilon_{ij} \quad (17.39)$$

where ϵ is the Lagrangian matrix. The second and third terms in eq. (17.39) vanish for an electric field perturbation. Thus,

$$\mu_f^{elec} = - \frac{\partial E_{elec}}{\partial F} = - 2 \sum_i^{MO} f_i h_{ii}^f = 2 \sum_i^{MO} f_i d_{ii}^f . \quad (17.40)$$

The results from eq. (17.33) for the derivative and eq. (17.34) for the expectation value formulae again are identical for the GRSCF wavefunction.

17.2.3 The Configuration Interaction (CI) Wavefunction

The energy first derivative including a nuclear perturbation for a CI wavefunction was given in Chapter 6 as

$$\frac{\partial E_{elec}}{\partial a} = \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij} . \quad (17.41)$$

Q and G are one- and two-electron reduced density matrices [10] and X is the Lagrangian matrix. Since the two-electron integral is not affected by an electric field perturbation, the expression for the dipole moment becomes

$$\mu_f^{elec} = - \frac{\partial E_{elec}}{\partial F} = - \sum_{ij}^{MO} Q_{ij} h_{ij}^f - 2 \sum_{ij}^{MO} U_{ij}^f X_{ij} \quad (17.42)$$

$$= \sum_{ij}^{MO} Q_{ij} d_{ij}^f - 2 \sum_{ij}^{MO} U_{ij}^f X_{ij} . \quad (17.43)$$

The first term in eqs. (17.42) and (17.43) corresponds to the expectation value given by eq. (17.34). For a CI wavefunction, explicit evaluation of the U^f matrices is necessary in order to properly determine the dipole moment. The related subject of the evaluation of the second term in eq. (17.42) (using the Z vector method) will be treated in Chapter 18.

17.2.4 The Multiconfiguration (MC) SCF Wavefunction

The general expression for the energy first derivative of an MCSCF wavefunction including a nuclear perturbation was given in Chapter 9 as

$$\frac{\partial E_{elec}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a - \sum_{ij}^{MO} S_{ij}^a x_{ij} . \quad (17.44)$$

Here γ and Γ are one- and two-electron reduced density matrices [10] and x is the Lagrangian matrix. With an electric field perturbation, the second and third terms vanish and the dipole moment becomes

$$\mu_f^{elec} = - \frac{\partial E_{elec}}{\partial F} = - \sum_{ij}^{MO} \gamma_{ij} h_{ij}^f = \sum_{ij}^{MO} \gamma_{ij} d_{ij}^f . \quad (17.45)$$

For an MCSCF wavefunction the first derivative and the expectation value equations produce the same results as was the case for CLSCF and GRSCF wavefunctions. It should be noted that the evaluation of the changes in the MO coefficients is *not* necessary to determine the dipole moment for these three types of wavefunctions. The CI wavefunction presents a more computationally difficult situation.

17.3 The Electric Polarizability

The electric polarizability is a second-order property with the components of the polarizability tensor given by [1-7]

$$\alpha_{fg} = - \frac{\partial^2 E_{elec}}{\partial F \partial G} \quad (17.46)$$

where F and G stand for the electric fields along the f and g axes. This equation may be rewritten using the definition of the electric dipole moment, eq. (17.33), as

$$\alpha_{fg} = - \frac{\partial}{\partial G} \left(\frac{\partial E_{elec}}{\partial F} \right) = \frac{\partial \mu_f^{elec}}{\partial G} \quad (17.47)$$

$$= - \frac{\partial}{\partial F} \left(\frac{\partial E_{elec}}{\partial G} \right) = \frac{\partial \mu_g^{elec}}{\partial F} . \quad (17.48)$$

17.3.1 The Closed-Shell SCF Wavefunction

An equation to evaluate the electric polarizability is obtained easily by combining eqs. (17.18), (17.38), and (17.47):

$$\alpha_{fg} = \frac{\partial \mu_f^{elec}}{\partial G} = -2 \sum_i^{d.o.} \left(\frac{\partial h_{ii}^f}{\partial G} \right) \quad (17.49)$$

$$= -2 \sum_i^{d.o.} \sum_m^{all} \left(U_{mi}^g h_{mi}^f + U_{mi}^g h_{im}^f \right) \quad (17.50)$$

$$= -4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^g h_{ij}^f \quad (17.51)$$

$$= -4 \sum_i^{virt. d.o.} \sum_j^{d.o.} U_{ij}^g h_{ij}^f - 4 \sum_i^{d.o.} \sum_j^{d.o.} U_{ij}^g h_{ij}^f \quad (17.52)$$

$$= -4 \sum_i^{virt. d.o.} \sum_j^{d.o.} U_{ij}^g h_{ij}^f - 2 \sum_{ij}^{d.o.} \left(U_{ij}^g + U_{ji}^g \right) h_{ij}^f \quad (17.53)$$

$$= -4 \sum_i^{virt. d.o.} \sum_j^{d.o.} U_{ij}^g h_{ij}^f . \quad (17.54)$$

Here *virt.* and *d.o.* denote virtual (unoccupied) and doubly occupied orbitals. In the last step of the derivation eq. (17.22) was used. The independent pairs in the U^f or U^g matrices are obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations with electric field perturbations (see Section 17.5).

An alternative expression may be obtained from the general equation for the second derivative of the electronic energy of the closed-shell (CL) SCF wavefunction given in Chapter 4:

$$\begin{aligned} \frac{\partial^2 E}{\partial a \partial b} &= 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\ &- 2 \sum_i^{d.o.} S_{ii}^{ab} \epsilon_i - 2 \sum_i^{d.o.} \eta_{ii}^{ab} \epsilon_i \\ &+ 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^a U_{ij}^b \epsilon_i \\ &+ 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} U_{ij}^a U_{kl}^b \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} , \end{aligned} \quad (17.55)$$

where the η^{ab} matrices were defined in Section 3.7

$$\eta_{ij}^{ab} = \sum_m^{all} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) . \quad (17.56)$$

For double electric field perturbations (i.e., the electric polarizability), the first three terms vanish and the resulting equation is

$$\alpha_{fg} = - \frac{\partial^2 E_{elec}}{\partial F \partial G} \quad (17.57)$$

$$\begin{aligned} &= 2 \sum_i^{d.o.} \eta_{ii}^{fg} \epsilon_i - 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^g F_{ij}^f + U_{ij}^f F_{ij}^g \right) - 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^f U_{ij}^g \epsilon_i \\ &- 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} U_{ij}^f U_{kl}^g \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} . \end{aligned} \quad (17.58)$$

The η^{fg} and skeleton (core) first derivative Fock matrices are defined by

$$\eta_{ii}^{fg} = 2 \sum_m^{all} U_{im}^f U_{im}^g , \quad (17.59)$$

$$F_{ij}^f = h_{ij}^f , \quad (17.60)$$

and

$$F_{ij}^g = h_{ij}^g . \quad (17.61)$$

Although eqs. (17.54) and (17.58) appear to be different, it may be proven that they are in fact mathematically equivalent. Using eqs. (17.22) and (17.59), the first and third terms of eq. (17.58) may be rewritten as

$$2 \sum_i^{d.o.} \eta_{ii}^{fg} \epsilon_i - 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^f U_{ij}^g \epsilon_i \quad (17.62)$$

$$= 4 \sum_i^{d.o.} \sum_m^{all} U_{im}^f U_{im}^g \epsilon_i - 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^f U_{ij}^g \epsilon_i \quad (17.63)$$

$$= 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^f U_{ij}^g (\epsilon_j - \epsilon_i) . \quad (17.64)$$

Using this result, eq. (17.58) may be reformulated as

$$\begin{aligned} \alpha_{fg} &= -4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^f \left[F_{ij}^g - (\epsilon_j - \epsilon_i) U_{ij}^g \right. \\ &\quad \left. + \sum_k^{all} \sum_l^{d.o.} U_{kl}^g \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \right] \\ &- 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^g F_{ij}^f . \end{aligned} \quad (17.65)$$

In Section 10.1 the first derivative of the Fock matrix with respect to a nuclear coordinate "a" was found as

$$\begin{aligned}\frac{\partial F_{ij}}{\partial a} &= F_{ij}^a - (\epsilon_j - \epsilon_i) U_{ij}^a - S_{ij}^a \epsilon_j \\ &+ \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} U_{kl}^a \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} .\end{aligned}\quad (17.66)$$

Referring to eq. (17.66), the terms in the square brackets in eq. (17.65) represent the first derivative of the Fock matrix with respect to the electric field G . Thus eq. (17.65) becomes

$$\alpha_{fg} = -4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^f \left(\frac{\partial F_{ij}}{\partial G} \right) - 4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^g F_{ij}^f . \quad (17.67)$$

For a CLSCF wavefunction the off-diagonal terms of the first derivative of the Fock matrix vanish, i.e.,

$$\frac{\partial F_{ij}}{\partial G} = 0 \quad \text{for } i \neq j \quad (17.68)$$

and the diagonal elements of the U^f matrix are zero from eq. (17.22)

$$U_{ii}^f = 0 . \quad (17.69)$$

Therefore, the expression for the polarizability is given by

$$\alpha_{fg} = -4 \sum_i^{\text{all d.o.}} \sum_j^{\text{d.o.}} U_{ij}^g h_{ij}^f \quad (17.70)$$

$$= -4 \sum_i^{\text{virt. d.o.}} \sum_j^{\text{d.o.}} U_{ij}^g h_{ij}^f . \quad (17.71)$$

Equation (17.71) is identical to eq. (17.54).

17.3.2 The General Restricted Open-Shell SCF Wavefunction

An equation to determine the electric polarizability for a general restricted open-shell wavefunction is derived in a manner similar to that for the closed-shell case. Using eqs. (17.18) and (17.40),

$$\alpha_{fg} = \frac{\partial \mu_f^{elec}}{\partial G} = -2 \sum_i^{MO} f_i \left(\frac{\partial h_{ii}^f}{\partial G} \right) \quad (17.72)$$

$$= -2 \sum_i^{MO} f_i \sum_m^{MO} \left(U_{mi}^g h_{mi}^f + U_{mi}^g h_{im}^f \right) \quad (17.73)$$

$$= -4 \sum_{ij}^{MO} f_i h_{ij}^f U_{ji}^g . \quad (17.74)$$

This equation may be further simplified to

$$\begin{aligned}\alpha_{fg} &= -4 \sum_{i>j}^{MO} f_i h_{ij}^f U_{ji}^g - 4 \sum_{i>j}^{MO} f_j h_{ji}^f U_{ij}^g \\ &\quad - 4 \sum_i^{MO} f_i h_{ii}^f U_{ii}^g\end{aligned}\quad (17.75)$$

$$= 4 \sum_{i>j}^{MO} (f_i - f_j) h_{ij}^f U_{ij}^g \quad (17.76)$$

$$= 4 \sum_{i>j}^{indep.\,pair} (f_i - f_j) h_{ij}^f U_{ij}^g . \quad (17.77)$$

Eqs. (17.22) and (17.69) and the symmetric property of the dipole moment integrals were employed in deriving eq. (17.77). In eq. (17.77) the summation runs over only the independent pairs, since the factor $(f_i - f_j)$ for any non-independent pairs is equal to zero. The U^f matrices are obtained by solving the CPHF equations with electric field perturbations (see Section 17.5).

An alternative equation may be derived from the general expression for the second derivative of the electronic energy for the GRSCF wavefunction given in Chapter 5:

$$\begin{aligned}\frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &\quad - 2 \sum_{ij}^{MO} S_{ij}^{ab} \epsilon_{ij} - 2 \sum_{ij}^{MO} \eta_{ij}^{ab} \epsilon_{ij} \\ &\quad + 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) + 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j \\ &\quad + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \left[2\alpha_{jl}(ij|kl) + \beta_{jl} \left\{ (ik|jl) + (il|jk) \right\} \right] .\end{aligned}\quad (17.78)$$

For double electric field perturbations, the first three terms disappear and the remainder is

$$\alpha_{fg} = - \frac{\partial^2 E_{elec}}{\partial F \partial G} \quad (17.79)$$

$$\begin{aligned}&= 2 \sum_{ij}^{MO} \eta_{ij}^{fg} \epsilon_{ij} - 4 \sum_{ij}^{MO} \left(U_{ij}^g \epsilon_{ji}^f + U_{ij}^f \epsilon_{ji}^g \right) - 4 \sum_{ijk}^{MO} U_{ij}^f U_{kj}^g \zeta_{ik}^j \\ &\quad - 4 \sum_{ijkl}^{MO} U_{ij}^f U_{kl}^g \left[2\alpha_{jl}(ij|kl) + \beta_{jl} \left\{ (ik|jl) + (il|jk) \right\} \right] .\end{aligned}\quad (17.80)$$

In this equation the η^{fg} and skeleton (core) first derivative Lagrangian matrices are defined

by

$$\eta_{ij}^{fg} = \sum_m^{MO} \left(U_{im}^f U_{jm}^g + U_{im}^g U_{jm}^f \right) , \quad (17.81)$$

$$\epsilon_{ij}^f = f_i h_{ij}^f , \quad (17.82)$$

and

$$\epsilon_{ij}^g = f_i h_{ij}^g . \quad (17.83)$$

Again, although eqs. (17.77) and (17.80) look superficially different, it may be proven that they are mathematically equivalent. Using eq. (17.81) and the variational condition on the MO space

$$\epsilon_{ij} - \epsilon_{ji} = 0 , \quad (17.84)$$

the first term of eq. (17.80) may be rewritten as

$$2 \sum_{ij}^{MO} \eta_{ij}^{fg} \epsilon_{ij} = 2 \sum_{ijm}^{MO} \left(U_{im}^f U_{jm}^g + U_{im}^g U_{jm}^f \right) \epsilon_{ij} \quad (17.85)$$

$$= 4 \sum_{ijk}^{MO} U_{ik}^f U_{jk}^g \epsilon_{ij} \quad (17.86)$$

$$= 4 \sum_{ijk}^{MO} U_{ij}^f U_{kj}^g \epsilon_{ik} . \quad (17.87)$$

Exploiting this result, eq. (17.80) may be reformulated as

$$\begin{aligned} \alpha_{fg} &= 4 \sum_{ij}^{MO} U_{ij}^f \left(\sum_k^{MO} U_{kj}^g \epsilon_{ik} - \epsilon_{ji}^g - \sum_k^{MO} U_{kj}^g \zeta_{ik}^j \right. \\ &\quad \left. - \sum_{kl}^{MO} U_{kl}^g \left[2\alpha_{jl}(ij|kl) + \beta_{jl} \left\{ (ik|jl) + (il|jk) \right\} \right] \right) \\ &\quad - 4 \sum_{ij}^{MO} U_{ij}^g \epsilon_{ji}^f . \end{aligned} \quad (17.88)$$

In Section 5.5 the first derivative of the Lagrangian matrix with respect to a nuclear coordinate "a" was developed as

$$\begin{aligned} \frac{\partial \epsilon_{ij}}{\partial a} &= \epsilon_{ij}^a + \sum_k^{MO} U_{ki}^a \zeta_{kj}^i + \sum_k^{MO} U_{kj}^a \epsilon_{ik} \\ &\quad + \sum_{kl}^{MO} U_{kl}^a \left[2\alpha_{il}(ij|kl) + \beta_{il} \left\{ (ik|jl) + (il|jk) \right\} \right] . \end{aligned} \quad (17.89)$$

Using eq. (17.89), equation (17.88) may be rewritten as

$$\begin{aligned}\alpha_{fg} &= 4 \sum_{ij}^{MO} U_{ij}^f \left[\sum_k^{MO} U_{kj}^g \epsilon_{ik} - \left(\frac{\partial \epsilon_{ji}}{\partial G} \right) + \sum_k^{MO} U_{ki}^g \epsilon_{jk} \right] \\ &- 4 \sum_{ij}^{MO} U_{ij}^g \epsilon_{ji}^f .\end{aligned}\quad (17.90)$$

The first derivative form of the variational condition on the MO space is

$$\frac{\partial \epsilon_{ij}}{\partial G} - \frac{\partial \epsilon_{ji}}{\partial G} = 0 . \quad (17.91)$$

Using relationships in eqs. (17.22) and (17.91), equation (17.90) may be further simplified to

$$\begin{aligned}\alpha_{fg} &= 2 \sum_{ij}^{MO} \left(U_{ij}^f + U_{ji}^f \right) \left[\sum_k^{MO} U_{kj}^g \epsilon_{ik} - \left(\frac{\partial \epsilon_{ji}}{\partial G} \right) + \sum_k^{MO} U_{ki}^g \epsilon_{jk} \right] \\ &- 4 \sum_{ij}^{MO} U_{ij}^g \epsilon_{ji}^f\end{aligned}\quad (17.92)$$

$$= -4 \sum_{ij}^{MO} U_{ij}^g \epsilon_{ji}^f \quad (17.93)$$

$$= -4 \sum_{ij}^{MO} f_j h_{ji}^f U_{ij}^g \quad (17.94)$$

$$= 4 \sum_{i>j}^{indep.\,pair} \left(f_i - f_j \right) h_{ij}^f U_{ij}^g . \quad (17.95)$$

Eq. (17.95) is seen to be identical to eq. (17.77).

17.3.3 The Configuration Interaction (CI) Wavefunction

An equation to evaluate the electric polarizability for a CI wavefunction may be obtained by differentiating eq. (17.42) with respect to a second electric field perturbation G , i.e.,

$$\alpha_{fg} = \frac{\partial \mu_f^{elec}}{\partial G} \quad (17.96)$$

$$= - \sum_{ij}^{MO} \left(\frac{\partial Q_{ij}}{\partial G} h_{ij}^f + Q_{ij} \frac{\partial h_{ij}^f}{\partial G} \right) - 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^f}{\partial G} X_{ij} + U_{ij}^f \frac{\partial X_{ij}}{\partial G} \right) . \quad (17.97)$$

In this equation an element of the one-electron reduced density matrix, Q_{ij} , is defined by [10]

$$Q_{ij} = \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} . \quad (17.98)$$

In general the derivatives of the CI coefficients do not vanish, although the derivatives of the coupling constants are zero. Thus, the first derivative of the one-electron reduced density matrix with respect to the variable G is given by

$$\frac{\partial Q_{ij}}{\partial G} = 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} Q_{ij}^{IJ} . \quad (17.99)$$

In Section 14.1 the first derivative of the Lagrangian matrix with respect to a nuclear coordinate "a" was derived as

$$\frac{\partial X_{ij}}{\partial a} = 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} X_{ij}^{IJ} + X_{ij}^a + \sum_k^{MO} U_{ki}^a X_{kj} + \sum_{kl}^{MO} U_{kl}^a Y_{ijkl} . \quad (17.100)$$

Exploiting eqs. (17.6), (17.18), (17.99) and (17.100), equation (17.97) may be rewritten as

$$\begin{aligned} \alpha_{fg} &= - \sum_{ij}^{MO} \left[2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} Q_{ij}^{IJ} h_{ij}^f \right] - \sum_{ij}^{MO} Q_{ij} \left[\sum_m^{MO} \left(U_{mi}^g h_{mj}^f + U_{mj}^g h_{im}^f \right) \right] \\ &- 2 \sum_{ij}^{MO} \left(U_{ij}^{fg} - \sum_m^{MO} U_{im}^g U_{mj}^f \right) X_{ij} \\ &- 2 \sum_{ij}^{MO} U_{ij}^f \left[2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} X_{ij}^{IJ} + X_{ij}^g + \sum_k^{MO} U_{ki}^g X_{kj} + \sum_{kl}^{MO} U_{kl}^g Y_{ijkl} \right] . \end{aligned} \quad (17.101)$$

In this equation the skeleton (core) first derivative Lagrangian matrices, "bare" Lagrangian matrices and Y matrix are

$$X_{ij}^f = \sum_m^{MO} Q_{jm} h_{im}^f , \quad (17.102)$$

$$X_{ij}^{IJ} = \sum_m^{MO} Q_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl) , \quad (17.103)$$

$$Y_{ijkl} = Q_{jl} h_{ik} + 2 \sum_{mn}^{MO} \left\{ G_{jlmn}(ik|mn) + 2G_{jmln}(im|kn) \right\} . \quad (17.104)$$

Rearranging the terms in eq. (17.101) one obtains

$$\alpha_{fg} = - 2 \sum_{ij}^{MO} U_{ij}^{fg} X_{ij} - 2 \sum_{ij}^{MO} \left(U_{ij}^g X_{ij}^f + U_{ij}^f X_{ij}^g \right)$$

$$\begin{aligned}
& - 2 \sum_{ijkl}^{MO} U_{ij}^f U_{kl}^g Y_{ijkl} \\
& - 2 \sum_{ij}^{MO} \sum_{IJ}^{CI} \left[C_I \frac{\partial C_J}{\partial G} \left(Q_{ij}^{IJ} h_{ij}^f + 2 U_{ij}^f X_{ij}^{IJ} \right) \right] . \quad (17.105)
\end{aligned}$$

An alternative equation may be derived from the general expression for the second derivative of the electronic energy for the CI wavefunction given in Chapter 6:

$$\begin{aligned}
\frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl} (ij|kl)^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} \\
&+ 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^a + U_{ij}^a X_{ij}^b \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl} \\
&- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (17.106)
\end{aligned}$$

For double electric field perturbations, the first two terms disappear and the resulting equation is

$$\alpha_{fg} = - \frac{\partial^2 E_{elec}}{\partial F \partial G} \quad (17.107)$$

$$\begin{aligned}
&= - 2 \sum_{ij}^{MO} U_{ij}^{fg} X_{ij} - 2 \sum_{ij}^{MO} \left(U_{ij}^g X_{ij}^f + U_{ij}^f X_{ij}^g \right) \\
&- 2 \sum_{ijkl}^{MO} U_{ij}^f U_{kl}^g Y_{ijkl} + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial F} \frac{\partial C_J}{\partial G} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (17.108)
\end{aligned}$$

Equivalence of the last terms in eqs. (17.105) and (17.108) may be proven in the following manner. In Section 6.7 the following relationships from the coupled perturbed configuration interaction (CPCI) equations were presented:

$$\begin{aligned}
& \sum_I^{CI} \frac{\partial C_I}{\partial a} \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} \right) \\
&= \sum_I^{CI} \frac{\partial C_I}{\partial b} \sum_J^{CI} C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) \quad (17.109)
\end{aligned}$$

$$= - \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (17.110)$$

Using these relationships the last term of eq. (17.108) may be manipulated as

$$2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial F} \frac{\partial C_J}{\partial G} \left(H_{IJ} - \delta_{IJ} E_{elec} \right)$$

$$= -2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \left(\frac{\partial H_{IJ}}{\partial F} - \delta_{IJ} \frac{\partial E_{elec}}{\partial F} \right) \quad (17.111)$$

$$= -2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \frac{\partial H_{IJ}}{\partial F} . \quad (17.112)$$

In the last step of the above manipulation, the first derivative form of the normalization condition for the CI coefficients

$$\sum_I^{CI} C_I \frac{\partial C_I}{\partial G} = 0 \quad (17.113)$$

was employed. In Section 6.4 the general form of the first derivative for the CI Hamiltonian matrix was derived as

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \quad (17.114)$$

$$= \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ijkl)^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} . \quad (17.115)$$

Using eq. (17.115) for electric field perturbations, equation (17.112) becomes

$$2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial F} \frac{\partial C_J}{\partial G} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \\ = -2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \left(\sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^f + 2 \sum_{ij}^{MO} U_{ij}^f X_{ij}^{IJ} \right) . \quad (17.116)$$

This result indicates that eqs. (17.105) and (17.108) are mathematically equivalent.

In equations (17.105) and (17.108), it is clearly seen that solutions to both the first- and second-order CPHF equations (see Section 17.5) and to the first-order CPCI equations (see Section 17.6) with respect to electric field perturbations are necessary to evaluate the electric polarizability at the CI level. This is a simple reflection of the fact that the polarizability is a second-order property. The related subject of the evaluation of the first terms in eq. (17.105) and (17.108) (using the Z vector method) will be discussed in Chapter 18.

17.3.4 The Multiconfiguration (MC) SCF Wavefunction

A simpler approach to the evaluation of the electric polarizability for an MCSCF wavefunction is derived using eqs. (17.18), (17.45) and (17.99):

$$\alpha_{fg} = \frac{\partial \mu_f^{elec}}{\partial G} = - \sum_{ij}^{MO} \left(\frac{\partial \gamma_{ij}}{\partial G} h_{ij}^f + \gamma_{ij} \frac{\partial h_{ij}^f}{\partial G} \right) \quad (17.117)$$

$$\begin{aligned}
&= - \sum_{ij}^{MO} \left[2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \gamma_{ij}^{IJ} h_{ij}^f \right] \\
&- \sum_{ij}^{MO} \gamma_{ij} \left[\sum_m^{MO} \left(U_{mi}^g h_{mj}^f + U_{mj}^g h_{im}^f \right) \right]
\end{aligned} \tag{17.118}$$

$$\begin{aligned}
&= - 2 \sum_{ij}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \gamma_{ij}^{IJ} h_{ij}^f \\
&- 2 \sum_{ijm}^{MO} \gamma_{ij} U_{mi}^g h_{mj}^f
\end{aligned} \tag{17.119}$$

$$\begin{aligned}
&= - 2 \sum_{ij}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \gamma_{ij}^{IJ} h_{ij}^f \\
&- 2 \sum_{ij}^{MO} U_{ij}^g x_{ij}^f .
\end{aligned} \tag{17.120}$$

In this equation the skeleton (core) first derivative Lagrangian matrices x^f matrix are

$$x_{ij}^f = \sum_m^{MO} \gamma_{jm} h_{im}^f , \tag{17.121}$$

and γ^{IJ} are the one-electron coupling constants [10].

An alternative equation may be obtained from the general expression for the second derivative of the MCSCF electronic energy. This second derivative expression was given in Chapter 9:

$$\begin{aligned}
\frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{ab} - \sum_{ij}^{MO} S_{ij}^{ab} x_{ij} - \sum_{ij}^{MO} \eta_{ij}^{ab} x_{ij} \\
&+ 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} \\
&- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) .
\end{aligned} \tag{17.122}$$

For double electric field perturbations, the first three terms vanish and the resulting equation is

$$\alpha_{fg} = - \frac{\partial^2 E_{elec}}{\partial F \partial G} \tag{17.123}$$

$$\begin{aligned}
&= \sum_{ij}^{MO} \eta_{ij}^{fg} x_{ij} - 2 \sum_{ij}^{MO} \left(U_{ij}^g x_{ij}^f + U_{ij}^f x_{ij}^g \right) - 2 \sum_{ijkl}^{MO} U_{ij}^f U_{kl}^g y_{ijkl} \\
&+ 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial F} \frac{\partial C_J}{\partial G} \left(H_{IJ} - \delta_{IJ} E_{elec} \right)
\end{aligned} \tag{17.124}$$

where the y matrix is

$$y_{ijkl} = \gamma_{jl}h_{ik} + 2 \sum_{mn}^{MO} \left\{ \Gamma_{jlmn}(ik|mn) + 2\Gamma_{jmkn}(im|kn) \right\} . \quad (17.125)$$

Although eqs. (17.120) and (17.124) appear different, it may be proved that they are mathematically equivalent. Using eq. (17.81) and the variational condition on the MO space

$$x_{ij} - x_{ji} = 0 , \quad (17.126)$$

the first term of eq. (17.124) may be rewritten as

$$\sum_{ij}^{MO} \eta_{ij}^{fg} x_{ij} = \sum_{ijm}^{MO} \left(U_{im}^f U_{jm}^g + U_{im}^g U_{jm}^f \right) x_{ij} \quad (17.127)$$

$$= 2 \sum_{ijk}^{MO} U_{ik}^f U_{jk}^g x_{ij} \quad (17.128)$$

$$= 2 \sum_{ijk}^{MO} U_{ij}^f U_{kj}^g x_{ik} . \quad (17.129)$$

Employing this result, equation (17.124) may be manipulated as

$$\begin{aligned} \alpha_{fg} &= 2 \sum_{ij}^{MO} U_{ij}^f \left[\sum_k^{MO} U_{kj}^g x_{ik} - x_{ij}^g - \sum_{kl}^{MO} U_{kl}^g y_{ijkl} \right] \\ &- 2 \sum_{ij}^{MO} U_{ij}^g x_{ij}^f \\ &+ 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial F} \frac{\partial C_J}{\partial G} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (17.130)$$

Using eqs. (17.100) and (17.116), equation (17.130) may be reformulated as

$$\begin{aligned} \alpha_{fg} &= 2 \sum_{ij}^{MO} U_{ij}^f \left[\sum_k^{MO} U_{kj}^g x_{ik} - \left(\frac{\partial x_{ij}}{\partial G} \right) + \sum_k^{MO} U_{ki}^g x_{kj} \right] \\ &+ 4 \sum_{ij}^{MO} U_{ij}^f \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} x_{ij}^{IJ} \\ &- 2 \sum_{ij}^{MO} U_{ij}^g x_{ij}^f \\ &- 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \left(\sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^f + 2 \sum_{ij}^{MO} U_{ij}^f x_{ij}^{IJ} \right) \end{aligned} \quad (17.131)$$

where the “bare” Lagrangian matrices x^{IJ} are

$$x_{ij}^{IJ} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jml}^{IJ}(im|kl) . \quad (17.132)$$

The first derivative form of the variational condition on the MO space is expressed as

$$\frac{\partial x_{ij}}{\partial G} - \frac{\partial x_{ji}}{\partial G} = 0 . \quad (17.133)$$

Using the relationships in eqs. (17.22) and (17.133), equation (17.131), may be further modified to

$$\begin{aligned} \alpha_{fg} &= \sum_{ij}^{MO} \left(U_{ij}^f + U_{ji}^f \right) \left[\sum_k^{MO} U_{kj}^g x_{ik} - \left(\frac{\partial x_{ij}}{\partial G} \right) + \sum_k^{MO} U_{ki}^g x_{kj} \right] \\ &+ 4 \sum_{ij}^{MO} U_{ij}^f \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} x_{ij}^{IJ} \\ &- 2 \sum_{ij}^{MO} U_{ij}^g x_{ij}^f \\ &- 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \left(\sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^f + 2 \sum_{ij}^{MO} U_{ij}^f x_{ij}^{IJ} \right) \end{aligned} \quad (17.134)$$

$$\begin{aligned} &= -2 \sum_{ij}^{MO} U_{ij}^g x_{ij}^f \\ &- 2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial G} \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^f . \end{aligned} \quad (17.135)$$

This equation is seen to be identical to eq. (17.120). The elements of the U^f and $\partial C_I/\partial F$ matrices are obtained by solving the first-order CPMCHF equations with respect to electric field perturbations (see Section 17.7). This is clearly a greatly simplified procedure compared to the more general CI case.

17.4 The Dipole Moment Derivative

Derivatives of the dipole moment with respect to nuclear coordinates are necessary to evaluate infrared (IR) intensities, an important goal of many quantum chemical studies. These derivatives are a second-order property and are expressed as

$$\frac{\partial \mu_f}{\partial a} = - \frac{\partial^2 E_{total}}{\partial a \partial F} = - \frac{\partial^2 E_{nuc}}{\partial a \partial F} - \frac{\partial^2 E_{elec}}{\partial a \partial F} . \quad (17.136)$$

The nuclear part of the second derivative is non-vanishing only when the direction of the electric field and the nuclear coordinate coincides:

$$\frac{\partial \mu_f^{nuc}}{\partial a} = - \frac{\partial^2 E_{nuc}}{\partial a \partial F} = e \sum_A^N Z_A . \quad (17.137)$$

The electronic part of the dipole moment derivative is given by

$$\frac{\partial \mu_f^{elec}}{\partial a} = - \frac{\partial^2 E_{elec}}{\partial a \partial F} = - \frac{\partial}{\partial a} \left(\frac{\partial E_{elec}}{\partial F} \right) = - \frac{\partial}{\partial F} \left(\frac{\partial E_{elec}}{\partial a} \right) . \quad (17.138)$$

Here “ a ” and F stand for the nuclear coordinate and electric field perturbations, respectively.

17.4.1 The Closed-Shell SCF Wavefunction

An expression for the dipole moment derivative using a closed-shell SCF wavefunction is obtained from eqs. (17.19) and (17.38):

$$\frac{\partial \mu_f^{elec}}{\partial a} = - \frac{\partial^2 E_{elec}}{\partial a \partial F} = - 2 \sum_i^{d.o.} \left(\frac{\partial h_{ii}^f}{\partial a} \right) \quad (17.139)$$

$$= - 2 \sum_i^{d.o.} \left[\sum_m^{all} \left(U_{mi}^a h_{mi}^f + U_{mi}^a h_{im}^f \right) + h_{ii}^{af} \right] \quad (17.140)$$

$$= - 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^a h_{ij}^f - 2 \sum_i^{d.o.} h_{ii}^{af} \quad (17.141)$$

$$= - 4 \sum_i^{virt. d.o.} \sum_j^{d.o.} U_{ij}^a h_{ij}^f - 4 \sum_{ij}^{d.o.} U_{ij}^a h_{ij}^f - 2 \sum_i^{d.o.} h_{ii}^{af} \quad (17.142)$$

$$= - 4 \sum_i^{virt. d.o.} \sum_j^{d.o.} U_{ij}^a h_{ij}^f - 2 \sum_{ij}^{d.o.} \left(U_{ij}^a + U_{ji}^a \right) h_{ij}^f - 2 \sum_i^{d.o.} h_{ii}^{af} . \quad (17.143)$$

Eq. (17.21) allows a simplification of the last equation to give

$$\frac{\partial \mu_f^{elec}}{\partial a} = - 4 \sum_i^{virt. d.o.} \sum_j^{d.o.} U_{ij}^a h_{ij}^f + 2 \sum_{ij}^{d.o.} S_{ij}^a h_{ij}^f - 2 \sum_i^{d.o.} h_{ii}^{af} . \quad (17.144)$$

Note that eq. (17.144) is *not* symmetric in terms of the variables “ a ” and F .

An alternative equation is derived using the general second derivative expression in eq. (17.55). For mixed perturbations the second and third terms in eq. (17.55) disappear, resulting in the following:

$$\begin{aligned} \frac{\partial \mu_f^{elec}}{\partial a} &= - 2 \sum_i^{d.o.} h_{ii}^{af} + 2 \sum_i^{d.o.} \eta_{ii}^{af} \epsilon_i \\ &- 4 \sum_i^{all} \sum_j^{d.o.} \left(U_{ij}^f F_{ij}^a + U_{ij}^a F_{ij}^f \right) - 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^a U_{ij}^f \epsilon_i \\ &- 4 \sum_i^{all} \sum_j^{d.o.} \sum_k^{all} \sum_l^{d.o.} U_{ij}^a U_{kl}^f \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \end{aligned} \quad (17.145)$$

where

$$\eta_{ii}^{af} = 2 \sum_m^{\text{all}} U_{im}^a U_{im}^f . \quad (17.146)$$

Eq. (17.145) is *symmetric* with respect to the variables “*a*” and *F*. It requires the evaluation of both the U^a and U^f matrices, while eq. (17.144) uses only the U^a matrices. Mathematical equivalence of eqs. (17.144) and (17.145) may be proved in a similar manner to that described in the preceding section.

17.4.2 The General Restricted Open-Shell SCF Wavefunction

In an analogous manner, an equation to determine the derivative of the dipole moment with respect to a nuclear coordinate may be obtained using eqs. (17.19) and (17.40):

$$\frac{\partial \mu_f^{\text{elec}}}{\partial a} = - \frac{\partial^2 E_{\text{elec}}}{\partial a \partial F} = - 2 \sum_i^{\text{MO}} f_i \left(\frac{\partial h_{ii}^f}{\partial a} \right) \quad (17.147)$$

$$= - 2 \sum_i^{\text{MO}} f_i \left[\sum_m^{\text{MO}} \left(U_{mi}^a h_{mi}^f + U_{mi}^a h_{im}^f \right) + h_{ii}^{af} \right] \quad (17.148)$$

$$= - 4 \sum_{ij}^{\text{MO}} f_i U_{ji}^a h_{ij}^f - 2 \sum_i^{\text{MO}} f_i h_{ii}^{af} \quad (17.149)$$

$$= - 4 \sum_{i>j}^{\text{MO}} f_i U_{ji}^a h_{ij}^f - 4 \sum_{i>j}^{\text{MO}} f_j U_{ij}^a h_{ji}^f - 4 \sum_i^{\text{MO}} f_i U_{ii}^a h_{ii}^f$$

$$- 2 \sum_i^{\text{MO}} f_i h_{ii}^{af} \quad (17.150)$$

$$= - 4 \sum_{i>j}^{\text{MO}} \left[- f_i \left(U_{ij}^a + S_{ij}^a \right) h_{ij}^f + f_j U_{ij}^a h_{ij}^f \right]$$

$$+ 2 \sum_i^{\text{MO}} f_i S_{ii}^a h_{ii}^f - 2 \sum_i^{\text{MO}} f_i h_{ii}^{af} \quad (17.151)$$

$$= 4 \sum_{i>j}^{\text{MO}} \left(f_i - f_j \right) U_{ij}^a h_{ij}^f + 4 \sum_{i>j}^{\text{MO}} f_i S_{ij}^a h_{ij}^f$$

$$+ 2 \sum_i^{\text{MO}} f_i S_{ii}^a h_{ii}^f - 2 \sum_i^{\text{MO}} f_i h_{ii}^{af} \quad (17.152)$$

$$= 4 \sum_{i>j}^{\text{indep. pair}} \left(f_i - f_j \right) U_{ij}^a h_{ij}^f + 4 \sum_{i>j}^{\text{MO}} f_i S_{ij}^a h_{ij}^f$$

$$+ 2 \sum_i^{\text{MO}} f_i S_{ii}^a h_{ii}^f - 2 \sum_i^{\text{MO}} f_i h_{ii}^{af} . \quad (17.153)$$

The summation in the first term of this equation runs over only independent molecular orbital pairs, since terms involving any non-independent pairs vanish. Note that eq. (17.153) is *not* symmetric with respect to the interchange of the variables “*a*” and *F*.

An alternative expression is derived using the general second derivative equation in eq. (17.78). For the cross perturbations, the second and third terms in eq. (17.78) vanish and one finds

$$\begin{aligned} \frac{\partial \mu_f^{elec}}{\partial a} &= -2 \sum_i^{MO} f_i h_{ii}^{af} + 2 \sum_{ij}^{MO} \eta_{ij}^{af} \epsilon_{ij} \\ &- 4 \sum_{ij}^{MO} \left(U_{ij}^f \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^f \right) - 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^f \zeta_{ik}^j \\ &- 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^f \left[2\alpha_{jl}(ij|kl) + \beta_{jl} \left\{ (ik|jl) + (il|jk) \right\} \right] \end{aligned} \quad (17.154)$$

where

$$\eta_{ij}^{af} = \sum_m^{MO} \left(U_{im}^a U_{jm}^f + U_{im}^f U_{jm}^a \right) . \quad (17.155)$$

Eq. (17.154) is *symmetric* in terms of the variables “*a*” and *F*. It requires evaluation of both the U^a and U^f matrices, while eq. (17.153) uses only the U^a matrices. Mathematical equivalence of these two equations may be proved in a similar manner to that shown in the preceding section.

