

Notes of Modern Quantum Chemistry, Szabo & Ostlund

WSR

July 1, 2020

Contents

0		4
1		4
1.1	4
1.2	4
1.3	4
1.4	N-D Complex Vector Spaces	4
1.4.1	Change of Basis	4
2		5
2.1	The Electronic Problem	5
2.1.1	Atomic Units	5
2.1.2	The B-O Approximation	5
2.1.3	The Antisymmetry or Pauli Exclusion Principle	5
2.2	Orbitals, Slater Determinants, and Basis Functions	5
2.2.1	Spin Orbitals and Spatial Orbitals	5
2.2.2	Hartree Products	5
2.2.3	Slater Determinants	5
2.2.4	The Hartree-Fock Approximation	5
2.2.5	The Minimal Basis H ₂ Model	5
2.2.6	Excited Determinants	5
2.3	Operators and Matrix Elements	5
2.3.1	Minimal Basis H ₂ Matrix Elements	5
2.3.2	Notations for 1- and 2-Electron Integrals	5
2.3.3	General Rules for Matrix Elements	6
2.4	Second Quantization	6
2.4.1	Creation and Annihilation Operators and Their Anticommutation Relations	6
2.5	Spin-Adapted Configurations	6
2.5.1	Spin Operators	6
2.5.2	Restricted Determinants and Spin-Adapted Configurations	7
3	The Hartree-Fock Approximation	7
3.1	The HF Equations	7
3.1.1	The Coulomb and Exchange Operators	7
3.1.2	The Fock Operator	7

3.2	Derivation of the HF Equations	7
3.2.1	Functional Variation	7
3.2.2	Minimization of the Energy of a Single Determinant	7
3.2.3	The Canonical HF Equations	7
3.3	Interpretation of Solutions to the HF Equations	7
3.3.1	Orbital Energies and Koopmans' Theorem	7
3.3.2	Brillouin's Theorem	8
3.3.3	The HF Hamiltonian	8
3.4	Restricted Closed-shell HF: The Roothaan Equations	8
3.4.1	Closed-shell HF: Restricted Spin Orbitals	8
3.4.2	Introduction of a Basis: The Roothaan Equations	8
3.4.3	The Charge Density	8
3.4.4	Expression for the Fock Matrix	8
3.4.5	Orthogonalization of the Basis	8
3.4.6	The SCF Procedure	9
3.4.7	Expectation Values and Population Analysis	9
3.5	Model Calculations on H_2 and HeH^+	9
3.5.1	The 1s Minimal STO-3G Basis Set	9
3.5.2	STO-3G H_2	9
3.5.3	An SCF Calculation on STO-3G HeH^+	9
3.6	Polyatomic Basis Sets	9
3.6.1	Contracted Gaussian Functions	9
3.6.2	Minimal Basis Sets: STO-3G	10
3.6.3	Double Zeta Basis Sets: 4-31G	10
3.6.4	Polarized Basis Sets: 6-31G* and 6-31G**	10
3.7	Some Illustrative Closed-shell Calculations	10
3.7.1	Total Energies	10
3.7.2	Ionization Potentials	10
3.7.3	Equilibrium Geometries	10
3.7.4	Population Analysis and Dipole Moments	10
3.8	Unrestricted Open-shell HF: The Pople-Nesbet Equations	10
3.8.1	Open-shell HF: Unrestricted Spin Orbitals	10
3.8.2	Introduction of a Basis: The Pople-Nesbet Equations	10
3.8.3	Unrestricted Density Matrices	10
3.8.4	Expression for the Fock Matrices	10
3.8.5	Solution of the Unrestricted SCF Equations	11
3.8.6	Illustrative Unrestricted Calculations	11
4	Configuration Interaction	11
4.1	Multiconfigurational Wave Functions and the Structure of Full CI Matrix	11
4.1.1	Intermediate Normalization and an Expression for the Correlation Energy	11
4.2	Doubly Exited CI	11
4.3	Some Illustrative Calculations	12
4.4	Natural Orbitals and the 1-Particle Reduced DM	12
4.5	The MCSCF and the GVB Methods	12
4.6	Truncated CI and the Size-consistency Problem	12
5	Pair and Coupled-pair Theories	12
5.1	The Independent Electron Pair Approximation	12

