Notes of **Modern Quantum Chemistry, Szabo & Ostlund**

wsr

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Contents

0

spatial mol orb $- \psi - i, j, k, ...$
spatial basis fxn $- \phi - \mu, \nu, \lambda, ...$
spin orb $- \chi$
occ mol orb $- a, b, c, ...$
vir mol orb $- r, s, t, ...$
exact many-elec wfn $- \Phi$
approx many-elec wfn $- \Psi$
exact energy $- \mathscr{E}$
approx energy $- E$

1

1.1

1.2

1.3

1.4   N-D Complex Vector Spaces

Suppose

$$\mathcal{O} \left| a \right\rangle = \left| b \right\rangle \tag{1.1}$$

$$\left\langle i \left| \mathcal{O} \right| j \right\rangle = O_{ij} \tag{1.2}$$

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

$$\left\langle a \right| \mathcal{O}^\dagger = \left\langle b \right| \tag{1.3}$$

$$\left\langle i \left| \mathcal{O}^\dagger \right| j \right\rangle = O_{ji}^* \tag{1.4}$$

1.4.1   Change of Basis

$$\left| \alpha \right\rangle = \sum_i \left| i \right\rangle \left\langle i | \alpha \right\rangle = \sum_i \left| i \right\rangle U_{i\alpha} \tag{1.5}$$

$$\left| i \right\rangle = \sum_\alpha \left| \alpha \right\rangle \left\langle i | \alpha \right\rangle = \sum_\alpha \left| \alpha \right\rangle U_{i\alpha}^* \tag{1.6}$$

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

$$\Omega_{\alpha\beta} = \left\langle \alpha \left| \mathcal{O} \right| \beta \right\rangle = ... \sum_{ij} U_{\alpha i}^* O_{ij} U_{j\beta} \tag{1.7}$$

or

$$\boldsymbol{\Omega} = \mathbf{U}^\dagger \mathbf{O} \mathbf{U} \tag{1.8}$$

4

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

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

It can be further shortened to

$$|\chi_i\chi_j\cdots\chi_k\rangle \tag{2.2}$$

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H_2 Model

gerade, ungerade

2.2.6 Excited Determinants

Suppose the ground state det

$$|\psi_0\rangle = |\chi_1\cdots\chi_a\cdots\chi_b\cdots\chi_N\rangle \tag{2.3}$$

thus, singly excited det

$$|\psi_a^r\rangle = |\chi_1\cdots\chi_r\cdots\chi_b\cdots\chi_N\rangle \tag{2.4}$$

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

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

2.3 Operators and Matrix Elements

2.3.1 Minimal Basis H_2 Matrix Elements

2.3.2 Notations for 1- and 2-Electron Integrals

For spin orb,
physicists'

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

5

$$\langle ij \,\|\, kl \rangle = \langle ij \,|\, kl \rangle - \langle ij \,|\, lk \rangle \tag{2.7}$$

chemists'

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

For spatial orb

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

2.3.3 General Rules for Matrix Elements

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

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

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

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

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

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

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

$$\langle K \,|\, \mathscr{H} \,|\, L \rangle = \langle mn \,\|\, pq \rangle = [mp|nq] - [mq|np] \tag{2.13}$$

2.4 Second Quantization

2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 \quad a_i a_j + a_j a_i = 0 \tag{2.14}$$

$$\{a_i, a_j^\dagger\} \equiv a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} \tag{2.15}$$

2.5 Spin-Adapted Configurations

2.5.1 Spin Operators

total spin

$$\hat{\mathscr{P}} = \sum_i^N \hat{\mathbf{s}}(i) \tag{2.16}$$

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

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

$$\hat{\mathscr{S}}^2 = \hat{\mathscr{S}}_+\hat{\mathscr{S}}_- - \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2 \tag{2.19}$$

$$\hat{\mathscr{S}}^2\ket{\Phi} = S(S+1)\ket{\Phi} \tag{2.20}$$

$$\hat{\mathscr{S}}_z\ket{\Phi} = M_S\ket{\Phi} \tag{2.21}$$

$$\hat{\mathscr{S}}_z\ket{ij\cdots k} = \frac{1}{2}(N^\alpha - N^\beta)\ket{ij\cdots k} \tag{2.22}$$

2.5.2 Restricted Determinants and Spin-Adapted Configurations

$$\ket{^1\Psi_1^2} = \frac{1}{\sqrt{2}}(\ket{1\bar{2}} + \ket{\bar{1}2}) = \frac{1}{\sqrt{2}}(\psi_1(1)\psi_2(2)\alpha(1)\beta(2) - \psi_2(1)...) \tag{2.23}$$