17.4.3 The Configuration Interaction (CI) Wavefunction

An expression for the dipole moment derivative for a CI wavefunction may be derived using eqs. (17.7), (17.19), (17.42), (17.99), and (17.100):

$$\frac{\partial \mu_f^{elec}}{\partial a} = -\frac{\partial^2 E_{elec}}{\partial a \partial F} \quad (17.156)$$

$$= -\sum_{ij}^{MO} \left(\frac{\partial Q_{ij}}{\partial a} h_{ij}^f + Q_{ij} \frac{\partial h_{ij}^f}{\partial a} \right) - 2 \sum_{ij}^{MO} \left(\frac{\partial U_{ij}^f}{\partial a} X_{ij} + U_{ij}^f \frac{\partial X_{ij}}{\partial a} \right) \quad (17.157)$$

$$\begin{aligned} &= -\sum_{ij}^{MO} \left[2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} Q_{ij}^{IJ} h_{ij}^f \right] \\ &- \sum_{ij}^{MO} Q_{ij} \left[\sum_m^{MO} \left(U_{mi}^a h_{mj}^f + U_{mj}^a h_{im}^f \right) + h_{ij}^{af} \right] \\ &- 2 \sum_{ij}^{MO} \left(U_{ij}^{af} - \sum_m^{MO} U_{im}^a U_{mj}^f \right) X_{ij} \end{aligned}$$

$$- 2 \sum_{ij}^{MO} U_{ij}^f \left[2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} X_{ij}^{IJ} + X_{ij}^a + \sum_k^{MO} U_{ki}^a X_{kj} + \sum_{kl}^{MO} U_{kl}^a Y_{ijkl} \right] . \quad (17.158)$$

The two types of skeleton (core) first derivative Lagrangian matrices for the CI wavefunction are

$$X_{ij}^a = \sum_m^{MO} Q_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl} (im|kl)^a \quad (17.159)$$

and

$$X_{ij}^f = \sum_m^{MO} Q_{jm} h_{im}^f . \quad (17.160)$$

Rearranging the terms in eq. (17.158) gives

$$\begin{aligned} \frac{\partial \mu_f^{elec}}{\partial a} &= - \sum_{ij}^{MO} Q_{ij} h_{ij}^{af} - 2 \sum_{ij}^{MO} U_{ij}^{af} X_{ij} \\ &- 2 \sum_{ij}^{MO} \left(U_{ij}^f X_{ij}^a + U_{ij}^a X_{ij}^f \right) - 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^f Y_{ijkl} \\ &- 2 \sum_{ij}^{MO} \sum_{IJ}^{CI} \left[C_I \frac{\partial C_J}{\partial a} \left(Q_{ij}^{IJ} h_{ij}^f + 2 U_{ij}^f X_{ij}^{IJ} \right) \right] . \end{aligned} \quad (17.161)$$

An alternative equation may be derived from the general expression for the second derivative of the electronic energy in eq. (17.106). For the cross perturbations, the second term in eq. (17.106) vanishes and the resulting equation is

$$\begin{aligned} \frac{\partial \mu_f^{elec}}{\partial a} &= - \sum_{ij}^{MO} Q_{ij} h_{ij}^{af} - 2 \sum_{ij}^{MO} U_{ij}^{af} X_{ij} \\ &- 2 \sum_{ij}^{MO} \left(U_{ij}^f X_{ij}^a + U_{ij}^a X_{ij}^f \right) - 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^f Y_{ijkl} \\ &+ 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial F} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (17.162)$$

Eq. (17.162) is *symmetric* in terms of the variables “*a*” and *F*. Mathematical equivalence of eqs. (17.161) and (17.162) may be proven in a similar manner to that of the preceding section. From the above equations it is evident that, for the formalism presented, the solution of both the first- and second-order CPHF equations (see Section 17.5) and the first-order CPCI equations (see Section 17.6) is necessary to evaluate the dipole moment derivative at the CI level. The related subject of the evaluation of the second terms in eq. (17.161) and (17.162) by the Z vector method will be described in Chapter 18.

17.4.4 The Multiconfiguration (MC) SCF Wavefunction

An equation to calculate the MCSCF derivative of the dipole moment with respect to a nuclear coordinate may be derived using eqs. (17.19), (17.45), and (17.99):

$$\frac{\partial \mu_f^{elec}}{\partial a} = - \frac{\partial^2 E_{elec}}{\partial a \partial F} = - \sum_{ij}^{MO} \left(\frac{\partial \gamma_{ij}}{\partial a} h_{ij}^f + \gamma_{ij} \frac{\partial h_{ij}^f}{\partial a} \right) \quad (17.163)$$

$$\begin{aligned} &= - \sum_{ij}^{MO} \left(2 \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{ij}^{IJ} h_{ij}^f \right) \\ &- \sum_{ij}^{MO} \gamma_{ij} \left[\sum_m^{MO} \left(U_{mi}^a h_{mj}^f + U_{mj}^a h_{im}^f \right) + h_{ij}^{af} \right] \end{aligned} \quad (17.164)$$

$$\begin{aligned} &= - 2 \sum_{ij}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{ij}^{IJ} h_{ij}^f \\ &- 2 \sum_{ijm}^{MO} \gamma_{ij} U_{mi}^a h_{mj}^f - \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{af} \end{aligned} \quad (17.165)$$

$$\begin{aligned} &= - 2 \sum_{ij}^{MO} \sum_{IJ}^{CI} C_I \frac{\partial C_J}{\partial a} \gamma_{ij}^{IJ} h_{ij}^f \\ &- 2 \sum_{ij}^{MO} U_{ij}^a x_{ij}^f - \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{af} \end{aligned} \quad (17.166)$$

Note that eq. (17.166) is *not* symmetric with respect to the interchange of the variables “*a*” and *F*.

An alternative equation is obtained from the general expression for the second derivative of the MCSCF electronic energy, which was given in eq. (17.122):

$$\begin{aligned} \frac{\partial \mu_f^{elec}}{\partial a} &= - \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{af} + \sum_{ij}^{MO} \eta_{ij}^{af} x_{ij} \\ &- 2 \sum_{ij}^{MO} \left(U_{ij}^f x_{ij}^a + U_{ij}^a x_{ij}^f \right) - 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^f y_{ijkl} \\ &+ 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial F} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) \end{aligned} \quad (17.167)$$

In these equations the two types of skeleton (core) first derivative Lagrangian matrices are

$$x_{ij}^a = \sum_m^{MO} \gamma_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmkl} (im|kl)^a , \quad (17.168)$$

and

$$x_{ij}^f = \sum_m^{MO} \gamma_{jm} h_{im}^f . \quad (17.169)$$

It is clearly seen that eq. (17.167) is *symmetric* with respect to the interchange of the variables “ a ” and F . The elements of the U^f , U^a , $\partial C_I/\partial a$, and $\partial C_I/\partial F$ matrices appearing in eq. (17.167) are obtained by solving the first-order CPMCHF equations with mixed perturbations (see Section 17.7). Eqs. (17.166) and (17.167) appear to be different, but their mathematical equivalence may be proven in a similar manner to that presented in the preceding section.

17.5 The Coupled Perturbed Hartree-Fock (CPHF) Equations Involving Electric Field Perturbations

The coupled perturbed Hartree-Fock (CPHF) simultaneous equations provide the derivatives of the MO coefficients with respect to perturbations. In this section the CPHF equations involving electric field perturbations are discussed.

17.5.1 The First-Order CPHF Equations for a Closed-Shell SCF Wavefunction

The general form of the first-order coupled perturbed Hartree-Fock (CPHF) equations was given in Section 10.1 as

$$(\epsilon_j - \epsilon_i) U_{ij}^a - \sum_k^{virt. d.o.} \sum_l A_{ij,kl} U_{kl}^a = B_{0,ij}^a . \quad (17.170)$$

The A and B_0 matrices in eq. (17.170) are

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) \quad (17.171)$$

and

$$B_{0,ij}^a = F_{ij}^a - S_{ij}^a \epsilon_j - \sum_{kl}^{d.o.} S_{kl}^a \left\{ 2(ij|kl) - (ik|jl) \right\} . \quad (17.172)$$

The skeleton (core) first derivative Fock matrices are

$$F_{ij}^a = h_{ij}^a + \sum_k^{d.o.} \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} . \quad (17.173)$$

In these equations *virt.* and *d.o.* denote the virtual (unoccupied) and doubly occupied orbitals, respectively.

For a first-order electric field perturbation the CPHF equations are formally the same as eq. (17.170):

$$\left(\epsilon_j - \epsilon_i\right)U_{ij}^f - \sum_k^{\text{virt. d.o.}} \sum_l^{\text{virt. d.o.}} A_{ij,kl} U_{kl}^f = B_{0,ij}^f . \quad (17.174)$$

The difference lies in the elements of the B_0^f matrices, which are

$$B_{0,ij}^f = F_{ij}^f = h_{ij}^f . \quad (17.175)$$

17.5.2 The Second-Order CPHF Equations for a Closed-Shell SCF Wavefunction

The general form of the second-order CPHF equations was developed in Section 10.4 as

$$\left(\epsilon_j - \epsilon_i\right)U_{ij}^{ab} - \sum_k^{\text{virt. d.o.}} \sum_l^{\text{virt. d.o.}} A_{ij,kl} U_{kl}^{ab} = B_{0,ij}^{ab} \quad (17.176)$$

where the A matrix was defined in eq. (17.171) and the B_0^{ab} matrices are

$$\begin{aligned} B_{0,ij}^{ab} &= F_{ij}^{ab} - \xi_{ij}^{ab} \epsilon_j - \sum_{kl}^{\text{d.o.}} \xi_{kl}^{ab} \left\{ 2(ij|kl) - (ik|jl) \right\} \\ &+ \sum_k^{\text{all}} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \\ &+ \sum_k^{\text{all}} \left(U_{ki}^a U_{kj}^b + U_{ki}^b U_{kj}^a \right) \epsilon_k \\ &+ \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} U_{km}^a U_{lm}^b A_{ij,kl} \\ &+ \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\ &+ \sum_{kl}^{\text{all d.o.}} \sum_m^{\text{d.o.}} \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\ &+ \sum_k^{\text{all d.o.}} \sum_l^{\text{d.o.}} \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right) . \end{aligned} \quad (17.177)$$

In eq. (17.177) the ξ^{ab} matrices, skeleton (core) second derivative Fock, and first derivative A matrices are defined by

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{\text{all}} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) , \quad (17.178)$$

$$F_{ij}^{ab} = h_{ij}^{ab} + \sum_k^{\text{d.o.}} \left\{ 2(ij|kk)^{ab} - (ik|jk)^{ab} \right\} , \quad (17.179)$$

and

$$A_{ij,kl}^a = 4(ij|kl)^a - (ik|jl)^a - (il|jk)^a . \quad (17.180)$$

For double electric field perturbations, the CPHF equations are formally the same as eq. (17.176):

$$(\epsilon_j - \epsilon_i) U_{ij}^{fg} - \sum_k^{\text{virt. d.o.}} \sum_l A_{ij,kl} U_{kl}^{fg} = B_{0,ij}^{fg} . \quad (17.181)$$

The elements of the B_0^{fg} matrices are given in a slightly simpler form as

$$\begin{aligned} B_{0,ij}^{fg} = & -\xi_{ij}^{fg} \epsilon_j - \sum_{kl}^{\text{d.o.}} \xi_{kl}^{fg} \left\{ 2(ij|kl) - (ik|jl) \right\} \\ & + \sum_k^{\text{all}} \left(U_{ki}^f F_{kj}^g + U_{ki}^g F_{kj}^f + U_{kj}^f F_{ik}^g + U_{kj}^g F_{ik}^f \right) \\ & + \sum_k^{\text{all}} \left(U_{ki}^f U_{kj}^g + U_{ki}^g U_{kj}^f \right) \epsilon_k \\ & + \sum_{kl}^{\text{all d.o.}} \sum_m U_{km}^f U_{lm}^g A_{ij,kl} \\ & + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{ki}^f U_{lm}^g + U_{ki}^g U_{lm}^f \right) A_{kj,lm} \\ & + \sum_{kl}^{\text{all d.o.}} \sum_m \left(U_{kj}^f U_{lm}^g + U_{kj}^g U_{lm}^f \right) A_{ik,lm} . \end{aligned} \quad (17.182)$$

The F^f and ξ^{fg} matrices appearing in eq. (17.182) are

$$F_{ij}^f = h_{ij}^f \quad (17.183)$$

and

$$\xi_{ij}^{fg} = \sum_m^{\text{all}} \left(U_{im}^f U_{jm}^g + U_{im}^g U_{jm}^f \right) . \quad (17.184)$$

For the cross perturbations, the CPHF equations again are formally the same as eq. (17.176):

$$(\epsilon_j - \epsilon_i) U_{ij}^{af} - \sum_k^{\text{virt. d.o.}} \sum_l A_{ij,kl} U_{kl}^{af} = B_{0,ij}^{af} . \quad (17.185)$$

The elements of the B_0^{af} matrices are

$$\begin{aligned}
 B_{0,ij}^{af} = & F_{ij}^{af} - \xi_{ij}^{af} \epsilon_j - \sum_{kl}^{d.o.} \xi_{kl}^{af} \left\{ 2(ij|kl) - (ik|jl) \right\} \\
 & + \sum_k^{all} \left(U_{ki}^a F_{kj}^f + U_{ki}^f F_{kj}^a + U_{kj}^a F_{ik}^f + U_{kj}^f F_{ik}^a \right) \\
 & + \sum_k^{all} \left(U_{ki}^a U_{kj}^f + U_{ki}^f U_{kj}^a \right) \epsilon_k \\
 & + \sum_{kl}^{all} \sum_m^{d.o.} U_{km}^a U_{lm}^f A_{ij,kl} \\
 & + \sum_{kl}^{all} \sum_m^{d.o.} \left(U_{ki}^a U_{lm}^f + U_{ki}^f U_{lm}^a \right) A_{kj,lm} \\
 & + \sum_{kl}^{all} \sum_m^{d.o.} \left(U_{kj}^a U_{lm}^f + U_{kj}^f U_{lm}^a \right) A_{ik,lm} \\
 & + \sum_k^{all} \sum_l^{d.o.} U_{kl}^f A_{ij,kl}^a .
 \end{aligned} \tag{17.186}$$

In eq. (17.186) the skeleton (core) second derivative Fock and ξ^{af} matrices are defined by

$$F_{ij}^{af} = h_{ij}^{af} \tag{17.187}$$

and

$$\xi_{ij}^{af} = \sum_m^{all} \left(U_{im}^a U_{jm}^f + U_{im}^f U_{jm}^a \right) . \tag{17.188}$$

17.5.3 The First-Order CPHF Equations for a General Restricted Open-Shell Wavefunction

The general form of the first-order CPHF equations for a general restricted open-shell wavefunction was given in Section 11.1 as

$$\sum_{k>l}^{indep.\,pair} \mathbf{A}_{ij,kl} U_{kl}^a = B_{0,ij}^a \tag{17.189}$$

where “*indep.pair*” denotes the independent pairs of molecular orbitals. The \mathbf{A} and B_0^a matrices are defined by

$$\begin{aligned}
 \mathbf{A}_{ij,kl} = & 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\
 & + (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl}) \left\{ (ik|jl) + (il|jk) \right\}
 \end{aligned}$$

$$+ \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) - \delta_{li}(\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj}(\zeta_{ki}^j - \epsilon_{ik}) \quad (17.190)$$

and

$$\begin{aligned} B_{0,ij}^a &= \epsilon_{ij}^a - \epsilon_{ji}^a \\ &- \sum_{k>l}^{all\ occ} S_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\ &\quad \left. + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) \right] \\ &- \sum_k^{occ} S_{kk}^a \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] . \end{aligned} \quad (17.191)$$

In the above summations, “all” implies a sum over both occupied and virtual (unoccupied) orbitals, while “occ” denotes a sum over only occupied orbitals. In the last equation the skeleton (core) first derivative Lagrangian matrices are defined as

$$\epsilon_{ij}^a = f_i h_{ij}^a + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} . \quad (17.192)$$

For the case of an electric field perturbation required here, the CPHF equations are formally the same as eq. (17.189):

$$\sum_{k>l}^{indep.\ pair} \mathbf{A}_{ij,kl} U_{kl}^f = B_{0,ij}^f . \quad (17.193)$$

The difference occurs in the elements of the B_0^f matrices, which are

$$B_{0,ij}^f = \epsilon_{ij}^f - \epsilon_{ji}^f \quad (17.194)$$

$$= f_i h_{ij}^f - f_j h_{ji}^f = (f_i - f_j) h_{ij}^f . \quad (17.195)$$

17.5.4 The Second-Order CPHF Equations for a General Restricted Open-Shell Wavefunction

The general form of the second-order CPHF equations was developed in Section 11.7 as

$$\sum_{k>l}^{indep.\ pair} \mathbf{A}_{ij,kl} U_{kl}^{ab} = B_{0,ij}^{ab} \quad (17.196)$$

where the \mathbf{A} matrix was defined in eq. (17.190) and the B_0^{ab} matrices are

$$\begin{aligned}
 B_{0,ij}^{ab} = & \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
 - & \sum_{k>l}^{\text{all occ}} \xi_{kl}^{ab} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\
 & \quad \left. + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) \right] \\
 - & \sum_k^{\text{occ}} \xi_{kk}^{ab} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\
 + & \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
 + & \sum_{klm}^{\text{all}} U_{km}^a U_{lm}^b \left[2(\alpha_{im} - \alpha_{jm})(ij|kl) + (\beta_{im} - \beta_{jm}) \{ (ik|jl) + (il|jk) \} \right] \\
 + & \sum_{kmn}^{\text{all}} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left[2(\alpha_{in} - \alpha_{jn})(kj|mn) \right. \\
 & \quad \left. + (\beta_{in} - \beta_{jn}) \{ (km|jn) + (kn|jm) \} \right] \\
 + & \sum_{kmn}^{\text{all}} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left[2(\alpha_{in} - \alpha_{jn})(ki|mn) \right. \\
 & \quad \left. + (\beta_{in} - \beta_{jn}) \{ (km|in) + (kn|im) \} \right] \\
 + & \sum_{kl}^{\text{all}} U_{kl}^a \left[2(\alpha_{il} - \alpha_{jl})(ij|kl)^b + (\beta_{il} - \beta_{jl}) \{ (ik|jl)^b + (il|jk)^b \} \right] \\
 + & \sum_{kl}^{\text{all}} U_{kl}^b \left[2(\alpha_{il} - \alpha_{jl})(ij|kl)^a + (\beta_{il} - \beta_{jl}) \{ (ik|jl)^a + (il|jk)^a \} \right] \\
 + & \sum_k^{\text{all}} \left[U_{ki}^a \left(\zeta_{kj}^{ib} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
 & \quad \left. - U_{kj}^a \left(\zeta_{ki}^{jb} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \quad . \tag{17.197}
 \end{aligned}$$

In eq. (17.197) the skeleton (core) second derivative Lagrangian and first derivative generalized Lagrangian matrices are defined by

$$\epsilon_{ij}^{ab} = f_i h_{ij}^{ab} + \sum_l^{\text{all}} \left\{ \alpha_{il}(ij|ll)^{ab} + \beta_{il}(il|jl)^{ab} \right\} \tag{17.198}$$

and

$$\zeta_{ij}^{la} = f_l h_{ij}^a + \sum_k^{\text{all}} \left\{ \alpha_{lk}(ij|kk)^a + \beta_{lk}(ik|jk)^a \right\} . \quad (17.199)$$

For the double electric field perturbations the second-order CPHF equations formally are the same as eq. (17.196)

$$\sum_{k>l}^{\text{indep. pair}} \mathbf{A}_{ij,kl} U_{kl}^{fg} = B_{0,ij}^{fg} \quad (17.200)$$

and the B_0^{fg} matrices are given in a somewhat simpler form as

$$\begin{aligned} B_{0,ij}^{fg} = & - \sum_{k>l}^{\text{all occ}} \xi_{kl}^{fg} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\ & \left. + \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) \right] \\ & - \sum_k^{\text{occ}} \xi_{kk}^{fg} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\ & + \sum_{kl}^{\text{all}} (U_{ki}^f U_{lj}^g + U_{ki}^g U_{lj}^f) (\zeta_{kl}^i - \zeta_{kl}^j) \\ & + \sum_{klm}^{\text{all}} U_{km}^f U_{lm}^g \left[2(\alpha_{im} - \alpha_{jm})(ij|kl) + (\beta_{im} - \beta_{jm}) \{ (ik|jl) + (il|jk) \} \right] \\ & + \sum_{kmn}^{\text{all}} (U_{ki}^f U_{mn}^g + U_{ki}^g U_{mn}^f) \left[2(\alpha_{in} - \alpha_{jn})(kj|mn) \right. \\ & \left. + (\beta_{in} - \beta_{jn}) \{ (km|jn) + (kn|jm) \} \right] \\ & + \sum_{kmn}^{\text{all}} (U_{kj}^f U_{mn}^g + U_{kj}^g U_{mn}^f) \left[2(\alpha_{in} - \alpha_{jn})(ki|mn) \right. \\ & \left. + (\beta_{in} - \beta_{jn}) \{ (km|in) + (kn|im) \} \right] \\ & + \sum_k^{\text{all}} \left[U_{ki}^f (\zeta_{kj}^{ig} - \epsilon_{jk}^g) + U_{ki}^g (\zeta_{kj}^{if} - \epsilon_{jk}^f) \right. \\ & \left. - U_{kj}^f (\zeta_{ki}^{jg} - \epsilon_{ik}^g) - U_{kj}^g (\zeta_{ki}^{jf} - \epsilon_{ik}^f) \right] . \end{aligned} \quad (17.201)$$

In this equation the skeleton (core) first derivative generalized Lagrangian matrices are defined by

$$\zeta_{ij}^{lf} = f_l h_{ij}^f . \quad (17.202)$$

For the mixed perturbations the second-order CPHF equations again are formally the same as eq. (17.196)

$$\sum_{k>l}^{indep.\,pair} \mathbf{A}_{ij,kl} U_{kl}^{af} = B_{0,ij}^{af} \quad (17.203)$$

and the B_0^{af} matrices are

$$\begin{aligned}
B_{0,ij}^{af} &= \epsilon_{ij}^{af} - \epsilon_{ji}^{af} \\
&- \sum_{k>l}^{all\,occ} \xi_{kl}^{af} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\
&\quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\
&- \sum_k^{occ} \xi_{kk}^{af} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\
&+ \sum_{kl}^{all} \left(U_{ki}^a U_{lj}^f + U_{ki}^f U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
&+ \sum_{klm}^{all} U_{km}^a U_{lm}^f \left[2(\alpha_{im} - \alpha_{jm})(ij|kl) + (\beta_{im} - \beta_{jm}) \{ (ik|jl) + (il|jk) \} \right] \\
&+ \sum_{kmn}^{all} \left(U_{ki}^a U_{mn}^f + U_{ki}^f U_{mn}^a \right) \left[2(\alpha_{in} - \alpha_{jn})(kj|mn) \right. \\
&\quad \left. + (\beta_{in} - \beta_{jn}) \{ (km|jn) + (kn|jm) \} \right] \\
&+ \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^f + U_{kj}^f U_{mn}^a \right) \left[2(\alpha_{in} - \alpha_{jn})(ki|mn) \right. \\
&\quad \left. + (\beta_{in} - \beta_{jn}) \{ (km|in) + (kn|im) \} \right] \\
&+ \sum_{kl}^{all} U_{kl}^f \left[2(\alpha_{il} - \alpha_{jl})(ij|kl)^a + (\beta_{il} - \beta_{jl}) \{ (ik|jl)^a + (il|jk)^a \} \right] \\
&+ \sum_k \left[U_{ki}^a \left(\zeta_{kj}^{if} - \epsilon_{jk}^f \right) + U_{ki}^f \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
&\quad \left. - U_{kj}^a \left(\zeta_{ki}^{jf} - \epsilon_{ik}^f \right) - U_{kj}^f \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \quad . \quad (17.204)
\end{aligned}$$

In this equation the skeleton (core) second derivative Lagrangian matrices are defined by

$$\epsilon_{ij}^{af} = f_i h_{ij}^{af} \quad . \quad (17.205)$$

17.6 The Coupled Perturbed Configuration Interaction Equations Involving Electric Field Perturbations

The coupled perturbed configuration interaction (CPCI) simultaneous equations provide the derivatives of the CI coefficients with respect to perturbations. In this section, the CPCI equations involving electric field perturbations are described.

17.6.1 The First-Order CPCI Equations

The general form for the first-order CPCI equations was developed in Section 12.1 and is

$$\sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} = - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J \quad (17.206)$$

where the first derivative of the CI Hamiltonian matrices is

$$\frac{\partial H_{IJ}}{\partial a} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \quad (17.207)$$

and the “bare” Lagrangian matrices are

$$X_{ij}^{IJ} = \sum_m^{MO} Q_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl) . \quad (17.208)$$

For an electric field perturbation the CPCI equations formally are the same as shown in eq. (17.206), with the displacement “ a ” replaced by the electric field F :

$$\sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial F} = - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial F} - \delta_{IJ} \frac{\partial E_{elec}}{\partial F} \right) C_J . \quad (17.209)$$

The elements of the derivative matrices on the rhs are of the forms (see Section 17.2)

$$\frac{\partial H_{IJ}}{\partial F} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^f + 2 \sum_{ij}^{MO} U_{ij}^f X_{ij}^{IJ} \quad (17.210)$$

and

$$\frac{\partial E_{elec}}{\partial F} = - \mu_f^{elec} = \sum_{ij}^{MO} Q_{ij} h_{ij}^f + 2 \sum_{ij}^{MO} U_{ij}^f X_{ij} \quad . \quad (17.211)$$

17.6.2 The Second-Order CPCI Equations

The general form for the second-order CPCI equations was given in Section 12.2 as

$$\begin{aligned}
 & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\
 &= - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\
 &\quad - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
 &\quad - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a}
 \end{aligned} \tag{17.212}$$

where the second derivative of the CI Hamiltonian matrices is

$$\begin{aligned}
 \frac{\partial^2 H_{IJ}}{\partial a \partial b} &= \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \\
 &\quad + 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJ^a} + U_{ij}^a X_{ij}^{IJ^b} \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} .
 \end{aligned} \tag{17.213}$$

The skeleton (core) first derivative “bare” Lagrangian and “bare” Y matrices appearing in eq. (17.213) are defined by

$$X_{ij}^{IJ^a} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl)^a \tag{17.214}$$

and

$$Y_{ijkl}^{IJ} = Q_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} \left\{ G_{jlmn}^{IJ}(ik|mn) + 2G_{jmln}^{IJ}(im|kn) \right\} . \tag{17.215}$$

For double electric field perturbations, the CPCI equations formally are [with suitable substitute variables] the same as given in eq. (17.212):

$$\begin{aligned}
 & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial F \partial G} \\
 &= - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial F \partial G} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial F \partial G} \right) C_J \\
 &\quad - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial F} - \delta_{IJ} \frac{\partial E_{elec}}{\partial F} + C_I \frac{\partial C_J}{\partial F} \right) \frac{\partial C_J}{\partial G} \\
 &\quad - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial G} - \delta_{IJ} \frac{\partial E_{elec}}{\partial G} + C_I \frac{\partial C_J}{\partial G} \right) \frac{\partial C_J}{\partial F} .
 \end{aligned} \tag{17.216}$$

The elements of the second derivative CI Hamiltonian matrices in eq. (17.216) are

$$\frac{\partial^2 H_{IJ}}{\partial F \partial G} = 2 \sum_{ij}^{MO} U_{ij}^{fg} X_{ij}^{IJ} + 2 \sum_{ij}^{MO} \left(U_{ij}^g X_{ij}^{IJf} + U_{ij}^f X_{ij}^{IJg} \right) + 2 \sum_{ijkl}^{MO} U_{ij}^f U_{kl}^g Y_{ijkl}^{IJ} , \quad (17.217)$$

in which the X^{IJf} matrix is

$$X_{ij}^{IJf} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^f . \quad (17.218)$$

The energy second derivative with respect to electric field perturbations was discussed in Section 17.3.

For cross perturbations, the CPCI equations again are formally the same as presented in eq. (17.212):

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial F} \\ &= - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial F} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial F} \right) C_J \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial F} \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial F} - \delta_{IJ} \frac{\partial E_{elec}}{\partial F} + C_I \frac{\partial C_J}{\partial F} \right) \frac{\partial C_J}{\partial a} . \end{aligned} \quad (17.219)$$

The elements of the second derivative CI Hamiltonian matrices in this equation are given by

$$\begin{aligned} \frac{\partial^2 H_{IJ}}{\partial a \partial F} &= \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{af} + 2 \sum_{ij}^{MO} U_{ij}^{af} X_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^f X_{ij}^{IJa} + U_{ij}^a X_{ij}^{IJf} \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^f Y_{ijkl}^{IJ} . \end{aligned} \quad (17.220)$$

The energy second derivative with respect to cross perturbations was described in Section 17.4. The first and second derivatives of the CI energy (electronic part), first- and second-order CPHF equations for U^a , U^f , and U^{af} , and the first-order CPCI equations for $\partial C_I / \partial a$ and $\partial C_I / \partial f$ must be evaluated *before* constructing the second-order CPCI equations.

17.7 The Coupled Perturbed Multiconfiguration Hartree-Fock Equations Involving Electric Field Perturbations

The coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) simultaneous equations provide the derivatives of both the MO coefficients and CI coefficients with respect to perturbations. These two derivatives are required to evaluate higher-order properties for MCSCF wavefunctions. In this section the CPMCHF equations involving electric field perturbations are described.

17.7.1 The First-Order CPMCHF Equations

The general form of the first-order CPMCHF equations was given in Section 14.1 as

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\mathbf{a}} \\ \partial \mathbf{C} / \partial \mathbf{a} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\mathbf{a}1} \\ \mathbf{B}_0^{\mathbf{a}2} \end{bmatrix} . \quad (17.221)$$

In this equation \mathbf{A}^{11} is the MO part and each element is given by

$$\begin{aligned} \mathbf{A}_{ij,kl}^{11} = & \delta_{li}x_{kj} - \delta_{lj}x_{ki} - \delta_{ki}x_{lj} + \delta_{kj}x_{li} \\ & + y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} . \end{aligned} \quad (17.222)$$

The \mathbf{A}^{22} term represents the CI part and is

$$\mathbf{A}_{I,J}^{22} = H_{IJ} - \delta_{IJ}E_{elec} + 2C_I C_J . \quad (17.223)$$

The \mathbf{A}^{21} ($\mathbf{A}^{21\dagger}$) term shows the CI-MO (or MO-CI) interactions with matrix elements

$$\mathbf{A}_{I,ij}^{21} = 2 \sum_J^{CI} C_J \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \quad (17.224)$$

where the “bare” Lagrangian matrices in this equation are defined by

$$x_{ij}^{IJ} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}^{IJ}(im|kl) . \quad (17.225)$$

The perturbative term for the MO space may be written as

$$\begin{aligned} B_{0,ij}^{\mathbf{a}1} = & -x_{ij}^{\mathbf{a}} + x_{ji}^{\mathbf{a}} \\ & + \sum_{k>l}^{MO} S_{kl}^{\mathbf{a}} \left(\delta_{ki}x_{lj} - \delta_{kj}x_{li} + y_{ijlk} - y_{jilk} \right) \\ & + \frac{1}{2} \sum_k^{MO} S_{kk}^{\mathbf{a}} \left(\delta_{ki}x_{kj} - \delta_{kj}x_{ki} + y_{ijkk} - y_{jikk} \right) \end{aligned} \quad (17.226)$$

where the x^a matrices are defined by

$$x_{ij}^a = \sum_m^{MO} \gamma_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl)^a . \quad (17.227)$$

For the CI space, the perturbation term is

$$\begin{aligned} B_{0,I}^{a2} &= - \sum_J^{CI} C_J H_{IJ}^a + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a x_{ji}^{IJ} \\ &\quad + \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a x_{ii}^{IJ} + C_I \frac{\partial E_{elec}}{\partial a} . \end{aligned} \quad (17.228)$$

In this equation the skeleton (core) first derivative Hamiltonian matrices are given by

$$H_{IJ}^a = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ}(ij|kl)^a . \quad (17.229)$$

For a first-order electric field perturbation, the CPMCHF equations formally are the same as in eq. (17.221), namely,

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^f \\ \partial \mathbf{C} / \partial \mathbf{F} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{f1} \\ \mathbf{B}_0^{f2} \end{bmatrix} . \quad (17.230)$$

The elements of the \mathbf{B}_0^{f1} matrices for the MO space are

$$B_{0,ij}^{f1} = -x_{ij}^f + x_{ji}^f \quad (17.231)$$

with the x^f matrix being

$$x_{ij}^f = \sum_m^{MO} \gamma_{jm} h_{im}^f . \quad (17.232)$$

For the CI space, the perturbation term is

$$B_{0,I}^{f2} = - \sum_J^{CI} C_J H_{IJ}^f + C_I \frac{\partial E_{elec}}{\partial F} \quad (17.233)$$

where the H_{IJ}^f matrix is given by

$$H_{IJ}^f = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^f . \quad (17.234)$$

17.7.2 The Second-Order CPMCHF Equations

The general form for the second-order CPMCHF equations was given in Section 14.4 as

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{ab} \\ \partial^2 \mathbf{C} / \partial \mathbf{a} \partial \mathbf{b} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{ab1} \\ \mathbf{B}_0^{ab2} \end{bmatrix} . \quad (17.235)$$

The elements of the \mathbf{A}^{11} , \mathbf{A}^{22} , and \mathbf{A}^{12} matrices were defined in the preceding section. The perturbation term for the MO space, \mathbf{B}_0^{ab1} , are given as

$$\begin{aligned} B_{0,ij}^{ab1} = & -x_{ij}^{ab} + x_{ji}^{ab} \\ & + \sum_{k>l}^{MO} \xi_{kl}^{ab} (\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijkl} - y_{jilk}) \\ & + \frac{1}{2} \sum_k^{MO} \xi_{kk}^{ab} (\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk}) \\ & - \sum_k^{MO} (U_{ki}^a x_{kj}^b - U_{kj}^a x_{ki}^b) - \sum_k^{MO} (U_{ki}^b x_{kj}^a - U_{kj}^b x_{ki}^a) \\ & - \sum_{kl}^{MO} U_{kl}^a (y_{ijkl}^b - y_{jikl}^b) - \sum_{kl}^{MO} U_{kl}^b (y_{ijkl}^a - y_{jikl}^a) \\ & - \sum_{kmn}^{MO} U_{mn}^b (U_{ki}^a y_{kjmn} - U_{kj}^a y_{kimn}) - \sum_{kmn}^{MO} U_{mn}^a (U_{ki}^b y_{kjmn} - U_{kj}^b y_{kimn}) \\ & - 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\ & \quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\} \\ & - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (x_{ij}^{IJ} - x_{ji}^{IJ}) \\ & - 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial a} \left(\frac{\partial x_{ij}^{IJ}}{\partial b} - \frac{\partial x_{ji}^{IJ}}{\partial b} \right) + \frac{\partial C_J}{\partial b} \left(\frac{\partial x_{ij}^{IJ}}{\partial a} - \frac{\partial x_{ji}^{IJ}}{\partial a} \right) \right\} \end{aligned} \quad (17.236)$$

where the x^{ab} and y^a matrices are defined by

$$x_{ij}^{ab} = \sum_m^{MO} \gamma_{jm} h_{im}^{ab} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl)^{ab} , \quad (17.237)$$

$$y_{ijkl}^a = \gamma_{jl} h_{ik}^a + 2 \sum_{mn}^{MO} \left\{ \Gamma_{jlmn}(ik|mn)^a + 2 \Gamma_{jmkn}(im|kn)^a \right\} . \quad (17.238)$$

The first derivative of the “bare” Lagrangian matrix was presented in Section 6.5 as

$$\frac{\partial x_{ij}^{IJ}}{\partial a} = x_{ij}^{IJ^a} + \sum_k^{MO} U_{ki}^a x_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^a y_{ijkl}^{IJ} \quad (17.239)$$

in which the x^{IJ^a} matrix is

$$x_{ij}^{IJ^a} = \sum_M^{MO} \gamma_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} \Gamma_{jmk}^{IJ} (im|kl)^a \quad . \quad (17.240)$$

The perturbation terms for the CI space, $\mathbf{B}_0^{\text{ab2}}$, are

$$\begin{aligned} B_{0,I}^{\text{ab2}} = & - \sum_J^{CI} C_J H_{IJ}^{ab} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} x_{ii}^{IJ} + C_I \frac{\partial^2 E_{\text{elec}}}{\partial a \partial b} \\ & - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\ & - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ} \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{\text{elec}}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{\text{elec}}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} \quad . \end{aligned} \quad (17.241)$$

In this equation the skeleton (core) second derivative Hamiltonian matrices are given by

$$H_{IJ}^{ab} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ} (ij|kl)^{ab} \quad , \quad (17.242)$$

whereas the first derivative of the Hamiltonian matrix was developed in Section 6.4 as

$$\frac{\partial H_{IJ}}{\partial a} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{IJ} (ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a x_{ij}^{IJ} \quad . \quad (17.243)$$

For double electric field perturbations the second-order CPMCHF equations are formally the same as eq. (17.235):

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\text{fg}} \\ \partial^2 \mathbf{C} / \partial \mathbf{F} \partial \mathbf{G} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\text{fg1}} \\ \mathbf{B}_0^{\text{fg2}} \end{bmatrix} \quad . \quad (17.244)$$

The \mathbf{B}_0^{fg1} matrices for the MO space are given as

$$\begin{aligned}
 B_{0,ij}^{fg1} = & \sum_{k>l}^{MO} \xi_{kl}^{fg} \left(\delta_{ki}x_{lj} - \delta_{kj}x_{li} + y_{ijkl} - y_{jilk} \right) \\
 & + \frac{1}{2} \sum_k^{MO} \xi_{kk}^{fg} \left(\delta_{ki}x_{kj} - \delta_{kj}x_{ki} + y_{ijkk} - y_{jikk} \right) \\
 & - \sum_k^{MO} \left(U_{ki}^f x_{kj}^g - U_{kj}^f x_{ki}^g \right) - \sum_k^{MO} \left(U_{ki}^g x_{kj}^f - U_{kj}^g x_{ki}^f \right) \\
 & - \sum_{kl}^{MO} U_{kl}^f \left(y_{ijkl}^g - y_{jikl}^g \right) - \sum_{kl}^{MO} U_{kl}^g \left(y_{ijkl}^f - y_{jikl}^f \right) \\
 & - \sum_{kmn}^{MO} U_{mn}^g \left(U_{ki}^f y_{kjmn} - U_{kj}^f y_{kimn} \right) - \sum_{kmn}^{MO} U_{mn}^f \left(U_{ki}^g y_{kjmn} - U_{kj}^g y_{kimn} \right) \\
 & - 4 \sum_{klmnp}^{MO} U_{kl}^f U_{mn}^g \left\{ \Gamma_{jlmp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\
 & \quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\} \\
 & - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial F} \frac{\partial C_J}{\partial G} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\
 & - 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial F} \left(\frac{\partial x_{ij}^{IJ}}{\partial G} - \frac{\partial x_{ji}^{IJ}}{\partial G} \right) + \frac{\partial C_J}{\partial G} \left(\frac{\partial x_{ij}^{IJ}}{\partial F} - \frac{\partial x_{ji}^{IJ}}{\partial F} \right) \right\} .
 \end{aligned} \tag{17.245}$$