5.1.1	Invariance under Unitary Transformations: An Example	13
5.1.2	Some Illustrative Calculations	13
5.2	Coupled-pair Theories	13
5.2.1	The Coupled-cluster Approximation	13
5.2.2	The Cluster Expansion of the Wave Function	14
5.2.3	Linear CCA and the Coupled-Electron Pair Approximation	14
5.2.4	Some Illustrative Calculations	14
5.3	Many-electron Theories with Single Particle Hamiltonians	14
5.3.1	The Relaxation Energy via CI, IEPA, CEPA and CCA	14
5.3.2	The Resonance Energy of Polyenes in Hückel Theory	14
6	Many-body Perturbation Theory	14
6.1	RS Perturbation Theory	14
6.2	Diagrammatic Representation of RS Perturbation Theory	14
6.2.1	Diagrammatic Perturbation Theory for Two States	14
6.2.2	Diagrammatic Perturbation Theory for N States	14
6.2.3	Summation of Diagrams	14
6.3	Orbital Perturbation Theory: One-Particle Perturbations	14
6.4	Diagrammatic Representation of Orbital Perturbation Theory	14
6.5	Perturbation Expansion of the Correlation Energy	14
6.6	The N -dependence of the RS Perturbation Expansion	15
6.7	Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy	15
6.7.1	Hugenholtz Diagrams	15
6.7.2	Goldstone Diagrams	15
6.7.3	Summation of Diagrams	15
6.7.4	What Is the Linked-Cluster Theorem?	15
6.8	Some Illustrative Calculations	15
7	The 1-Particle Many-body Green's Function	15
7.1	Green's Function in Single-Particle Systems	15
7.2	The 1-Particle Many-body Green's Function	15
7.2.1	The Self-Energy	16
7.2.2	The Solution of the Dyson Equation	16
7.3	Application of the Formalism to H_2 and HeH^+	16
A	Integral Evaluation with 1s Primitive Gaussians	16
B	2-Electron Self-consistent-field Program	16
C	Analytic Derivative Methods and Geometry Optimization	16
C.1	Introduction	16
C.2	General Considerations	16
C.3	Analytic Derivatives	16
C.4	Optimization Techniques	17
C.5	Some Optimization Algorithms	17
C.6	Transition States	18
C.7	Constrained Variation	18
D	Molecular Integrals for H_2 as a Function of Bond Length	18

0

spatial mol orb – $\psi - i, j, k, \dots$
 spatial basis fcn – $\phi - \mu, \nu, \lambda, \dots$
 spin orb – χ
 occ mol orb – a, b, c, \dots
 vir mol orb – r, s, t, \dots
 exact many-elec wfn – Φ
 approx many-elec wfn – Ψ
 exact energy – \mathcal{E}
 approx energy – E

1

1.1

1.2

1.3

1.4 N-D Complex Vector Spaces

Suppose

$$\mathcal{O} |a\rangle = |b\rangle \quad (1.1)$$

$$\langle i | \mathcal{O} | j \rangle = O_{ij} \quad (1.2)$$

def the **adjoint** of \mathcal{O} as \mathcal{O}^\dagger

$$\langle a | \mathcal{O}^\dagger = \langle b | \quad (1.3)$$

$$\langle i | \mathcal{O}^\dagger | j \rangle = O_{ji}^* \quad (1.4)$$

1.4.1 Change of Basis

$$|\alpha\rangle = \sum_i |i\rangle \langle i | \alpha \rangle = \sum_i |i\rangle U_{i\alpha} \quad (1.5)$$

$$|i\rangle = \sum_\alpha |\alpha\rangle \langle i | \alpha \rangle = \sum_\alpha |\alpha\rangle U_{i\alpha}^* \quad (1.6)$$

If i, α are all orthonormal, \mathbf{U} must be unitary.

$$\Omega_{\alpha\beta} = \langle \alpha | \mathcal{O} | \beta \rangle = \dots \sum_{ij} U_{\alpha i}^* O_{ij} U_{j\beta} \quad (1.7)$$

or

$$\mathbf{\Omega} = \mathbf{U}^\dagger \mathbf{O} \mathbf{U} \quad (1.8)$$

2

2.1 The Electronic Problem

2.1.1 Atomic Units

2.1.2 The B-O Approximation

2.1.3 The Antisymmetry or Pauli Exclusion Principle

2.2 Orbitals, Slater Determinants, and Basis Functions

2.2.1 Spin Orbitals and Spatial Orbitals

2.2.2 Hartree Products

2.2.3 Slater Determinants

def

$$|\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix} \quad (2.1)$$

It can be further shortened to

$$|\chi_i\chi_j\cdots\chi_k\rangle \quad (2.2)$$

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H₂ Model

gerade, ungerade

2.2.6 Excited Determinants

Suppose the ground state det

$$|\psi_0\rangle = |\chi_1\cdots\chi_a\cdots\chi_b\cdots\chi_N\rangle \quad (2.3)$$

thus, singly excited det

$$|\psi_a^r\rangle = |\chi_1\cdots\chi_r\cdots\chi_b\cdots\chi_N\rangle \quad (2.4)$$

$$|\psi_{ab}^{rs}\rangle = |\chi_1\cdots\chi_r\cdots\chi_s\cdots\chi_N\rangle \quad (2.5)$$

How does program determine what dets can exist? by gerade/ungerade?