3 The Hartree-Fock Approximation

3.1 The HF Equations

3.1.1 The Coulomb and Exchange Operators

$$\mathscr{J}_b(1) = \int \mathrm{d}x_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \tag{3.1}$$

$$\mathscr{K}_b(1) = \int \mathrm{d}x_2 \chi_b^*(2) r_{12}^{-1} \hat{\mathscr{P}}_{12} \chi_b(2) \tag{3.2}$$

$$= \int \mathrm{d}x_2 \chi_b^*(2) r_{12}^{-1} \chi_b(1) \hat{\mathscr{P}}_{12} \tag{3.3}$$

$$\bra{\chi_a(1)} \mathscr{J}_b(1) \ket{\chi_a(1)} = J_{ab} \tag{3.4}$$

$$\bra{\chi_a(1)} \mathscr{K}_b(1) \ket{\chi_a(1)} = K_{ab} \tag{3.5}$$

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

$$\varepsilon_i = \bra{i}h\ket{i} + \sum_b \braket{ib \| ib} \tag{3.6}$$

$$= \bra{i}h\ket{i} + \sum_b (\braket{ib | ib} - \braket{ib | bi}) \tag{3.7}$$

Koopmans' Theorem

$$\mathrm{IP} = -\varepsilon_a \quad \mathrm{EA} = -\varepsilon_r \tag{3.8}$$

Koopmans' EA is often bad.

3.3.2 Brillouin's Theorem

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_a^r \rangle = 0 \tag{3.9}$$

3.3.3 The HF Hamiltonian

$$\mathscr{H}_0 = \sum_i^N f(i) \tag{3.10}$$

3.4 Restricted Closed-shell HF: The Roothaan Equations

3.4.1 Closed-shell HF: Restricted Spin Orbitals

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

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

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1} \tag{3.12}$$

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

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \tag{3.13}$$

Symmetric Orthogonalization

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

(linear dependence must be removed)

Canonical Orthogonalization

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

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

$$\tilde{\mathbf{X}} = ... \tag{3.16}$$

thus

$$\phi'_\mu = \sum_\nu^K \phi_\nu \tilde{X}_{\nu\mu} \qquad \mu = 1, 2, \cdots, K-m \tag{3.17}$$

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

$$\phi' = \phi \mathbf{X} \tag{3.18}$$

$$\psi = \phi \mathbf{C} \tag{3.19}$$

we have

$$\psi = \phi' \mathbf{X}^{-1} \mathbf{C} \tag{3.20}$$

Let

$$\mathbf{C}' = \mathbf{X}^{-1} \mathbf{C} \qquad or \ \mathbf{C} = \mathbf{X} \mathbf{C}' \tag{3.21}$$

thus

$$\mathbf{F} \mathbf{X} \mathbf{C}' = \mathbf{S} \mathbf{X} \mathbf{C}' \varepsilon \tag{3.22}$$

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

def:

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \tag{3.24}$$

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

$$N = \sum_\mu \sum_\nu P_{\mu\nu} S_{\mu\nu} = \operatorname{tr} \mathbf{PS} \tag{3.25}$$

Mulliken:

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu} \tag{3.26}$$

Löwin:

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

3.5   Model Calculations on H_2 and HeH^+

3.5.1   The $1s$ Minimal STO-3G Basis Set

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

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 $p_x, p_y, ...$)

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]

9

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

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

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

3.8.2 Introduction of a Basis: The Pople-Nesbet Equations

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S}\mathbf{C}^\alpha \boldsymbol{\varepsilon}^\alpha \tag{3.31}$$

$$\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S}\mathbf{C}^\beta \boldsymbol{\varepsilon}^\beta \tag{3.32}$$

3.8.3 Unrestricted Density Matrices

spin density

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

$$\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta \tag{3.34}$$

3.8.4 Expression for the Fock Matrices

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

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

4 Configuration Interaction

4.1 Multiconfigurational Wave Functions and the Structure of Full CI Matrix

1.
$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, S \rangle = 0 \tag{4.1}$$

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:
$$|\Phi_0\rangle = |\Psi_0\rangle + ... \tag{4.2}$$

thus
$$\langle \Psi_0 \,|\, \Phi_0 \rangle = 0 \tag{4.3}$$

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

4.2 Doubly Exited CI

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

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

def
$$B_{rasb} = \langle \Psi_{ab}^{rs} |\, \mathscr{H} \,|\, \Psi_0 \rangle \tag{4.7}$$
$$D_{rasb,tcud} = \langle \Psi_{ab}^{rs} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{cd}^{tu} \rangle \tag{4.8}$$
$$c_{rasb} = c_{ab}^{rs} \tag{4.9}$$

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

then diagonalize.
Another way:
$$E_{\text{corr}} = -\mathbf{B}^\dagger (\mathbf{D} - E_{\text{corr}}\mathbf{1})^{-1} \mathbf{B} \tag{4.11}$$

solve it iteratively.