In this equation the y^f matrices are defined by

$$y_{ijkl}^f = \gamma_{jl} h_{ik}^f , \tag{17.246}$$

and the first derivatives of the “bare” Lagrangian matrices are

$$\frac{\partial x_{ij}^{IJ}}{\partial F} = x_{ij}^{IJf} + \sum_m^{MO} U_{ki}^f x_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^f y_{ijkl}^{IJ} \tag{17.247}$$

with

$$x_{ij}^{IJf} = \sum_m^{MO} \gamma_{jm}^{IJ} h_{im}^f . \tag{17.248}$$

For the CI space the \mathbf{B}_0^{fg2} matrices are

$$B_{0,I}^{fg2} = 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{fg} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{fg} x_{ii}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial F \partial G}$$

$$\begin{aligned}
& - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^g x_{ij}^{IJf} + U_{ij}^f x_{ij}^{IJg} \right) \\
& - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^f U_{kl}^g y_{ijkl}^{IJ} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial F} - \delta_{IJ} \frac{\partial E_{elec}}{\partial F} + C_I \frac{\partial C_J}{\partial F} \right) \frac{\partial C_J}{\partial G} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial G} - \delta_{IJ} \frac{\partial E_{elec}}{\partial G} + C_I \frac{\partial C_J}{\partial G} \right) \frac{\partial C_J}{\partial F} .
\end{aligned} \quad (17.249)$$

In this equation the first derivative of the Hamiltonian matrix is expressed as

$$\frac{\partial H_{IJ}}{\partial F} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^f + 2 \sum_{ij}^{MO} U_{ij}^f x_{ij}^{IJ} . \quad (17.250)$$

For the mixed perturbations the second-order CPMCHF equations again are formally the same as eq. (17.235):

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\text{af}} \\ \partial^2 \mathbf{C} / \partial \mathbf{a} \partial \mathbf{F} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\text{af1}} \\ \mathbf{B}_0^{\text{af2}} \end{bmatrix} . \quad (17.251)$$

The $\mathbf{B}_0^{\text{af1}}$ matrices for the MO space are given by

$$\begin{aligned}
B_{0,ij}^{af1} &= -x_{ij}^{af} + x_{ji}^{af} \\
&+ \sum_{k>l}^{MO} \xi_{kl}^{af} \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijlk} - y_{jilk} \right) \\
&+ \frac{1}{2} \sum_k^{MO} \xi_{kk}^{af} \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right) \\
&- \sum_k^{MO} \left(U_{ki}^a x_{kj}^f - U_{kj}^a x_{ki}^f \right) - \sum_k^{MO} \left(U_{ki}^f x_{kj}^a - U_{kj}^f x_{ki}^a \right) \\
&- \sum_{kl}^{MO} U_{kl}^a \left(y_{ijkl}^f - y_{jikl}^f \right) - \sum_{kl}^{MO} U_{kl}^f \left(y_{ijkl}^a - y_{jikl}^a \right) \\
&- \sum_{kmn}^{MO} U_{mn}^f \left(U_{ki}^a y_{kjmn} - U_{kj}^a y_{kimn} \right) - \sum_{kmn}^{MO} U_{mn}^a \left(U_{ki}^f y_{kjmn} - U_{kj}^f y_{kimn} \right) \\
&- 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^f \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\
&\quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\}
\end{aligned}$$

$$\begin{aligned}
& - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial F} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\
& - 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial a} \left(\frac{\partial x_{ij}^{IJ}}{\partial F} - \frac{\partial x_{ji}^{IJ}}{\partial F} \right) + \frac{\partial C_J}{\partial F} \left(\frac{\partial x_{ij}^{IJ}}{\partial a} - \frac{\partial x_{ji}^{IJ}}{\partial a} \right) \right\} .
\end{aligned} \quad (17.252)$$

In this equation the x^{af} matrices are defined by their elements as

$$x_{ij}^{af} = \sum_m^{MO} \gamma_{jm} h_{im}^{af} . \quad (17.253)$$

For the CI space the \mathbf{B}_0^{af2} matrices are

$$\begin{aligned}
B_{0,I}^{af2} &= - \sum_J^{CI} C_J H_{IJ}^{af} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{af} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{af} x_{ii}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial F} \\
&- 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^f x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^f} \right) \\
&- 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^f y_{ijkl}^{IJ} \\
&- \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial F} \\
&- \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial F} - \delta_{IJ} \frac{\partial E_{elec}}{\partial F} + C_I \frac{\partial C_J}{\partial F} \right) \frac{\partial C_J}{\partial a} .
\end{aligned} \quad (17.254)$$

In the equation the H_{IJ}^{af} matrices are given by their elements as

$$H_{IJ}^{af} = \sum_{ij}^{MO} \gamma_{ij}^{IJ} h_{ij}^{af} . \quad (17.255)$$

17.8 The Coupled Perturbed Equations for Multiple Perturbations

In the preceding three sections, three different types of coupled perturbed equations, CPHF, CPCI, and CPMCHF equations, have been discussed. For any *real* perturbations, each type of coupled perturbed equation has the same \mathbf{A} matrix. It is, therefore, possible and economical to simultaneously solve the coupled perturbed equations for multiple first-order (p, q, r, \dots) and second-order (pq, pr, qr, \dots) perturbations;

for the first-order perturbations,

$$[\mathbf{A}] \begin{bmatrix} \mathbf{U}^P & \mathbf{U}^Q & \mathbf{U}^R \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^P & \mathbf{B}_0^Q & \mathbf{B}_0^R \end{bmatrix} , \quad (17.256)$$

and for the second-order perturbations,

$$[\mathbf{A}] \begin{bmatrix} \mathbf{U}^{PQ} & \mathbf{U}^{PR} & \mathbf{U}^{QR} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{PQ} & \mathbf{B}_0^{PR} & \mathbf{B}_0^{QR} \end{bmatrix} . \quad (17.257)$$

In these two equations the \mathbf{U} matrices denote unknown variables. The corresponding \mathbf{A} matrices and the general form of \mathbf{B}_0^P and \mathbf{B}_0^{PQ} matrices are summarized as follows:

For the closed-shell CPHF equations

$$\mathbf{A}_{ij,kl} = \delta_{ik}\delta_{jl}(\epsilon_j - \epsilon_i) - \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} , \quad (17.258)$$

$$B_{0,ij}^p = F_{ij}^p - S_{ij}^p\epsilon_j - \sum_{kl}^{d.o.} S_{kl}^p \left\{ 2(ij|kl) - (ik|jl) \right\} , \quad (17.259)$$

$$\begin{aligned} B_{0,ij}^{pq} &= F_{ij}^{pq} - \xi_{ij}^{pq}\epsilon_j - \sum_{kl}^{d.o.} \xi_{kl}^{pq} \left\{ 2(ij|kl) - (ik|jl) \right\} \\ &+ \sum_k^{all} \left(U_{ki}^p F_{kj}^q + U_{ki}^q F_{kj}^p + U_{kj}^p F_{ik}^q + U_{kj}^q F_{ik}^p \right) \\ &+ \sum_k^{all} \left(U_{ki}^p U_{kj}^q + U_{ki}^q U_{kj}^p \right) \epsilon_k \\ &+ \sum_{kl}^{all} \sum_m^{d.o.} U_{km}^p U_{lm}^q A_{ij,kl} \\ &+ \sum_{kl}^{all} \sum_m^{d.o.} \left(U_{ki}^p U_{lm}^q + U_{ki}^q U_{lm}^p \right) A_{kj,lm} \\ &+ \sum_{kl}^{all} \sum_m^{d.o.} \left(U_{kj}^p U_{lm}^q + U_{kj}^q U_{lm}^p \right) A_{ik,lm} \\ &+ \sum_k^{all} \sum_l^{d.o.} \left(U_{kl}^p A_{ij,kl}^q + U_{kl}^q A_{ij,kl}^p \right) . \end{aligned} \quad (17.260)$$

Note that the \mathbf{A} matrix in eq. (17.258) is different from the A matrix in eq. (17.171).

For the general restricted open-shell CPHF equations

$$\mathbf{A}_{ij,kl} = 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl)$$

$$\begin{aligned}
& + \left(\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl} \right) \left\{ (ik|jl) + (il|jk) \right\} \\
& + \delta_{ki} \left(\zeta_{lj}^i - \epsilon_{jl} \right) - \delta_{kj} \left(\zeta_{li}^j - \epsilon_{il} \right) - \delta_{li} \left(\zeta_{kj}^i - \epsilon_{jk} \right) + \delta_{lj} \left(\zeta_{ki}^j - \epsilon_{ik} \right) , \\
\end{aligned} \tag{17.261}$$

$$\begin{aligned}
B_{0,ij}^p &= \epsilon_{ij}^p - \epsilon_{ji}^p \\
&- \sum_{k>l}^{\text{all occ}} S_{kl}^p \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \left\{ (ik|jl) + (il|jk) \right\} \right. \\
&\quad \left. + \delta_{ki} \left(\zeta_{lj}^i - \epsilon_{jl} \right) - \delta_{kj} \left(\zeta_{li}^j - \epsilon_{il} \right) \right] \\
&- \sum_k^{\text{occ}} S_{kk}^p \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] , \\
\end{aligned} \tag{17.262}$$

$$\begin{aligned}
B_{0,ij}^{pq} &= \epsilon_{ij}^{pq} - \epsilon_{ji}^{pq} \\
&- \sum_{k>l}^{\text{all occ}} \xi_{kl}^{pq} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \left\{ (ik|jl) + (il|jk) \right\} \right. \\
&\quad \left. + \delta_{ki} \left(\zeta_{lj}^i - \epsilon_{jl} \right) - \delta_{kj} \left(\zeta_{li}^j - \epsilon_{il} \right) \right] \\
&- \sum_k^{\text{occ}} \xi_{kk}^{pq} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\
&+ \sum_{kl}^{\text{all}} \left(U_{ki}^p U_{lj}^q + U_{ki}^q U_{lj}^p \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
&+ \sum_{klm}^{\text{all}} U_{km}^p U_{lm}^q \left[2(\alpha_{im} - \alpha_{jm})(ij|kl) + (\beta_{im} - \beta_{jm}) \left\{ (ik|jl) + (il|jk) \right\} \right] \\
&+ \sum_{kmn}^{\text{all}} \left(U_{ki}^p U_{mn}^q + U_{ki}^q U_{mn}^p \right) \left[2(\alpha_{in} - \alpha_{jn})(kj|mn) \right. \\
&\quad \left. + (\beta_{in} - \beta_{jn}) \left\{ (km|jn) + (kn|jm) \right\} \right] \\
&+ \sum_{kmn}^{\text{all}} \left(U_{kj}^p U_{mn}^q + U_{kj}^q U_{mn}^p \right) \left[2(\alpha_{in} - \alpha_{jn})(ki|mn) \right. \\
&\quad \left. + (\beta_{in} - \beta_{jn}) \left\{ (km|in) + (kn|im) \right\} \right] \\
&+ \sum_{kl}^{\text{all}} U_{kl}^p \left[2(\alpha_{il} - \alpha_{jl})(ij|kl)^q + (\beta_{il} - \beta_{jl}) \left\{ (ik|jl)^q + (il|jk)^q \right\} \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_{kl}^{all} U_{kl}^q \left[2(\alpha_{il} - \alpha_{jl})(ij|kl)^p + (\beta_{il} - \beta_{jl}) \left\{ (ik|jl)^p + (il|jk)^p \right\} \right] \\
& + \sum_k^{all} \left[U_{ki}^p \left(\zeta_{kj}^{iq} - \epsilon_{jk}^q \right) + U_{ki}^q \left(\zeta_{kj}^{ip} - \epsilon_{jk}^p \right) \right. \\
& \quad \left. - U_{kj}^p \left(\zeta_{ki}^{jq} - \epsilon_{ik}^q \right) - U_{kj}^q \left(\zeta_{ki}^{jp} - \epsilon_{ik}^p \right) \right] \quad . \tag{17.263}
\end{aligned}$$

For the CPCI equations

$$\mathbf{A}_{I,J} = H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \quad , \tag{17.264}$$

$$B_{0,I}^p = - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial p} - \delta_{IJ} \frac{\partial E_{elec}}{\partial p} \right) C_J \quad , \tag{17.265}$$

$$\begin{aligned}
B_{0,I}^{pq} &= - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial p \partial q} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial p \partial q} \right) C_J \\
&- \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial p} - \delta_{IJ} \frac{\partial E_{elec}}{\partial p} + C_I \frac{\partial C_J}{\partial p} \right) \frac{\partial C_J}{\partial q} \\
&- \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial q} - \delta_{IJ} \frac{\partial E_{elec}}{\partial q} + C_I \frac{\partial C_J}{\partial q} \right) \frac{\partial C_J}{\partial p} \quad . \tag{17.266}
\end{aligned}$$

For the CPMCHF equations

$$\begin{aligned}
\mathbf{A}_{ij,kl}^{11} &= \delta_{li} x_{kj} - \delta_{lj} x_{ki} - \delta_{ki} x_{lj} + \delta_{kj} x_{li} \\
&+ y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} \quad , \tag{17.267}
\end{aligned}$$

$$\mathbf{A}_{I,ij}^{22} = H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \quad , \tag{17.268}$$

$$\mathbf{A}_{I,ij}^{21} = 2 \sum_J^{CI} C_J \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \quad , \tag{17.269}$$

$$\begin{aligned}
B_{0,ij}^{p1} &= -x_{ij}^p + x_{ji}^p \\
&+ \sum_{k>l}^{MO} S_{kl}^p \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijlk} - y_{jilk} \right) \\
&+ \frac{1}{2} \sum_k^{MO} S_{kk}^p \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right) \quad , \tag{17.270}
\end{aligned}$$

$$\begin{aligned}
B_{0,I}^{p2} = & - \sum_J^{CI} C_J H_{IJ}^p + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^p x_{ji}^{IJ} \\
& + \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^p x_{ii}^{IJ} + C_I \frac{\partial E_{elec}}{\partial p} ,
\end{aligned} \tag{17.271}$$

$$\begin{aligned}
B_{0,ij}^{pq1} = & - x_{ij}^{pq} + x_{ji}^{pq} \\
& + \sum_{k>l}^{MO} \xi_{kl}^{pq} \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijkl} - y_{jilk} \right) \\
& + \frac{1}{2} \sum_k^{MO} \xi_{kk}^{pq} \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right) \\
& - \sum_k^{MO} \left(U_{ki}^p x_{kj}^q - U_{kj}^p x_{ki}^q \right) - \sum_k^{MO} \left(U_{ki}^q x_{kj}^p - U_{kj}^q x_{ki}^p \right) \\
& - \sum_{kl}^{MO} U_{kl}^p \left(y_{ijkl}^q - y_{jikl}^q \right) - \sum_{kl}^{MO} U_{kl}^q \left(y_{ijkl}^p - y_{jikl}^p \right) \\
& - \sum_{kmn}^{MO} U_{mn}^q \left(U_{ki}^p y_{kjmn} - U_{kj}^p y_{kimn} \right) - \sum_{kmn}^{MO} U_{mn}^p \left(U_{ki}^q y_{kjmn} - U_{kj}^q y_{kimn} \right) \\
& - 4 \sum_{klmnp}^{MO} U_{kl}^p U_{mn}^q \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\
& \quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\} \\
& - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial p} \frac{\partial C_J}{\partial q} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\
& - 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial p} \left(\frac{\partial x_{ij}^{IJ}}{\partial q} - \frac{\partial x_{ji}^{IJ}}{\partial q} \right) + \frac{\partial C_J}{\partial q} \left(\frac{\partial x_{ij}^{IJ}}{\partial p} - \frac{\partial x_{ji}^{IJ}}{\partial p} \right) \right\} ,
\end{aligned} \tag{17.272}$$

$$\begin{aligned}
B_{0,I}^{pq2} = & - \sum_J^{CI} C_J H_{IJ}^{pq} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{pq} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{pq} x_{ii}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial p \partial q} \\
& - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^q x_{ij}^{IJp} + U_{ij}^p x_{ij}^{IJq} \right) \\
& - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^p U_{kl}^q y_{ijkl}^{IJ} \\
& - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial p} - \delta_{IJ} \frac{\partial E_{elec}}{\partial p} + C_I \frac{\partial C_J}{\partial p} \right) \frac{\partial C_J}{\partial q}
\end{aligned}$$

$$- \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial q} - \delta_{IJ} \frac{\partial E_{elec}}{\partial q} + C_I \frac{\partial C_J}{\partial q} \right) \frac{\partial C_J}{\partial p} . \quad (17.273)$$

It should be noted, however, that solutions to the first-order equations are usually required in order to construct the second-order coupled perturbed equations.

References

1. H. Eyring, J. Walter, and G.E. Kimball, *Quantum Chemistry*, Chapters 8 and 17, John Wiley & Sons, New York, 1944.
2. K.S. Pitzer, *Quantum Chemistry*, Chapter 12 and Appendix 20, Prentice-Hall, Englewood Cliffs, N.J. 1953.
3. J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, *Molecular Theory of Gases and Liquids*, Chapters 12 and 13, John Wiley & Sons, New York, 1954.
4. A.D. Buckingham and J.A. Pople, Proc. Roy. Soc. **A68**, 905 (1955).
5. A.D. Buckingham, Quart. Rev. **13**, 183 (1959).
6. K. Thomsen and P. Swanstrøm, Mol. Phys. **26**, 735 (1973).
7. P. Lazzeretti, B. Cadile, and U. Pincelli, Int. J. Quantum Chem. **10**, 771 (1976).
8. H. Hellmann, *Einführung in die Quantenchemie*, Franz Deuticke, Leipzig, Germany, 1937.
9. R.P. Feynman, Phys. Rev. **56**, 340 (1939).
10. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.

Suggested Reading

1. R.D. Amos, Chem. Phys. Lett. **108**, 185 (1984).
2. Y. Yamaguchi, M.J. Frisch, J.F. Gaw, H.F. Schaefer, and J.S. Binkley, J. Chem. Phys. **84**, 2262 (1986).
3. R. Amos, in *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry Part I*, K.P. Lawley editor, John Wiley & Sons, New York, Vol. 67, p.99 (1987).
4. C.E. Dykstra, S.-Y. Liu, and D.J. Malik, in *Advances in Chemical Physics*, I. Prigogine and S.A. Rice editors, John Wiley & Sons, New York, Vol. 75, p.37 (1989).

Chapter 18

The Z Vector Method

In order to obtain energy derivatives for the configuration interaction (CI) wavefunction, information concerning the derivatives of the MO coefficients of the reference wavefunction is required. These quantities are usually obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations for an SCF reference function and the coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) equations for an MCSCF reference function. Such procedures require $3N$ (N being the number of atoms) sets of unknowns for first-order and $3N(3N+1)/2$ sets of unknowns for second-order derivatives. The Z vector method considers this problem from a different point of view and allows much smaller sets of unknowns. The method has proven very powerful whenever applicable. In this chapter, the principle of the Z vector method is explained using analytic derivatives for the CI wavefunction as the most common example.

18.1 The Z Vector Method and First Derivative Properties for the CI Wavefunction

The first derivative of the electronic energy for the CI wavefunction was derived in Chapter 6 and is

$$\frac{\partial E_{elec}}{\partial a} = \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij} . \quad (18.1)$$

In this equation Q and G are the one- and two-electron reduced density matrices [1] and h_{ij}^a and $(ij|kl)^a$ are the skeleton (core) parts of the one- and two-electron derivative integrals. The Lagrangian matrix for the CI wavefunction X is defined by

$$X_{ij} = \sum_m^{MO} Q_{jm} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl) . \quad (18.2)$$

The U^a matrices, which are related to the first derivatives of the MO coefficients with respect to nuclear coordinates (see Chapter 3), are obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations in the following matrix form:

$$\mathbf{A} \mathbf{U}^a = \mathbf{B}_0^a . \quad (18.3)$$

For a closed-shell SCF wavefunction the \mathbf{A} matrix elements were found in Chapter 10 to be

$$\mathbf{A}_{ij,kl} = \delta_{ik}\delta_{jl}(\epsilon_j - \epsilon_i) - \left\{ 4(ij|kl) - (ik|jl) - (il|jk) \right\} \quad (18.4)$$

and the \mathbf{B}_0^a matrix elements are

$$B_{0,ij}^a = F_{ij}^a - S_{ij}^a\epsilon_j - \sum_{kl}^{d.o.} S_{kl}^a \left\{ 2(ij|kl) - (ik|jl) \right\} . \quad (18.5)$$

The skeleton (core) first derivative Fock matrix, F^a , is defined by

$$F_{ij}^a = h_{ij}^a + \sum_k^{d.o.} \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} . \quad (18.6)$$

In eq. (18.4) ϵ_i stand for orbital energies. The third term in eq. (18.1) may be written in matrix form [2] as

$$2 \sum_{ij}^{MO} U_{ij}^a X_{ij} = 2 \mathbf{X}^T \mathbf{U}^a \quad (18.7)$$

where \mathbf{X}^T stands for the transpose of the \mathbf{X} matrix. Equation (18.3) is rewritten as

$$\mathbf{U}^a = \mathbf{A}^{-1} \mathbf{B}_0^a . \quad (18.8)$$

Combining eqs. (18.7) and (18.8), the third term of eq. (18.1) becomes

$$2 \sum_{ij}^{MO} U_{ij}^a X_{ij} = 2 \mathbf{X}^T \mathbf{U}^a \quad (18.9)$$

$$= 2 \mathbf{X}^T \mathbf{A}^{-1} \mathbf{B}_0^a \quad (18.10)$$

$$= 2 \mathbf{Z}^T \mathbf{B}_0^a . \quad (18.11)$$

The \mathbf{Z} vector in this equation is defined by

$$\mathbf{Z}^T = \mathbf{X}^T \mathbf{A}^{-1} \quad (18.12)$$

which in turn may be written

$$\mathbf{A}^T \mathbf{Z} = \mathbf{X} . \quad (18.13)$$

The elements of the **Z** vector are obtained by solution of the simultaneous equations, eq. (18.13), and the third term of eq. (18.1) may be evaluated through

$$2 \sum_{ij}^{MO} U_{ij}^a X_{ij} = 2 \sum_{ij}^{MO} B_{0,ij}^a Z_{ij} , \quad (18.14)$$

where the elements of \mathbf{B}_0^a were defined in eq. (18.5). In eq. (18.3) the simultaneous equations were solved for $3N$ (N being the number of atoms in the molecule) degrees of freedom, while in eq. (18.11) the simultaneous equations are solved for only one degree of freedom. This is a significant saving in the work involved in solving these equations. The \mathbf{B}_0^a matrices in eq. (18.3) contain the perturbed Fock matrices with respect to nuclear perturbations. The Lagrangian matrix in eqs. (18.2) and (18.13) involves the first derivative of the CI energy with respect to changes in the MO coefficients.

The first derivative of the CI energy with respect to an electric field perturbation, i.e., the electric dipole moment (electronic part), was obtained in Chapter 17 as

$$\mu_f^{elec} = - \frac{\partial E_{elec}}{\partial F} \quad (18.15)$$

$$= - \sum_{ij}^{MO} Q_{ij} h_{ij}^f - 2 \sum_{ij}^{MO} U_{ij}^f X_{ij} \quad (18.16)$$

$$= \sum_{ij}^{MO} Q_{ij} d_{ij}^f - 2 \sum_{ij}^{MO} U_{ij}^f X_{ij} . \quad (18.17)$$

Here the matrix d^f stands for the dipole moment matrix described in Section 17.1. The corresponding CPHF equations to evaluate the elements of U^f are

$$\mathbf{A} \mathbf{U}^f = \mathbf{B}_0^f . \quad (18.18)$$

For a closed-shell SCF wavefunction the \mathbf{B}_0^f matrices were given in Section 17.5 by

$$B_{0,ij}^f = F_{ij}^f = h_{ij}^f . \quad (18.19)$$

In a similar manner as for the nuclear perturbations, these equations for the dipole moment may be manipulated to yield

$$2 \sum_{ij}^{MO} U_{ij}^f X_{ij} = 2 \mathbf{X}^T \mathbf{U}^f \quad (18.20)$$

$$= 2 \mathbf{X}^T \mathbf{A}^{-1} \mathbf{B}_0^f \quad (18.21)$$

$$= 2 \mathbf{Z}^T \mathbf{B}_0^f . \quad (18.22)$$

The **Z** vector here is the *same* quantity defined in eq. (18.12). In eq. (18.18) the simultaneous equations were solved for three degrees (x, y, and z) of freedom, while in eq. (18.22) they are solved for only one degree of freedom.

In the Z vector method, corrections due to the first-order changes of the MO coefficients are reformulated in general as

$$\sum_{ij}^{MO} U_{ij}^p X_{ij} = \sum_{ij}^{MO} B_{0,ij}^p Z_{ij} . \quad (18.23)$$

A superscript “*p*” stands for any real first-order perturbation. The Z vector is obtained by solving the simultaneous equations

$$\mathbf{A}^T \mathbf{Z} = \mathbf{X} . \quad (18.24)$$

The corresponding **A** matrix for the reference wavefunction (other than the closed-shell SCF wavefunction; see Chapters 11, 13 and 14) is used in solving eq. (18.24). With the Z vector evaluated, any first-order correction terms, expressed in the general form of eq. (18.23), with respect to different types of “*p*” perturbations may be evaluated simultaneously. However, the corresponding **B**₀^{*p*} matrices must be available. The above argument is *not* limited necessarily to the CI wavefunction. In principle, the Z vector method is applicable whenever equations of the form of eqs. (18.23) and (18.24) are valid. In practice, the details are somewhat more complex because of the relation

$$U_{ij}^p + U_{ji}^p + S_{ij}^p = 0 \quad (18.25)$$

due to the first derivative of the orthonormality of the molecular orbitals discussed in Section 3.7. The equations, eq. (18.24), have to be rewritten in terms of the independent pairs of U_{ij}^p [3]. This does not affect the significance of the Z vector method.

18.2 The Z Vector Method and Second Derivative Properties for the CI Wavefunction

The second derivative of the electronic energy for the CI wavefunction was formulated in Chapter 6 and is given by

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^a + U_{ij}^a X_{ij}^b \right) + 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \end{aligned} \quad (18.26)$$

The skeleton (core) first derivative Lagrangian matrices appearing in eq. (18.26) are defined by

$$X_{ij}^a = \sum_m^{MO} Q_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^a , \quad (18.27)$$

and the Y matrix by

$$Y_{ijkl} = Q_{jl}h_{ik} + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn) + 4 \sum_{mn}^{MO} G_{jmfn}(im|kn) . \quad (18.28)$$

The U^{ab} matrices, which are related to the second derivatives of the MO coefficients with respect to nuclear coordinates (see Chapter 3), are obtained straightforwardly by solving the following second-order CPHF equations:

$$\mathbf{A} \mathbf{U}^{ab} = \mathbf{B}_0^{ab} . \quad (18.29)$$

For a closed-shell SCF wavefunction the \mathbf{A} matrix is given in eq. (18.4) and the \mathbf{B}_0^{ab} matrices were found in Chapter 10 to be

$$\begin{aligned} B_{0,ij}^{ab} &= F_{ij}^{ab} - \xi_{ij}^{ab}\epsilon_j - \sum_{kl}^{d.o.} \xi_{kl}^{ab} \left\{ 2(ij|kl) - (ik|jl) \right\} \\ &+ \sum_k^{all} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \\ &+ \sum_k^{all} \left(U_{ki}^a U_{kj}^b + U_{ki}^b U_{kj}^a \right) \epsilon_k \\ &+ \sum_{kl}^{all d.o.} \sum_m U_{km}^a U_{lm}^b A_{ij,kl} \\ &+ \sum_{kl}^{all d.o.} \sum_m \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\ &+ \sum_{kl}^{all d.o.} \sum_m \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\ &+ \sum_k^{all d.o.} \sum_l \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right) . \end{aligned} \quad (18.30)$$

In this equation the ξ^{ab} matrices, the skeleton (core) second derivative Fock matrices, and the A matrix and its skeleton (core) first derivative matrices are defined by

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{all} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) , \quad (18.31)$$

$$F_{ij}^{ab} = h_{ij}^{ab} + \sum_k^{d.o.} \left\{ 2(ij|kk)^{ab} - (ik|jk)^{ab} \right\} , \quad (18.32)$$

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) , \quad (18.33)$$

$$A_{ij,kl}^a = 4(ij|kl)^a - (ik|jl)^a - (il|jk)^a . \quad (18.34)$$

Note that the A matrix in eq. (18.33) is a different quantity from the \mathbf{A} matrix in eq. (18.4). The third term in eq. (18.26) is written in matrix form [2] as

$$2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} = 2 \mathbf{X}^T \mathbf{U}^{ab} , \quad (18.35)$$

and equation (18.29) is rewritten as

$$\mathbf{U}^{ab} = \mathbf{A}^{-1} \mathbf{B}_0^{ab} . \quad (18.36)$$

Combining eqs. (18.35) and (18.36), the third term of eq. (18.26) becomes

$$2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} = 2 \mathbf{X}^T \mathbf{U}^{ab} \quad (18.37)$$

$$= 2 \mathbf{X}^T \mathbf{A}^{-1} \mathbf{B}_0^{ab} \quad (18.38)$$

$$= 2 \mathbf{Z}^T \mathbf{B}_0^{ab} \quad (18.39)$$

where the \mathbf{Z} vector was defined by eqs. (18.12) and (18.13). Thus, this term may be evaluated through

$$2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} = 2 \sum_{ij}^{MO} B_{0,ij}^{ab} Z_{ij} , \quad (18.40)$$

where the elements of \mathbf{B}_0^{ab} matrices were defined in eq. (18.30).

In eq. (18.29), the simultaneous equations were solved for $3N(N+1)/2$ degrees of freedom, while in eq. (18.39) these equations are solved for only one degree of freedom. This represents a substantial saving in computational effort. In the evaluation of second derivatives of the CI wavefunction, however, the U^a matrices must be explicitly obtained prior to application of eq. (18.26).

The second derivative of the CI energy with respect to electric field perturbations, i.e., the electric polarizability, was given in Section 17.3 as

$$\alpha_{fg} = - \frac{\partial^2 E_{elec}}{\partial F \partial G} \quad (18.41)$$

$$= - 2 \sum_{ij}^{MO} U_{ij}^{fg} X_{ij} - 2 \sum_{ij}^{MO} \left(U_{ij}^g X_{ij}^f + U_{ij}^f X_{ij}^g \right)$$

$$- 2 \sum_{ijkl}^{MO} U_{ij}^f U_{kl}^g Y_{ijkl} \\ + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial F} \frac{\partial C_J}{\partial G} \left(H_{IJ} - \delta_{IJ} E_{elec} \right) . \quad (18.42)$$

The skeleton (core) first derivative matrices appearing in this equation were given in Section 17.3 as

$$X_{ij}^f = \sum_m^{MO} Q_{jm} h_{im}^f . \quad (18.43)$$

The corresponding second-order CPHF equations to evaluate the elements of U^{fg} are

$$\mathbf{A} \mathbf{U}^{fg} = \mathbf{B}_0^{fg} . \quad (18.44)$$

For a closed-shell SCF wavefunction the \mathbf{B}_0^{fg} matrices were found in Section 17.5 to be

$$\begin{aligned} B_{0,ij}^{fg} &= -\xi_{ij}^{fg} \epsilon_j - \sum_{kl}^{d.o.} \xi_{kl}^{fg} \left\{ 2(ij|kl) - (ik|jl) \right\} \\ &+ \sum_k^{all} \left(U_{ki}^f F_{kj}^g + U_{ki}^g F_{kj}^f + U_{kj}^f F_{ik}^g + U_{kj}^g F_{ik}^f \right) \\ &+ \sum_k^{all} \left(U_{ki}^f U_{kj}^g + U_{ki}^g U_{kj}^f \right) \epsilon_k \\ &+ \sum_{kl}^{all} \sum_m^{d.o.} U_{km}^f U_{lm}^g A_{ij,kl} \\ &+ \sum_{kl}^{all} \sum_m^{d.o.} \left(U_{ki}^f U_{lm}^g + U_{ki}^g U_{lm}^f \right) A_{kj,lm} \\ &+ \sum_{kl}^{all} \sum_m^{d.o.} \left(U_{kj}^f U_{lm}^g + U_{kj}^g U_{lm}^f \right) A_{ik,lm} . \end{aligned} \quad (18.45)$$

In this equation the ξ^{fg} matrices and the skeleton (core) first derivative Fock matrices are defined by

$$\xi_{ij}^{fg} = \sum_m^{all} \left(U_{im}^f U_{jm}^g + U_{im}^g U_{jm}^f \right) \quad (18.46)$$

and

$$F_{ij}^f = h_{ij}^f . \quad (18.47)$$

In a similar way as for the nuclear perturbations, these CPHF equations for the polarizability may be treated as

$$2 \sum_{ij}^{MO} U_{ij}^{fg} X_{ij} = 2 \mathbf{X}^T \mathbf{U}^{fg} \quad (18.48)$$

$$= 2 \mathbf{X}^T \mathbf{A}^{-1} \mathbf{B}_0^{fg} \quad (18.49)$$

$$= 2 \mathbf{Z}^T \mathbf{B}_0^{fg} . \quad (18.50)$$

The **Z** vector in eq. (18.50) is again the *same* quantity defined in eq. (18.12). In eq. (18.44) the simultaneous equations were solved for six degrees (xx, xy, xz, yy, yz, and zz) of freedom, while in eq. (18.50) they are solved for only one degree of freedom.

In the Z vector method the term due to the second-order changes of the MO coefficients may be reformulated in general as

$$\sum_{ij}^{MO} U_{ij}^{pq} X_{ij} = \sum_{ij}^{MO} B_{0,ij}^{pq} Z_{ij} \quad (18.51)$$

where the superscript “pq” stands for any real second-order perturbations. The **Z** vector is obtained by solving the simultaneous equations given in eq. (18.24). The Z vector method is applicable whenever equations like (18.23), (18.24), and (18.51) can be formulated. If the **Z** vector is determined any second-order correction terms, given in the general form of eq. (18.51), with respect to different types (including mixed or crossed) of perturbations, may be evaluated simultaneously. However, the corresponding B_0^{pq} matrices must be available. The above approach is valid to any order of perturbation and for any property. In practice, the details are somewhat more complicated due to the linear dependence of the elements of the U^{pq} matrices, i.e.,

$$U_{ij}^{pq} + U_{ji}^{pq} + \xi_{ij}^{pq} = 0 \quad (18.52)$$

where

$$\xi_{ij}^{pq} = S_{ij}^{pq} + \sum_m^{\text{all}} \left(U_{im}^p U_{jm}^q + U_{im}^q U_{jm}^p - S_{im}^p S_{jm}^q - S_{im}^q S_{jm}^p \right) . \quad (18.53)$$

The simultaneous equations, eq. (18.24), must be modified in terms of the independent pairs of the U^{pq} matrices [4]. This does not diminish the importance of the Z vector method.

References

1. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic Press, New York, 1976.
2. N.C. Handy and H.F. Schaefer, J. Chem. Phys. **81**, 5031 (1984).
3. J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, and H.F. Schaefer, J. Chem. Phys. **85**, 963 (1986).
4. T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, J. Chem. Phys. **85**, 3930 (1986).

Chapter 19

Applications of Analytic Derivatives

In this chapter, some chemical applications of the analytic derivative techniques developed in the earlier chapters are illustrated. This chapter takes a somewhat historical viewpoint and focuses on a few of the key early studies of chemical reactions by derivative methods. In particular, differences in the results between SCF and correlated levels of theory obtained with derivative methodology will be highlighted. The application of analytic derivative techniques to ensure the precise determination of the equilibrium geometries of relatively weakly bound molecular complexes will be illustrated. The systematics of the changes in molecular properties including structures, dipole moments, and harmonic vibrational frequencies with basis set and theoretical method will be illustrated for two molecules. The evolution of derivative techniques has aided greatly in the production of a number of critical papers addressing the question of what level of theory is necessary to reach agreement with experiment for various molecular properties. In addition, the use of derivative methods to aid in the full (i.e., beyond the harmonic approximation) vibrational analysis of two triatomic molecules will be considered. The immense practical advantages of the use of analytic derivatives in characterizing the nature of stationary points for larger molecules will be examined.

Some of the quantitative results in this chapter have been superseded in very recent times by more elaborate methods of including electron correlation and perhaps most notably by the various coupled cluster (CC) approaches augmented by their own analytic derivative schemes. Nonetheless, the examples demonstrate clearly the importance of derivative approaches to real chemical problems and should give the reader an appreciation of the practical necessity of such methods.

Table 19.1 summarizes some of the common applications of analytic gradients in chemistry.

Table 19.1 A summary of some common applications of analytic derivatives in chemistry. This table is applicable to variational wavefunctions (i.e., SCF, CI, and MCSCF) and X is a nuclear coordinate or electric field perturbation.

Order	Energy Derivative	Applications
Zeroth	E	Relative energies Minima and transition states Electronic states
First	$\frac{\partial^1 E}{\partial X^1}$	Stationary point location Finite differences Force constants Infrared intensities Electric dipole moment
Second	$\frac{\partial^2 E}{\partial X^2}$	Geometry optimization Force constants Harmonic vibrational frequencies Reaction path Hamiltonian Infrared intensities Electric polarizabilities
Higher	$\frac{\partial^3 E}{\partial X^3}$ $\frac{\partial^4 E}{\partial X^4}$	Cubic force constants Vibration-rotation interaction constants Raman intensities Electric hyperpolarizabilities Quartic force constants Vibrational anharmonic constants Electric higher-order hyperpolarizabilities

19.1 Unimolecular Isomerization of HCN

Conceptually if not always experimentally or theoretically the simplest chemical reactions are isomerizations. A particularly important example of this reaction type is the methyl isocyanide, CH₃NC, to methyl cyanide, CH₃CN, rearrangement. This reaction was a key test of unimolecular kinetics models such as RRKM. An early study of the analogous reaction of HCN was undertaken by Pearson, Schaefer, and Wahlgren without the use of analytic derivatives [1]. Through a careful but computationally tedious mapping of the potential energy surface at the SCF level supplemented by surface fits and CI level work on the stationary points, the conceptually and chemically significant intrinsic reaction coordinate or minimum energy path was determined. This important early study inspired the first chemical application of the configuration interaction (CI) analytic gradient method by Brooks *et al.* [2]. At the equilibrium geometries of both the linear reactant (HCN) and product (HNC) there are only two geometrical degrees of freedom, while there are three at the transition state. Thus the optimization of the equilibrium points could be done by using energy only methods. However, the ease of geometry optimization of the stationary points and particularly of the transition state, the precision of the various geometrical parameters determined, and the confidence in the results improved dramatically with the use of SCF and CI gradients. Figure 19.1 presents the three stationary point geometries at both the double zeta plus polarization (DZP) SCF and CISD levels of theory. Experimental structures for HCN and HNC also are shown. The lengthening of bonded and shortening of nonbonded distances in the transition state with the inclusion of electron correlation is evident. Such changes in transition state geometry have now been observed in many such reactions as derivative techniques have allowed the study of numerous chemical processes. The reaction barriers without correction for zero-point vibrational energy (ZPVE) changes were 40.0 and 36.3 kcal/mol with the SCF and CI theoretical models. Thus for this isomerization, the effects of electron correlation lower the reaction barrier by *ca.* 10 % and thus the SCF and CISD energetics agree reasonably well.