2.3 Operators and Matrix Elements

2.3.1 Minimal Basis H₂ Matrix Elements

2.3.2 Notations for 1- and 2-Electron Integrals

For spin orb,
physicists'

$$\langle ij | kl \rangle = \left\langle \chi_i(1)\chi_j(2) \left| \frac{1}{r_{12}} \right| \chi_k(1)\chi_l(2) \right\rangle \quad (2.6)$$

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle \quad (2.7)$$

chemists'

$$[ij|kl] = \left\langle \chi_i(1)\chi_j(1) \left| \frac{1}{r_{12}} \right| \chi_k(2)\chi_l(2) \right\rangle \quad (2.8)$$

For spatial orb

$$(ij|kl) = \left\langle \psi_i(1)\psi_j(1) \left| \frac{1}{r_{12}} \right| \psi_k(2)\psi_l(2) \right\rangle \quad (2.9)$$

2.3.3 General Rules for Matrix Elements

$$1. |K\rangle = |\cdots mn \cdots\rangle$$

$$\langle K | \mathcal{H} | K \rangle = \sum_m^N \langle m | h | m \rangle + \frac{1}{2} \sum_m^N \sum_n^N \langle mn || mn \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_n^N ([mm|nn] - [mn|nm]) \quad (2.10)$$

or (Since $[mm|mm] - [mm|mm] = 0$)

$$\langle K | \mathcal{H} | K \rangle = \sum_m^N [m|h|m] + \sum_m^N \sum_{n>m}^N ([mm|nn] - [mn|nm]) \quad (2.11)$$

$$2. |K\rangle = |\cdots mn \cdots\rangle, |L\rangle = |\cdots pn \cdots\rangle$$

$$\langle K | \mathcal{H} | L \rangle = \langle m | h | p \rangle + \sum_n^N \langle mn || pn \rangle = [m|h|p] + \sum_n^N ([mp|nn] - [mn|np]) \quad (2.12)$$

$$3. |K\rangle = |\cdots mn \cdots\rangle, |L\rangle = |\cdots pq \cdots\rangle$$

$$\langle K | \mathcal{H} | L \rangle = \langle mn || pq \rangle = [mp|nq] - [mq|np] \quad (2.13)$$

2.4 Second Quantization

2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 \quad a_i a_j + a_j a_i = 0 \quad (2.14)$$

$$\{a_i, a_j^\dagger\} \equiv a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} \quad (2.15)$$

2.5 Spin-Adapted Configurations

2.5.1 Spin Operators

total spin

$$\hat{\mathcal{S}} = \sum_i^N \hat{\mathbf{s}}(i) \quad (2.16)$$

$$\hat{\mathcal{S}}_x = \sum_i^N \hat{\mathbf{s}}_x(i) \quad (2.17)$$

$$\hat{\mathcal{S}}_+ = \sum_i^N \hat{\mathbf{s}}_+(i) \quad (2.18)$$

$$\hat{\mathcal{S}}^2 = \hat{\mathcal{S}}_+ \hat{\mathcal{S}}_- - \hat{\mathcal{S}}_z + \hat{\mathcal{S}}_z^2 \quad (2.19)$$

$$\hat{\mathcal{S}}^2 |\Phi\rangle = S(S+1) |\Phi\rangle \quad (2.20)$$

$$\hat{\mathcal{S}}_z |\Phi\rangle = M_S |\Phi\rangle \quad (2.21)$$

$$\hat{\mathcal{S}}_z |ij \cdots k\rangle = \frac{1}{2}(N^\alpha - N^\beta) |ij \cdots k\rangle \quad (2.22)$$

2.5.2 Restricted Determinants and Spin-Adapted Configurations

$$|^1\Psi_1^2\rangle = \frac{1}{\sqrt{2}}(|1\bar{2}\rangle + |\bar{1}2\rangle) = \frac{1}{\sqrt{2}}(\psi_1(1)\psi_2(2)\alpha(1)\beta(2) - \psi_2(1)\psi_1(2)\alpha(1)\beta(2)) \quad (2.23)$$