11

4.3 Some Illustrative Calculations

4.4 Natural Orbitals and the 1-Particle Reduced DM

reduced density function

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

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

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

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

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

$$\eta_i = \sum_k \chi_k U_{ki} \tag{4.15}$$

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

def

$$\boldsymbol{\lambda} = \mathbf{U}^\dagger \boldsymbol{\gamma} \mathbf{U} \tag{4.17}$$

find a $\mathbf{U}$ to make $\boldsymbol{\lambda}$ diagonal, thus

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

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

$$E_{\mathrm{corr}} = \sum_{a<b} e_{ab} \tag{5.1}$$

$$e_{ab} = \sum_{r<s} c_{ab}^{rs} \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{ab}^{rs} \rangle \tag{5.2}$$

IEPA: Do CID for each pair separately.
Do some approx., we get Epstein-Nesbet pair corr. E:

$$e_{ab}^{\mathrm{EN}} = -\sum_{r<s} \frac{|\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{ab}^{rs} \rangle|^2}{\langle \Psi_{ab}^{rs} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{ab}^{rs} \rangle} \tag{5.3}$$

more approx., first-order pair E:

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

5.1.1 Invariance under Unitary Transformations: An Example

2 independent H_2
MOs localized on the 2 monomers: $1_1, 2_1, 1_2, 2_2$
delocalized MOs:

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

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

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

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

5.1.2 Some Illustrative Calculations

IEPA is not variational.
IEPA is not invariant to unitary tranformations.
works bad for Ne and N_2.

5.2 Coupled-pair Theories

Ignore single, triple, etc.

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

then

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

$$\langle \Psi_{ab}^{rs} \,|\, \mathscr{H} \,|\, \Psi_0\rangle + \sum_{c<d,t<u} \langle \Psi_{ab}^{rs} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{cd}^{tu}\rangle c_{cd}^{tu} + \sum_{c<d,t<u} \langle \Psi_{ab}^{rs} \,|\, \mathscr{H} \,|\, \Psi_{abcd}^{rstu}\rangle c_{abcd}^{rstu} = E_{\text{corr}} c_{ab}^{rs}$$

$$\cdots \tag{5.11}$$

How to truncate/decouple?

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

5.2.1 The Coupled-cluster Approximation

Suppose

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} * c_{cd}^{tu} = ... \tag{5.12}$$

13

thus

$$\langle \Psi_{ab}^{rs} | \mathscr{H} | \Psi_0 \rangle + \sum_{c<d,t<u} \langle \Psi_{ab}^{rs} | \mathscr{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu}$$

$$+ \sum_{c<d,t<u} \langle \Psi_{ab}^{rs} | \mathscr{H} | \Psi_{abcd}^{rstu} \rangle (c_{ab}^{rs} * c_{cd}^{tu}) = \left(\sum_{c<d,t<u} \langle \Psi_0 | \mathscr{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs} \tag{5.13}$$

after some tricks

$$\langle \Psi_{ab}^{rs} | \mathscr{H} | \Psi_0 \rangle + \sum_{c<d,t<u} \langle \Psi_{ab}^{rs} | \mathscr{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu}$$

$$+ \sum_{c<d,t<u} \langle \Psi_0 | \mathscr{H} | \Psi_{cd}^{tu} \rangle \left(c_{ab}^{rs} c_{cd}^{tu} - < c_{ab}^{rs} * c_{cd}^{tu} > \right) = \left(\sum_{c<d,t<u} \langle \Psi_0 | \mathscr{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs} \tag{5.14}$$

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

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

linear CCA: set $< c_{ab}^{rs} * c_{cd}^{tu} > = 0$ in (5.15)

$$E_{\text{corr}}(\text{L-CCA}) = -\mathbf{B}^\dagger \mathbf{D}^{-1} \mathbf{B} \tag{5.16}$$

L-CCA is size-consistent.

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:

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

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

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

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)

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

7.1 Green's Function in Single-Particle Systems

Solve Eq for $\mathbf{a}$

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

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

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

HF Green's function

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

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

i.e.

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

7.2.1 The Self-Energy

Dyson equation

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

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

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

where

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

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

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

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

i.e.

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

C.3 Analytic Derivatives

for HF

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

where

$$Q_{\nu\mu} = 2 \sum_a \varepsilon_a C_{\mu a} C_{\nu a} \tag{C.7}$$

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
```

17

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

Quasi-Newton Optimization
Murtagh-Sargent

$$\mathbf{q}_n = -\alpha_{n-1}\mathbf{G}_{n-1}\mathbf{f}_{n-1} \tag{C.8}$$

1. Set $\alpha_0 = 1$ and $\mathbf{G_0} = \mathbf{1}$.
   While $(E_1 > E_0)$ set $\alpha_0 \leftarrow \alpha_0/2$

2.

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

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

$$T_k = \mathbf{U}_k^\dagger \mathbf{U}_k \tag{C.11}$$

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

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

$$\alpha_k = 1 \tag{C.13}$$

3.

$$\mathbf{q}_k = -\alpha_{k-1}\mathbf{G}_{k-1}\mathbf{f}_{k-1} \tag{C.14}$$

$$\tag{C.15}$$

C.6 Transition States

C.7 Constrained Variation

D Molecular Integrals for H$_2$ as a Function of Bond Length