The use of analytic derivatives, and more specifically SCF level first derivatives, was of great value in providing the input to one of the earliest reaction path Hamiltonian studies by Gray, Miller, Yamaguchi, and Schaefer [3]. This study of the HCN → HNC reaction required the evaluation of force constants along the reaction coordinate to define the reaction path Hamiltonian of Miller, Handy, and Adams [4]. The labor in the repeated computation of force constants was reduced significantly by the availability of the analytic SCF gradient. The use of force constants from more reliable correlated wavefunctions in approximate kinetic models like the reaction path Hamiltonian is much more efficient and accurate with analytic schemes than with any sort of numerical differencing approach. There have been extensive developments of methods to determine intrinsic reaction coordinates which depend on the availability of analytic higher derivatives of SCF and correlated methods. (For a recent article, see Page, Doubleday, and McIver [5].) The potential energy surface for the hydrogen cyanide-hydrogen isocyanide isomerization has remained of interest to the present day (see, e.g., Bentley, Bowman, Gazdy, Lee, and Dateo [6]).

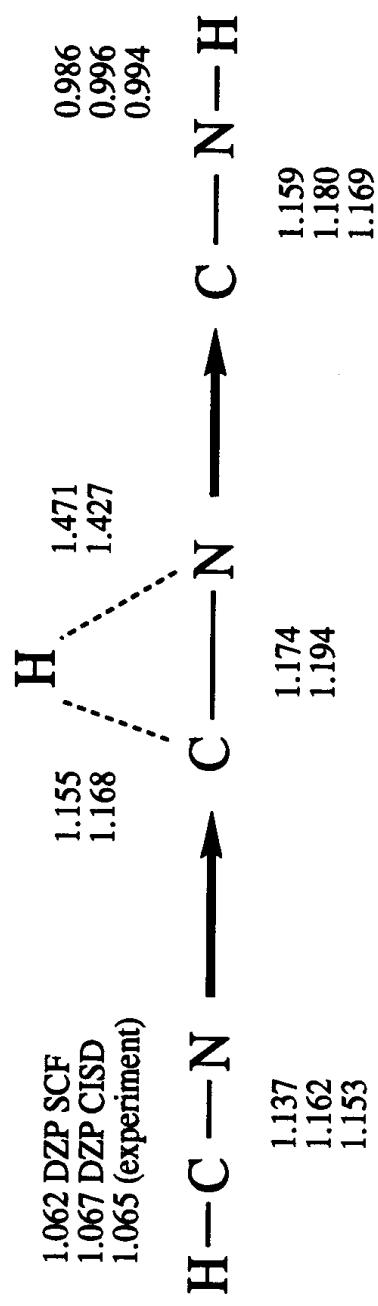


Figure 19.1 DZP SCF and CISD optimized structures for hydrogen cyanide, the isomerization transition state, and hydrogen isocyanide. Experimental results for the stable molecules also are shown.

19.2 Formaldehyde Dissociation

The photochemically initiated dissociation of formaldehyde to molecular or radical products ranks as perhaps the most completely understood of all polyatomic unimolecular reactions. The use of analytic derivative methods has been critical in building up a reliable theoretical description of these reactions and especially of the transition state structures involved. Two key reviews on spectroscopic and photochemical aspects of formaldehyde were given by Clouthier and Ramsay [7] and by Moore and Weisshaar [8]. More recent experimental results on the molecular and radical dissociations may be found in Guyer, Polik, and Moore [9] and in Chuang, Foltz, and Moore [10].

Early pioneering *ab initio* theoretical studies of the molecular decomposition by Jaffe and Morokuma [11] and of the radical dissociations by Hayes and Morokuma [12] and Fink [13] are of particular note. Although these early papers made no use of analytic derivative methods, they did provide extraordinarily valuable information to supplement various orbital and state symmetry analyses of the reactions. An early study of both the molecular and radical processes on the ground state surface (closed-shell singlet) was carried out by Goddard and Schaefer [14] using fledgling SCF analytic first derivative technology. Another very early use (1981) of analytic CI gradient schemes was the thorough theoretical study by Goddard, Yamaguchi, and Schaefer [15] of the molecular dissociation of formaldehyde. It is with this study that the formaldehyde example considered here will commence.

The DZP SCF and CISD geometries for formaldehyde, the molecular dissociation transition state, and the molecular products, H₂ and CO, are shown in Figure 19.2. These structures are taken from Scuseria and Schaefer [16] although essentially comparable results on the transition state were given in [15]. The most notable feature of the transition state at both the SCF and correlated levels is its distortion to C_s symmetry from C_{2v} to avoid an otherwise orbitally forbidden process. Comparable geometrical results also are shown in Figure 19.2 with the same two theoretical methods but with a larger triple zeta plus double polarization (TZ2P) basis set [16]. It should be mentioned that, particularly in the region of transition state structures where bond breaking and formation occur, the condition of a zero analytic gradient makes the precise location of such stationary points possible. The simple energy only versus coordinate mapping of a potential energy surface to locate transition states would not only be highly computationally inefficient but also rather inaccurate. Geometrical uncertainty arises due to the flatness of the potential energy hypersurface with respect to certain degrees of freedom at the transition state. In addition, relatively standard sets of internal coordinates which reduce couplings between various modes can be chosen for the equilibrium structures of most molecules. However, such couplings can be important in transition state structures, making the availability of approximate Hessians derived from analytic derivatives crucial to the geometry optimization.

The classical (no zero-point vibrational energy (ZPVE) correction) barrier height to the molecular dissociation of formaldehyde was predicted to be 101.9 kcal/mol at the TZ2P SCF level and 95.0 kcal/mol at the CISD level with the same basis set [16]. Analytic second SCF derivatives and finite differencing of analytic CI gradients allowed the reliable determination

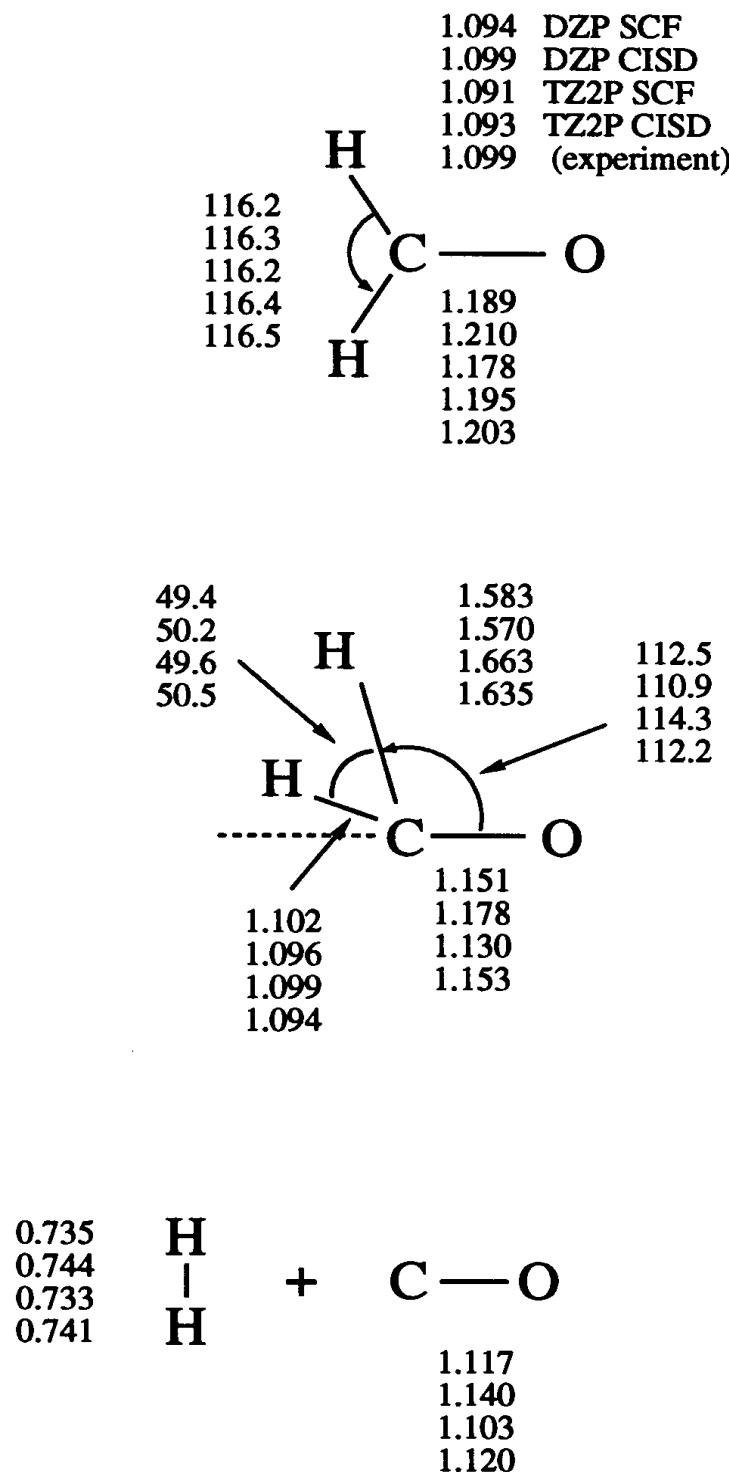


Figure 19.2 DZP and TZ2P SCF and CISD optimized geometries for formaldehyde, the molecular dissociation transition state, and the molecular products H_2 and CO .

of the harmonic vibrational frequencies not only for reactants and products but also for the transition state. These frequencies were then used to predict the effects of changes in ZPVE upon the barrier height. The ZPVE corrected TZ2P SCF barrier became 96.0 kcal/mol and the CISD result with this basis was 89.5 kcal/mol. It is clear that the ability to consistently predict harmonic vibrational frequencies and thus zero-point vibrational energies by analytic derivative approaches can have important energetic consequences when comparisons are drawn to experiment. It must be noted that still higher levels of electron correlation treatment (coupled cluster singles and doubles (CCSD) and coupled cluster including single, double, and linearized triple excitations (CCSDT-1)) and the associated gradient technology [16] finally result in a best prediction of an activation barrier of 81.4 kcal/mol in good agreement with the most reliable experimental value of 78.0 to 81.1 kcal/mol [9].

Consideration of the radical dissociation of formaldehyde by Yates, Yamaguchi, and Schaefer [17] involved the application of restricted open-shell SCF, CASSCF, and CISD analytic derivatives to the lowest triplet surface and to the formyl radical. Basis sets employed ranged from DZP through quadruple zeta plus triple polarization (QZ3P). Higher level correlation corrections (CISD + Q) to the energies at lower level optimized geometries also were carried out to set the stage for a comparison with experiment [10].

The origin of the exit channel barrier in the triplet state radical dissociation of formaldehyde has been understood in terms of avoided crossings [12,13], but a high level theoretical description with rigorous geometry optimization and stationary point vibrational analyses via analytic derivative methods had been lacking. Similarly, the importance of the triplet dissociation mechanism had not been established firmly by experiment until the study by Moore and co-workers [10]. The T₁ exit barrier height at 0 K was determined to lie in the range of 2.9 to 6.0 kcal/mol. This barrier is defined as the energy required for the hydrogen atom and formyl radical to approach from infinite separation and combine to yield triplet formaldehyde at its C_s equilibrium geometry.

Several key results of Yates *et al.* [17] will be discussed, but first we note a concluding remark from that paper. In order to estimate the energy difference between two stationary points to an accuracy of 2 kcal/mol, complete geometry optimizations and harmonic vibrational analyses of all species are required. In addition, these predictions must be made with large basis sets including multiple sets of polarization functions and at correlated levels including excitations beyond the simple CISD model. The determination of optimized structures and harmonic vibrational frequencies would be essentially impossible without at least the first analytic derivative of the various quantum chemical methods described in this book.

Figure 19.3 contains the CISD optimized geometries for ground state formaldehyde, for the pyramidalized equilibrium structure of the lowest triplet state, for the strongly nonplanar transition state to radical dissociation, and for one of the products, the ground state formyl radical. Note that large basis sets have been used and the geometries precisely determined with analytic gradient techniques. The two predicted equilibrium structures for ground and triplet state formaldehyde are of interest since the ground state structure is in

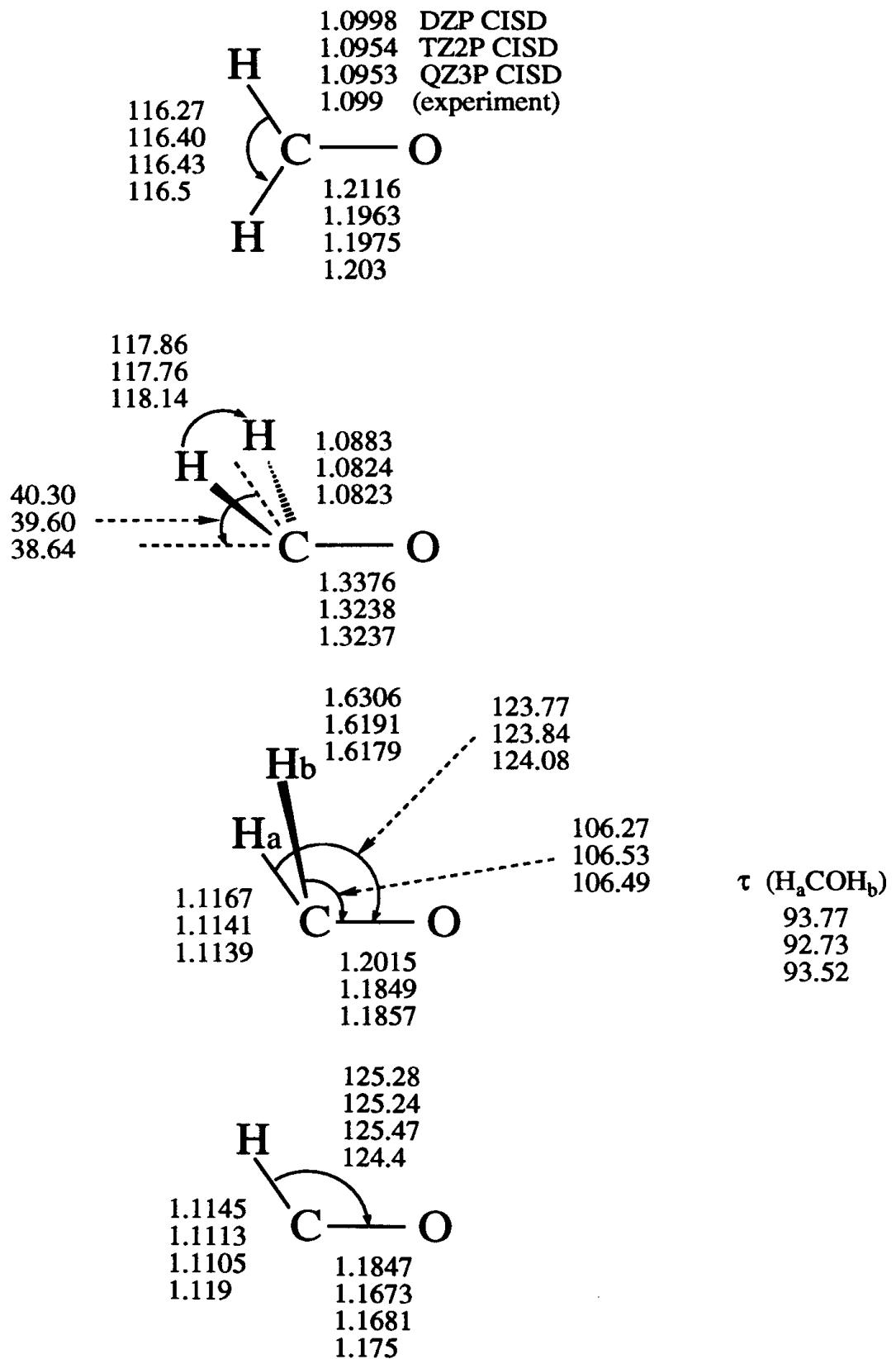


Figure 19.3 DZP, TZ2P, and QZ3P CISD optimized structures for ground state formaldehyde, for the lowest ($^3\text{A}''$) excited state, for the radical dissociation transition state, and for the ground state formyl radical.

excellent agreement with experiment while the triplet structure is not [7]. In fact, the experimental parameters for this excited electronic state are effective values derived from a double-well potential function. The high-level theoretical prediction may be a more reliable source of information for the geometry of triplet H₂CO and especially for the CO bond distance than existing experimental results. At the transition state the leaving hydrogen atom is almost perpendicular to the HCO plane. This interesting feature was suggested in the experiments of Bersohn and coworkers [18] and in the theoretical study by Hayes and Morokuma [12]. At the CISD levels, the presence of one and only one imaginary vibrational frequency establishes unequivocally that the stationary point is a true transition state. In this case, finite differences of CISD analytic first derivatives were employed and the value of the imaginary frequency lies between 1381*i* and 1443*i* cm⁻¹ depending on the basis set. Clearly it would have been impossible to locate and characterize completely a low symmetry point in a 7-dimensional space (the energy plus 6 geometrical coordinates) without analytic derivatives. The predicted structures of the product formyl radical are also in very good agreement with experiment.

The classical CISD exit barrier heights for triplet formaldehyde range from 8.6 to 9.7 kcal/mol depending on basis set. ZPVE changes determined from the theoretical harmonic frequencies increase these values to 10.4 to 11.5 kcal/mol. Higher-order electron correlation effects introduced by an approximate account of quadruple excitations and the use of a still larger set of polarization functions including f type Gaussians on carbon and oxygen (2df,2pd) gave a classical barrier of 6.0 kcal/mol. The CISD harmonic vibrational frequencies gave a ZPVE change as noted above and thus a barrier of 7.8 kcal/mol, which is within 2 kcal/mol of the experimental findings of Chuang, Foltz, and Moore [10].

19.3 Dissociation of *cis*-Glyoxal → H₂ + 2 CO

The “triple whammy” decomposition of glyoxal to three small closed-shell molecules via a single transition state was a novel and initially controversial suggestion by Osamura and Schaefer [19]. A Woodward-Hoffmann type orbital symmetry analysis indicated that the triple dissociation was allowed and thus a reasonably low activation barrier might be anticipated. The energy scale for the description “reasonably low” refers to the approximately 80 kcal/mol required if glyoxal were to decompose first to formaldehyde and then the H₂CO were to dissociate to H₂ and CO as discussed in the previous section. This prediction in an otherwise rather uncontroversial paper on the barrier to internal rotation of ground state (closed-shell singlet) glyoxal led on to more detailed theoretical work by Osamura, Schaefer, Dupuis, and Lester [20] and most recently by Scuseria and Schaefer [21]. Critically important experiments in establishing the validity of the unimolecular triple dissociation of glyoxal were performed by Hepburn, Buss, Butler, and Lee [22]. Although now well established for glyoxal, it should be noted that triple whammy reactions remain exceedingly rare, with the only other reasonably well studied example being the triple dissociation of s-tetrazine examined by Scheiner, Scuseria, and Schaefer [23] and by Scuseria and Schaefer [24].

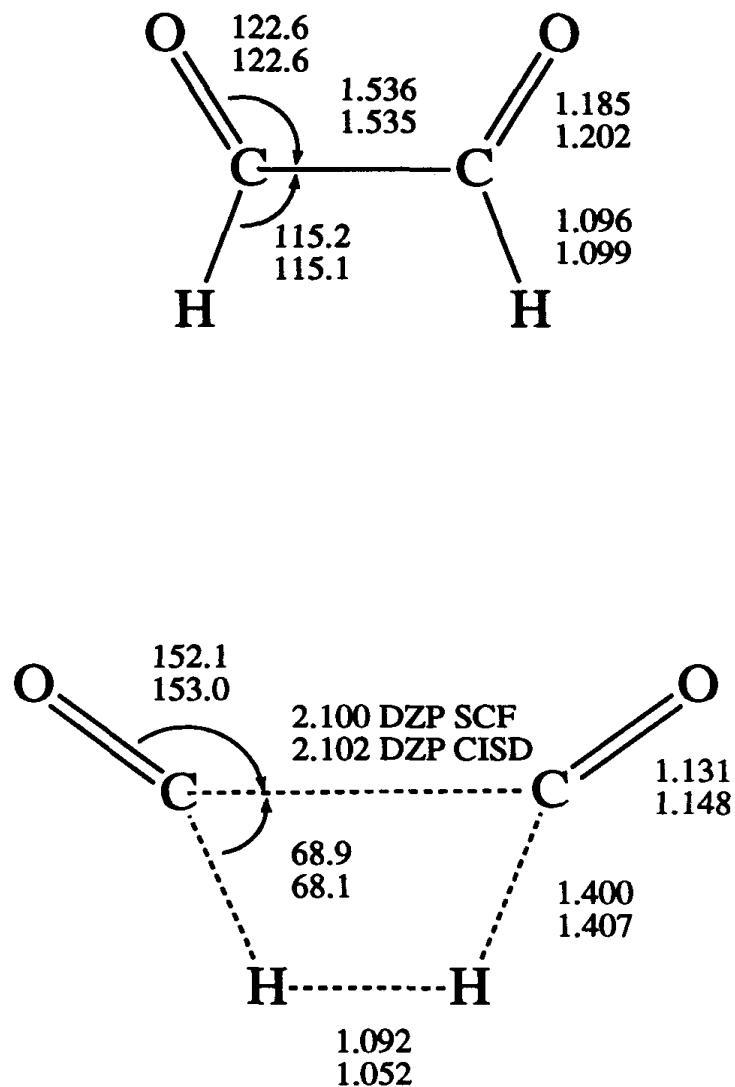


Figure 19.4 DZP SCF and DZP CISD optimized structures for *cis*-glyoxal (C_{2v}) and for the planar stationary point (C_{2v}) corresponding to the unimolecular triple dissociation of glyoxal.

Figure 19.4 presents DZP SCF and CISD structures for *cis*-glyoxal and for the planar stationary point corresponding to the unimolecular triple dissociation of glyoxal as determined by Scuseria and Schaefer [21]. As discussed by Osamura *et al.* [20], the DZP SCF stationary point has two imaginary vibrational frequencies. The smaller one, $96i\text{ cm}^{-1}$, leads to an energetically close by but nonplanar transition state. The DZP CISD transition state is likely to undergo a similar distortion to a nonplanar structure. The larger imaginary frequency, $2161i\text{ cm}^{-1}$ with the DZP SCF method, corresponds to the true reaction coordinate. The knowledge of the distortion of the transition state to nonplanarity is of course a result of an analytic second derivative-based SCF level vibrational analysis. Analytic derivative approaches prevented any assumption regarding the planarity of the transition state from going unchallenged. The DZP SCF and CISD transition state structures are remarkably similar. Only the CO bond lengths, which increased by 0.017 \AA and the HH distance which changed from 1.092 \AA (SCF) to 1.052 \AA (CISD), varied noticeably as electron correlation was included. The C-C bond being broken is 2.100 or 2.102 \AA in length at the DZP SCF and CISD levels and thus very much longer than in *cis*-glyoxal. Such a severe geometrical distortion must have an energetic price.

The energetics of this unusual triple dissociation have always been the key issue in comparison with experiment. The experiments of Hepburn *et al.* [22] place a rigorous upper bound on the activation energy of 62.9 kcal/mol . This value corresponds to the zero-point energy of S_1 glyoxal, and when excited to this level and following internal conversion to the S_0 surface, molecular hydrogen and carbon monoxide were observed. Using the DZP SCF harmonic vibrational frequencies to estimate the ZPVE, the planar stationary points for the triple dissociation, a larger TZ2P basis set, and higher level coupled cluster correlation schemes (CCSD and CCSDT-1), Scuseria and Schaefer [21] carefully extrapolated to an activation barrier of 54.6 kcal/mol . Experimental estimates of the E_a of approximately 47 to 50 kcal/mol have been given. Beyond question, the triple whammy mechanism for fragmentation is energetically feasible under the experimental conditions for glyoxal photodissociation.

19.4 The Hydrogen Fluoride Dimer, $(HF)_2$

Analytic derivative based approaches can be of particular value in determining the equilibrium geometries and the vibrational frequencies of relatively weakly bound molecular complexes. One very important example is the hydrogen bonded HF dimer which has been studied extensively both experimentally and theoretically. The experimental value of the binding energy, D_e , is 4.56 kcal/mol . Pine and Lafferty [25] studied the rotational structure of and vibrational predissociation in the HF stretching bands of the HF dimer. Gaw, Yamaguchi, Vincent, and Schaefer [26] predicted the vibrational frequency shifts in the hydrogen fluoride dimer relative to the monomer at the DZP SCF and CISD levels. The low frequency fundamentals of the HF dimer have been extracted by Quack and Suhm [27]. The effects of considerably more extended basis sets along with SCF, CISD, and CCSD methods on the properties of $(HF)_2$ were examined very recently by Collins, Morihashi, Yamaguchi,

and Schaefer [28].

The experiments of Pine and Lafferty indicated that in the dimer the free H-F stretch is at 3929 cm^{-1} and the hydrogen bonded H-F fundamental at 3868 cm^{-1} [25]. These bands are red shifted by 32 and 93 cm^{-1} , respectively, relative to the free monomer value of 3961 cm^{-1} . The study of Gaw *et al.* [26] used SCF and CISD analytic gradients to greatly increase the precision of the theoretical data on this complex. Care was taken with the CI method to consider size consistency effects and to take the value of the “monomer” properties from a supermolecular computation. The DZP SCF and CISD structures for the hydrogen fluoride monomer and dimer are shown in Figure 19.5. The predicted red shifts of -47 and -105 cm^{-1} at the DZP CISD level are in reasonable agreement with the experimental results of -32 and -93 cm^{-1} . These shifts may be correlated with the very slight increases in the HF distances on proceeding from the monomer to the dimer. These bond length changes are only a few thousandths of an Ångstrom and yet they can be reliably determined not only at the SCF but also at the CISD levels with the application of analytic derivative-based geometry optimization procedures.

The higher level TZ2P and QZ3P SCF and CISD structures also are shown in Figure 19.5. The eventual nearly quantitative agreement of the geometry and vibrational frequencies with experiment for this dimer required the application of coupled cluster gradient techniques by Collins *et al.* [28]. For example, the equilibrium dissociation energy was within 0.2 kcal/mol of experiment provided correlated methods such as CISD or CCSD and large basis sets such as quadruple zeta plus triple polarization (QZ3P) were employed. Even the CISD results represent an important step along the road to chemical truth. At the QZ3P CISD level the F-F distance in the dimer was 2.764 \AA in comparison with the experimental value of $2.72 \pm 0.003\text{ \AA}$ from the microwave spectrum [29]. The experimental values of the two angles presented in the figure are 63 ± 6 and 10 ± 6 degrees, in good accord with the predictions.

The QZ3P CISD shifts for the H-F stretches were -39 and -105 cm^{-1} . Comparison with the DZP CISD values indicate only modest changes in these two quantities. However, Collins *et al.* [28] have shown that at the QZ3P CCSD level, again using analytic derivatives for very precise geometry optimizations and vibrational frequency analyses, these red shifts became -35 and -94 cm^{-1} in essentially quantitative agreement with experiment. In dealing with quantities on a scale of tens of wavenumbers, there can be no doubt of the value of analytic derivative methods in avoiding the numerical errors inherent in finite difference procedures.

The extraction of the low energy harmonic frequencies for the weakly bound HF dimer is very far from trivial. Sophisticated analyses of potential energy surfaces by Quack and Suhm [27] give harmonic values for the symmetric bend of 483 to 487 cm^{-1} , for the F-F stretch of 148 to 153 cm^{-1} , for the antisymmetric stretch of 211 to 212 cm^{-1} , and for the out-of-plane bend of 401 cm^{-1} . The ranges of values follow from different models for the potential energy hypersurface. In the same order the QZ3P CISD harmonic values for these low frequencies are 565, 155, 221, and 462 cm^{-1} and the QZ3P CCSD level predictions are

0.9034 DZP SCF
0.9206 DZP CISD
0.8978 TZ2P SCF
0.9131 TZ2P CISD
0.8974 QZ3P SCF
0.9125 QZ3P CISD

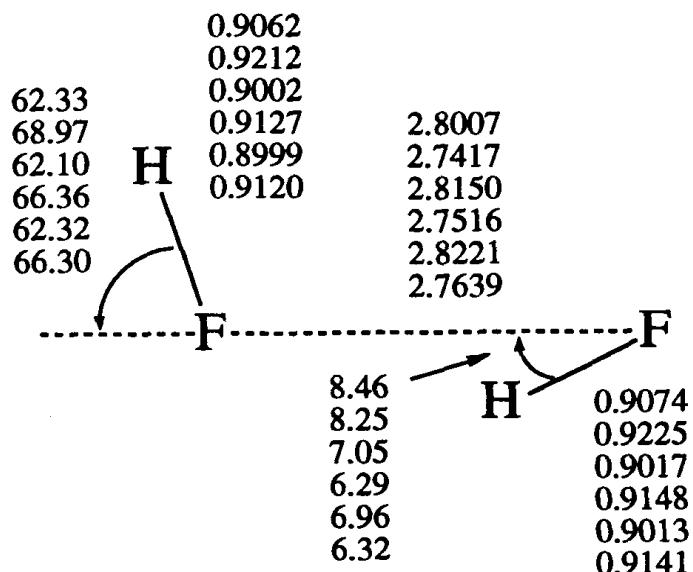


Figure 19.5 DZP, TZ2P, and QZ3P optimized geometries for the hydrogen fluoride monomer and dimer at the SCF and CISD levels of theory.

561, 154, 218, and 454 cm⁻¹. Agreement is generally satisfactory for these low modes and difficulty with the extraction of the harmonic frequencies from the experimental data cannot be ruled out as one source of any remaining discrepancy.

19.5 Systematics of Molecular Properties

There can be little doubt that a major benefit of the efficiency of derivative methods has been the possibility of examining a large number of molecules with systematic variations in basis set and theoretical approach. Another early application of the CISD analytic gradient method was just such a study of vibrational frequencies in a series of small polyatomic molecules by Yamaguchi and Schaefer [30]. These studies have been continued at the coupled cluster level by Besler, Scuseria, Scheiner, and Schaefer (CCSD) [31], by Thomas, DeLeeuw, Vacek and Schaefer (coupled cluster singles, doubles, and perturbative triples, CCSD(T)) [32], and by Thomas, DeLeeuw, Vacek, Crawford, Yamaguchi, and Schaefer (larger basis set CCSD(T)) [33]. Tables 19.2 and 19.3 present the energies, geometries, harmonic vibrational frequencies, infrared intensities and dipole moments of ground state H₂O and H₂CO at the DZP and TZ2P SCF and CISD levels of theory. Water is certainly the most carefully studied molecule by theoreticians and the results on formaldehyde may be put into context with reference to Section 19.2.

Two basis sets, two methods, and two molecules obviously do not represent a systematic study. However, the flavor of such research can be appreciated even with reference to only this restricted set of data. The key question in such work is what basis set and method will produce results with a consistent level of agreement with experiment. Although not uniformly recommended by quantum chemists, an empirical scaling of molecular properties such as vibrational frequencies is possible if a uniformly good agreement is attained relative to experimental results.

Table 19.2 presents the DZP and TZ2P SCF and CISD values for the structure, dipole moment, and harmonic vibrational frequencies of H₂O. As would be expected, the O-H bond lengths increase with the inclusion of electron correlation and agree within 0.005 Å with experiment at the DZP or TZ2P CISD levels of theory. The bond angle change from SCF to CISD is larger, reflecting the softer nature of the potential for this geometrical coordinate. The best predicted values are within 0.5 degrees of experiment. The dipole moment is the most accessible experimental measure of the molecular electronic charge distribution. SCF values for this moment are almost invariably too large with correlation leading to a decrease. At the TZ2P CISD level the dipole moment of water is predicted to be 1.940 Debye, or approximately 0.09 Debye greater than experiment. For these small molecules, the vibrational analyses have been carried out to yield the harmonic frequencies most directly comparable to the theoretical results. There is a decrease in the vibrational frequencies on proceeding from SCF to CISD, especially for the modes dominated by bond stretching. With the TZ2P CISD model, the predicted harmonic frequencies are 2.9, 3.2, and 2.5 % greater than experiment for the symmetric stretch, the bend, and the asymmetric stretch,

Table 19.2 Molecular properties of H₂O taken from Refs. [32] and [33].

Basis set	SCF		CISD		
	DZP	TZ2P	DZP	TZ2P	Expt.
Energy (<i>Hartree</i>)	-76.04695	-76.06135	-76.25751	-76.31169	
r_e (OH) (Å)	0.9441	0.9400	0.9585	0.9523	0.9572 0.9578
θ_e (HOH) (deg.)	106.6	106.3	104.9	104.9	104.5
μ (Debye)	2.180	1.988	2.144	1.940	1.8473
ω_1 (a_1) (cm^{-1})	4164	4139	3967	3943	3832
ω_2 (a_1)	1751	1764	1693	1702	1649
ω_3 (b_2)	4287	4238	4090	4042	3943
I_1 (a_1) (km/mol)	20.5	14.8	6.6	6.2	2.2
I_2 (a_1)	108.0	96.4	83.2	75.7	53.6
I_3 (b_2)	73.8	80.7	37.4	53.6	44.6

respectively. Infrared intensities are rather more difficult either to predict or to measure quantitatively. There is a general trend for the predicted intensities of water to decrease with the inclusion of correlation. The highest level TZ2P CISD infrared intensities in the table are all greater than experiment.

Table 19.3 presents the DZP and TZ2P SCF and CISD results on ground state formaldehyde. The geometry, dipole moment, and harmonic vibrational frequencies with their associated infrared intensities are given. The trends follow the same pattern as discussed above for the water molecule. The C=O distance of 1.1949 Å at the TZ2P CISD level is approximately 0.008 Å, or 0.7 % shorter than experiment. The CH bond length is 0.006 Å shorter than experiment and the HCH bond angle 0.1 degrees less than experiment at the highest level of theory presented here. The SCF level dipole moments are 2.781 and 2.698 Debye and decrease to 2.513 and 2.450 Debye with the CISD method. The experimental dipole moment is in the range of 2.323 to 2.331 Debye. Again for formaldehyde, the harmonic vibrational frequencies have been determined. The average absolute percentage deviation of the TZ2P CISD harmonic frequencies from the more recent experimental re-

Table 19.3 Molecular properties of H₂CO taken from Refs. [32] and [33].

Basis set	SCF		CISD		
	DZP	TZ2P	DZP	TZ2P	Expt.
Energy (<i>Hartree</i>)	-113.89533	-113.91388	-114.22312	-114.28902	
r_e (CO) (Å)	1.1888	1.1778	1.2102	1.1949	1.203
r_e (CH) (Å)	1.0943	1.0911	1.0988	1.0929	1.099
θ_e (HCH) (deg.)	116.2	116.2	116.3	116.4	116.5
μ (<i>Debye</i>)	2.781	2.698	2.513	2.450	2.323
ω_1 (a_1) (cm^{-1})	3149	3102	3080	3024	2978
ω_2 (a_1)	2007	1987	1877	1865	1778
ω_3 (a_1)	1656	1655	1600	1592	1529
ω_4 (b_1)	1335	1342	1247	1255	1191
ω_5 (b_2)	3227	3175	3162	3097	2997
ω_6 (b_2)	1367	1374	1310	1321	1299
I_1 (a_1) (km/mol)	72.7	63.9	66.4	60.8	75.5
I_2 (a_1)	158.0	155.0	94.6	100.2	74.0
I_3 (a_1)	14.0	19.1	7.7	12.2	11.2
I_4 (b_1)	1.7	2.1	3.5	3.5	6.5
I_5 (b_2)	112.1	107.5	109.5	105.2	87.6
I_6 (b_2)	19.3	22.0	13.0	15.4	9.9

Table 19.4 Theoretical and experimental vibrational anharmonic constants (in cm^{-1}) of H_2O , Ref. [34].

Basis set	SCF		CISD		
	DZP	TZP	DZP	TZP	Expt.
χ_{11}	-40.08	-38.40	-44.2	-41.2	-42.6
χ_{12}	-15.63	-14.65	-17.1	-14.2	-15.9
χ_{13}	-157.21	-150.86	-170.3	-159.5	-165.8
χ_{22}	-19.99	-20.70	-15.9	-15.4	-16.8
χ_{23}	-17.92	-17.12	-20.7	-18.8	-20.3
χ_{33}	-45.36	-43.84	-49.3	-46.7	-47.6

sults is approximately 3 %. The infrared intensities show a general decrease on going from SCF to CISD with the same basis set. The predicted intensities are again larger than the experimental values.

It should be recalled that the analytic SCF first and second derivatives and the CISD first derivatives were critical to the determination of the above properties to the precision reported. The examples considered and many more in the literature clearly indicate the possibility of generating accurate structural and spectroscopic information from an *ab initio* approach.

19.6 Vibrational Analysis: Anharmonic Effects

The harmonic vibrational frequencies of larger molecules are of greatest interest to chemists. However, high resolution molecular spectroscopy has developed into a major subdiscipline of chemical physics, and it is in this research field that predictions of higher-order effects such as vibration-rotation interaction constants, vibrational anharmonic constants, and centrifugal distortion constants become crucial. Two systematic studies of the prediction of molecular vibrational anharmonicity and vibration-rotation interaction by Clabo *et al.* [34] and Allen *et al.* [35] have appeared. These researchers used analytic SCF third derivatives to determine theoretically a number of anharmonic molecular properties.

It has been noted that the SCF cubic force field as well as the quartic force field obtained from finite differences of the cubic force constants show surprisingly little variation with basis set. For many anharmonic properties, the values predicted via SCF higher (i.e., third and

Table 19.5 Complete quartic force fields for CO₂, Ref. [35].

In internal coordinates				In normal coordinates				
Constant	SCF	CISD	Expt.	Constant	SCF	CISD	Expt.	
f_{rr}	19.067	17.421	16.022	ω_1	1507.2	1426.4	1354.3,	1353.7
$f_{rr'}$	2.342	1.754	1.2613	ω_2	768.3	705.9	672.9,	672.7
$f_{\alpha\alpha}$	0.977	0.847	0.785	ω_3	2550.7	2468.7	2396.3,	2396.4
f_{rrr}	-138.6	-124.7	-113.9	ϕ_{111}	-274.3	-267.6	-274.7,	-273.0
$f_{rrr'}$	-2.917	-2.564	-3.909	ϕ_{122}	165.5	164.3	149.4,	150.5
$f_{\alpha\alpha r}$	-1.232	-1.149	-1.218	ϕ_{133}	-547.1	-522.9	-498.3,	-506.1
f_{rrrr}	750.1	695.3	630.0	ϕ_{1111}	39.2	40.7	46.1,	43.1
$f_{rrrr'}$	4.125	6.831	22.06	ϕ_{1122}	-47.0	-47.4	-44.6,	-48.0
$f_{rrr'r'}$	10.086	6.098	12.090	ϕ_{1133}	78.9	80.2	78.1,	82.6
$f_{\alpha\alpha rr}$	0.066	0.692	2.015	ϕ_{2222}	81.2	88.9	58.8,	65.4
$f_{\alpha\alpha rr'}$	3.047	2.558	3.740	ϕ_{2233}	-115.1	-113.5	-110.2,	-112.4
$f_{\alpha\alpha\alpha\alpha}$	2.422	2.594	1.106	ϕ_{3333}	176.5	169.2	151.2,	160.4

fourth) derivatives appeared to have converged with respect to basis set variation at the DZP basis level. Good agreement between theoretical anharmonic constants and experiment was attained with a CISD harmonic force field coupled with the corresponding SCF cubic and/or quartic force constants using the same basis set. Thus, the SCF higher derivative methods have real practical value in the prediction or interpretation of the finer details of molecular spectra.