3 The Hartree-Fock Approximation

3.1 The HF Equations

3.1.1 The Coulomb and Exchange Operators

$$\mathcal{J}_b(1) = \int dx_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \quad (3.1)$$

$$\mathcal{K}_b(1) = \int dx_2 \chi_b^*(2) r_{12}^{-1} \hat{\mathcal{P}}_{12} \chi_b(2) \quad (3.2)$$

$$= \int dx_2 \chi_b^*(2) r_{12}^{-1} \chi_b(1) \hat{\mathcal{P}}_{12} \quad (3.3)$$

$$\langle \chi_a(1) | \mathcal{J}_b(1) | \chi_a(1) \rangle = J_{ab} \quad (3.4)$$

$$\langle \chi_a(1) | \mathcal{K}_b(1) | \chi_a(1) \rangle = K_{ab} \quad (3.5)$$

3.1.2 The Fock Operator

3.2 Derivation of the HF Equations

3.2.1 Functional Variation

3.2.2 Minimization of the Energy of a Single Determinant

3.2.3 The Canonical HF Equations

3.3 Interpretation of Solutions to the HF Equations

3.3.1 Orbital Energies and Koopmans' Theorem

$$\varepsilon_i = \langle i | h | i \rangle + \sum_b \langle ib | ib \rangle \quad (3.6)$$

$$= \langle i | h | i \rangle + \sum_b (\langle ib | ib \rangle - \langle ib | bi \rangle) \quad (3.7)$$

Koopmans' Theorem

$$\text{IP} = -\varepsilon_a \quad \text{EA} = -\varepsilon_r \quad (3.8)$$

Koopmans' EA is often bad.

3.3.2 Brillouin's Theorem

$$\langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle = 0 \quad (3.9)$$

3.3.3 The HF Hamiltonian

$$\mathcal{H}_0 = \sum_i^N f(i) \quad (3.10)$$

3.4 Restricted Closed-shell HF: The Roothaan Equations

3.4.1 Closed-shell HF: Restricted Spin Orbitals

$$E_0 = 2 \sum_a h_{aa} + \sum_a \sum_b (2J_{ab} - K_{ab}) \quad (3.11)$$

3.4.2 Introduction of a Basis: The Roothaan Equations

3.4.3 The Charge Density

3.4.4 Expression for the Fock Matrix

3.4.5 Orthogonalization of the Basis

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1} \quad (3.12)$$

\mathbf{S} can be diagonalized by unitary matrix \mathbf{U} :

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \quad (3.13)$$

Symmetric Orthogonalization

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U} \mathbf{s}^{-1/2} \mathbf{U}^\dagger \quad (3.14)$$

(linear dependence must be removed)

Canonical Orthogonalization

$$\mathbf{X} = \mathbf{U} \mathbf{S}^{-1/2} = \mathbf{U} \mathbf{s}^{-1/2} \mathbf{U}^\dagger \quad (3.15)$$

Suppose \mathbf{s} has m small values, we make a truncated $K \times (K - m)$ matrix

$$\tilde{\mathbf{X}} = \dots \quad (3.16)$$

thus

$$\phi'_\mu = \sum_\nu^K \phi_\nu \tilde{X}_{\nu\mu} \quad \mu = 1, 2, \dots, K - m \quad (3.17)$$

However, calculate 2e integrals in transformed matrix is very time-consuming.
Since

$$\phi' = \phi \mathbf{X} \quad (3.18)$$

$$\psi = \phi \mathbf{C} \quad (3.19)$$

we have

$$\psi = \phi' \mathbf{X}^{-1} \mathbf{C} \quad (3.20)$$

Let

$$\mathbf{C}' = \mathbf{X}^{-1} \mathbf{C} \quad \text{or} \quad \mathbf{C} = \mathbf{X} \mathbf{C}' \quad (3.21)$$

thus

$$\mathbf{F} \mathbf{X} \mathbf{C}' = \mathbf{S} \mathbf{X} \mathbf{C}' \varepsilon \quad (3.22)$$

$$(\mathbf{X}^\dagger \mathbf{F} \mathbf{X}) \mathbf{C}' = (\mathbf{X}^\dagger \mathbf{S} \mathbf{X}) \mathbf{C}' \varepsilon = \mathbf{C}' \varepsilon \quad (3.23)$$

def:

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \quad (3.24)$$

3.4.6 The SCF Procedure

P. 148

I think \mathbf{C}' should be $(K - m) \times K$.

3.4.7 Expectation Values and Population Analysis

$$N = \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} = \text{tr } \mathbf{P} \mathbf{S} \quad (3.25)$$

Mulliken:

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{P} \mathbf{S})_{\mu\mu} \quad (3.26)$$

Löwin:

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2})_{\mu\mu} \quad (3.27)$$

3.5 Model Calculations on H_2 and HeH^+

3.5.1 The 1s Minimal STO-3G Basis Set

$$\alpha = \alpha_{(\zeta=1.0)} \times \zeta^2 \quad (3.28)$$

3.5.2 STO-3G H_2

3.5.3 An SCF Calculation on STO-3G HeH^+

3.6 Polyatomic Basis Sets

3.6.1 Contracted Gaussian Functions

Notation: (pGTO)/[cGTO] (ignore p_x, p_y, \dots)

STO-3G	(6s3p/3s)/[2s1p/1s]
4-31G	(8s4p/4s)/[3s2p/2s]
T. Dunning (JCP 1970)	(9s5p/4s)/[3s2p/2s]
6-31G* (sph)	(10s4p1d)/[3s2p1d/2s]
6-31G** (sph)	(10s4p1d/4s1p)/[3s2p1d/2s1p]

3.6.2 Minimal Basis Sets: STO-3G

3.6.3 Double Zeta Basis Sets: 4-31G

3.6.4 Polarized Basis Sets: 6-31G* and 6-31G**

What's D polarized basis?

Cartesian: xx, yy, zz, xy, yz, xz

Spherical: $3z^2 - r^2, x^2 - y^2, xy, yz, zx$, (r^2 is removed)

3.7 Some Illustrative Closed-shell Calculations

3.7.1 Total Energies

3.7.2 Ionization Potentials

3.7.3 Equilibrium Geometries

3.7.4 Population Analysis and Dipole Moments

3.8 Unrestricted Open-shell HF: The Pople-Nesbet Equations

3.8.1 Open-shell HF: Unrestricted Spin Orbitals

$$f^\alpha(1) = h(1) + \sum_a^{N_\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N_\beta} J_a^\beta(1) \quad (3.29)$$

$$E_0 = \sum_a h_{aa} + \frac{1}{2} \sum_a^{N_\alpha} \sum_b^{N_\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2} \sum_a^{N_\beta} \sum_b^{N_\beta} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N_\alpha} \sum_b^{N_\beta} J_{ab}^{\alpha\beta} \quad (3.30)$$

3.8.2 Introduction of a Basis: The Pople-Nesbet Equations

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S} \mathbf{C}^\alpha \boldsymbol{\varepsilon}^\alpha \quad (3.31)$$

$$\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S} \mathbf{C}^\beta \boldsymbol{\varepsilon}^\beta \quad (3.32)$$

3.8.3 Unrestricted Density Matrices

spin density

$$\rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \quad (3.33)$$

$$\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta \quad (3.34)$$

3.8.4 Expression for the Fock Matrices

$$F_{\mu\nu}^\alpha = H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma [P_{\lambda\sigma}^T(\mu\nu|\sigma\lambda) - P_{\lambda\sigma}^\alpha(\mu\lambda|\sigma\nu)] \quad (3.35)$$

$$F_{\mu\nu}^\beta = H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma [P_{\lambda\sigma}^T(\mu\nu|\sigma\lambda) - P_{\lambda\sigma}^\beta(\mu\lambda|\sigma\nu)] \quad (3.36)$$

3.8.5 Solution of the Unrestricted SCF Equations

3.8.6 Illustrative Unrestricted Calculations

4 Configuration Interaction

4.1 Multiconfigurational Wave Functions and the Structure of Full CI Matrix

1.

$$\langle \Psi_0 | \mathcal{H} | S \rangle = 0 \quad (4.1)$$

2. Slater dets which differ by > 2 spin orbitals are zero.
Non-zero blocks are sparse.

3. Single excitations have a very small effect on the ground state energy, but not small for dipole and excited states.

4.1.1 Intermediate Normalization and an Expression for the Correlation Energy

Intermediate Normalization:

$$|\Phi_0\rangle = |\Psi_0\rangle + \dots \quad (4.2)$$

thus

$$\langle \Psi_0 | \Phi_0 \rangle = 0 \quad (4.3)$$

thus

$$E_{\text{corr}} = \langle \Psi_0 | \mathcal{H} - E_0 | \Phi_0 \rangle = \sum_{c < d, t < u} c_{cd}^{tu} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle \quad (4.4)$$

4.2 Doubly Exited CI

$$\sum_{c < d, t < u} c_{cd}^{tu} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle = E_{\text{corr}} \quad (4.5)$$

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c < d, t < u} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle = c_{ab}^{rs} E_{\text{corr}} \quad (4.6)$$

def

$$B_{rasb} = \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle \quad (4.7)$$

$$D_{rasb,tcud} = \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle \quad (4.8)$$

$$c_{rasb} = c_{ab}^{rs} \quad (4.9)$$

thus

$$\begin{pmatrix} 0 & \mathbf{B}^\dagger \\ \mathbf{B} & \mathbf{D} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix} \quad (4.10)$$

then diagonalize.