In Table 19.4, DZP and triple zeta plus polarization (TZP) SCF and CISD values of the vibrational anharmonic constants of H₂O are presented [34]. Obviously, the magnitudes of these constants are much smaller than the harmonic constants. It should be recalled that the full quartic force field for H₂O has been known quite accurately from experiment for some time. Note that the DZP and TZP SCF values for the vibrational anharmonic constants are reasonably close, demonstrating the convergence with respect to basis set mentioned above. In addition, the SCF and CISD results with the larger basis sets are quite comparable to the experimental values. The average absolute percentage deviation of the TZP CISD vibrational anharmonic constants from experiment is only 4.5 %.

Table 19.5 displays the complete quartic force fields in both internal and normal coordinates for CO₂ [35]. The TZ2P CISD cubic and quartic internal coordinate force constants agree with experiment better than the SCF values in four of the nine cases. In normal coordinates the predicted force fields are in good agreement with the best experimental results. The average percentage errors of the cubic and quartic constants are only 5.8 % and 3.8 % at the TZ2P SCF and CISD levels (neglecting the one large discrepancy for ϕ_{2222}). Some deficiency in the description of the bending of this multiply bonded system probably accounts for the error in ϕ_{2222} and a larger basis set including f-type Gaussian functions may be needed.

Though much more could be said, it is perhaps sufficient to note two points. First, the anharmonic constants derived from large basis set SCF work are reliable enough to be useful to the experimental spectroscopist. Second, the higher analytic derivatives from SCF theory are essential to the accurate and efficient prediction of anharmonic effects.

19.7 Larger Molecules: Structural Certainty

It has long been recognized that the analytic derivative techniques have particular value in the study of larger molecules of low symmetry. As most large molecules have relatively low symmetry, analytic gradient techniques are likely to be of particular value in the areas of theoretical organic chemistry and biochemistry. As the number of degrees of freedom in a molecule without symmetry varies as 3N-6 (where N is the number of nuclei), the advantage of obtaining both an energy and all the analytic derivatives at any given geometry increases rapidly with N. Certainly for N greater than 3 the efficiency and the accuracy of analytic derivatives will be needed in any quantitative study of molecular structure.

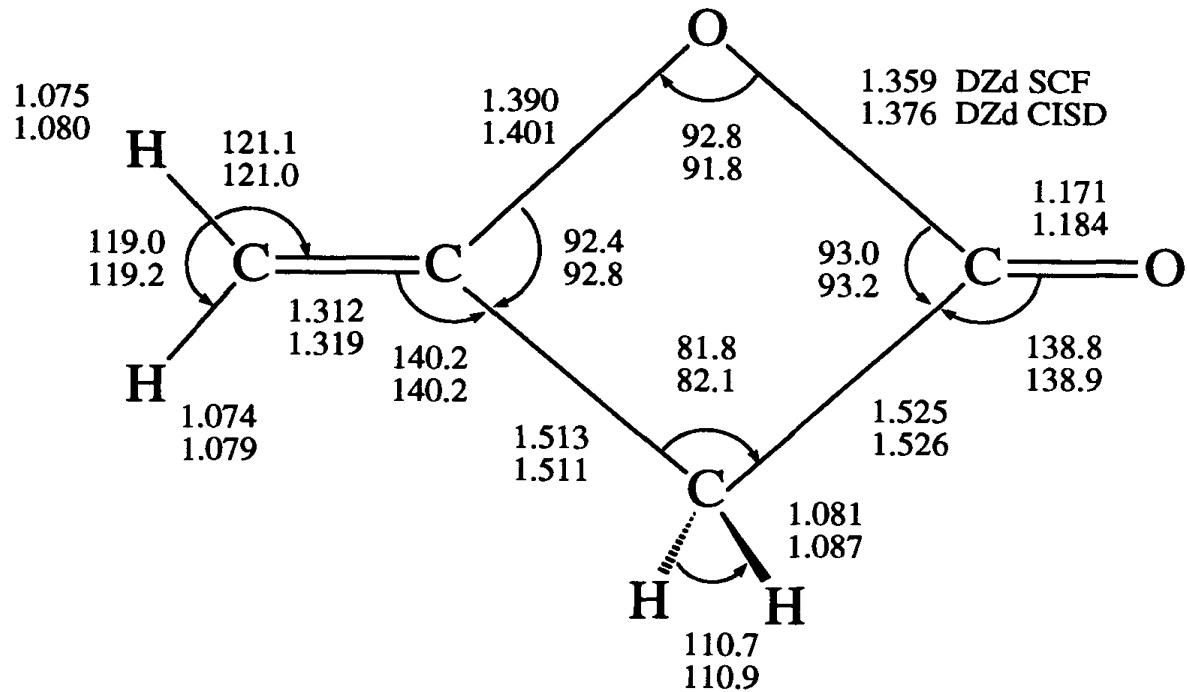


Figure 19.6 Theoretical predictions of the equilibrium geometry of diketene employing the double zeta plus heavy atom d function (DZd) basis set and the SCF and CISD methods. All bond distances are in Ångströms.

Diketene is an important and frequently studied molecule as evidenced by the substantial review by Clemens [36]. However, there have been no recent X-ray crystallographic, electron diffraction or microwave experiments to establish a highly accurate experimental structure for this important organic molecule. Thus Seidl and Schaefer [37,38] set out to determine the geometry of diketene from a systematic theoretical approach. The harmonic vibrational frequencies also were predicted at the DZP SCF level of theory using analytic second derivatives and were used to suggest a reassignment of certain bands in the experimental infrared spectrum.

The most important feature of the study was a reliable prediction of the equilibrium structure. Figure 19.6 presents the DZd SCF and CISD optimized geometries for the diketene molecule. The DZd basis contains d polarization functions on carbon and oxygen but differs from DZP in omitting p polarization functions on hydrogen. Diketene contains 10 atoms and is of C_s symmetry and thus there are 18 geometrical degrees of freedom. In order to efficiently and precisely locate a minimum in a space with this number of variables, the use of SCF and CISD analytic derivatives is mandatory.

Particular attention was drawn to the C-O bond length adjacent to the CC double bond, the C-O bond distance next to the CO double bond, and the length of the C=O bond. All of the predicted values, even with the inclusion of electron correlation by the CISD approach, differed markedly from early crystal structure results. However, the precisely located equilibrium structure from theory produced rotational constants in good agreement with a microwave study and also was in accord with early electron diffraction work. A final study of the structure of diketene at the DZd CCSD level, again with analytic gradients, further increased the reliability of the theoretical predictions. Further x-ray diffraction crystal structure analysis of diketene appears necessary.

References

1. P.K. Pearson, H.F. Schaefer, and U. Wahlgren, *J. Chem. Phys.* **62**, 350 (1975).
2. B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **72**, 4652 (1980).
3. S.K. Gray, W.H. Miller, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **73**, 2733 (1980).
4. W.H. Miller, N.C. Handy, and J.E. Adams, *J. Chem. Phys.* **72**, 99 (1980).
5. M. Page, C. Doubleday, and J.W. McIver, *J. Chem. Phys.* **93**, 5634 (1990).
6. J.A. Bentley, J.M. Bowman, B. Gazdy, T.J. Lee, and C.E. Dateo, *Chem. Phys. Lett.* **198**, 563 (1992).
7. D.J. Clouthier and D.A. Ramsay, *Ann. Rev. Phys. Chem.* **34**, 31 (1983).
8. C.B. Moore and J.C. Weisshaar, *Ann. Rev. Phys. Chem.* **34**, 525 (1983).
9. D.R. Guyer, W.F. Polik, and C.B. Moore, *J. Chem. Phys.* **84**, 6519 (1986).
10. M.-C. Chuang, M.F. Foltz, and C.B. Moore, *J. Chem. Phys.* **87**, 3855 (1987).
11. R.L. Jaffe and K. Morokuma, *J. Chem. Phys.* **64**, 4881 (1976).

12. D.M. Hayes and K. Morokuma, *Chem. Phys. Lett.* **12**, 539 (1972).
13. W.H. Fink, *J. Am. Chem. Soc.* **94**, 1073 (1972).
14. J.D. Goddard and H.F. Schaefer, *J. Chem. Phys.* **70**, 5117 (1979).
15. J.D. Goddard, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **75**, 3459 (1981).
16. G.E. Scuseria and H.F. Schaefer, *J. Chem. Phys.* **90**, 3629 (1989).
17. B.F. Yates, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **93**, 8798 (1990).
18. J. Solomon, C. Jonah, P. Chandra, and R. Bersohn, *J. Chem. Phys.* **55**, 1908 (1971).
19. Y. Osamura and H.F. Schaefer, *J. Chem. Phys.* **74**, 4576 (1981).
20. Y. Osamura, H.F. Schaefer, M. Dupuis, and W.A. Lester, *J. Chem. Phys.* **75**, 5828 (1981).
21. G.E. Scuseria and H.F. Schaefer, *J. Am. Chem. Soc.* **111**, 7761 (1989).
22. J.W. Hepburn, R.J. Buss, L.J. Butler, and Y.T. Lee, *J. Phys. Chem.* **87**, 3638 (1983).
23. A.C. Scheiner, G.E. Scuseria, and H.F. Schaefer, *J. Am. Chem. Soc.* **108**, 8160 (1986).
24. G.E. Scuseria and H.F. Schaefer, *J. Phys. Chem.* **94**, 5552 (1990).
25. A.S. Pine and W.J. Lafferty, *J. Chem. Phys.* **78**, 2154 (1983).
26. J.F. Gaw, Y. Yamaguchi, M.A. Vincent, and H.F. Schaefer, *J. Am. Chem. Soc.* **106**, 3133 (1984).
27. M. Quack and M.A. Suhm, *J. Chem. Phys.* **95**, 28 (1991).
28. C.L. Collins, K. Morihashi, Y. Yamaguchi, and H.F. Schaefer, to be published.
29. B.J. Howard, T.R. Dyke, and W. Klemperer, *J. Chem. Phys.* **81**, 5417 (1984).
30. Y. Yamaguchi and H.F. Schaefer, *J. Chem. Phys.* **73**, 2310 (1980).
31. B.H. Besler, G.E. Scuseria, A.C. Scheiner, and H.F. Schaefer, *J. Chem. Phys.* **89**, 360 (1988).
32. J.R. Thomas, B.J. DeLeeuw, G. Vacek, and H.F. Schaefer, *J. Chem. Phys.* **98**, 1336 (1993).
33. J.R. Thomas, B.J. DeLeeuw, G. Vacek, T.D. Crawford, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **99**, 403 (1993).
34. D.A. Clabo, W.D. Allen, R.B. Remington, Y. Yamaguchi, and H.F. Schaefer, *Chem. Phys.* **123**, 187 (1988).
35. W.D. Allen, Y. Yamaguchi, A.G. Császár, D.A. Clabo, R.B. Remington, and H.F. Schaefer, *Chem. Phys.* **145**, 427 (1990).
36. R.J. Clemens, *Chem. Rev.* **86**, 241 (1986).
37. E.T. Seidl and H.F. Schaefer, *J. Am. Chem. Soc.* **112**, 1493 (1990).
38. E.T. Seidl and H.F. Schaefer, *J. Phys. Chem.* **96**, 657 (1992).

Suggested Reading

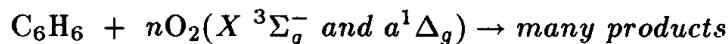
1. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986.
2. H.F. Schaefer and Y. Yamaguchi, *J. Mol. Struct.* **135**, 369 (1986).
3. T.H. Dunning, Jr. Editor, *Advances in Molecular Electronic Structure Theory: Calculation and Characterization of Molecular Potential Energy Surfaces*, JAI Press, Greenwich, Connecticut, 1990.

Chapter 20

The Future

The most obvious statement one can make regarding the future is that we will see *ab initio* analytic derivative studies of *much larger* molecules. If one looks at theoretical chemistry today (May 1993), there are two primary forces behind this drive: the desire to study clusters, associated in large part with the discovery [1] of C₆₀; and the inevitable spread of chemical methods into biology [2]. In the former category, systems as large as the P₆₈ phosphorus cluster and C₁₂₀ carbon cluster have been studied *ab initio*, using not million dollar supercomputers but modestly priced computer workstations [3,4]. In the latter category biological systems as large as the six base pair fragment C₁₁₆H₁₃₈N₄₆O₆₈P₁₀ of DNA have been subjected to all-electron *ab initio* quantum mechanical methods [5]. The very largest systems studied at a given moment in time will be examined at the self-consistent-field (SCF) level of theory, but second-order perturbation theory is also rapidly being extended to very large molecules [6]. With the undiminished, continuing advances in computational power per dollar, and with complementary advances in theoretical/computational methods, it seems likely that the examples cited above will appear routine by the year 2000.

In the hope (perhaps wishful thinking) of achieving a measure of permanence for this monograph, we have focused on theoretical methods and largely limited coverage to the SCF, MCSCF, and configuration interaction (CI) methods. The mathematical techniques required to develop analytic derivative methods for the increasingly important perturbation and coupled cluster methods are closely related [7,8]. Furthermore, key references to perturbation and coupled cluster analytic derivative methods are included in the present bibliography. Also, as the applications chapter immediately preceding demonstrates via several examples, the coupled cluster methods CCSD and CCSD(T) are particularly promising amongst high-level theoretical methods [9,10]. Before the turn of the century, one expects these sophisticated new methods to be regularly applied to rather complicated reactive systems [11] such as the combustion reaction of benzene with molecular oxygen:



By the year 2000 it seems likely that theory will be a full partner with experiment in de-

mystifying the mechanisms of moderate-sized chemical reactions such as the above benzene plus oxygen example.

Theoretical methods that are currently available and highly efficient include SCF and MP2 (Møller-Plesset second-order perturbation theory) analytic first and second derivatives. In the same category but presently applicable to smaller systems are analytic gradients for the CISD, CCSD, and CCSD(T) methods, as well as SCF third and fourth derivative methods. Since this book is decidedly oriented towards methods, a reasonable concluding question is, "What are the most urgently needed new developments in analytic derivative theory ?" From a thoroughly pragmatic perspective, the answer may be open-ended (i.e., applicable to large molecular systems) highly efficient analytic second derivative techniques for the CISD, CCSD, and CCSD(T) methods. The fundamental theory has been established for the first two methods (CISD [12] and CCSD [13]) and preliminary applications have been reported. However, these methods are (a) only marginally more efficient than the use of numerical finite differences of analytic first derivatives and (b) have been thus far restricted in applicability due to the large number of intermediate quantities stored in memory. The unrelenting drop in the cost of computer memory is already making limitation (b) above less important. However, some new theoretical ideas are probably needed to address the efficiency problem (a). The ready availability of highly efficient coupled cluster analytic second derivative methods would surely open exciting new vistas for computational quantum chemistry.

References

1. R.F. Curl and R.E. Smalley, *Scientific American*, October, 1991, pages 54-63.
2. W.G. Richards, *Pure and Applied Chem.* **65**, 231 (1993).
3. R. Ahlrichs, personal communication.
4. G.E. Scuseria, personal communication.
5. C.F. Melius, M.E. Colvin, and C.L. Janssen, private communication.
6. N.C. Handy, R.D. Amos, J.F. Gaw, J.E. Rice, and E.D. Simandiras, *Chem. Phys. Lett.* **120**, 151 (1985); M. Häser, J. Almlöf, and G.E. Scuseria, *Chem. Phys. Lett.* **181**, 497 (1991).
7. J. Gauss and D. Cremer, *Adv. Quantum Chem.* **23**, 206 (1992).
8. A.C. Scheiner, G.E. Scuseria, J.E. Rice, T.J. Lee, and H.F. Schaefer, *J. Chem. Phys.* **87**, 5361 (1987).
9. J.R. Thomas, B.J. DeLeeuw, G. Vacek, and H.F. Schaefer, *J. Chem. Phys.* **98**, 1336 (1993).
10. G.E. Scuseria and T.J. Lee, *J. Chem. Phys.* **93**, 5851 (1990).
11. J.A. Miller and G.A. Fisk, "Combustion Chemistry", pages 22-46, August 31, 1987 *Chemical & Engineering News*.
12. T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, *J. Chem. Phys.* **85**, 3930 (1986).
13. H. Koch, H. J. Aa. Jensen, P. Jørgensen, T. Helgaker, G.E. Scuseria, and H.F. Schaefer, *J. Chem. Phys.* **92**, 4924 (1990).

Appendix A

Some Elementary Definitions

Electronic Hamiltonian

$$\mathbf{H}_{elec} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_A^N \frac{Z_A}{r_{iA}} + \sum_{i>j}^n \frac{1}{r_{ij}} \quad (\text{A.1})$$

$$= \sum_i^n \mathbf{h}(i) + \sum_{i>j}^n \frac{1}{r_{ij}} \quad (\text{A.2})$$

LCAO-MO Approximation

$$\phi_i(r) = \sum_{\mu}^{AO} C_{\mu}^i \chi_{\mu}(r) \quad (\text{A.3})$$

Slater-Type Orbital (STO)

$$\chi_{\mu}^{STO}(r) = N x^l y^m z^n \exp(-\zeta r) \quad (\text{A.4})$$

Gaussian-Type Orbital (GTO)

$$\chi_{\mu}^{GTO}(r) = N x^l y^m z^n \exp(-\alpha r^2) \quad (\text{A.5})$$

Appendix B

Definition of Integrals

Atomic Orbital (AO) Integrals

$$S_{\mu\nu} = \int \chi_{\mu}^{*}(1)\chi_{\nu}(1)d\tau_1 = \langle \chi_{\mu} | \chi_{\nu} \rangle \quad (\text{B.1})$$

$$h_{\mu\nu} = \int \chi_{\mu}^{*}(1)\mathbf{h}(1)\chi_{\nu}(1)d\tau_1 = \langle \chi_{\mu} | \mathbf{h} | \chi_{\nu} \rangle \quad (\text{B.2})$$

$$(\mu\nu|\rho\sigma) = \int \int \chi_{\mu}^{*}(1)\chi_{\nu}(1)\frac{1}{r_{12}}\chi_{\rho}^{*}(2)\chi_{\sigma}(2)d\tau_1 d\tau_2 = [\chi_{\mu}\chi_{\nu}|\frac{1}{r_{12}}|\chi_{\rho}\chi_{\sigma}] \quad (\text{B.3})$$

Molecular Orbital (MO) Integrals

$$S_{ij} = \int \phi_i^{*}(1)\phi_j(1)d\tau_1 \quad (\text{B.4})$$

$$= \langle \phi_i | \phi_j \rangle \quad (\text{B.5})$$

$$= \sum_{\mu\nu}^{AO} C_{\mu}^{i*} C_{\nu}^j S_{\mu\nu} \quad (\text{B.6})$$

$$h_{ij} = \int \phi_i^{*}(1)\mathbf{h}(1)\phi_j(1)d\tau_1 \quad (\text{B.7})$$

$$= \langle \phi_i | \mathbf{h} | \phi_j \rangle \quad (\text{B.8})$$

$$= \sum_{\mu\nu}^{AO} C_{\mu}^{i*} C_{\nu}^j h_{\mu\nu} \quad (\text{B.9})$$

$$(ij|kl) = \int \int \phi_i^*(1)\phi_j(1) \frac{1}{r_{12}} \phi_k^*(2)\phi_l(2) d\tau_1 d\tau_2 \quad (\text{B.10})$$

$$= [\phi_i \phi_j | \frac{1}{r_{12}} | \phi_k \phi_l] \quad (\text{B.11})$$

$$= \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^{i*} C_\nu^j C_\rho^{k*} C_\sigma^l (\mu\nu|\rho\sigma) \quad (\text{B.12})$$

Appendix C

Electronic Energy Expressions

Closed-Shell Self-Consistent-Field (CLSCF)

$$E_{elec} = 2 \sum_i^{d.o.} h_{ii} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj) - (ij|ij) \right\} \quad (C.1)$$

General Restricted Open-Shell Self-Consistent-Field (GRSCF)

$$E_{elec} = 2 \sum_i^{all} f_i h_{ii} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad (C.2)$$

Configuration Interaction (CI)

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (C.3)$$

$$= \sum_{IJ}^{CI} C_I C_J \left[Q_{ij}^{IJ} h_{ij} + G_{ijkl}^{IJ}(ij|kl) \right] \quad (C.4)$$

$$= \sum_{ij}^{MO} Q_{ij} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl) \quad (C.5)$$

Two-Configuration (TC) SCF and Paired Excitation Multiconfiguration (PEMC) SCF

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (C.6)$$

$$= \sum_{IJ}^{CI} C_I C_J \left[2 \sum_i^{MO} f_i^{IJ} h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}^{IJ}(ii|jj) + \beta_{ij}^{IJ}(ij|ij) \right\} \right] \quad (C.7)$$

$$= 2 \sum_i^{MO} f_i h_{ii} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad (C.8)$$

Multiconfiguration (MC) SCF

$$E_{elec} = \sum_{IJ}^{CI} C_I C_J H_{IJ} \quad (C.9)$$

$$= \sum_{IJ}^{CI} C_I C_J \left[\gamma_{ij}^{IJ} h_{ij} + \Gamma_{ijkl}^{IJ}(ij|kl) \right] \quad (C.10)$$

$$= \sum_{ij}^{MO} \gamma_{ij} h_{ij} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl) \quad (C.11)$$

Appendix D

Relationships between Reduced Density Matrices and Coupling Constant Matrices

CI

$$Q_{ij} = \sum_{IJ}^{CI} C_I C_J Q_{ij}^{IJ} \quad (D.1)$$

$$G_{ijkl} = \sum_{IJ}^{CI} C_I C_J G_{ijkl}^{IJ} \quad (D.2)$$

TCSCF and PEMCSCF

$$f_i = \sum_{IJ}^{CI} C_I C_J f_i^{IJ} \quad (D.3)$$

$$\alpha_{ij} = \sum_{IJ}^{CI} C_I C_J \alpha_{ij}^{IJ} \quad (D.4)$$

$$\beta_{ij} = \sum_{IJ}^{CI} C_I C_J \beta_{ij}^{IJ} \quad (D.5)$$

MCSCF

$$\gamma_{ij} = \sum_{IJ}^{CI} C_I C_J \gamma_{ij}^{IJ} \quad (\text{D.6})$$

$$\Gamma_{ijkl} = \sum_{IJ}^{CI} C_I C_J \Gamma_{ijkl}^{IJ} \quad (\text{D.7})$$

Appendix E

Fock and Lagrangian Matrices

CLSCF

$$F_{ij} = h_{ij} + \sum_k^{d.o.} \left\{ 2(ij|kk) - (ik|jk) \right\} \quad (\text{E.1})$$

GRSCF

$$\epsilon_{ij} = f_i h_{ij} + \sum_l^{all} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} \quad (\text{E.2})$$

CI

$$X_{ij} = \sum_m^{MO} Q_{jm} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl) \quad (\text{E.3})$$

TCSCF and PEMCSCF

$$\epsilon_{ij} = f_i h_{ij} + \sum_l^{MO} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} \quad (\text{E.4})$$

MCSCF

$$x_{ij} = \sum_m^{MO} \gamma_{jm} h_{im} + 2 \sum_{mkl}^{MO} \Gamma_{jmkl}(im|kl) \quad (\text{E.5})$$

Appendix F

Variational Conditions and Constraints

CLSCF

$$F_{ij} = \delta_{ij}\epsilon_i \quad (\text{F.1})$$

$$S_{ij} = \delta_{ij} \quad (\text{F.2})$$

GRSCF

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad (\text{F.3})$$

$$S_{ij} = \delta_{ij} \quad (\text{F.4})$$

CI

$$\sum_J^{CI} C_J \left(H_{IJ} - \delta_{IJ} E_{elec} \right) = 0 \quad (\text{F.5})$$

$$\sum_I^{CI} C_I^2 = 1 \quad (\text{F.6})$$

TCSCF and PEMCSCF

$$\epsilon_{ij} - \epsilon_{ji} = 0 \quad (\text{F.7})$$

$$S_{ij} = \delta_{ij} \quad (\text{F.8})$$

$$\sum_J^{CI} C_J (H_{IJ} - \delta_{IJ} E_{elec}) = 0 \quad (\text{F.9})$$

$$\sum_I^{CI} C_I^2 = 1 \quad (\text{F.10})$$

MCSCF

$$x_{ij} - x_{ji} = 0 \quad (\text{F.11})$$

$$S_{ij} = \delta_{ij} \quad (\text{F.12})$$

$$\sum_J^{CI} C_J (H_{IJ} - \delta_{IJ} E_{elec}) = 0 \quad (\text{F.13})$$

$$\sum_I^{CI} C_I^2 = 1 \quad (\text{F.14})$$

Appendix G

Definition of U Matrices

$$\frac{\partial C_\mu^i}{\partial a} = \sum_m^{MO} U_{mi}^a C_\mu^m \quad (G.1)$$

$$\frac{\partial^2 C_\mu^i}{\partial a \partial b} = \sum_m^{MO} U_{mi}^{ab} C_\mu^m \quad (G.2)$$

$$\frac{\partial^3 C_\mu^i}{\partial a \partial b \partial c} = \sum_m^{MO} U_{mi}^{abc} C_\mu^m \quad (G.3)$$

$$\frac{\partial^4 C_\mu^i}{\partial a \partial b \partial c \partial d} = \sum_m^{MO} U_{mi}^{abcd} C_\mu^m \quad (G.4)$$

Appendix H

Relationships among U Matrices

$$\frac{\partial U_{ij}^a}{\partial b} = U_{ij}^{ab} - \sum_k^{MO} U_{ik}^b U_{kj}^a \quad (\text{H.1})$$

$$\frac{\partial U_{ij}^{ab}}{\partial c} = U_{ij}^{abc} - \sum_k^{MO} U_{ik}^c U_{kj}^{ab} \quad (\text{H.2})$$

$$\frac{\partial U_{ij}^{abc}}{\partial d} = U_{ij}^{abcd} - \sum_k^{MO} U_{ik}^d U_{kj}^{abc} \quad (\text{H.3})$$

Appendix I

Definition of Skeleton (Core) Derivative Integrals

Zeroth-Order Definition

$$S_{ij} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j S_{\mu\nu} \quad (I.1)$$

$$h_{ij} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j h_{\mu\nu} \quad (I.2)$$

$$(ij|kl) = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma) \quad (I.3)$$

First Derivatives

$$S_{ij}^a = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial S_{\mu\nu}}{\partial a} \quad (I.4)$$

$$h_{ij}^a = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} \quad (I.5)$$

$$(ij|kl)^a = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial(\mu\nu|\rho\sigma)}{\partial a} \quad (I.6)$$

Second Derivatives

$$S_{ij}^{ab} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} \quad (I.7)$$

$$h_{ij}^{ab} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b} \quad (I.8)$$

$$(ij|kl)^{ab} = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^2 (\mu\nu|\rho\sigma)}{\partial a \partial b} \quad (I.9)$$

Third Derivatives

$$S_{ij}^{abc} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial^3 S_{\mu\nu}}{\partial a \partial b \partial c} \quad (I.10)$$

$$h_{ij}^{abc} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial^3 h_{\mu\nu}}{\partial a \partial b \partial c} \quad (I.11)$$

$$(ij|kl)^{abc} = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^3 (\mu\nu|\rho\sigma)}{\partial a \partial b \partial c} \quad (I.12)$$

Fourth Derivatives

$$S_{ij}^{abcd} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial^4 S_{\mu\nu}}{\partial a \partial b \partial c \partial d} \quad (I.13)$$

$$h_{ij}^{abcd} = \sum_{\mu\nu}^{AO} C_\mu^i C_\nu^j \frac{\partial^4 h_{\mu\nu}}{\partial a \partial b \partial c \partial d} \quad (I.14)$$

$$(ij|kl)^{abcd} = \sum_{\mu\nu\rho\sigma}^{AO} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^4 (\mu\nu|\rho\sigma)}{\partial a \partial b \partial c \partial d} \quad (I.15)$$

Appendix J

First Derivative Expressions for MO Integrals

Overlap Integral

$$\frac{\partial S_{ij}}{\partial a} = S_{ij}^a + \sum_m^{MO} \left(U_{mi}^a S_{mj} + U_{mj}^a S_{im} \right) \quad (J.1)$$

$$= S_{ij}^a + U_{ji}^a + U_{ij}^a = 0 \quad (J.2)$$

One-Electron Integral

$$\frac{\partial h_{ij}}{\partial a} = h_{ij}^a + \sum_m^{MO} \left(U_{mi}^a h_{mj} + U_{mj}^a h_{im} \right) \quad (J.3)$$

Two-Electron Integral

$$\begin{aligned} \frac{\partial(ij|kl)}{\partial a} = & (ij|kl)^a + \sum_m^{MO} \left(U_{mi}^a(mj|kl) + U_{mj}^a(im|kl) \right. \\ & \left. + U_{mk}^a(ij|ml) + U_{ml}^a(ij|km) \right) \end{aligned} \quad (J.4)$$

Appendix K

Expressions for Skeleton (Core) Derivatives

Derivative Overlap Integrals

$$\frac{\partial S_{ij}^a}{\partial b} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{mi}^b S_{mj}^a + U_{mj}^b S_{im}^a \right) \quad (\text{K.1})$$

$$\frac{\partial S_{ij}^{ab}}{\partial c} = S_{ij}^{abc} + \sum_m^{MO} \left(U_{mi}^c S_{mj}^{ab} + U_{mj}^c S_{im}^{ab} \right) \quad (\text{K.2})$$

$$\frac{\partial S_{ij}^{abc}}{\partial d} = S_{ij}^{abcd} + \sum_m^{MO} \left(U_{mi}^d S_{mj}^{abc} + U_{mj}^d S_{im}^{abc} \right) \quad (\text{K.3})$$

Derivative One-Electron Integrals

$$\frac{\partial h_{ij}^a}{\partial b} = h_{ij}^{ab} + \sum_m^{MO} \left(U_{mi}^b h_{mj}^a + U_{mj}^b h_{im}^a \right) \quad (\text{K.4})$$

$$\frac{\partial h_{ij}^{ab}}{\partial c} = h_{ij}^{abc} + \sum_m^{MO} \left(U_{mi}^c h_{mj}^{ab} + U_{mj}^c h_{im}^{ab} \right) \quad (\text{K.5})$$

$$\frac{\partial h_{ij}^{abc}}{\partial d} = h_{ij}^{abcd} + \sum_m^{MO} \left(U_{mi}^d h_{mj}^{abc} + U_{mj}^d h_{im}^{abc} \right) \quad (\text{K.6})$$

Derivative Two-Electron Integrals

$$\frac{\partial(ij|kl)^a}{\partial b} = (ij|kl)^{ab} + \sum_m^{MO} \left(U_{mi}^b(mj|kl)^a + U_{mj}^b(im|kl)^a \right. \\ \left. + U_{mk}^b(ij|ml)^a + U_{ml}^b(ij|km)^a \right) \quad (\text{K.7})$$

$$\frac{\partial(ij|kl)^{ab}}{\partial c} = (ij|kl)^{abc} + \sum_m^{MO} \left(U_{mi}^c(mj|kl)^{ab} + U_{mj}^c(im|kl)^{ab} \right. \\ \left. + U_{mk}^c(ij|ml)^{ab} + U_{ml}^c(ij|km)^{ab} \right) \quad (\text{K.8})$$

$$\frac{\partial(ij|kl)^{abc}}{\partial d} = (ij|kl)^{abcd} + \sum_m^{MO} \left(U_{mi}^d(mj|kl)^{abc} + U_{mj}^d(im|kl)^{abc} \right. \\ \left. + U_{mk}^d(ij|ml)^{abc} + U_{ml}^d(ij|km)^{abc} \right) \quad (\text{K.9})$$

Appendix L

Second Derivative Expressions for MO Integrals

Overlap Integral

$$\begin{aligned} \frac{\partial^2 S_{ij}}{\partial a \partial b} &= S_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} \\ &+ \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \end{aligned} \quad (\text{L.1})$$

$$= S_{ij}^{ab} + \eta_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} \quad (\text{L.2})$$

$$= \xi_{ij}^{ab} + U_{ji}^{ab} + U_{ij}^{ab} = 0 \quad (\text{L.3})$$

where

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \quad (\text{L.4})$$

and

$$\eta_{ij}^{ab} = \sum_m^{MO} \left(U_{im}^a U_{jm}^b + U_{im}^b U_{jm}^a - S_{im}^a S_{jm}^b - S_{im}^b S_{jm}^a \right) \quad (\text{L.5})$$

One-Electron Integral

$$\begin{aligned}
\frac{\partial^2 h_{ij}}{\partial a \partial b} &= h_{ij}^{ab} \\
&+ \sum_m^{MO} \left(U_{mi}^{ab} h_{mj} + U_{mj}^{ab} h_{im} \right) \\
&+ \sum_m^{MO} \left(U_{mi}^a h_{mj}^b + U_{mi}^b h_{mj}^a + U_{nj}^a h_{im}^b + U_{nj}^b h_{im}^a \right) \\
&+ \sum_{mn}^{MO} \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) h_{mn}
\end{aligned} \tag{L.6}$$

Two-Electron Integral

$$\begin{aligned}
\frac{\partial^2 (ij|kl)}{\partial a \partial b} &= (ij|kl)^{ab} \\
&+ \sum_m^{MO} \left\{ U_{mi}^{ab} (mj|kl) + U_{mj}^{ab} (im|kl) + U_{mk}^{ab} (ij|ml) + U_{ml}^{ab} (ij|km) \right\} \\
&+ \sum_m^{MO} \left\{ U_{mi}^a (mj|kl)^b + U_{mj}^a (im|kl)^b + U_{mk}^a (ij|ml)^b + U_{ml}^a (ij|km)^b \right. \\
&\quad \left. + U_{mi}^b (mj|kl)^a + U_{mj}^b (im|kl)^a + U_{mk}^b (ij|ml)^a + U_{ml}^b (ij|km)^a \right\} \\
&+ \sum_{mn}^{MO} \left\{ \left(U_{mi}^a U_{nj}^b + U_{mi}^b U_{nj}^a \right) (mn|kl) + \left(U_{mi}^a U_{nk}^b + U_{mi}^b U_{nk}^a \right) (mj|nl) \right. \\
&\quad \left. + \left(U_{mi}^a U_{nl}^b + U_{mi}^b U_{nl}^a \right) (mj|kn) + \left(U_{mj}^a U_{nk}^b + U_{mj}^b U_{nk}^a \right) (im|nl) \right. \\
&\quad \left. + \left(U_{mj}^a U_{nl}^b + U_{mj}^b U_{nl}^a \right) (im|kn) + \left(U_{mk}^a U_{nl}^b + U_{mk}^b U_{nl}^a \right) (ij|mn) \right\}
\end{aligned} \tag{L.7}$$

Appendix M

Definition of Skeleton (Core) Derivative Matrices for Closed-Shell SCF Wavefunctions

Zeroth-Order Definition

$$F_{ij} = h_{ij} + \sum_k^{d.o.} \left\{ 2(ij|kk) - (ik|jk) \right\} \quad (\text{M.1})$$

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) \quad (\text{M.2})$$

$$E_{clsfc} = 2 \sum_i^{d.o.} h_{ii} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj) - (ij|ij) \right\} \quad (\text{M.3})$$

First Derivatives

$$F_{ij}^a = h_{ij}^a + \sum_k^{d.o.} \left\{ 2(ij|kk)^a - (ik|jk)^a \right\} \quad (\text{M.4})$$

$$A_{ij,kl}^a = 4(ij|kl)^a - (ik|jl)^a - (il|jk)^a \quad (\text{M.5})$$

$$E_{clsfc}^a = 2 \sum_i^{d.o.} h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \quad (\text{M.6})$$

Second Derivatives

$$F_{ij}^{ab} = h_{ij}^{ab} + \sum_k^{d.o.} \left\{ 2(ij|kk)^{ab} - (ik|jk)^{ab} \right\} \quad (\text{M.7})$$

$$A_{ij,kl}^{ab} = 4(ij|kl)^{ab} - (ik|jl)^{ab} - (il|jk)^{ab} \quad (\text{M.8})$$

$$E_{clsrf}^{ab} = 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \quad (\text{M.9})$$

Third Derivatives

$$F_{ij}^{abc} = h_{ij}^{abc} + \sum_k^{d.o.} \left\{ 2(ij|kk)^{abc} - (ik|jk)^{abc} \right\} \quad (\text{M.10})$$

$$A_{ij,kl}^{abc} = 4(ij|kl)^{abc} - (ik|jl)^{abc} - (il|jk)^{abc} \quad (\text{M.11})$$

$$E_{clsrf}^{abc} = 2 \sum_i^{d.o.} h_{ii}^{abc} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{abc} - (ij|ij)^{abc} \right\} \quad (\text{M.12})$$

Fourth Derivatives

$$F_{ij}^{abcd} = h_{ij}^{abcd} + \sum_k^{d.o.} \left\{ 2(ij|kk)^{abcd} - (ik|jk)^{abcd} \right\} \quad (\text{M.13})$$

$$A_{ij,kl}^{abcd} = 4(ij|kl)^{abcd} - (ik|jl)^{abcd} - (il|jk)^{abcd} \quad (\text{M.14})$$

$$E_{clsrf}^{abcd} = 2 \sum_i^{d.o.} h_{ii}^{abcd} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{abcd} - (ij|ij)^{abcd} \right\} \quad (\text{M.15})$$

Appendix N

Expressions for Skeleton (Core) Derivative Matrices for Closed-Shell SCF Wavefunctions

Fock Matrices

$$\frac{\partial F_{ij}}{\partial a} = F_{ij}^a + \sum_k^{all} \left\{ U_{ki}^a F_{kj} + U_{kj}^a F_{ik} \right\} + \sum_k^{all} \sum_l^{d.o.} U_{kl}^a A_{ij,kl} \quad (N.1)$$

$$\frac{\partial F_{ij}^a}{\partial b} = F_{ij}^{ab} + \sum_k^{all} \left\{ U_{ki}^b F_{kj}^a + U_{kj}^b F_{ik}^a \right\} + \sum_k^{all} \sum_l^{d.o.} U_{kl}^b A_{ij,kl}^a \quad (N.2)$$

$$\frac{\partial F_{ij}^{ab}}{\partial c} = F_{ij}^{abc} + \sum_k^{all} \left\{ U_{ki}^c F_{kj}^{ab} + U_{kj}^c F_{ik}^{ab} \right\} + \sum_k^{all} \sum_l^{d.o.} U_{kl}^c A_{ij,kl}^{ab} \quad (N.3)$$

$$\frac{\partial F_{ij}^{abc}}{\partial d} = F_{ij}^{abcd} + \sum_k^{all} \left\{ U_{ki}^d F_{kj}^{abc} + U_{kj}^d F_{ik}^{abc} \right\} + \sum_k^{all} \sum_l^{d.o.} U_{kl}^d A_{ij,kl}^{abc} \quad (N.4)$$

A Matrices

$$\frac{\partial A_{ij,kl}}{\partial a} = A_{ij,kl}^a + \sum_m^{all} \left\{ U_{mi}^a A_{mj,kl} + U_{mj}^a A_{im,kl} + U_{mk}^a A_{ij,ml} + U_{ml}^a A_{ij,km} \right\} \quad (N.5)$$

$$\frac{\partial A_{ij,kl}^a}{\partial b} = A_{ij,kl}^{ab} + \sum_m^{all} \left\{ U_{mi}^b A_{mj,kl}^a + U_{mj}^b A_{im,kl}^a + U_{mk}^b A_{ij,ml}^a + U_{ml}^b A_{ij,km}^a \right\} \quad (\text{N.6})$$

$$\frac{\partial A_{ij,kl}^{ab}}{\partial c} = A_{ij,kl}^{abc} + \sum_m^{all} \left\{ U_{mi}^c A_{mj,kl}^{ab} + U_{mj}^c A_{im,kl}^{ab} + U_{mk}^c A_{ij,ml}^{ab} + U_{ml}^c A_{ij,km}^{ab} \right\} \quad (\text{N.7})$$

$$\frac{\partial A_{ij,kl}^{abc}}{\partial d} = A_{ij,kl}^{abcd} + \sum_m^{all} \left\{ U_{mi}^d A_{mj,kl}^{abc} + U_{mj}^d A_{im,kl}^{abc} + U_{mk}^d A_{ij,ml}^{abc} + U_{ml}^d A_{ij,km}^{abc} \right\} \quad (\text{N.8})$$

Energies

$$\frac{\partial E_{clsrf}}{\partial a} = 2 \sum_i^{d.o.} h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^a F_{ij} \quad (\text{N.9})$$

$$= E_{clsrf}^a + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^a F_{ij} \quad (\text{N.10})$$

$$\frac{\partial E_{clsrf}^a}{\partial b} = 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^b F_{ij}^a \quad (\text{N.11})$$

$$= E_{clsrf}^{ab} + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^b F_{ij}^a \quad (\text{N.12})$$

$$\frac{\partial E_{clsrf}^{ab}}{\partial c} = 2 \sum_i^{d.o.} h_{ii}^{abc} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{abc} - (ij|ij)^{abc} \right\} + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^c F_{ij}^{ab} \quad (\text{N.13})$$

$$= E_{clsrf}^{abc} + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^c F_{ij}^{ab} \quad (\text{N.14})$$

$$\frac{\partial E_{clsrf}^{abc}}{\partial d} = 2 \sum_i^{d.o.} h_{ii}^{abcd} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{abcd} - (ij|ij)^{abcd} \right\} + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^d F_{ij}^{abc} \quad (\text{N.15})$$

$$= E_{clsrf}^{abcd} + 4 \sum_i^{all} \sum_j^{d.o.} U_{ij}^d F_{ij}^{abc} \quad (\text{N.16})$$

Appendix O

Definition of Skeleton (Core) Derivative Matrices for General Restricted Open-Shell SCF Wavefunctions

Zeroth-Order Definition

$$\epsilon_{ij} = f_i h_{ij} + \sum_l^{\text{all}} \left\{ \alpha_{il}(ij|ll) + \beta_{il}(il|jl) \right\} \quad (\text{O.1})$$

$$\zeta_{ij}^l = f_l h_{ij} + \sum_k^{\text{all}} \left\{ \alpha_{lk}(ij|kk) + \beta_{lk}(ik|jk) \right\} \quad (\text{O.2})$$

$$\tau_{ij,kl}^{mn} = 2\alpha_{mn}(ij|kl) + \beta_{mn} \left\{ (ik|jl) + (il|jk) \right\} \quad (\text{O.3})$$

$$E_{grscf} = 2 \sum_i^{\text{all}} f_i h_{ii} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij) \right\} \quad (\text{O.4})$$

First Derivatives

$$\epsilon_{ij}^a = f_i h_{ij}^a + \sum_l^{\text{all}} \left\{ \alpha_{il}(ij|ll)^a + \beta_{il}(il|jl)^a \right\} \quad (\text{O.5})$$

$$\zeta_{ij}^{la} = f_l h_{ij}^a + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk)^a + \beta_{lk}(ik|jk)^a \right\} \quad (O.6)$$

$$\tau_{ij,kl}^{mn^a} = 2\alpha_{mn}(ij|kl)^a + \beta_{mn} \left\{ (ik|jl)^a + (il|jk)^a \right\} \quad (O.7)$$

$$E_{grscf}^a = 2 \sum_i^{all} f_i h_{ii}^a + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \quad (O.8)$$

Second Derivatives

$$\epsilon_{ij}^{ab} = f_i h_{ij}^{ab} + \sum_l^{all} \left\{ \alpha_{il}(ij|ll)^{ab} + \beta_{il}(il|jl)^{ab} \right\} \quad (O.9)$$

$$\zeta_{ij}^{lab} = f_l h_{ij}^{ab} + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk)^{ab} + \beta_{lk}(ik|jk)^{ab} \right\} \quad (O.10)$$

$$\tau_{ij,kl}^{mn^{ab}} = 2\alpha_{mn}(ij|kl)^{ab} + \beta_{mn} \left\{ (ik|jl)^{ab} + (il|jk)^{ab} \right\} \quad (O.11)$$

$$E_{grscf}^{ab} = 2 \sum_i^{all} f_i h_{ii}^{ab} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \quad (O.12)$$

Third Derivatives

$$\epsilon_{ij}^{abc} = f_i h_{ij}^{abc} + \sum_l^{all} \left\{ \alpha_{il}(ij|ll)^{abc} + \beta_{il}(il|jl)^{abc} \right\} \quad (O.13)$$

$$\zeta_{ij}^{abc} = f_l h_{ij}^{abc} + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk)^{abc} + \beta_{lk}(ik|jk)^{abc} \right\} \quad (O.14)$$

$$\tau_{ij,kl}^{mn^{abc}} = 2\alpha_{mn}(ij|kl)^{abc} + \beta_{mn} \left\{ (ik|jl)^{abc} + (il|jk)^{abc} \right\} \quad (O.15)$$

$$E_{grscf}^{abc} = 2 \sum_i^{all} f_i h_{ii}^{abc} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{abc} + \beta_{ij}(ij|ij)^{abc} \right\} \quad (O.16)$$

Fourth Derivatives

$$\epsilon_{ij}^{abcd} = f_i h_{ij}^{abcd} + \sum_l^{all} \left\{ \alpha_{il}(ij|ll)^{abcd} + \beta_{il}(il|jl)^{abcd} \right\} \quad (O.17)$$

$$\zeta_{ij}^{abcd} = f_l h_{ij}^{abcd} + \sum_k^{all} \left\{ \alpha_{lk}(ij|kk)^{abcd} + \beta_{lk}(ik|jk)^{abcd} \right\} \quad (O.18)$$

$$\tau_{ij,kl}^{mnabcd} = 2\alpha_{mn}(ij|kl)^{abcd} + \beta_{mn} \left\{ (ik|jl)^{abcd} + (il|jk)^{abcd} \right\} \quad (O.19)$$

$$E_{grscf}^{abcd} = 2 \sum_i^{all} f_i h_{ii}^{abcd} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{abcd} + \beta_{ij}(ij|ij)^{abcd} \right\} \quad (O.20)$$

Appendix P

Expressions for Skeleton (Core) Derivative Matrices for General Restricted Open-Shell SCF Wavefunctions

Lagrangian Matrices

$$\frac{\partial \epsilon_{ij}^a}{\partial a} = \epsilon_{ij}^a + \sum_k^{all} \left\{ U_{ki}^a \zeta_{kj}^i + U_{kj}^a \epsilon_{ik} \right\} + \sum_{kl}^{all} U_{kl}^a \tau_{ij,kl}^{il} \quad (\text{P.1})$$

$$\frac{\partial \epsilon_{ij}^a}{\partial b} = \epsilon_{ij}^{ab} + \sum_k^{all} \left\{ U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right\} + \sum_{kl}^{all} U_{kl}^b \tau_{ij,kl}^{il^a} \quad (\text{P.2})$$

$$\frac{\partial \epsilon_{ij}^{ab}}{\partial c} = \epsilon_{ij}^{abc} + \sum_k^{all} \left\{ U_{ki}^c \zeta_{kj}^{iab} + U_{kj}^c \epsilon_{ik}^{ab} \right\} + \sum_{kl}^{all} U_{kl}^c \tau_{ij,kl}^{il^{ab}} \quad (\text{P.3})$$

$$\frac{\partial \epsilon_{ij}^{abc}}{\partial d} = \epsilon_{ij}^{abcd} + \sum_k^{all} \left\{ U_{ki}^d \zeta_{kj}^{iabc} + U_{kj}^d \epsilon_{ik}^{abc} \right\} + \sum_{kl}^{all} U_{kl}^d \tau_{ij,kl}^{il^{abc}} \quad (\text{P.4})$$

Generalized Lagrangian Matrices

$$\frac{\partial \zeta_{ij}^l}{\partial a} = \zeta_{ij}^{la} + \sum_m^{all} \left\{ U_{mi}^a \zeta_{mj}^l + U_{mj}^a \zeta_{im}^l \right\} + \sum_{mn}^{all} U_{mn}^a \tau_{ij,mn}^{ln} \quad (\text{P.5})$$

$$\frac{\partial \zeta_{ij}^{l^a}}{\partial b} = \zeta_{ij}^{l^{ab}} + \sum_m^{all} \left\{ U_{mi}^b \zeta_{mj}^{l^a} + U_{mj}^b \zeta_{im}^{l^a} \right\} + \sum_{mn}^{all} U_{mn}^b \tau_{ij,mn}^{ln^a} \quad (\text{P.6})$$

$$\frac{\partial \zeta_{ij}^{l^{ab}}}{\partial c} = \zeta_{ij}^{l^{abc}} + \sum_m^{all} \left\{ U_{mi}^c \zeta_{mj}^{l^{ab}} + U_{mj}^c \zeta_{im}^{l^{ab}} \right\} + \sum_{mn}^{all} U_{mn}^c \tau_{ij,mn}^{ln^{ab}} \quad (\text{P.7})$$

$$\frac{\partial \zeta_{ij}^{l^{abc}}}{\partial d} = \zeta_{ij}^{l^{abcd}} + \sum_m^{all} \left\{ U_{mi}^d \zeta_{mj}^{l^{abc}} + U_{mj}^d \zeta_{im}^{l^{abc}} \right\} + \sum_{mn}^{all} U_{mn}^d \tau_{ij,mn}^{ln^{abc}} \quad (\text{P.8})$$

τ Matrices

$$\frac{\partial \tau_{ij,kl}^{mn}}{\partial a} = \tau_{ij,kl}^{mn^a} + \sum_p^{all} \left\{ U_{pi}^a \tau_{pj,kl}^{mn} + U_{pj}^a \tau_{ip,kl}^{mn} + U_{pk}^a \tau_{ij,pl}^{mn} + U_{pl}^a \tau_{ij,kp}^{mn} \right\} \quad (\text{P.9})$$

$$\frac{\partial \tau_{ij,kl}^{mn^a}}{\partial b} = \tau_{ij,kl}^{mn^{ab}} + \sum_p^{all} \left\{ U_{pi}^b \tau_{pj,kl}^{mn^a} + U_{pj}^b \tau_{ip,kl}^{mn^a} + U_{pk}^b \tau_{ij,pl}^{mn^a} + U_{pl}^b \tau_{ij,kp}^{mn^a} \right\} \quad (\text{P.10})$$

$$\frac{\partial \tau_{ij,kl}^{mn^{ab}}}{\partial c} = \tau_{ij,kl}^{mn^{abc}} + \sum_p^{all} \left\{ U_{pi}^c \tau_{pj,kl}^{mn^{ab}} + U_{pj}^c \tau_{ip,kl}^{mn^{ab}} + U_{pk}^c \tau_{ij,pl}^{mn^{ab}} + U_{pl}^c \tau_{ij,kp}^{mn^{ab}} \right\} \quad (\text{P.11})$$

$$\frac{\partial \tau_{ij,kl}^{mn^{abc}}}{\partial d} = \tau_{ij,kl}^{mn^{abcd}} + \sum_p^{all} \left\{ U_{pi}^d \tau_{pj,kl}^{mn^{abc}} + U_{pj}^d \tau_{ip,kl}^{mn^{abc}} + U_{pk}^d \tau_{ij,pl}^{mn^{abc}} + U_{pl}^d \tau_{ij,kp}^{mn^{abc}} \right\} \quad (\text{P.12})$$

Energies

$$\begin{aligned} \frac{\partial E_{grscf}}{\partial a} &= 2 \sum_i^{all} f_i h_{ii}^a + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} + 4 \sum_{ij}^{all} U_{ij}^a \epsilon_{ji} \\ &\quad (\text{P.13}) \end{aligned}$$

$$= E_{grscf}^a + 4 \sum_{ij}^{all} U_{ij}^a \epsilon_{ji} \quad (\text{P.14})$$

$$\frac{\partial E_{grscf}^a}{\partial b} = 2 \sum_i^{all} f_i h_{ii}^{ab} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} + 4 \sum_{ij}^{all} U_{ij}^b \epsilon_{ji}^a \quad (\text{P.15})$$

$$= E_{grscf}^{ab} + 4 \sum_{ij}^{all} U_{ij}^b \epsilon_{ji}^a \quad (\text{P.16})$$

$$\frac{\partial E_{grscf}^{ab}}{\partial c} = 2 \sum_i^{all} f_i h_{ii}^{abc} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{abc} + \beta_{ij}(ij|ij)^{abc} \right\} + 4 \sum_{ij}^{all} U_{ij}^c \epsilon_{ji}^{ab} \quad (\text{P.17})$$

$$= E_{grscf}^{abc} + 4 \sum_{ij}^{all} U_{ij}^c \epsilon_{ji}^{ab} \quad (\text{P.18})$$

$$\frac{\partial E_{grscf}^{abc}}{\partial d} = 2 \sum_i^{all} f_i h_{ii}^{abcd} + \sum_{ij}^{all} \left\{ \alpha_{ij}(ii|jj)^{abcd} + \beta_{ij}(ij|ij)^{abcd} \right\} + 4 \sum_{ij}^{all} U_{ij}^d \epsilon_{ji}^{abc} \quad (\text{P.19})$$

$$= E_{grscf}^{abcd} + 4 \sum_{ij}^{all} U_{ij}^d \epsilon_{ji}^{abc} \quad (\text{P.20})$$

Appendix Q

Definition of Skeleton (Core) Derivative “Bare” Matrices for CI and MCSCF Wavefunctions

Zeroth-Order Definition

$$H_{IJ} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl) \quad (Q.1)$$

$$X_{ij}^{IJ} = \sum_m^{MO} Q_{jm}^{IJ} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl) \quad (Q.2)$$

$$Y_{ijkl}^{IJ} = Q_{jl}^{IJ} h_{ik} + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ}(ik|mn) + 4 \sum_{mn}^{MO} G_{jmkn}^{IJ}(im|kn) \quad (Q.3)$$

First Derivatives

$$H_{IJ}^a = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^a \quad (Q.4)$$

$$X_{ij}^{IJ^a} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl)^a \quad (Q.5)$$

$$Y_{ijkl}^{IJ^a} = Q_{jl}^{IJ} h_{ik}^a + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ}(ik|mn)^a + 4 \sum_{mn}^{MO} G_{jmkn}^{IJ}(im|kn)^a \quad (Q.6)$$

Second Derivatives

$$H_{IJ}^{ab} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^{ab} \quad (\text{Q.7})$$

$$X_{ij}^{IJab} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^{ab} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl)^{ab} \quad (\text{Q.8})$$

$$Y_{ijkl}^{IJab} = Q_{jl}^{IJ} h_{ik}^{ab} + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ}(ik|mn)^{ab} + 4 \sum_{mn}^{MO} G_{jmkn}^{IJ}(im|kn)^{ab} \quad (\text{Q.9})$$

Third Derivatives

$$H_{IJ}^{abc} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{abc} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^{abc} \quad (\text{Q.10})$$

$$X_{ij}^{IJabc} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^{abc} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl)^{abc} \quad (\text{Q.11})$$

$$Y_{ijkl}^{IJabc} = Q_{jl}^{IJ} h_{ik}^{abc} + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ}(ik|mn)^{abc} + 4 \sum_{mn}^{MO} G_{jmkn}^{IJ}(im|kn)^{abc} \quad (\text{Q.12})$$

Fourth Derivatives

$$H_{IJ}^{abcd} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij}^{abcd} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl)^{abcd} \quad (\text{Q.13})$$

$$X_{ij}^{IJabcd} = \sum_m^{MO} Q_{jm}^{IJ} h_{im}^{abcd} + 2 \sum_{mkl}^{MO} G_{jmkl}^{IJ}(im|kl)^{abcd} \quad (\text{Q.14})$$

$$Y_{ijkl}^{IJabcd} = Q_{jl}^{IJ} h_{ik}^{abcd} + 2 \sum_{mn}^{MO} G_{jlmn}^{IJ}(ik|mn)^{abcd} + 4 \sum_{mn}^{MO} G_{jmkn}^{IJ}(im|kn)^{abcd} \quad (\text{Q.15})$$

Appendix R

Expressions for Skeleton (Core) Derivative Hamiltonian Matrices for CI and MCSCF Wavefunctions

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \quad (\text{R.1})$$

$$\frac{\partial H_{IJ}^a}{\partial b} = H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^b X_{ij}^{IJ^a} \quad (\text{R.2})$$

$$\frac{\partial H_{IJ}^{ab}}{\partial c} = H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^c X_{ij}^{IJ^{ab}} \quad (\text{R.3})$$

$$\frac{\partial H_{IJ}^{abc}}{\partial d} = H_{IJ}^{abcd} + 2 \sum_{ij}^{MO} U_{ij}^d X_{ij}^{IJ^{abc}} \quad (\text{R.4})$$

Appendix S

Definition of Skeleton (Core) Derivative Lagrangian and Y Matrices for CI and MCSCF Wavefunctions

Zeroth-Order Definition

$$X_{ij} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJ} \quad (S.1)$$

$$= \sum_m^{MO} Q_{jm} h_{im} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl) \quad (S.2)$$

$$Y_{ijkl} = \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJ} \quad (S.3)$$

$$= Q_{jl} h_{ik} + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn) + 4 \sum_{mn}^{MO} G_{jmkn}(im|kn) \quad (S.4)$$

First Derivatives

$$X_{ij}^a = \sum_{IJ}^{CI} C_I C_J X_{ij}^{IJa} \quad (S.5)$$

$$= \sum_m^{MO} Q_{jm} h_{im}^a + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^a \quad (S.6)$$

$$Y_{ijkl}^a = \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJ^a} \quad (S.7)$$

$$= Q_{jl} h_{ik}^a + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn)^a + 4 \sum_{mn}^{MO} G_{jmkn}(im|kn)^a \quad (S.8)$$

Second Derivatives

$$X_{ij}^{ab} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{ab} \quad (S.9)$$

$$= \sum_m^{MO} Q_{jm} h_{im}^{ab} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^{ab} \quad (S.10)$$

$$Y_{ijkl}^{ab} = \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJ^{ab}} \quad (S.11)$$

$$= Q_{jl} h_{ik}^{ab} + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn)^{ab} + 4 \sum_{mn}^{MO} G_{jmkn}(im|kn)^{ab} \quad (S.12)$$

Third Derivatives

$$X_{ij}^{abc} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{abc} \quad (S.13)$$

$$= \sum_m^{MO} Q_{jm} h_{im}^{abc} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^{abc} \quad (S.14)$$

$$Y_{ijkl}^{abc} = \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJ^{abc}} \quad (S.15)$$

$$= Q_{jl} h_{ik}^{abc} + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn)^{abc} + 4 \sum_{mn}^{MO} G_{jmkn}(im|kn)^{abc} \quad (S.16)$$

Fourth Derivatives

$$X_{ij}^{abcd} = \sum_{IJ}^{CI} C_I C_J X_{ij}^{abcd} \quad (S.17)$$

$$= \sum_m^{MO} Q_{jm} h_{im}^{abcd} + 2 \sum_{mkl}^{MO} G_{jmkl}(im|kl)^{abcd} \quad (S.18)$$

$$Y_{ijkl}^{abcd} = \sum_{IJ}^{CI} C_I C_J Y_{ijkl}^{IJabcd} \quad (S.19)$$

$$= Q_{jl} h_{ik}^{abcd} + 2 \sum_{mn}^{MO} G_{jlmn}(ik|mn)^{abcd} + 4 \sum_{mn}^{MO} G_{jmkn}(im|kn)^{abcd} \quad (S.20)$$

Appendix T

Derivative Expressions for Skeleton (Core) “Bare” Matrices for CI and MCSCF Wavefunctions

“Bare” Lagrangian Matrices

$$\frac{\partial X_{ij}^{IJ}}{\partial a} = X_{ij}^{IJ^a} + \sum_k^{MO} U_{ki}^a X_{kj}^{IJ} + \sum_{kl}^{MO} U_{kl}^a Y_{ijkl}^{IJ} \quad (\text{T.1})$$

$$\frac{\partial X_{ij}^{IJ^a}}{\partial b} = X_{ij}^{IJ^{ab}} + \sum_k^{MO} U_{ki}^b X_{kj}^{IJ^a} + \sum_{kl}^{MO} U_{kl}^b Y_{ijkl}^{IJ^a} \quad (\text{T.2})$$

$$\frac{\partial X_{ij}^{IJ^{ab}}}{\partial c} = X_{ij}^{IJ^{abc}} + \sum_k^{MO} U_{ki}^c X_{kj}^{IJ^{ab}} + \sum_{kl}^{MO} U_{kl}^c Y_{ijkl}^{IJ^{ab}} \quad (\text{T.3})$$

$$\frac{\partial X_{ij}^{IJ^{abc}}}{\partial d} = X_{ij}^{IJ^{abcd}} + \sum_k^{MO} U_{ki}^d X_{kj}^{IJ^{abc}} + \sum_{kl}^{MO} U_{kl}^d Y_{ijkl}^{IJ^{abc}} \quad (\text{T.4})$$

“Bare” Y Matrices

$$\begin{aligned} \frac{\partial Y_{ijkl}^{IJ}}{\partial a} &= Y_{ijkl}^{IJ^a} + \sum_p^{MO} U_{pi}^a Y_{pjkl}^{IJ} + \sum_p^{MO} U_{pk}^a Y_{ijpl}^{IJ} \\ &+ 4 \sum_{mnp}^{MO} U_{pm}^a \left\{ G_{jlmn}^{IJ}(ik|pn) + G_{jmtn}^{IJ}(ip|kn) + G_{jnlm}^{IJ}(in|kp) \right\} \end{aligned} \quad (\text{T.5})$$

$$\begin{aligned} \frac{\partial Y_{ijkl}^{IJ^a}}{\partial b} &= Y_{ijkl}^{IJ^{ab}} + \sum_p^{MO} U_{pi}^b Y_{pjkl}^{IJ^a} + \sum_p^{MO} U_{pk}^b Y_{ijpl}^{IJ^a} \\ &+ 4 \sum_{mnp}^{MO} U_{pm}^b \left\{ G_{jlmn}^{IJ}(ik|pn)^a + G_{jmkn}^{IJ}(ip|kn)^a + G_{jnkm}^{IJ}(in|kp)^a \right\} \end{aligned} \quad (\text{T.6})$$

$$\begin{aligned} \frac{\partial Y_{ijkl}^{IJ^{ab}}}{\partial c} &= Y_{ijkl}^{IJ^{abc}} + \sum_p^{MO} U_{pi}^c Y_{pjkl}^{IJ^{ab}} + \sum_p^{MO} U_{pk}^c Y_{ijpl}^{IJ^{ab}} \\ &+ 4 \sum_{mnp}^{MO} U_{pm}^c \left\{ G_{jlmn}^{IJ}(ik|pn)^{ab} + G_{jmkn}^{IJ}(ip|kn)^{ab} + G_{jnkm}^{IJ}(in|kp)^{ab} \right\} \end{aligned} \quad (\text{T.7})$$

$$\begin{aligned} \frac{\partial Y_{ijkl}^{IJ^{abc}}}{\partial d} &= Y_{ijkl}^{IJ^{abcd}} + \sum_p^{MO} U_{pi}^d Y_{pjkl}^{IJ^{abc}} + \sum_p^{MO} U_{pk}^d Y_{ijpl}^{IJ^{abc}} \\ &+ 4 \sum_{mnp}^{MO} U_{pm}^d \left\{ G_{jlmn}^{IJ}(ik|pn)^{abc} + G_{jmkn}^{IJ}(ip|kn)^{abc} + G_{jnkm}^{IJ}(in|kp)^{abc} \right\} \end{aligned} \quad (\text{T.8})$$

Appendix U

Derivative Expressions for Hamiltonian Matrices for CI and MCSCF Wavefunctions

Zeroth-Order Definition

$$H_{IJ} = \sum_{ij}^{MO} Q_{ij}^{IJ} h_{ij} + \sum_{ijkl}^{MO} G_{ijkl}^{IJ}(ij|kl) \quad (\text{U.1})$$

First Derivative

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}^{IJ} \quad (\text{U.2})$$

Second Derivative

$$\begin{aligned} \frac{\partial^2 H_{IJ}}{\partial a \partial b} &= H_{IJ}^{ab} + 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij}^{IJ} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^{IJ^a} + U_{ij}^a X_{ij}^{IJ^b} \right) \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl}^{IJ} \end{aligned} \quad (\text{U.3})$$

Third Derivative

$$\begin{aligned}
\frac{\partial^3 H_{IJ}}{\partial a \partial b \partial c} = & H_{IJ}^{abc} + 2 \sum_{ij}^{MO} U_{ij}^{abc} X_{ij}^{IJ} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{IJc} + U_{ij}^{bc} X_{ij}^{IJa} + U_{ij}^{ca} X_{ij}^{IJb} \right) \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{IJbc} + U_{ij}^b X_{ij}^{IJca} + U_{ij}^c X_{ij}^{IJab} \right) \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{IJc} + U_{ij}^b U_{kl}^c Y_{ijkl}^{IJa} + U_{ij}^c U_{kl}^a Y_{ijkl}^{IJb} \right) \\
& + 8 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c + U_{ij}^b U_{kl}^c U_{mn}^a + U_{ij}^c U_{kl}^a U_{mn}^b \right) \sum_p^{MO} G_{jlnp}^{IJ}(ik|mp)
\end{aligned} \tag{U.4}$$

Fourth Derivative

$$\begin{aligned}
\frac{\partial^4 H_{IJ}}{\partial a \partial b \partial c \partial d} = & H_{IJ}^{abcd} + 2 \sum_{ij}^{MO} U_{ij}^{abcd} X_{ij}^{IJ} \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{abc} X_{ij}^{IJd} + U_{ij}^{abd} X_{ij}^{IJc} + U_{ij}^{acd} X_{ij}^{IJb} + U_{ij}^{bcd} X_{ij}^{IJa} \right) \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^{ab} X_{ij}^{IJcd} + U_{ij}^{ac} X_{ij}^{IJbd} + U_{ij}^{ad} X_{ij}^{IJbc} \right. \\
& \quad \left. + U_{ij}^{bc} X_{ij}^{IJad} + U_{ij}^{bd} X_{ij}^{IJac} + U_{ij}^{cd} X_{ij}^{IJab} \right) \\
& + 2 \sum_{ij}^{MO} \left(U_{ij}^a X_{ij}^{IJbcd} + U_{ij}^b X_{ij}^{IJcad} + U_{ij}^c X_{ij}^{IJdab} + U_{ij}^d X_{ij}^{IJabc} \right) \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{abc} U_{kl}^d + U_{ij}^{abd} U_{kl}^c + U_{ij}^{acd} U_{kl}^b + U_{ij}^{bcd} U_{kl}^a \right) Y_{ijkl}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^{cd} + U_{ij}^{ac} U_{kl}^{bd} + U_{ij}^{ad} U_{kl}^{bc} \right) Y_{ijkl}^{IJ} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^c + U_{ij}^{bc} U_{kl}^a + U_{ij}^{ca} U_{kl}^b \right) Y_{ijkl}^{IJd}
\end{aligned}$$

$$\begin{aligned}
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{ab} U_{kl}^d + U_{ij}^{bd} U_{kl}^a + U_{ij}^{ab} U_{kl}^b \right) Y_{ijkl}^{IJc} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^a + U_{ij}^{ac} U_{kl}^d + U_{ij}^{ad} U_{kl}^c \right) Y_{ijkl}^{IJb} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^{cd} U_{kl}^b + U_{ij}^{bd} U_{kl}^c + U_{ij}^{bc} U_{kl}^d \right) Y_{ijkl}^{IJa} \\
& + 2 \sum_{ijkl}^{MO} \left(U_{ij}^a U_{kl}^b Y_{ijkl}^{IJcd} + U_{ij}^a U_{kl}^c Y_{ijkl}^{IJbd} + U_{ij}^a U_{kl}^d Y_{ijkl}^{IJbc} \right. \\
& \quad \left. + U_{ij}^c U_{kl}^d Y_{ijkl}^{IJab} + U_{ij}^b U_{kl}^d Y_{ijkl}^{IJca} + U_{ij}^b U_{kl}^c Y_{ijkl}^{IJad} \right) \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^{ab} U_{kl}^c U_{mn}^d + U_{ij}^{ac} U_{kl}^b U_{mn}^d + U_{ij}^{ad} U_{kl}^b U_{mn}^c \right. \\
& \quad \left. + U_{ij}^{bc} U_{kl}^a U_{mn}^d + U_{ij}^{bd} U_{kl}^a U_{mn}^c + U_{ij}^{cd} U_{kl}^a U_{mn}^b \right) Z_{ijklmn}^{IJ} \\
& + 2 \sum_{ijklmn}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c Z_{ijklmn}^{IJd} + U_{ij}^a U_{kl}^b U_{mn}^d Z_{ijklmn}^{IJc} \right. \\
& \quad \left. + U_{ij}^a U_{kl}^c U_{mn}^d Z_{ijklmn}^{IJb} + U_{ij}^b U_{kl}^c U_{mn}^d Z_{ijklmn}^{IJa} \right) \\
& + 8 \sum_{ijklmno}^{MO} \left(U_{ij}^a U_{kl}^b U_{mn}^c U_{op}^d + U_{ij}^a U_{kl}^c U_{mn}^b U_{op}^d + U_{ij}^a U_{kl}^d U_{mn}^b U_{op}^c \right) \\
& \quad \times G_{jlnp}^{IJ}(ik|mo)
\end{aligned} \tag{U.5}$$

Appendix V

First and Second Electronic Energy Derivatives

CLSCF

First Derivative

$$\begin{aligned} \frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{d.o.} h_{ii}^a + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^a - (ij|ij)^a \right\} \\ &- 2 \sum_i^{d.o.} S_{ii}^a \epsilon_i \end{aligned} \quad (\text{V.1})$$

Second Derivative

$$\begin{aligned} \frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{d.o.} h_{ii}^{ab} + \sum_{ij}^{d.o.} \left\{ 2(ii|jj)^{ab} - (ij|ij)^{ab} \right\} \\ &- 2 \sum_i^{d.o.} S_{ii}^{ab} \epsilon_i - 2 \sum_i^{d.o.} \eta_{ii}^{ab} \epsilon_i \\ &+ 4 \sum_i^{all d.o.} \sum_j^{d.o.} \left(U_{ij}^b F_{ij}^a + U_{ij}^a F_{ij}^b \right) \\ &+ 4 \sum_i^{all d.o.} \sum_j^{d.o.} U_{ij}^a U_{ij}^b \epsilon_i + 4 \sum_i^{all d.o.} \sum_j^{d.o.} \sum_k^{all d.o.} \sum_l^{d.o.} U_{ij}^a U_{kl}^b A_{ij,kl} \end{aligned} \quad (\text{V.2})$$

GRSCF

First Derivative

$$\begin{aligned}\frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{\text{all}} f_i h_{ii}^a + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{\text{all}} S_{ij}^a \epsilon_{ij}\end{aligned}\quad (\text{V.3})$$

Second Derivative

$$\begin{aligned}\frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{\text{all}} f_i h_{ii}^{ab} + \sum_{ij}^{\text{all}} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &- 2 \sum_{ij}^{\text{all}} S_{ij}^{ab} \epsilon_{ij} - 2 \sum_{ij}^{\text{all}} \eta_{ij}^{ab} \epsilon_{ij} \\ &+ 4 \sum_{ij}^{\text{all}} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{\text{all}} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{\text{all}} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl}\end{aligned}\quad (\text{V.4})$$

CI

First Derivative

$$\begin{aligned}\frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^a + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^a \\ &+ 2 \sum_{ij}^{MO} U_{ij}^a X_{ij}\end{aligned}\quad (\text{V.5})$$

Second Derivative

$$\begin{aligned}\frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} Q_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} G_{ijkl}(ij|kl)^{ab} \\ &+ 2 \sum_{ij}^{MO} U_{ij}^{ab} X_{ij} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b X_{ij}^a + U_{ij}^a X_{ij}^b \right) \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b Y_{ijkl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right)\end{aligned}\quad (\text{V.6})$$

TCSCF and PEMCSCF

First Derivative

$$\begin{aligned}\frac{\partial E_{elec}}{\partial a} &= 2 \sum_i^{MO} f_i h_{ii}^a + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^a + \beta_{ij}(ij|ij)^a \right\} \\ &- 2 \sum_{ij}^{MO} S_{ij}^a \epsilon_{ij}\end{aligned}\quad (\text{V.7})$$

Second Derivative

$$\begin{aligned}\frac{\partial^2 E_{elec}}{\partial a \partial b} &= 2 \sum_i^{MO} f_i h_{ii}^{ab} + \sum_{ij}^{MO} \left\{ \alpha_{ij}(ii|jj)^{ab} + \beta_{ij}(ij|ij)^{ab} \right\} \\ &- 2 \sum_{ij}^{MO} S_{ij}^{ab} \epsilon_{ij} - 2 \sum_{ij}^{MO} \eta_{ij}^{ab} \epsilon_{ij} \\ &+ 4 \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^a + U_{ij}^a \epsilon_{ji}^b \right) \\ &+ 4 \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^j + 4 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right)\end{aligned}\quad (\text{V.8})$$

MCSCF

First Derivative

$$\begin{aligned}\frac{\partial E_{elec}}{\partial a} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^a + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^a \\ &- \sum_{ij}^{MO} S_{ij}^a x_{ij}\end{aligned}\quad (\text{V.9})$$

Second Derivative

$$\begin{aligned}\frac{\partial^2 E_{elec}}{\partial a \partial b} &= \sum_{ij}^{MO} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl}^{MO} \Gamma_{ijkl}(ij|kl)^{ab} \\ &- \sum_{ij}^{MO} S_{ij}^{ab} x_{ij} - \sum_{ij}^{MO} \eta_{ij}^{ab} x_{ij} \\ &+ 2 \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^a + U_{ij}^a x_{ij}^b \right) \\ &+ 2 \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl} \\ &- 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(H_{IJ} - \delta_{IJ} E_{elec} \right)\end{aligned}\quad (\text{V.10})$$

Appendix W

First and Second Derivatives of Fock and Lagrangian Matrices

CLSCF

First-Order

$$\begin{aligned} \frac{\partial F_{ij}}{\partial a} &= F_{ij}^a + \sum_k^{\text{all}} U_{ki}^a F_{kj} + \sum_k^{\text{all}} U_{kj}^a F_{ik} \\ &+ \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^a A_{ij,kl} \end{aligned} \quad (\text{W.1})$$

Second-Order

$$\begin{aligned} \frac{\partial^2 F_{ij}}{\partial a \partial b} &= F_{ij}^{ab} + \sum_k^{\text{all}} U_{ki}^{ab} F_{kj} + \sum_k^{\text{all}} U_{kj}^{ab} F_{ik} \\ &+ \sum_k^{\text{all}} \sum_l^{\text{d.o.}} U_{kl}^{ab} A_{ij,kl} \\ &+ \sum_k^{\text{all}} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \\ &+ \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) F_{kl} \\ &+ \sum_{kl}^{\text{all}} \sum_m^{\text{d.o.}} U_{km}^a U_{lm}^b A_{ij,kl} \end{aligned}$$

$$\begin{aligned}
& + \sum_{kl}^{\text{all}} \sum_m^{\text{d.o.}} \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\
& + \sum_{kl}^{\text{all}} \sum_m^{\text{d.o.}} \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\
& + \sum_k^{\text{all}} \sum_l^{\text{d.o.}} \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right)
\end{aligned} \tag{W.2}$$

GRSCF

First-Order

$$\begin{aligned}
\frac{\partial \epsilon_{ij}}{\partial a} &= \epsilon_{ij}^a + \sum_k^{\text{all}} U_{ki}^a \zeta_{kj}^i + \sum_k^{\text{all}} U_{kj}^a \epsilon_{ik} \\
&+ \sum_{kl}^{\text{all}} U_{kl}^a \tau_{ij,kl}^{il}
\end{aligned} \tag{W.3}$$

Second-Order

$$\begin{aligned}
\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} &= \epsilon_{ij}^{ab} + \sum_k^{\text{all}} U_{ki}^{ab} \zeta_{kj}^i + \sum_k^{\text{all}} U_{kj}^{ab} \epsilon_{ik} \\
&+ \sum_{kl}^{\text{all}} U_{kl}^{ab} \tau_{ij,kl}^{il} \\
&+ \sum_{kl}^{\text{all}} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \zeta_{kl}^i \\
&+ \sum_{klm}^{\text{all}} U_{km}^a U_{lm}^b \tau_{ij,kl}^{im} \\
&+ \sum_{kmn}^{\text{all}} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \tau_{kj,mn}^{in} \\
&+ \sum_{kmn}^{\text{all}} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ik,mn}^{in} \\
&+ \sum_{kl}^{\text{all}} \left(U_{kl}^a \tau_{ij,kl}^{ilb} + U_{kl}^b \tau_{ij,kl}^{ila} \right) \\
&+ \sum_k^{\text{all}} \left(U_{ki}^a \zeta_{kj}^{ib} + U_{kj}^a \epsilon_{ik}^b + U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right)
\end{aligned} \tag{W.4}$$

TCSCF and PEMCSCF

First-Order

$$\begin{aligned}
\frac{\partial \epsilon_{ij}}{\partial a} &= 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} \epsilon_{ij}^{IJ} \\
&+ \epsilon_{ij}^a + \sum_k^{MO} \left(U_{ki}^a \zeta_{kj}^i + U_{kj}^a \epsilon_{ik} \right) \\
&+ \sum_{kl}^{MO} U_{kl}^a \tau_{ij,kl}^{il}
\end{aligned} \tag{W.5}$$

Second-Order

$$\begin{aligned}
\frac{\partial^2 \epsilon_{ij}}{\partial a \partial b} &= 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \epsilon_{ij}^{IJ} + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} \epsilon_{ij}^{IJ} \\
&+ 2 \sum_I^{CI} C_I \sum_J^{CI} \left(\frac{\partial C_J}{\partial a} \frac{\partial \epsilon_{ij}^{IJ}}{\partial b} + \frac{\partial C_J}{\partial b} \frac{\partial \epsilon_{ij}^{IJ}}{\partial a} \right) \\
&+ \epsilon_{ij}^{ab} + \sum_k^{MO} U_{ki}^{ab} \zeta_{kj}^i + \sum_k^{MO} U_{kj}^{ab} \epsilon_{ik} \\
&+ \sum_{kl}^{MO} U_{kl}^{ab} \tau_{ij,kl}^{il} \\
&+ \sum_{kl}^{MO} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \zeta_{kl}^i \\
&+ \sum_{klm}^{MO} U_{km}^a U_{lm}^b \tau_{ij,kl}^{im} \\
&+ \sum_{kmn}^{MO} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \tau_{kj,mn}^{in} \\
&+ \sum_{kmn}^{MO} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \tau_{ik,mn}^{in} \\
&+ \sum_{kl}^{MO} \left(U_{kl}^a \tau_{ij,kl}^{ilb} + U_{kl}^b \tau_{ij,kl}^{ila} \right) \\
&+ \sum_k^{MO} \left(U_{ki}^a \zeta_{kj}^{ib} + U_{kj}^a \epsilon_{ik}^b + U_{ki}^b \zeta_{kj}^{ia} + U_{kj}^b \epsilon_{ik}^a \right)
\end{aligned} \tag{W.6}$$