Another way:

$$E_{\text{corr}} = -\mathbf{B}^\dagger (\mathbf{D} - E_{\text{corr}} \mathbf{1})^{-1} \mathbf{B} \quad (4.11)$$

solve it iteratively.

4.3 Some Illustrative Calculations

4.4 Natural Orbitals and the 1-Particle Reduced DM

reduced density function

$$\rho(\mathbf{x}_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) \Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \quad (4.12)$$

1st-order reduced DM, or 1-P reduced DM

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) \Phi(\mathbf{x}'_1, \cdots, \mathbf{x}_N) \quad (4.13)$$

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_{ij} \chi_i(\mathbf{x}_1) \gamma_{ij} \chi_j^*(\mathbf{x}'_1) \quad (4.14)$$

def an orthonormal basis $\{\eta_i\}$ (natural spin orb),

$$\eta_i = \sum_k \chi_k U_{ki} \quad (4.15)$$

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_{kl} \eta_k(\mathbf{x}_1) (\mathbf{U}^\dagger \gamma \mathbf{U})_{kl} \eta_l^*(\mathbf{x}'_1) \quad (4.16)$$

def

$$\lambda = \mathbf{U}^\dagger \gamma \mathbf{U} \quad (4.17)$$

find a \mathbf{U} to make λ diagonal, thus

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_i \lambda_i \eta_i(\mathbf{x}_1) \eta_i^*(\mathbf{x}'_1) \quad (4.18)$$

λ_i is called the occupation number of the natural spin orbs.

4.5 The MCSCF and the GVB Methods

4.6 Truncated CI and the Size-consistency Problem

Truncated CI is not size-consistent.

5 Pair and Coupled-pair Theories

5.1 The Independent Electron Pair Approximation

Full CI

$$E_{\text{corr}} = \sum_{a < b} e_{ab} \quad (5.1)$$

$$e_{ab} = \sum_{r < s} c_{ab}^{rs} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle \quad (5.2)$$

IEPA: Do CID for each pair separately.

Do some approx., we get Epstein-Nesbet pair corr. E:

$$e_{ab}^{\text{EN}} = - \sum_{r < s} \frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle|^2}{\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle} \quad (5.3)$$

more approx., first-order pair E:

$$e_{ab}^{\text{FO}} = \sum_{r < s} \frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (5.4)$$

5.1.1 Invariance under Unitary Transformations: An Example

2 independent H₂

MOs localized on the 2 monomers: 1₁, 2₁, 1₂, 2₂

delocalized MOs:

$$a = \frac{1}{\sqrt{2}}(1_1 + 1_2) \quad (5.5)$$

$$b = \frac{1}{\sqrt{2}}(1_1 - 1_2) \quad (5.6)$$

$$r = \frac{1}{\sqrt{2}}(2_1 - 2_2) \quad (5.7)$$

$$s = \frac{1}{\sqrt{2}}(2_1 + 2_2) \quad (5.8)$$

5.1.2 Some Illustrative Calculations

IEPA is not variational.

IEPA is not invariant to unitary transformations.

works bad for Ne and N₂.

5.2 Coupled-pair Theories

Ignore single, triple, etc.

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{a < b, r < s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{a < b < c < d, r < s < t < u} c_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle + \dots \quad (5.9)$$

then

$$\sum_{c < d, t < u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} = E_{\text{corr}} \quad (5.10)$$

$$\begin{aligned} & \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{abcd}^{rstu} \rangle c_{abcd}^{rstu} = E_{\text{corr}} c_{ab}^{rs} \\ & \dots \end{aligned} \quad (5.11)$$

How to truncate/decouple?

$c_{abcd}^{rstu} := 0 \Rightarrow \text{CID}$,
or, use CC.

5.2.1 The Coupled-cluster Approximation

Suppose

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} * c_{cd}^{tu} = \dots \quad (5.12)$$

thus

$$\begin{aligned} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \\ + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{abcd}^{rstu} \rangle (c_{ab}^{rs} * c_{cd}^{tu}) = \left(\sum_{c < d, t < u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs} \end{aligned} \quad (5.13)$$

after some tricks

$$\begin{aligned} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \\ + \sum_{c < d, t < u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle (c_{ab}^{rs} c_{cd}^{tu} - \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle) = \left(\sum_{c < d, t < u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs} \end{aligned} \quad (5.14)$$

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} - \sum_{c < d, t < u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = 0 \quad (5.15)$$

along with (5.10), we get the energy of Coupled-Pair Many-Electron Theory (CPMET), aka CCA.

CCA is derived by J. Čížek and J. Paldus.

CC is size-consistent.

CC is invariant to unitary transformations of degenerate orbitals.

But, CC is not variational.

5.2.2 The Cluster Expansion of the Wave Function

5.2.3 Linear CCA and the Coupled-Electron Pair Approximation

5.2.4 Some Illustrative Calculations

5.3 Many-electron Theories with Single Particle Hamiltonians

5.3.1 The Relaxation Energy via CI, IEPA, CEPA and CCA

5.3.2 The Resonance Energy of Polyenes in Hückel Theory

6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

6.2.2 Diagrammatic Perturbation Theory for N States

6.2.3 Summation of Diagrams

6.3 Orbital Perturbation Theory: One-Particle Perturbations

6.4 Diagrammatic Representation of Orbital Perturbation Theory

6.5 Perturbation Expansion of the Correlation Energy

MPPT:

$$E_0^{(0)} = \sum_a \varepsilon_a \quad (6.1)$$

$$E_0^{(1)} = -\frac{1}{2} \sum_{ab} \langle ab \| ab \rangle \quad (6.2)$$

$$E_0^{(2)} = \sum_{a < b, r < s} \frac{|\langle ab \| rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (6.3)$$

6.6 The N -dependence of the RS Perturbation Expansion

6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy

6.7.1 Hugenholtz Diagrams

- H1. numerator $\rightarrow \prod_{\text{dot}} \langle in, in \| out, out \rangle$
- H2. denominator $\rightarrow \prod_{\text{adjacent dots}} \left(\sum \varepsilon_{\text{holes}} - \sum \varepsilon_{\text{particles}} \right)$
- H3. sign $\rightarrow (-1)^{h+l}$ (h : # of holes; l : # of closed loops)
- H5. weight factor 2^{-k} (k : # of equivalent line pairs)

6.7.2 Goldstone Diagrams

6.7.3 Summation of Diagrams

6.7.4 What Is the Linked-Cluster Theorem?

6.8 Some Illustrative Calculations

7 The 1-Particle Many-body Green's Function

7.1 Green's Function in Single-Particle Systems

Solve Eq for \mathbf{a}

$$(E\mathbf{1} - \mathbf{H}_0)\mathbf{a} = \mathbf{b} \rightarrow \mathbf{G}_0(E) = (E\mathbf{1} - \mathbf{H}_0)^{-1} \quad (7.1)$$

$$(E - \mathcal{H}_0)a(x) = b(x) \rightarrow G_0(x, x', E) = \sum_{\alpha} \frac{\psi_{\alpha}(x)\psi_{\alpha}^*(x')}{E - E_{\alpha}^{(0)}} \quad (7.2)$$

7.2 The 1-Particle Many-body Green's Function

HF Green's function

$$G_0(\mathbf{x}, \mathbf{x}', E) = \sum_i \frac{\chi_i(\mathbf{x})\chi_i^*(\mathbf{x}')}{E - \varepsilon_i} \quad (7.3)$$

$$[G_0(E)]_{ij} = \frac{\delta_{ij}}{E - \varepsilon_i} \quad (7.4)$$

i.e.

$$\mathbf{G}_0(E) = (E\mathbf{1} - \varepsilon)^{-1} \quad (7.5)$$

7.2.1 The Self-Energy

Dyson equation

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\mathbf{\Sigma}(E)\mathbf{G}(E) \quad (7.6)$$

7.2.2 The Solution of the Dyson Equation

7.3 Application of the Formalism to H_2 and HeH^+

A Integral Evaluation with 1s Primitive Gaussians

B 2-Electron Self-consistent-field Program

C Analytic Derivative Methods and Geometry Optimization

C.1 Introduction

C.2 General Considerations

$$E(\mathbf{X}_1) = E(\mathbf{X}) + \mathbf{q}^\dagger \mathbf{f}(\mathbf{X}) + \frac{1}{2} \mathbf{q}^\dagger \mathbf{H}(\mathbf{X}) \mathbf{q} + \dots \quad (\text{C.1})$$

where

$$\mathbf{q} = \mathbf{X}_1 - \mathbf{X} \quad f_i = \frac{\partial E(\mathbf{X})}{\partial X_i} \quad H_{ij} = \frac{\partial^2 E(\mathbf{X})}{\partial X_i \partial X_j} \quad (\text{C.2})$$

$$\mathbf{f}(\mathbf{X}_1) = \mathbf{f}(\mathbf{X}) + \mathbf{H}(\mathbf{X})\mathbf{q} \quad (\text{C.3})$$