CI and MCSCF

First-Order

$$\begin{aligned} \frac{\partial X_{ij}}{\partial a} = & 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial C_J}{\partial a} X_{ij}^{IJ} \\ & + X_{ij}^a + \sum_k^{MO} U_{ki}^a X_{kj} + \sum_{kl}^{MO} U_{kl}^a Y_{ijkl} \end{aligned} \quad (\text{W.7})$$

Second-Order

$$\begin{aligned} \frac{\partial^2 X_{ij}}{\partial a \partial b} = & 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} X_{ij}^{IJ} + 2 \sum_I^{CI} C_I \sum_J^{CI} \frac{\partial^2 C_J}{\partial a \partial b} X_{ij}^{IJ} \\ & + 2 \sum_I^{CI} C_I \sum_J^{CI} \left[\frac{\partial C_J}{\partial a} \frac{\partial X_{ij}^{IJ}}{\partial b} + \frac{\partial C_J}{\partial b} \frac{\partial X_{ij}^{IJ}}{\partial a} \right] \\ & + X_{ij}^{ab} + \sum_k^{MO} U_{ki}^{ab} X_{kj} + \sum_{kl}^{MO} U_{kl}^{ab} Y_{ijkl} \\ & + \sum_k^{MO} U_{ki}^a X_{kj}^b + \sum_k^{MO} U_{ki}^b X_{kj}^a \\ & + \sum_{kl}^{MO} U_{kl}^a Y_{ijkl}^b + \sum_{kl}^{MO} U_{kl}^b Y_{ijkl}^a \\ & + \sum_{kmn}^{MO} U_{ki}^a U_{mn}^b Y_{kjmn} + \sum_{kmn}^{MO} U_{ki}^b U_{mn}^a Y_{kjmn} \\ & + 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ G_{jlnp}(ik|mp) + G_{jnlp}(im|kp) + G_{jpln}(ip|km) \right\} \end{aligned} \quad (\text{W.8})$$

Appendix X

Coupled Perturbed Hartree-Fock (CPHF) Equations for Closed-Shell SCF Wavefunctions

First-Order Equations

$$(\epsilon_j - \epsilon_i) U_{ij}^a - \sum_k^{virt. d.o.} \sum_l A_{ij,kl} U_{kl}^a = B_{0,ij}^a \quad (X.1)$$

$$A_{ij,kl} = 4(ij|kl) - (ik|jl) - (il|jk) \quad (X.2)$$

$$B_{0,ij}^a = F_{ij}^a - S_{ij}^a \epsilon_j - \sum_{kl}^{d.o.} S_{kl}^a \left\{ 2(ij|kl) - (ik|jl) \right\} \quad (X.3)$$

Second-Order Equations

$$(\epsilon_j - \epsilon_i) U_{ij}^{ab} - \sum_k^{virt. d.o.} \sum_l A_{ij,kl} U_{kl}^{ab} = B_{0,ij}^{ab} \quad (X.4)$$

$$\begin{aligned} B_{0,ij}^{ab} &= F_{ij}^{ab} - \xi_{ij}^{ab} \epsilon_j - \sum_{kl}^{d.o.} \xi_{kl}^{ab} \left\{ 2(ij|kl) - (ik|jl) \right\} \\ &+ \sum_k^{all} \left(U_{ki}^a F_{kj}^b + U_{ki}^b F_{kj}^a + U_{kj}^a F_{ik}^b + U_{kj}^b F_{ik}^a \right) \end{aligned}$$

$$\begin{aligned}
& + \sum_k^{\text{all}} \left(U_{ki}^a U_{kj}^b + U_{ki}^b U_{kj}^a \right) \epsilon_k \\
& + \sum_{kl}^{\text{all}} \sum_m^{\text{d.o.}} U_{km}^a U_{lm}^b A_{ij,kl} \\
& + \sum_{kl}^{\text{all}} \sum_m^{\text{d.o.}} \left(U_{ki}^a U_{lm}^b + U_{ki}^b U_{lm}^a \right) A_{kj,lm} \\
& + \sum_{kl}^{\text{all}} \sum_m^{\text{d.o.}} \left(U_{kj}^a U_{lm}^b + U_{kj}^b U_{lm}^a \right) A_{ik,lm} \\
& + \sum_k^{\text{all}} \sum_l^{\text{d.o.}} \left(U_{kl}^a A_{ij,kl}^b + U_{kl}^b A_{ij,kl}^a \right)
\end{aligned} \tag{X.5}$$

Appendix Y

Coupled Perturbed Hartree-Fock (CPHF) Equations for General Restricted Open-Shell SCF Wavefunctions

First-Order Equations

$$\sum_{k>l}^{indep.\,pair} \mathbf{A}_{ij,kl} U_{kl}^a = B_{0,ij}^a \quad (\text{Y.1})$$

$$\begin{aligned} \mathbf{A}_{ij,kl} &= 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\ &+ (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl})\{(ik|jl) + (il|jk)\} \\ &+ \delta_{ki}\left(\zeta_{lj}^i - \epsilon_{jl}\right) - \delta_{kj}\left(\zeta_{li}^j - \epsilon_{il}\right) - \delta_{li}\left(\zeta_{kj}^i - \epsilon_{jk}\right) + \delta_{lj}\left(\zeta_{ki}^j - \epsilon_{ik}\right) \end{aligned} \quad (\text{Y.2})$$

$$\begin{aligned} B_{0,ij}^a &= \epsilon_{ij}^a - \epsilon_{ji}^a \\ &- \sum_{k>l}^{all\,occ} S_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk})\{(ik|jl) + (il|jk)\} \right. \\ &\quad \left. + \delta_{ki}\left(\zeta_{lj}^i - \epsilon_{jl}\right) - \delta_{kj}\left(\zeta_{li}^j - \epsilon_{il}\right) \right] \\ &- \sum_k^{occ} S_{kk}^a \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \end{aligned} \quad (\text{Y.3})$$

Second-Order Equations

$$\sum_{k>l}^{indep.\,pair} \mathbf{A}_{ij,kl} U_{kl}^{ab} = B_{0,ij}^{ab} \quad (\text{Y.4})$$

$$\begin{aligned}
B_{0,ij}^{ab} &= \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
&- \sum_{k>l}^{all\,occ} \xi_{kl}^{ab} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\
&\quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\
&- \sum_k^{occ} \xi_{kk}^{ab} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\
&+ \sum_{kl}^{all} \left(U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a \right) \left(\zeta_{kl}^i - \zeta_{kl}^j \right) \\
&+ \sum_{klm}^{all} U_{km}^a U_{lm}^b \left(\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm} \right) \\
&+ \sum_{kmn}^{all} \left(U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a \right) \left(\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn} \right) \\
&+ \sum_{kmn}^{all} \left(U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a \right) \left(\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn} \right) \\
&+ \sum_{kl}^{all} U_{kl}^a \left(\tau_{ij,kl}^{il^b} - \tau_{ji,kl}^{jl^b} \right) + \sum_{kl}^{all} U_{kl}^b \left(\tau_{ij,kl}^{il^a} - \tau_{ji,kl}^{jl^a} \right) \\
&+ \sum_k^{all} \left[U_{ki}^a \left(\zeta_{kj}^{ib} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{ia} - \epsilon_{jk}^a \right) \right. \\
&\quad \left. - U_{kj}^a \left(\zeta_{ki}^{jb} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{ja} - \epsilon_{ik}^a \right) \right] \quad (\text{Y.5})
\end{aligned}$$

Appendix Z

Coupled Perturbed Configuration Interaction (CPCI) Equations

First-Order Equations

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial C_J}{\partial a} \\ &= - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} \right) C_J \end{aligned} \quad (Z.1)$$

Second-Order Equations

$$\begin{aligned} & \sum_J^{CI} \left(H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J \right) \frac{\partial^2 C_J}{\partial a \partial b} \\ &= - \sum_J^{CI} \left(\frac{\partial^2 H_{IJ}}{\partial a \partial b} - \delta_{IJ} \frac{\partial^2 E_{elec}}{\partial a \partial b} \right) C_J \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\ & - \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a} \end{aligned} \quad (Z.2)$$

Appendix AA

Coupled Perturbed Paired Excitation Multiconfiguration Hartree-Fock (CPPEMCHF) Equations

First-Order Equations

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\mathbf{a}} \\ \partial \mathbf{C} / \partial \mathbf{a} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\mathbf{a}1} \\ \mathbf{B}_0^{\mathbf{a}2} \end{bmatrix} \quad (\text{AA.1})$$

$$\begin{aligned} \mathbf{A}_{ij,kl}^{11} &= 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\ &+ (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl})\{(ik|jl) + (il|jk)\} \\ &+ \delta_{ki}(\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj}(\zeta_{li}^j - \epsilon_{il}) - \delta_{li}(\zeta_{kj}^i - \epsilon_{jk}) + \delta_{lj}(\zeta_{ki}^j - \epsilon_{ik}) \end{aligned} \quad (\text{AA.2})$$

$$\mathbf{A}_{I,J}^{22} = \frac{1}{2} (H_{IJ} - \delta_{IJ} E_{elec} + 2C_I C_J) \quad (\text{AA.3})$$

$$\mathbf{A}_{I,ij}^{21} = -2 \sum_J^{CI} C_J (\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ}) \quad (\text{AA.4})$$

$$\begin{aligned}
B_{0,ij}^{a1} &= \epsilon_{ij}^a - \epsilon_{ji}^a \\
&- \sum_{k>l}^{all\ occ} S_{kl}^a \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\
&\quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\
&- \sum_k^{occ} S_{kk}^a \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right]
\end{aligned} \tag{AA.5}$$

$$\begin{aligned}
B_{0,I}^{a2} &= -\frac{1}{2} \sum_J^{CI} C_J H_{IJ}^a + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^a \epsilon_{ij}^{IJ} \\
&+ \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^a \epsilon_{ii}^{IJ} + \frac{1}{2} C_I \frac{\partial E_{elec}}{\partial a}
\end{aligned} \tag{AA.6}$$

Second-Order Equations

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\mathbf{ab}} \\ \partial^2 \mathbf{C} / \partial \mathbf{a} \partial \mathbf{b} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\mathbf{ab}1} \\ \mathbf{B}_0^{\mathbf{ab}2} \end{bmatrix} \tag{AA.7}$$

$$\begin{aligned}
B_{0,ij}^{\mathbf{ab}1} &= \epsilon_{ij}^{ab} - \epsilon_{ji}^{ab} \\
&- \sum_{k>l}^{all\ occ} \xi_{kl}^{ab} \left[2(\alpha_{ik} - \alpha_{jk})(ij|kl) + (\beta_{ik} - \beta_{jk}) \{ (ik|jl) + (il|jk) \} \right. \\
&\quad \left. + \delta_{ki} (\zeta_{lj}^i - \epsilon_{jl}) - \delta_{kj} (\zeta_{li}^j - \epsilon_{il}) \right] \\
&- \sum_k^{occ} \xi_{kk}^{ab} \left[(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk) \right] \\
&+ \sum_{kl}^{MO} (U_{ki}^a U_{lj}^b + U_{ki}^b U_{lj}^a) (\zeta_{kl}^i - \zeta_{kl}^j) \\
&+ \sum_{klm}^{MO} U_{km}^a U_{lm}^b (\tau_{ij,kl}^{im} - \tau_{ji,kl}^{jm}) \\
&+ \sum_{kmn}^{MO} (U_{ki}^a U_{mn}^b + U_{ki}^b U_{mn}^a) (\tau_{kj,mn}^{in} - \tau_{jk,mn}^{jn}) \\
&+ \sum_{kmn}^{MO} (U_{kj}^a U_{mn}^b + U_{kj}^b U_{mn}^a) (\tau_{ik,mn}^{in} - \tau_{ki,mn}^{jn})
\end{aligned}$$

$$\begin{aligned}
& + \sum_{kl}^{MO} U_{kl}^a \left(\tau_{ij,kl}^{il^b} - \tau_{ji,kl}^{jl^b} \right) + \sum_{kl}^{MO} U_{kl}^b \left(\tau_{ij,kl}^{il^a} - \tau_{ji,kl}^{jl^a} \right) \\
& + \sum_k^{MO} \left[U_{ki}^a \left(\zeta_{kj}^{i^b} - \epsilon_{jk}^b \right) + U_{ki}^b \left(\zeta_{kj}^{i^a} - \epsilon_{jk}^a \right) \right. \\
& \quad \left. - U_{kj}^a \left(\zeta_{ki}^{j^b} - \epsilon_{ik}^b \right) - U_{kj}^b \left(\zeta_{ki}^{j^a} - \epsilon_{ik}^a \right) \right] \\
& + 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ} \right) \\
& + 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial a} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial b} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial b} \right) + \frac{\partial C_J}{\partial b} \left(\frac{\partial \epsilon_{ij}^{IJ}}{\partial a} - \frac{\partial \epsilon_{ji}^{IJ}}{\partial a} \right) \right\}
\end{aligned} \tag{AA.8}$$

$$\begin{aligned}
B_{0,I}^{ab2} &= -\frac{1}{2} \sum_J^{CI} C_J H_{IJ}^{ab} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} \epsilon_{ij}^{IJ} \\
&+ \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} \epsilon_{ii}^{IJ} + \frac{1}{2} C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \\
&- 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b \epsilon_{ji}^{IJ^a} + U_{ij}^a \epsilon_{ji}^{IJ^b} \right) \\
&- 2 \sum_J^{CI} C_J \sum_{ijk}^{MO} U_{ij}^a U_{kj}^b \zeta_{ik}^{jIJ} \\
&- 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b \tau_{ij,kl}^{jlIJ} \\
&- \frac{1}{2} \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
&- \frac{1}{2} \sum_J^{CI} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a}
\end{aligned} \tag{AA.9}$$

Appendix BB

Coupled Perturbed Multiconfiguration Hartree-Fock (CPMCHF) Equations

First-Order Equations

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\mathbf{a}} \\ \partial \mathbf{C} / \partial \mathbf{a} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\mathbf{a}1} \\ \mathbf{B}_0^{\mathbf{a}2} \end{bmatrix} \quad (\text{BB.1})$$

$$\begin{aligned} \mathbf{A}_{ij,kl}^{11} = & \delta_{li}x_{kj} - \delta_{lj}x_{ki} - \delta_{ki}x_{lj} + \delta_{kj}x_{li} \\ & + y_{ijkl} - y_{jikl} - y_{ijlk} + y_{jilk} \end{aligned} \quad (\text{BB.2})$$

$$\mathbf{A}_{I,J}^{22} = H_{IJ} - \delta_{IJ}E_{elec} + 2C_I C_J \quad (\text{BB.3})$$

$$\mathbf{A}_{I,ij}^{21} = 2 \sum_J^{CI} C_J \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \quad (\text{BB.4})$$

$$\begin{aligned} B_{0,ij}^{\mathbf{a}1} = & -x_{ij}^{\mathbf{a}} + x_{ji}^{\mathbf{a}} \\ & + \sum_{k>l}^{MO} S_{kl}^{\mathbf{a}} \left(\delta_{ki}x_{lj} - \delta_{kj}x_{li} + y_{ijlk} - y_{jilk} \right) \\ & + \frac{1}{2} \sum_k^{MO} S_{kk}^{\mathbf{a}} \left(\delta_{ki}x_{kj} - \delta_{kj}x_{ki} + y_{ijkk} - y_{jikk} \right) \end{aligned} \quad (\text{BB.5})$$

$$\begin{aligned} B_{0,I}^{\mathbf{a}2} = & - \sum_J^{CI} C_J H_{IJ}^{\mathbf{a}} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} S_{ij}^{\mathbf{a}} x_{ji}^{IJ} \\ & + \sum_J^{CI} C_J \sum_i^{MO} S_{ii}^{\mathbf{a}} x_{ii}^{IJ} + C_I \frac{\partial E_{elec}}{\partial a} \end{aligned} \quad (\text{BB.6})$$

Second-Order Equations

$$\begin{bmatrix} \mathbf{A}^{11} & \mathbf{A}^{21\dagger} \\ \mathbf{A}^{21} & \mathbf{A}^{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^{\mathbf{ab}} \\ \partial^2 \mathbf{C} / \partial \mathbf{a} \partial \mathbf{b} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_0^{\mathbf{ab}1} \\ \mathbf{B}_0^{\mathbf{ab}2} \end{bmatrix} \quad (\text{BB.7})$$

$$\begin{aligned}
B_{0,ij}^{ab1} = & -x_{ij}^{ab} + x_{ji}^{ab} \\
& + \sum_{k>l}^{MO} \xi_{kl}^{ab} \left(\delta_{ki} x_{lj} - \delta_{kj} x_{li} + y_{ijkl} - y_{jilk} \right) \\
& + \frac{1}{2} \sum_k^{MO} \xi_{kk}^{ab} \left(\delta_{ki} x_{kj} - \delta_{kj} x_{ki} + y_{ijkk} - y_{jikk} \right) \\
& - \sum_k^{MO} \left(U_{ki}^a x_{kj}^b - U_{kj}^a x_{ki}^b \right) - \sum_k^{MO} \left(U_{ki}^b x_{kj}^a - U_{kj}^b x_{ki}^a \right) \\
& - \sum_{kl}^{MO} U_{kl}^a \left(y_{ijkl}^b - y_{jikl}^b \right) - \sum_{kl}^{MO} U_{kl}^b \left(y_{ijkl}^a - y_{jikl}^a \right) \\
& - \sum_{kmn}^{MO} U_{mn}^b \left(U_{ki}^a y_{kjmn} - U_{kj}^a y_{kimn} \right) - \sum_{kmn}^{MO} U_{mn}^a \left(U_{ki}^b y_{kjmn} - U_{kj}^b y_{kimn} \right) \\
& - 4 \sum_{klmnp}^{MO} U_{kl}^a U_{mn}^b \left\{ \Gamma_{jlnp}(ik|mp) + \Gamma_{jnlp}(im|kp) + \Gamma_{jpln}(ip|km) \right. \\
& \quad \left. - \Gamma_{ilnp}(jk|mp) - \Gamma_{inlp}(jm|kp) - \Gamma_{ipln}(jp|km) \right\} \\
& - 2 \sum_{IJ}^{CI} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} \left(x_{ij}^{IJ} - x_{ji}^{IJ} \right) \\
& - 2 \sum_I^{CI} C_I \sum_J^{CI} \left\{ \frac{\partial C_J}{\partial a} \left(\frac{\partial x_{ij}^{IJ}}{\partial b} - \frac{\partial x_{ji}^{IJ}}{\partial b} \right) + \frac{\partial C_J}{\partial b} \left(\frac{\partial x_{ij}^{IJ}}{\partial a} - \frac{\partial x_{ji}^{IJ}}{\partial a} \right) \right\}
\end{aligned} \quad (\text{BB.8})$$

$$\begin{aligned}
B_{0,I}^{ab2} = & - \sum_J^{CI} C_J H_{IJ}^{ab} + 2 \sum_J^{CI} C_J \sum_{i>j}^{MO} \xi_{ij}^{ab} x_{ji}^{IJ} + \sum_J^{CI} C_J \sum_i^{MO} \xi_{ii}^{ab} x_{ii}^{IJ} + C_I \frac{\partial^2 E_{elec}}{\partial a \partial b} \\
& - 2 \sum_J^{CI} C_J \sum_{ij}^{MO} \left(U_{ij}^b x_{ij}^{IJ^a} + U_{ij}^a x_{ij}^{IJ^b} \right) \\
& - 2 \sum_J^{CI} C_J \sum_{ijkl}^{MO} U_{ij}^a U_{kl}^b y_{ijkl}^{IJ}
\end{aligned}$$

$$\begin{aligned}
 & - \sum_J^{O_I} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E_{elec}}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b} \\
 & - \sum_J^{O_I} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E_{elec}}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a}
 \end{aligned} \tag{BB.9}$$

Bibliographical Survey on Analytic Energy Derivatives

1968

J. Gerratt and I.M. Mills, J. Chem. Phys. **49**, 1719 (1968).

"Force constants and dipole-moment derivatives of molecules from perturbed Hartree-Fock calculations. I"

J. Gerratt and I.M. Mills, J. Chem. Phys. **49**, 1730 (1968).

"Force constants and dipole-moment derivatives of molecules from perturbed Hartree-Fock calculations. II. Applications to limited basis-set SCF-MO wavefunctions"

1969

P. Pulay, Mol. Phys. **17**, 197 (1969).

"Ab initio calculation of force constants and equilibrium geometries in polyatomic molecules. I. Theory"

1970

R. Moccia, Chem. Phys. Lett. **5**, 260 (1970).

"Variable bases in SCF MO calculations"

P. Pulay, Mol. Phys. **18**, 473 (1970).

"Ab initio calculation of force constants and equilibrium geometries in polyatomic molecules. II. Force constants of water"

1971

P. Pulay, Mol. Phys. **21**, 329 (1971).

"Ab initio calculation of force constants and equilibrium geometries. III. Second-row hydrides"

1973

- K. Thomsen and P. Swanstrøm, Mol. Phys. **26**, 735 (1973).
"Calculation of molecular one-electron properties using coupled Hartree-Fock methods I. Computational scheme"
K. Thomsen and P. Swanstrøm, Mol. Phys. **26**, 751 (1973).
"Calculation of molecular one-electron properties using coupled Hartree-Fock methods II. The water molecule"

1974

- R. Moccia, Int. J. Quantum Chem. **8**, 293 (1974).
"Static and dynamic first- and second-order properties by variational wave functions"

1975

- H.B. Schlegel, S. Wolfe, and F. Bernardi, J. Chem. Phys. **63**, 3632 (1975).
"Ab initio computation of force constants. I. The second and third period hydrides"
M. Jaszuński and A.J. Sadlej, Theor. Chim. Acta **40**, 157 (1975).
"Coupled multiconfiguration self-consistent field (MC SCF) perturbation theory"

1976

- M. Dupuis, J. Rys, and H.F. King, J. Chem. Phys. **65**, 111 (1976).
"Evaluation of molecular integrals over Gaussian basis functions"

1977

- A. Komornicki, K. Ishida, K. Morokuma, R. Ditchfield, and M. Conrad, Chem. Phys. Lett. **45**, 595 (1977).
"Efficient determination and characterization of transition states using ab initio methods"
M. Jaszuński and A.J. Sadlej, Int. J. Quantum Chem. **11**, 233 (1977).
"Analytic techniques for the coupled multiconfiguration SCF perturbation theory"
J.L. Dodds, R. McWeeny, and A.J. Sadlej, Mol. Phys. **34**, 1779 (1977).
"Self-consistent perturbation theory. Generalization for perturbation-dependent non-orthogonal basis set"

1978

- A. Tachibana, K. Yamashita, T. Yamabe, and K. Fukui, Chem. Phys. Lett. **59**, 255 (1978).
"Exact formula for the gradient of the CI potential energy hypersurface"
M. Dupuis and H.F. King, J. Chem. Phys. **68**, 3998 (1978).
"Molecular symmetry. II. Gradient of electronic energy with respect to nuclear coordinates"

1979

S. Kato and K. Morokuma, Chem. Phys. Lett. **65**, 19 (1979).

"Energy gradient in a multi-configurational SCF formalism and its application to geometry optimization of trimethylene diradicals"

J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, Int. J. Quantum Chem. **S13**, 225 (1979).

"Derivative studies in Hartree-Fock and Møller-Plesset theories"

P. Pulay, G. Fogarasi, F. Pang, and J.E. Boggs, J. Am. Chem. Soc. **101**, 2550 (1979).

"Systematic ab initio gradient calculation of molecular geometries, force constants, and dipole moment derivatives"

D.J. DeFrees, B.A. Levi, S.K. Pollack, W.J. Hehre, J.S. Binkley, and J.A. Pople, J. Am. Chem. Soc. **101**, 4085 (1979).

"Effect of electron correlation on theoretical equilibrium geometries"

A. Komornicki and J.W. McIver, Jr., J. Chem. Phys. **70**, 2014 (1979).

"An efficient ab initio method for computing infrared and Raman intensities: Application to ethylene"

J.D. Goddard, N.C. Handy, and H.F. Schaefer, J. Chem. Phys. **71**, 1525 (1979).

"Gradient techniques for open-shell restricted Hartree-Fock and multiconfiguration self-consistent-field methods"

1980

G.T. Daborn, W.I. Ferguson, and N.C. Handy, Chem. Phys. **50**, 255 (1980).

"The calculation of second-order molecular properties at the configuration interaction level of theory"

B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, Y. Yamaguchi, and H.F. Schaefer, J. Chem. Phys. **72**, 4652 (1980).

"Analytic gradients from correlated wave functions via the two-particle density matrix and the unitary group approach"

R. Krishnan, H.B. Schlegel, and J.A. Pople, J. Chem. Phys. **72**, 4654 (1980).

"Derivative studies in configuration-interaction theory"

Y. Yamaguchi and H.F. Schaefer, J. Chem. Phys. **73**, 2310 (1980).

"A systematic theoretical study of harmonic vibrational frequencies: The ammonium ion NH_4^+ and other simple molecules"

1981

M. Dupuis, J. Chem. Phys. **74**, 5758 (1981).

"Energy derivatives for configuration interaction wave functions"

- T. Takada, M. Dupuis, and H.F. King, *J. Chem. Phys.* **75**, 332 (1981).
“Molecular symmetry. III. Second derivatives of electronic energy with respect to nuclear coordinates”
- Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **75**, 2919 (1981).
“Analytic configuration interaction (CI) gradient techniques for potential energy hypersurfaces. A method for open-shell molecular wave functions”

1982

- Y. Osamura, Y. Yamaguchi, P. Saxe, M.A. Vincent, J.F. Gaw, and H.F. Schaefer, *Chem. Phys.* **72**, 131 (1982).
“Unified theoretical treatment of analytic first and second energy derivatives in open-shell Hartree-Fock theory”
- T.U. Helgaker, *Int. J. Quantum Chem.* **21**, 939 (1982).
“Simple derivation of the potential energy gradient for an arbitrary electronic wave function”
- Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 383 (1982).
“Generalization of analytic configuration interaction (CI) gradient techniques for potential energy hypersurfaces, including a solution to the coupled perturbed Hartree-Fock equations for multiconfiguration SCF molecular wave functions”
- H.B. Schlegel, *J. Chem. Phys.* **77**, 3676 (1982).
“An efficient algorithm for calculating ab initio energy gradients using s, p cartesian Gaussians”
- P. Saxe, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **77**, 5647 (1982).
“Analytic second derivatives in restricted Hartree-Fock theory. A method for high-spin open-shell molecular wave functions”
- R.F. Hout, Jr., B.A. Levi, and W.J. Hehre, *J. Comp. Chem.* **3**, 234 (1982).
“Effect of electron correlation on theoretical vibrational frequencies”

1983

- M.A. Vincent, P. Saxe, and H.F. Schaefer, *Chem. Phys. Lett.* **94**, 351 (1983).
“Rotational invariance in analytic first, second and third energy derivative studies in molecular electronic structure theory”
- H. Teramae, T. Yamabe, C. Satoko, and A. Imamura, *Chem. Phys. Lett.* **101**, 149 (1983).
“Energy gradient in the ab initio Hartree-Fock crystal-orbital formalism of one-dimensional infinite polymers”
- D.J. Fox, Y. Osamura, M.R. Hoffmann, J.F. Gaw, G. Fitzgerald, Y. Yamaguchi, and H.F. Schaefer, *Chem. Phys. Lett.* **102**, 17 (1983).
“Analytic energy second derivatives for general correlated wavefunctions, including a solution of the first-order coupled-perturbed configuration-interaction equations”

- Y. Yamaguchi, Y. Osamura, and H.F. Schaefer, *J. Am. Chem. Soc.* **105**, 7506 (1983).
 "Analytic energy second derivatives for two-configuration self-consistent-field wave functions. Application to twisted ethylene and to the trimethylene diradical"
- Y. Yamaguchi, Y. Osamura, G. Fitzgerald, and H.F. Schaefer, *J. Chem. Phys.* **78**, 1607 (1983).
 "Analytic force constants for post-Hartree-Fock wave functions: The simplest case"
- P. Pulay, *J. Chem. Phys.* **78**, 5043 (1983).
 "Second and third derivatives of variational energy expressions : Application to multiconfigurational self-consistent field wave functions"
- P. Jørgensen and J. Simons, *J. Chem. Phys.* **79**, 334 (1983).
 "Ab initio analytical molecular gradients and Hessians"
- R.N. Camp, H.F. King, J.W. McIver, Jr., and D. Mullally, *J. Chem. Phys.* **79**, 1088 (1983).
 "Analytical force constants for MCSCF wave functions"
- J. Simons and P. Jørgensen, *J. Chem. Phys.* **79**, 3599 (1983).
 "First and second anharmonicities of the MCSCF energy"
- J. Rys, M. Dupuis, and H.F. King, *J. Comp. Chem.* **4**, 154 (1983).
 "Computation of electron repulsion integrals using the Rys quadrature method"
- T. Takada, M. Dupuis, and H.F. King, *J. Comp. Chem.* **4**, 234 (1983).
 "Molecular symmetry. IV. The coupled perturbed Hartree-Fock method"
- P. Pulay, *J. Mol. Struct.* **103**, 57 (1983).
 "Gradients in coupled pair theories"
- Y. Osamura, Y. Yamaguchi, P. Saxe, D.J. Fox, M.A. Vincent, and H.F. Schaefer, *J. Mol. Struct.* **103**, 183 (1983).
 "Analytic second derivative techniques for self-consistent-field wave functions. A new approach to the solution of the coupled perturbed Hartree-Fock equations"

1984

- J.F. Gaw and N.C. Handy, *Ann. Rep. Prog. Chem. (Sect. C, Physical Chemistry, The Chemical Society, London)* **81**, 291 (1984).
 "Derivatives of the potential energy hypersurface by analytic techniques"
- J. Simons, P. Jørgensen, and T.U. Helgaker, *Chem. Phys.* **86**, 413 (1984).
 "Higher molecular-deformation derivatives of the configuration-interaction energy"
- M. Page, P. Saxe, G.F. Adams, and B.H. Lengsfeld, *Chem. Phys. Lett.* **104**, 587 (1984).
 "Exploiting rotational and translational invariance of the energy in derivative calculations in quantum chemistry"

- M. Kertesz, Chem. Phys. Lett. **106**, 443 (1984).
“The gradient of the total energy for metals”
- R.D. Amos, Chem. Phys. Lett. **108**, 185 (1984).
“Dipole moment derivatives of H₂O and H₂S”
- R.D. Amos, Chem. Phys. Lett. **108**, 347 (1984).
“Structure and harmonic vibrational frequencies of the carbon suboxide molecule using analytic derivative methods”
- C.E. Dykstra and P.G. Jasien, Chem. Phys. Lett. **109**, 388 (1984).
“Derivative Hartree-Fock theory to all orders”
- J. Simons and P. Jørgensen, Int. J. Quantum Chem. **25**, 1135 (1984).
“Geometrical derivatives of dipole moments and polarizabilities”
- T.U. Helgaker and J. Almlöf, Int. J. Quantum Chem. **26**, 275 (1984).
“A second-quantization approach to the analytical evaluation of response properties for perturbation-dependent basis sets”
- L. Adamowicz, W.D. Laidig, and R.J. Bartlett, Int. J. Quantum Chem. **S18**, 245 (1984).
“Analytic gradients for the coupled-cluster method”
- H.B. Schlegel, J.S. Binkley, and J.A. Pople, J. Chem. Phys. **80**, 1976 (1984).
“First and second derivatives of two electron integrals over cartesian Gaussians using Rys polynomials”
- M.R. Hoffmann, D.J. Fox, J.F. Gaw, Y. Osamura, Y. Yamaguchi, R.S. Grev, G. Fitzgerald, H.F. Schaefer, P.J. Knowles, and N.C. Handy, J. Chem. Phys. **80**, 2660 (1984).
“Analytic energy second derivatives for general MCSCF wave functions”
- M. Page, P. Saxe, G.F. Adams, and B.H. Lengsfeld, J. Chem. Phys. **81**, 434 (1984).
“Multireference CI gradients and MCSCF second derivatives”
- N.C. Handy and H.F. Schaefer, J. Chem. Phys. **81**, 5031 (1984).
“On the evaluation of analytic energy derivatives for correlated wave functions”
- J.F. Gaw, Y. Yamaguchi, and H.F. Schaefer, J. Chem. Phys. **81**, 6395 (1984).
“Analytic third derivatives for self-consistent-field wave functions”

1985

- N.C. Handy, R.D. Amos, J.F. Gaw, J.E. Rice, and E.D. Simandiras, Chem. Phys. Lett. **120**, 151 (1985).
“The elimination of singularities in derivative calculations”

- J.F. Gaw and N.C. Handy, Chem. Phys. Lett. **121**, 321 (1985).
 "Ab initio quadratic, cubic and quartic force constants for the calculation of spectroscopic constants"
- J.E. Rice and R.D. Amos, Chem. Phys. Lett. **122**, 585 (1985).
 "On the efficient evaluation of analytic energy gradients"
- J. Almlöf and P.R. Taylor, Int. J. Quantum Chem. **27**, 743 (1985).
 "Molecular properties from perturbation theory : A unified treatment of energy derivatives"
- G. Fitzgerald, R. Harrison, W.D. Laidig, and R.J. Bartlett, J. Chem. Phys. **82**, 4379 (1985).
 "Third-order MBPT gradients"
- G. Fitzgerald and H.F. Schaefer, J. Chem. Phys. **83**, 1162 (1985).
 "Analytic energy derivative methods for excited singlet states of the same symmetry as the electronic ground state"

1986

- Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, Chem. Phys. **103**, 227 (1986).
 "Second-order coupled perturbed Hartree-Fock equations for closed-shell and open-shell self-consistent-field wavefunctions"
- J.F. Gaw, Y. Yamaguchi, R.B. Remington, Y. Osamura, and H.F. Schaefer, Chem. Phys. **109**, 237 (1986).
 "Analytic energy third derivatives for open-shell self-consistent-field wavefunctions"
- R.J. Harrison, G.B. Fitzgerald, W.D. Laidig, and R.J. Bartlett, Chem. Phys. Lett. **124**, 291 (1986).
 "Analytic MBPT(2) second derivatives"
- R.D. Amos, Chem. Phys. Lett. **124**, 376 (1986).
 "Calculation of polarizability derivatives using analytic gradient methods"
- H. Sellers, Int. J. Quantum Chem. **30**, 433 (1986).
 "Analytical force constant calculation as a minimization problem"
- M.J. Frisch, Y. Yamaguchi, J.F. Gaw, H.F. Schaefer, and J.S. Binkley, J. Chem. Phys. **84**, 531 (1986).
 "Analytic Raman intensities from molecular electronic wave functions"
- Y. Yamaguchi, M.J. Frisch, J.F. Gaw, H.F. Schaefer, and J.S. Binkley, J. Chem. Phys. **84**, 2262 (1986).
 "Analytic evaluation and basis set dependence of intensities of infrared spectra"
- S. Obara and A. Saika, J. Chem. Phys. **84**, 3963 (1986).
 "Efficient recursive computation of molecular integrals over cartesian Gaussian functions"

H.F. King and A. Komornicki, J. Chem. Phys. **84**, 5645 (1986).

"Analytic computation of energy derivatives. Relationships among partial derivatives of a variationally determined function"

T.U. Helgaker, J. Almlöf, H. J. Aa. Jensen, and P. Jørgensen, J. Chem. Phys. **84**, 6266 (1986).

"Molecular Hessian for large-scale MCSCF wave functions"

J.E. Rice, R.D. Amos, N.C. Handy, T.J. Lee, and H.F. Schaefer, J. Chem. Phys. **85**, 963 (1986).

"The analytic configuration interaction gradient method : Application to the cyclic and open isomers of the S₃ molecule"

T.J. Lee, N.C. Handy, J.E. Rice, A.C. Scheiner, and H.F. Schaefer, J. Chem. Phys. **85**, 3930 (1986).

"The efficient evaluation of configuration interaction analytic energy second derivatives : Application to hydrogen thioperoxide, HSOH"

J.F. Gaw, Y. Yamaguchi, H.F. Schaefer, and N.C. Handy, J. Chem. Phys. **85**, 5132 (1986).

"Generalization of analytic energy third derivatives for the RHF closed-shell wave function: Derivative energy and integral formalisms and the prediction of vibration-rotation interaction constants"

K. Faegri and J. Almlöf, J. Comp. Chem. **7**, 396 (1986).

"Energy-optimized GTO basis sets for LCAO calculations. A gradient approach"

H.F. Schaefer and Y. Yamaguchi, J. Mol. Struct. **135**, 369 (1986).

"A new dimension to quantum chemistry: Theoretical methods for the analytic evaluation of first, second, and third derivatives of the molecular electronic energy with respect to nuclear coordinates"

Y. Yamaguchi, M.J. Frisch, T.J. Lee, H.F. Schaefer, and J.S. Binkley, Theor. Chim. Acta, **69**, 337 (1986).

"Analytic evaluation of infrared intensities and polarizabilities by two-configuration self-consistent-field wave functions"

P. Pulay and S. Saebø, Theor. Chim. Acta, **69**, 357 (1986).

"Orbital-invariant formulation and second-order gradient evaluation in Møller-Plesset perturbation theory"

1987

E.D. Simandiras, R.D. Amos, and N.C. Handy, Chem. Phys. **114**, 9 (1987).

"The analytic evaluation of second-order Møller-Plesset (MP2) dipole moment derivatives"

- E.D. Simandiras, N.C. Handy, and R.D. Amos, Chem. Phys. Lett. **133**, 324 (1987).
 "On the high accuracy of MP2-optimised geometries and harmonic frequencies with large basis sets"
- B.H. Lengsfield, S. Havriliak, M.E. Colvin, and H.F. Schaefer, Chem. Phys. Lett. **135**, 340 (1987).
 "Analytic MCSCF infrared intensities: Application to formaldehyde"
- J. Gauss and D. Cremer, Chem. Phys. Lett. **138**, 131 (1987).
 "Implementation of analytical energy gradients of third- and fourth-order Møller-Plesset perturbation theory"
- M.R. Hoffmann and J. Simons, Chem. Phys. Lett. **142**, 451 (1987).
 "Analytical energy gradients for a unitary coupled-cluster theory"
- R. Shepard, Int. J. Quantum Chem. **31**, 33 (1987).
 "Geometrical energy derivative evaluation with MRCI wave functions"
- G.E. Scuseria, A.C. Scheiner, J.E. Rice, T.J. Lee, and H.F. Schaefer, Int. J. Quantum Chem. **S21**, 495 (1987).
 "Analytic evaluation of energy gradients for the single and double excitation coupled cluster (CCSD) wave function: A comparison with configuration interaction (CISD, CISDT, and CISDTQ) results for the harmonic vibrational frequencies, infrared intensities, dipole moment, and inversion barrier of ammonia"
- G. Tonachini and H.B. Schlegel, J. Chem. Phys. **87**, 514 (1987).
 "Hartree-Fock energy derivatives with respect to basis set exponents. Integral derivatives using Rys polynomials"
- A.C. Scheiner, G.E. Scuseria, J.E. Rice, T.J. Lee, and H.F. Schaefer, J. Chem. Phys. **87**, 5361 (1987).
 "Analytic evaluation of energy gradients for the single and double excitation coupled cluster (CCSD) wave function: Theory and application"
- A.P.L. Rendell, G.B. Bacskay, N.S. Hush, and N.C. Handy, J. Chem. Phys. **87**, 5976 (1987).
 "The analytic configuration interaction gradient method: The calculation of one electron properties"
- T.J. Lee, W.D. Allen, and H.F. Schaefer, J. Chem. Phys. **87**, 7062 (1987).
 "The analytic evaluation of energy first derivatives for two-configuration self-consistent-field configuration interaction (TCSCF-CI) wavefunctions. Application to ozone and ethylene"
- W.D. Allen and H.F. Schaefer, J. Chem. Phys. **87**, 7076 (1987).
 "An examination of the $2\ ^1A_1$ states of formaldehyde and ketene including analytic configuration interaction energy first derivatives for singlet excited electronic states of the same symmetry as the ground state"

Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *Theor. Chim. Acta* **72**, 71 (1987).
"Generalization of analytic energy derivatives for configuration interaction wave functions"

Y. Osamura, Y. Yamaguchi, and H.F. Schaefer, *Theor. Chim. Acta* **72**, 93 (1987).
"Correspondence between higher order energy derivative formalisms for restricted Hartree-Fock and correlated wavefunctions"

1988

M. Duran, Y. Yamaguchi, R.B. Remington, and H.F. Schaefer, *Chem. Phys.* **122**, 201 (1988).

"Analytic energy second derivatives for paired-excited multi-configuration self-consistent-field wavefunctions. Application of the PEMCSCF model to H₂O, CH₂, HCN, HCCCH, H₂CO, NH₃, CH₄, and C₂H₄"

D.A. Clabo, Jr., W.D. Allen, R.B. Remington, Y. Yamaguchi, and H.F. Schaefer, *Chem. Phys.* **123**, 187 (1988).