Let $\mathbf{X}_1 = \mathbf{X}_e$

$$\mathbf{f}(\mathbf{X}) = -\mathbf{H}(\mathbf{X})\mathbf{q} \quad (\text{C.4})$$

i.e.

$$\mathbf{q} = -\mathbf{H}^{-1}(\mathbf{X})\mathbf{f}(\mathbf{X}) \quad (\text{C.5})$$

C.3 Analytic Derivatives

for HF

$$\begin{aligned} \frac{\partial E}{\partial X_A} &= \sum_{\mu\nu} P_{\nu\mu} \frac{\partial H_{\mu\nu}^{\text{core}}}{\partial X_A} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\nu\mu} P_{\lambda\sigma} \frac{\partial(\mu\nu||\sigma\lambda)}{\partial X_A} + \frac{\partial V_{NN}}{\partial X_A} \\ &\quad + \sum_{\mu\nu} \frac{\partial P_{\nu\mu}}{\partial X_A} H_{\mu\nu}^{\text{core}} + \sum_{\mu\nu\lambda\sigma} \frac{\partial P_{\nu\mu}}{\partial X_A} P_{\lambda\sigma} (\mu\nu||\sigma\lambda) \\ &= \dots \\ &= \sum_{\mu\nu} P_{\nu\mu} \frac{\partial H_{\mu\nu}^{\text{core}}}{\partial X_A} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\nu\mu} P_{\lambda\sigma} \frac{\partial(\mu\nu||\sigma\lambda)}{\partial X_A} + \frac{\partial V_{NN}}{\partial X_A} \\ &\quad - \sum_{\mu\nu} Q_{\nu\mu} \frac{\partial S_{\mu\nu}}{\partial X_A} \end{aligned} \quad (\text{C.6})$$

where

$$Q_{\nu\mu} = 2 \sum_a \varepsilon_a C_{\mu a} C_{\nu a} \quad (\text{C.7})$$

C.4 Optimization Techniques

C.5 Some Optimization Algorithms

Nelder-Mead Optimization

```
find(h)
while(true):
    X* = (1+a) Xbar - a X[h]
    if Emin < E* < E[h] :
        update(X[h], X*)
    elif E* < Emin:
        X** = v X* + (1-v) Xbar
        if E** < Emin:
            update(X[h], X**)
        else:
            update(X[h], X*)
    else:
        X** = b X[h] + (1-b) Xbar
```

```

if E** > E[h]:
    pass
else:
    update(X[h], X**)

```

Quasi-Newton Optimization

Murtagh-Sargent

$$\mathbf{q}_n = -\alpha_{n-1} \mathbf{G}_{n-1} \mathbf{f}_{n-1} \quad (\text{C.8})$$

1. Set $\alpha_0 = 1$ and $\mathbf{G}_0 = \mathbf{1}$.
While ($E_1 > E_0$) set $\alpha_0 \leftarrow \alpha_0/2$
- 2.

$$\mathbf{U}_k = -\alpha_{k-1} \mathbf{G}_{k-1} \mathbf{f}_{k-1} - \mathbf{G}_{k-1} (\mathbf{f}_k - \mathbf{f}_{k-1}) = -\mathbf{G}_{k-1} [\mathbf{f}_k + \mathbf{f}_{k-1} (\alpha_{k-1} - 1)] \quad (\text{C.9})$$

$$a_k^{-1} = \mathbf{U}_k^\dagger \mathbf{d}_k = \mathbf{U}_k^\dagger (\mathbf{f}_k - \mathbf{f}_{k-1}) \quad (\text{C.10})$$

$$T_k = \mathbf{U}_k^\dagger \mathbf{U}_k \quad (\text{C.11})$$

if $a_k^{-1} < 10^{-5} T_k$ or $a_k \mathbf{U}_k^\dagger \mathbf{f}_{k-1} > 10^{-5}$, goto step 1
else

$$\mathbf{G}_k = \mathbf{G}_{k-1} + a_k \mathbf{U}_k \mathbf{U}_k^\dagger \quad (\text{C.12})$$

$$\alpha_k = 1 \quad (\text{C.13})$$

- 3.

$$\mathbf{q}_k = -\alpha_{k-1} \mathbf{G}_{k-1} \mathbf{f}_{k-1} \quad (\text{C.14})$$

$$(\text{C.15})$$

C.6 Transition States

C.7 Constrained Variation

D Molecular Integrals for H₂ as a Function of Bond Length