"A systematic study of molecular vibrational anharmonicity and vibration-rotation interaction by self-consistent-field higher-derivative methods. Asymmetric top molecules"

G.E. Scuseria and H.F. Schaefer, *Chem. Phys. Lett.* **146**, 23 (1988).

"Analytic evaluation of energy gradients for the single, double, and linearized triple excitation coupled cluster CCSDT-1 wavefunction: Theory and applications"

J. Gauss and D. Cremer, *Chem. Phys. Lett.* **150**, 280 (1988).

"Analytic evaluation of energy gradients in quadratic configuration interaction theory"

G.W. Trucks, J.D. Watts, E.A. Satter, and R.J. Bartlett, *Chem. Phys. Lett.* **153**, 490 (1988).

"Analytical MBPT(4) gradients"

H. Sellers, *Int. J. Quantum Chem.* **38**, 271 (1988).

"Variational energy derivatives and perturbation theory"

J.E. Rice, T.J. Lee, and N.C. Handy, *J. Chem. Phys.* **88**, 7011 (1988).

"The analytic energy gradient for the coupled pair functional method"

B.H. Besler, G.E. Scuseria, A.C. Scheiner, and H.F. Schaefer, *J. Chem. Phys.* **89**, 360 (1988).

"A systematic theoretical study of harmonic vibrational frequencies: The single and double excitation coupled cluster (CCSD) method"

T.J. Lee, R.B. Remington, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **89**, 408 (1988).

"The effects of triple and quadruple excitations in configuration interaction procedures for the quantum mechanical prediction of molecular properties"

- S. Obara and A. Saika, J. Chem. Phys. **89**, 1540 (1988).
“General recurrence formulas for molecular integrals over cartesian Gaussian functions”
- P. Jørgensen and T.U. Helgaker, J. Chem. Phys. **89**, 1560 (1988).
“Møller-Plesset energy derivatives”
- I.L. Alberts and N.C. Handy, J. Chem. Phys. **89**, 2107 (1988).
“Møller-Plesset third order calculations with large basis sets”
- M. Head-Gordon and J.A. Pople, J. Chem. Phys. **89**, 5777 (1988).
“A method for two-electron Gaussian integral and integral derivative evaluation using recurrence relations”
- M. Duran, Y. Yamaguchi, Y. Osamura, and H.F. Schaefer, J. Mol. Struct. **163**, 389 (1988).
“Analytic energy third derivatives for two-configuration self-consistent-field wavefunctions”
- M. Head-Gordon and J.A. Pople, J. Phys. Chem. **92**, 3063 (1988).
“Optimization of wave function and geometry in the finite basis Hartree-Fock method”
- M. Duran, Y. Yamaguchi, and H.F. Schaefer, J. Phys. Chem. **92**, 3070 (1988).
“Analytic energy second derivative for open-shell two-configuration self-consistent-field wave functions: Application to carbyne and silyne least-motion insertion reactions”
- 1989**
- D. Jayatilaka, R.D. Amos, and N. Koga, Chem. Phys. Lett. **163**, 151 (1989).
“Analytic second derivatives with model potentials at SCF and MP2 levels”
- J. Gauss and D. Cremer, Chem. Phys. Lett. **163**, 549 (1989).
“Analytical differentiation of the energy contribution due to triple excitations in quadratic configuration interaction theory”
- K. Hashimoto and Y. Osamura, Chem. Phys. Lett. **164**, 353 (1989).
“Analytic energy gradients with respect to orbital exponents for molecular SCF wavefunctions”
- J.D. Watts, G.W. Trucks, and R.J. Bartlett, Chem. Phys. Lett. **164**, 502 (1989).
“Coupled-cluster, unitary coupled-cluster and MBPT(4) open-shell analytical gradient methods”
- M. Head-Gordon, J.A. Pople, and M.J. Frisch, Int. J. Quantum Chem. **23**, 291 (1989).
“Quadratically convergent simultaneous optimization of wavefunction and geometry”

- M. Duran, J.L. Andrés, A. Lledós, and J. Bertrán, *J. Chem. Phys.* **90**, 328 (1989).
“Influence of an external uniform electric field on harmonic vibrational frequencies.
Analytic energy second derivatives for closed-shell restricted Hartree-Fock functions
with an applied uniform electric field”
- M. Duran, Y. Yamaguchi, R.B. Remington, Y. Osamura, and H.F. Schaefer, *J. Chem. Phys.* **90**, 334 (1989).
“Analytic energy third derivatives for paired-excited multiconfiguration self-consistent-field wavefunctions”
- H.B. Schlegel, *J. Chem. Phys.* **90**, 5630 (1989).
“Analytical second derivatives of two electron integrals over s and p cartesian Gaussians”
- T. Helgaker and P. Jørgensen, *Theor. Chim. Acta* **75**, 111 (1989).
“Configuration-interaction energy derivatives in a fully variational formulation”
- Y. Osamura, *Theor. Chim. Acta* **76**, 113 (1989).
“Analytic expression of the second derivatives of electronic energy for full configuration interaction wave functions”

1990

- W.D. Allen, Y. Yamaguchi, A.G. Császár, D.A. Clabo, Jr., R.B. Remington, and H.F. Schaefer, *Chem. Phys.* **145**, 427 (1990).
“A systematic study of molecular vibrational anharmonicity and vibration-rotation interaction by self-consistent-field higher-derivative methods. Linear polyatomic molecules”
- Y. Yamaguchi, I.L. Alberts, J.D. Goddard, and H.F. Schaefer, *Chem. Phys.* **147**, 309 (1990).
“Use of the molecular orbital Hessian for self-consistent-field (SCF) wavefunctions”
- M.J. Frish, M. Head-Gordon, and J.A. Pople, *Chem. Phys. Lett.* **166**, 275 (1990).
“A direct MP2 gradient method”
- M.J. Frish, M. Head-Gordon, and J.A. Pople, *Chem. Phys. Lett.* **166**, 281 (1990).
“Semi-direct algorithms for the MP2 energy and gradient”
- H. Koch, H. J. Aa. Jensen, P. Jørgensen, T. Helgaker, G.E. Scuseria, and H.F. Schaefer, *J. Chem. Phys.* **92**, 4924 (1990).
“Coupled cluster energy derivatives. Analytic Hessian for the closed-shell coupled cluster singles and doubles wave function: Theory and applications”

1991

- J. Gauss, W.J. Lauderdale, J.F. Stanton, J.D. Watts, and R.J. Bartlett, *Chem. Phys. Lett.* **182**, 207 (1991).
“Analytic energy gradient for open-shell coupled-cluster singles and doubles (CCSD)
calculations using restricted open-shell Hartree-Fock (ROHF) reference functions”

- R. Kobayashi, R.D. Amos, and N.C. Handy, *Chem. Phys. Lett.* **184**, 195 (1991).
“The analytic gradient of the perturbative triple excitations correction to the Brueckner doubles method”
- S.M. Colwell, D. Jayatilaka, P.E. Maslen, R.D. Amos, and N.C. Handy, *Int. J. Quantum Chem.* **40**, 179 (1991).
“Higher analytic derivatives. I. A new implementation for the third derivative of the SCF energy”
- J.F. Stanton, J.D. Watts, and R.J. Bartlett, *J. Chem. Phys.* **94**, 404 (1991).
“Harmonic vibrational frequencies and infrared intensities from analytic fourth-order many-body perturbation theory gradients”
- J.E. Rice and N.C. Handy, *J. Chem. Phys.* **94**, 4959 (1991).
“The calculation of frequency-dependent polarizabilities as pseudo-energy derivatives”
- T. Busch, A.D. Esposti, and H.-J. Werner, *J. Chem. Phys.* **94**, 6708 (1991).
“Analytical energy gradients for multiconfiguration self-consistent field wave functions with frozen core orbitals”
- J. Gauss, J.F. Stanton, and R.J. Bartlett, *J. Chem. Phys.* **95**, 2623 (1991).
“Coupled-cluster open-shell analytic gradients: Implementation of the direct product decomposition approach in energy gradient calculations”
- J. Gauss, J.F. Stanton, and R.J. Bartlett, *J. Chem. Phys.* **95**, 2639 (1991).
“Analytic evaluation of energy gradients at the coupled-cluster singles and doubles level using quasi-restricted Hartree-Fock open-shell reference functions”
- R.S. Grev, C.L. Janssen, and H.F. Schaefer, *J. Chem. Phys.* **95**, 5128 (1991).
“Concerning zero-point vibrational energy corrections to electronic energies”
- P.E. Maslen, D. Jayatilaka, S.M. Colwell, R.D. Amos, and N.C. Handy, *J. Chem. Phys.* **95**, 7409 (1991).
“Higher analytic derivatives. II. The fourth derivative of self-consistent-field energy”
- N.A. Burton, Y. Yamaguchi, I.L. Alberts, and H.F. Schaefer, *J. Chem. Phys.* **95**, 7466 (1991).
“Interpretation of excited state Hartree-Fock analytic derivative anomalies for NO₂ and HCO₂ using the molecular orbital Hessian”
- M.W. Wong, K.B. Wiberg, and M. Frisch, *J. Chem. Phys.* **95**, 8991 (1991).
“Hartree-Fock second derivatives and electric field properties in a solvent reaction field: Theory and application”
- H. Horn, H. Weiß, M. Häser, M. Ehrig, and R. Ahlrichs, *J. Comp. Chem.* **12**, 1058 (1991).
“Prescreening of two-electron integral derivatives in SCF gradient and Hessian calculations”

1992

- K. Hashimoto and Y. Osamura, Can. J. Chem. **70**, 547 (1992).
“Orbital exponent optimization for molecular self-consistent-field wave functions including polarization function”
- J.F. Stanton, J. Gauss, and R.J. Bartlett, Chem. Phys. Lett. **195**, 194 (1992).
“Analytic evaluation of second derivatives using second-order many-body perturbation theory and unrestricted Hartree-Fock reference functions”
- D.J. Tozer, J.S. Andrews, R.D. Amos, and N.C. Handy, Chem. Phys. Lett. **199**, 229 (1992).
“Gradient theory applied to restricted (open-shell) Møller-Plesset theory”
- J.D. Watts, J. Gauss, and R.J. Bartlett, Chem. Phys. Lett. **200**, 1 (1992).
“Open-shell analytical energy gradients for triple excitation many-body, coupled-cluster methods: MBPT(4), CCSD+T(CCSD), CCSD(T), and QCISD(T)”
- R. Shepard, H. Lischka, P.G. Szalay, T. Kovar, and M. Ernzerhof, J. Chem. Phys. **96**, 2085 (1992).
“A general multireference configuration interaction gradient program”
- H. Tokiwa, H. Ichikawa, and Y. Osamura, J. Chem. Phys. **96**, 6018 (1992).
“Concerning analytic derivatives of kinetic and potential energies in the Hartree-Fock theory”
- J. Cioslowski and J.V. Ortiz, J. Chem. Phys. **96**, 8379 (1992).
“One-electron density matrices and energy gradients in second-order electron propagator theory”
- D. Jayatilaka, P.E. Maslen, R.D. Amos, and N.C. Handy, Mol. Phys. **75**, 271 (1992).
“Higher analytic derivatives. III. Geometrical derivatives of the dipole and dipole polarizabilities”
- T. Helgaker and P. R. Taylor, Theor. Chim. Acta **83**, 177 (1992).
“On the evaluation of derivatives of Gaussian integrals”

1993

- J.R. Thomas, B.J. DeLeeuw, G. Vacek, and H.F. Schaefer, J. Chem. Phys. **98**, 1336 (1993).
“A systematic theoretical study of the harmonic vibrational frequencies for polyatomic molecules: The single, double, and perturbative triple excitation coupled-cluster [CCSD(T)] method”
- K. Ishida, J. Chem. Phys. **98**, 2176 (1993).
“General formula evaluation of the electron-repulsion integral (ERI) and its derivatives over Gaussian-type orbitals. II. ERI evaluation improved”

- W.D. Allen and A.G. Császár, *J. Chem. Phys.* **98**, 2983 (1993).
“On the ab initio determination of higher-order force constants at nonstationary reference geometries”
- J.D. Watts, J. Gauss, and R.J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
“Coupled-cluster methods with noniterative triple excitations for restricted open-shell Hartree-Fock and other general single determinant reference functions. Energies and analytical gradients”
- Y. Yamaguchi, R.B. Remington, J.F. Gaw, H.F. Schaefer, and G. Frenking, *J. Chem. Phys.* **98**, 8749 (1993).
“Use of canonical orbital energy derivatives for closed-shell self-consistent-field wave functions”
- J.R. Thomas, B.J. DeLeeuw, G. Vacek, T.D. Crawford, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **99**, 403 (1993).
“The balance between theoretical method and basis set quality: A systematic study of equilibrium geometries, dipole moments, harmonic vibrational frequencies, and infrared intensities”
- A. Willetts and J.E. Rice, *J. Chem. Phys.* **99**, 426 (1993).
“A study of solvent effects on hyperpolarizabilities: The reaction field model applied to acetonitrile”

Index

Activation energy (barrier), 369, 371, 373
Active space, 20, 111, 119, 175, 197
A matrix, 60, 129, 151, 181, 204, 296, 332, 359
 first derivative, 133
Anharmonicity (constants), 6, 218, 364, 379
Antisymmetrizer, 12, 111
Atomic orbital (AO), 12, 29, 309
Averaged Fock operator
 GRSCF, 150
 MCSCF, 202
 PEMCSCF, 180

Bare generalized Lagrangian matrix
 PEMCSCF, 116, 174, 275
 TCSCF, 105
Bare Lagrangian matrix
 CI, 90, 168, 252, 321, 340
 first derivative CI, 90
 first derivative MCSCF, 195, 346, 347
 first derivative PEMCSCF, 173
 MCSCF, 122, 194, 199, 261, 326, 343
 PEMCSCF, 115, 173, 274
 second derivative MCSCF, 210
 TCSCF, 103
Bare τ matrix
 PEMCSCF, 117, 174, 275
 TCSCF, 105
Bare Y (y) matrix
 CI, 92, 170, 252, 341
 first derivative MCSCF, 206
 MCSCF, 125, 195, 262
Bare Z (z) matrix
 CI, 231
 first derivative CI, 234
Basis set, 12, 376

Born-Oppenheimer approximation, 10, 24, 25, 55

Canonical orbitals, 128
Carbon dioxide (CO_2), 380, 381
Classical barrier height, 367
Closed-shell SCF (CLSCF) wavefunction, 5, 13, 22, 53, 128, 293
Complete active space self-consistent-field (CASSCF) wavefunction, 4, 20, 119, 369
Configuration interaction (CI) wavefunction, 4, 16, 23, 83, 166, 218, 249, 355, 364, 385
Configuration interaction with singles and doubles (CISD), 18, 365, 367, 373, 376, 381, 383
Configuration state function (CSF), 4, 16, 18
Contracted Gaussian functions, 13
Core
 electrons, 18
 orbitals, 18, 202
Correlated wavefunction, 3, 249, 256, 363
 CASSCF, 4, 20, 119, 369
 CI, 4, 16, 23, 83, 166, 218, 249, 355, 364, 385
 GVB, 5, 98, 110, 270
 MCSCF, 4, 18, 119, 193, 258, 364, 385
 PEMCSCF, 5, 98, 110, 170, 270
 TCSCF, 5, 98, 270
Correspondence equations (relationships), 6, 249, 256, 270, 271, 274, 278, 285, 293, 298
Coulomb integrals
 MO basis, 14
Coulomb operator, 14, 21, 54, 70

- Coupled cluster (CC) methods, 363
 Coupled cluster with single, double and linearized triple excitations (CCSDT-1) wavefunction, 369, 373
 Coupled cluster with singles and doubles and perturbative triples (CCSD(T)) wavefunction, 376, 385
 Coupled cluster with singles and doubles (CCSD) wavefunction, 369, 373, 374, 376, 383, 385
 Coupled perturbed configuration interaction (CPCI) equations, 6, 26, 94, 96, 166, 221, 248, 251, 253, 256, 322, 323, 330, 340
 electric field perturbations
 first-order, 340
 second-order, 341
 mixed (cross) perturbations
 second-order, 342
 multiple perturbations, 352
 nuclear perturbations
 first-order, 166, 221, 340
 second-order, 169, 221, 341
 Coupled perturbed Hartree-Fock (CPHF) equations, 4, 26, 63, 79, 87, 96, 128, 144, 248, 250, 251, 253, 256, 290, 292, 300, 303, 315, 318, 323, 330, 332, 355
 electric field perturbations
 CLSCF first-order, 333, 357
 CLSCF second-order, 334, 361
 GRSCF first-order, 336
 GRSCF second-order, 338
 mixed (cross) perturbations
 CLSCF second-order, 334
 GRSCF second-order, 339
 multiple perturbations
 CLSCF, 350
 GRSCF, 350
 nuclear perturbations
 CLSCF first-order, 128, 332, 356
 CLSCF second-order, 134, 333, 359
 GRSCF first-order, 144, 335
 GRSCF second-order, 158, 336
 Coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) equations, 5, 26, 87, 126, 193, 260, 264, 270, 326, 332, 343, 355
 electric field perturbations
 first-order, 344
 second-order, 346
 mixed (cross) perturbations
 second-order, 348
 multiple perturbations, 352
 nuclear perturbations
 first-order, 194, 343
 second-order, 208, 345
 Coupled perturbed paired excitation multiconfiguration Hartree-Fock (CPPEMCHF) equations, 6, 118, 172, 274, 278, 284
 nuclear perturbations
 first-order, 172
 second-order, 182
 Coupled perturbed two-configuration Hartree-Fock (CPTCHF) equations, 109
 see also CPPEMCHF
 Coupling constants
 see One-electron coupling constants
 see Two-electron coupling constants
 Cross perturbations
 see Mixed perturbations
 Deleted virtual approximation, 18
 Density matrix
 CLSCF, 15, 22, 57
 GRSCF, 73
 Diagonality
 CLSCF Fock matrix, 54, 128, 304
 GRSCF averaged Fock matrix, 150
 MCSCF averaged Fock matrix, 202
 PEMCSCF averaged Fock matrix, 180
 Diketene, 383
 Dipole moment
 see Electric dipole moment
 Dipole moment derivative
 see Electric dipole moment derivative

- Dipole moment integral
AO basis, 310
MO basis, 310
- Doublet state, 69
- Double zeta plus heavy atom polarization (DZd) basis set, 383
- Double zeta plus polarization (DZP) basis set, 365, 367, 373, 376, 381
- Eigenfunction, 11
- Eigenvalue, 9, 18
- Electric dipole moment, 312, 376
CI, 313, 357
CLSCF, 312
GRSCF, 313
MCSCF, 314
- Electric dipole moment derivative, 326
CI, 329
CLSCF, 327
GRSCF, 328
MCSCF, 331
- Electric field, 6, 29, 308, 364
- Electric hyperpolarizability, 364
- Electric polarizability, 314, 360, 364
CI, 320, 360
CLSCF, 315
GRSCF, 317
MCSCF, 323
- Electronic energy, 10, 13
CI, 17, 23, 84, 219, 249
CLSCF, 13, 22, 53, 293
GRSCF, 68, 285
MCSCF, 19, 120, 258
PEMCSCF, 111, 114, 270
TCSCF, 99, 101
- Electronic energy first derivative
CI, 84, 220, 250, 313, 355
CLSCF, 55, 295, 304, 312
GRSCF, 71, 286, 313
MCSCF, 121, 259, 314
PEMCSCF, 115, 272
TCSCF, 102
- Electronic energy fourth derivative
CI, 224, 246, 253
CLSCF, 300, 306
- GRSCF, 290
MCSCF, 264
PEMCSCF, 278
- Electronic energy second derivative
CI, 94, 221, 251, 322, 358
CLSCF, 60, 63, 296, 304, 315
GRSCF, 76, 79, 286, 318
MCSCF, 124, 259, 324
PEMCSCF, 116, 272
TCSCF, 106
- Electronic energy third derivative
CI, 222, 233, 251
CLSCF, 298, 305
GRSCF, 288
MCSCF, 260
PEMCSCF, 274
- Electronic Hamiltonian operator, 10, 84
- Energy
expectation value, 10, 13
nuclear repulsion, 10, 25, 51
orbital, 14, 15, 54, 129, 150, 180, 202, 304
total, 10, 25
see also Electronic energy
- Energy weighted density matrix
CI, 88
CLSCF, 57
GRSCF, 73
MCSCF, 123
- Exchange integrals
MO, 14
- Exchange operator, 14, 54, 70
- Finite difference method, 3, 364
- First derivative
CI bare Lagrangian matrix, 90
CI bare Z matrix, 234
CI coefficients normalization condition, 85, 168, 221, 323
CI Hamiltonian matrix, 89, 168, 220, 252, 323, 340
CI Lagrangian matrix, 321
CLSCF A matrix, 133
CLSCF Fock matrix, 58, 129, 298, 317
CLSCF orbital energy, 131, 305

- GRSCF averaged Fock matrix, 151
 GRSCF generalized Lagrangian matrix, 154
 GRSCF Lagrangian matrix, 74, 145, 319
 GRSCF τ matrix, 155
 MCSCF averaged Fock matrix, 204
 MCSCF bare Lagrangian matrix, 195, 346, 347
 MCSCF bare y matrix, 206
 MCSCF Hamiltonian matrix, 121, 199, 346, 348
 MCSCF Lagrangian matrix, 195, 261
 MO orthonormality condition, 36, 38, 56, 88, 123, 129, 146, 178, 196, 200, 259, 311, 358
 nuclear repulsion energy, 51
 one-electron AO integral, 33, 310
 one-electron MO integral, 39, 41
 one-electron reduced density matrix
 CI, 321
 MCSCF, 203
 PEMCSCF, 181
 orbital energy, 131, 305
 overlap AO integral, 32
 overlap MO integral, 34, 37
 PEMCSCF averaged Fock matrix, 181
 PEMCSCF bare Lagrangian matrix, 173
 PEMCSCF Hamiltonian matrix, 115, 177, 276
 PEMCSCF Lagrangian matrix, 174
 TCSCF Hamiltonian matrix, 103
 two-electron AO integral, 33
 two-electron MO integral, 43, 47
 see also Electronic energy first derivative
- Fock matrix
 CLSCF, 14, 15, 22, 54, 128, 293
 first derivative, 58, 129, 298, 317
- Fock operator
 CLSCF, 14, 54
 MCSCF, 121
- Formaldehyde (H_2CO), 367, 371, 376
 Formyl radical (HCO), 369
 Fourth derivative
 CI Hamiltonian matrix, 235
 MO orthonormality condition, 264
 see also Electronic energy fourth derivative
 Frozen core approximation, 18
 Full CI, 4, 18, 20
- Gaussian-type orbital (GTO), 3, 12
 Generalized Fock operator
 GRSCF, 16, 70, 144
 MCSCF, 121
 PEMCSCF, 114, 172
 TCSCF, 101
- Generalized Lagrangian matrix
 GRSCF, 75, 145, 287
 PEMCSCF, 117, 174, 272
 TCSCF, 106
- Generalized valence bond (GVB) wavefunction, 5, 98, 110, 270
- General restricted open-shell SCF (GRSCF) wavefunction, 5, 16, 68, 144, 285
- Geometry optimization, 364
 Glyoxal, 371
- Hamiltonian matrix
 CI, 17, 84, 166, 219, 250
 first derivative CI, 89, 168, 220, 252, 323, 340
 first derivative MCSCF, 121, 199, 346, 348
 first derivative PEMCSCF, 115, 177, 276
 first derivative TCSCF, 103
 fourth derivative CI, 235
 MCSCF, 19, 120, 198, 258
 PEMCSCF, 111, 177, 271
 second derivative CI, 92, 170, 221, 252, 341, 342
 second derivative MCSCF, 124, 213
 second derivative PEMCSCF, 116, 187, 281

- second derivative TCSCF, 104
TCSCF, 99
third derivative CI, 228, 254
Hamiltonian operator, 9, 29, 308
Harmonic vibrational frequencies, 3, 363, 376
Hartree-Fock approximation, 11
Hartree-Fock equations, 14
Hartree-Fock (HF) wavefunction, 11, 13
Hellmann-Feynman theorem, 312
Hessian, 3, 24, 367
Hessian index, 24
High-spin open-shell, 69, 99, 110, 175
Hydrogen cyanide (HCN), 365
Hydrogen fluoride (HF), 373
Hydrogen fluoride dimer [(HF)₂], 373
Hydrogen isocyanide (HNC), 365
hyperpolarizability
 see Electric hyperpolarizability
Imaginary frequency, 3, 371, 373
Independent and non-independent pairs
 CLSCF, 131, 315
 GRSCF, 148, 150, 318, 329
 MCSCF, 197, 206
 PEMCSCF, 175, 180
Infrared (IR) intensities, 326, 364, 376
Intrinsic reaction coordinate, 365
Kinetic energy, 10
Koopmans' theorem, 129
Kronecker delta function, 14
Lagrange's method of undetermined multipliers, 167, 177, 199
Lagrangian matrix
 CI, 87, 90, 168, 250, 355
 first derivative CI, 321
 first derivative GRSCF, 74, 145, 319
 first derivative MCSCF, 195, 261
 first derivative PEMCSCF, 174
 GRSCF, 16, 70, 144, 285
 MCSCF, 20, 121, 194, 199, 258
 PEMCSCF, 114, 173, 271
 second derivative GRSCF, 156, 162
second derivative MCSCF, 211
second derivative PEMCSCF, 184
TCSCF, 102
Laplacian operator, 9
Linear combination of atomic orbitals-molecular orbital (LCAO-MO), 5, 9, 11, 15, 29
Linear dependency, 178, 195, 200, 362
Minimal basis set, 13
Minimum energy path, 365
Mixed (cross) perturbations, 308, 311, 326
Modified derivative Lagrangian matrix
 CI first, 252
 CI second, 255
 CLSCF first, 300
 CLSCF second, 301, 303
 GRSCF first, 289
 GRSCF second, 290
 MCSCF first, 261
 MCSCF second, 267
 PEMCSCF first, 276
 PEMCSCF second, 279
Molecular orbital (MO), 12, 29
MO orthonormality condition, 14, 36, 56, 258, 311
CLSCF, 14, 56
MCSCF, 19, 258
first derivative, 36, 38, 56, 88, 123, 129, 146, 178, 196, 200, 259, 311, 358
fourth derivative, 264
second derivative, 34, 39, 62, 96, 108, 118, 126, 136, 160, 189, 213, 259, 311, 362
third derivative, 261
Multiconfiguration self-consistent-field (MCSCF) wavefunction, 4, 18, 119, 193, 258, 364, 385
Multiple perturbations, 349
Newton-Raphson method, 4, 24
Normalization condition of
 CI coefficients, 16, 83, 166, 219, 250
 CLSCF MO coefficients, 16

- MCSCF CI coefficients, 19, 119, 199
- PEMCSCF CI coefficients, 111, 177
- TCSCF CI coefficients, 99
- Normalization constant, 12
- Nuclear perturbation, 4, 29, 364
- Nuclear repulsion energy, 10, 25, 51
 - first derivative, 51
 - second derivative, 51
- Occupation number, 68, 150, 180
- Occupied orbital, 16, 22, 31, 68, 144, 148
- One-electron coupling constant
 - CI, 17, 84, 167, 219, 250, 321
 - GRSCF, 16, 68
 - MCSCF, 19, 120, 199, 258, 324
 - PEMCSCF, 111, 270
 - TCSCF, 99
- One-electron integral
 - AO basis, 15, 21, 33
 - first derivative AO basis, 33, 310
 - first derivative MO basis, 39, 41
 - MO basis, 14, 17, 20, 39
 - second derivative AO basis, 33, 310
 - second derivative MO basis, 39, 42
- One-electron operator, 10, 14, 21, 54, 70, 121
- One-electron reduced density matrix
 - CI AO basis, 23, 87, 250
 - CI MO basis, 17, 23, 84, 167, 219, 250, 321
 - first derivative
 - CI, 321
 - MCSCF, 203
 - PEMCSCF, 181
 - MCSCF AO basis, 123
 - MCSCF MO basis, 19, 120, 199, 258
 - PEMCSCF MO basis, 113, 270
 - TCSCF MO basis, 100
- Open-shell SCF wavefunction, 16, 68, 285
- Open-shell singlet, 68, 70
- Orbital energies, 14, 15, 54, 129, 150, 180, 202, 304
 - first derivative CLSCF, 131, 305
- Orbital exponent, 12
- Orthogonality, 11
- Orthonormality condition
 - see MO orthonormality condition
- Overlap integral
 - AO basis, 15, 32
 - first derivative AO basis, 32
 - first derivative MO basis, 34, 37
 - MO basis, 14
 - second derivative AO basis, 32
 - second derivative MO basis, 34, 39
- Paired excitation MCSCF (PEMCSCF)
 - wavefunction, 5, 98, 110, 172, 270
- Pauli exclusion principle, 12
- Permutation operator, 14
- Perturbations
 - electric field, 6, 29, 308, 364
 - mixed (cross), 308, 311, 326
 - multiple, 349
 - nuclear, 4, 6, 29, 308
- Polarizability
 - see Electric polarizability
- Potential energy, 10
- Potential energy (hyper) surface (PES), 3, 24
- Primitive Gaussian functions, 13
- Quadruple zeta plus triple polarization (QZ3P) basis set, 369, 374
- Quartet state, 69
- Raman intensities, 364
- Reaction coordinate, 24, 365, 373
- Reaction path Hamiltonian, 364, 365
- Reduced density matrices
 - see One-electron reduced density matrix
 - see Two-electron reduced density matrix
- Reference wavefunction (or configuration), 5, 18, 87, 355
- Restricted Hartree-Fock (RHF), 53, 68, 128, 144, 256
- Rys polynomial, 3
- Saddle point, 24

- Second derivative
CI coefficients normalization condition, 170
CI Hamiltonian matrix, 92, 170, 221, 252, 341, 342
CLSCF, Fock matrix, 136, 138
GRSCF, Lagrangian matrix, 156, 162
MCSCF bare Lagrangian matrix, 210
MCSCF Hamiltonian matrix, 124, 213
MCSCF Lagrangian matrix, 211
MO orthonormality condition, 34, 39, 62, 96, 108, 118, 126, 136, 160, 189, 213, 259, 311, 362
nuclear repulsion energy, 51
one-electron AO integral, 33, 310
one-electron MO integral, 39, 42
overlap AO integral, 32
overlap MO integral, 34, 37, 39
PEMCSCF bare Lagrangian matrix, 183
PEMCSCF Hamiltonian matrix, 116, 187, 281
PEMCSCF Lagrangian matrix, 184
TCSCF Hamiltonian matrix, 104
two-electron AO integral, 34
two-electron MO integral, 43, 49
see also Electronic energy second derivative
Secular equation, 15
Shell, 73, 147, 150, 175, 180
Simultaneous equations, 357
CI, 168, 169
CLSCF, 131
GRSCF, 148
MCSCF, 194, 201
PEMCSCF, 179
Skeleton (core) first derivative
CI bare Lagrangian matrix, 91, 170, 252, 341, 342
CI bare Y matrix, 255
CI bare Z matrix, 235
CI Hamiltonian matrix, 90, 168, 252
CI Lagrangian matrix, 92, 170, 233, 251, 321, 330, 358, 361
CI Y matrix, 234, 253
CI Z matrix, 248, 256
CLSCF A matrix, 133, 298, 334, 359
CLSCF Fock matrix, 59, 129, 296, 316, 332, 334, 356, 361
GRSCF averaged Fock matrix, 151
GRSCF generalized Lagrangian matrix, 154, 288, 338
GRSCF Lagrangian matrix, 75, 145, 287, 319, 336
GRSCF τ matrix, 154, 288
MCSCF averaged Fock matrix, 204
MCSCF bare Lagrangian matrix, 125, 195, 262, 346, 347
MCSCF bare y matrix, 207, 209, 267
MCSCF Hamiltonian matrix, 121, 199, 344
MCSCF Lagrangian matrix, 125, 195, 260, 324, 331, 344
MCSCF y matrix, 209, 263, 345, 347
MCSCF z matrix, 267
one-electron MO integral, 40, 310
overlap MO integral, 35
PEMCSCF averaged Fock matrix, 181
PEMCSCF bare generalized Lagrangian matrix, 184, 278
PEMCSCF bare Lagrangian matrix, 116, 174, 275
PEMCSCF bare τ matrix, 184, 278
PEMCSCF generalized Lagrangian matrix, 184, 274
PEMCSCF Hamiltonian matrix, 115, 177, 276
PEMCSCF Lagrangian matrix, 117, 174, 273
PEMCSCF τ matrix, 184, 274
TCSCF bare Lagrangian matrix, 105
TCSCF Hamiltonian matrix, 103
TCSCF Lagrangian matrix, 105
two-electron MO integral, 46
Skeleton (core) fourth derivative
CI Hamiltonian matrix, 237

Skeleton (core) second derivative
 CI bare Lagrangian matrix, 229, 255
 CI Hamiltonian matrix, 93, 170, 252
 CI Lagrangian matrix, 229, 233, 253
 CI Y matrix, 248, 256
 CLSCF A matrix, 301
 CLSCF Fock matrix, 133, 298, 334, 335, 359
 GRSCF generalized Lagrangian matrix, 290
 GRSCF Lagrangian matrix, 154, 288, 337, 339
 GRSCF τ matrix, 290
 MCSCF bare Lagrangian matrix, 209, 266
 MCSCF Hamiltonian matrix, 124, 214, 262, 346, 349
 MCSCF Lagrangian matrix, 209, 263, 345, 349
 MCSCF y matrix, 267
 one-electron MO integral, 40, 310
 overlap MO integral, 35
 PEMCSCF bare Lagrangian matrix, 184, 278
 PEMCSCF generalized Lagrangian matrix, 278
 PEMCSCF Hamiltonian matrix, 116, 188, 276
 PEMCSCF Lagrangian matrix, 184, 274
 PEMCSCF τ matrix, 278
 TCSCF Hamiltonian matrix, 105
 two-electron MO integral, 46
 Skeleton (core) third derivative
 CI bare Lagrangian matrix, 237
 CI Hamiltonian matrix, 229, 254
 CI Lagrangian matrix, 237, 247, 256
 CLSCF Fock matrix, 301
 GRSCF Lagrangian matrix, 290
 MCSCF Hamiltonian matrix, 266
 MCSCF Lagrangian matrix, 267
 PEMCSCF Hamiltonian matrix, 281
 PEMCSCF Lagrangian matrix, 278
 Slater determinant, 12

Slater-type orbital (STO), 12
 Spatial orbital, 12
 Spin function, 12
 Spin-orbitals, 11
 Split valence basis set, 13
 Stationary point, 3, 24, 308, 363
 s-Tetrazine, 371
 Symmetric relationships
 one-electron
 AO integral, 21
 MO integral, 21
 reduced density matrix AO, 23
 reduced density matrix MO, 17
 τ matrix, 147
 two-electron
 AO integral, 21
 coupling constant MO, 207
 MO integral, 21
 reduced density matrix AO, 23
 reduced density matrix MO, 17
 τ matrix
 GRSCF, 75, 145, 287
 PEMCSCF, 117, 174, 273
 TCSCF, 106
 Third derivative
 CI Hamiltonian matrix, 228, 254
 MO orthonormality condition, 261
 see also Electronic energy third derivative
 Total energy, 10, 25
 CI, 84
 CLSCF, 54
 GRSCF, 68
 MCSCF, 120
 PEMCSCF, 114
 TCSCF, 101
 Transition state, 3, 24, 364
 Triplet state, 69, 369
 Triple zeta plus double polarization (TZ2P) basis set, 367, 374, 376
 Triple zeta plus polarization (TZP) basis set, 381
 Two-configuration self-consistent field (TCSCF) wavefunction, 5, 98, 270

- Two-electron coupling constant
CI, 17, 84, 167, 219, 250
GRSCF, 16, 68
MCSCF, 19, 120, 200, 207, 258
PEMCSCF, 111, 270
TCSCF, 99
- Two-electron integral
AO basis, 15, 21, 33
first derivative AO basis, 33
first derivative MO basis, 43, 47
MO basis, 17, 21, 43
second derivative AO basis, 33
second derivative MO basis, 43, 49
- Two-electron operator, 21, 34, 121
- Two-electron reduced density matrix
CI AO basis, 23, 87
CI MO basis, 17, 23, 84, 167, 219, 250
MCSCF AO basis, 123
MCSCF MO basis, 19, 120, 200, 258
PEMCSCF MO basis, 113, 270
TCSCF MO basis, 101
- U matrices, 27, 31, 309, 350, 356
- Unitary transformation, 128, 150, 180, 202, 294
- Unoccupied orbitals
see Virtual orbitals
- Variational conditions, 11, 14, 18, 19
CI space, 18, 84, 166, 219, 250
CLSCF MO space, 14, 54, 128, 293, 304
GRSCF MO space, 16, 71, 144, 285, 319
MCSCF CI space, 20, 120, 198
MCSCF MO space, 20, 121, 194, 258, 325
PEMCSCF CI space, 115, 177
PEMCSCF MO space, 114, 172, 271
TCSCF CI space, 102
TCSCF MO space, 102
- Variation method, 10
- Variation principle, 11
- Virtual orbitals, 18, 31, 68, 71, 130, 144, 148, 202, 304
- Water (H_2O), 376, 381
- Wavefunction
CASSCF, 4, 20, 119, 369
CI, 4, 16, 23, 83, 166, 218, 249, 355, 364, 385
CLSCF, 5, 13, 22, 53, 128, 293
GRSCF, 5, 16, 68, 144, 285
GVB, 5, 98, 110, 270
MCSCF, 4, 18, 119, 193, 258, 364, 385
PEMCSCF, 5, 98, 110, 172, 270
TCSCF, 5, 98, 270
- Wigner's 2n+1 theorem, 25
- Y (y) matrix
CI, 92, 170, 251, 321, 359
MCSCF, 125, 195, 260, 325
- Zero-point vibrational energy (ZPVE), 365, 369
- Z (z) matrix
CI, 231, 255
MCSCF, 267
- Z vector method, 6, 26, 87, 96, 314, 323, 330, 355