

# Notes of Modern Quantum Chemistry, Szabo & Ostlund

WSR

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## 0 Preface

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

## 1 Mathematical Review

### 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  $i, \alpha$  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 Many-electron Wave Functions and Operators

### 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 H<sub>2</sub> 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 H<sub>2</sub> Matrix Elements

### 2.3.2 Notations for 1- and 2-Electron Integrals

For spin orb,  
physicists'

$$\langle ij | kl \rangle = \left\langle \chi_i(1)\chi_j(2) \left| \frac{1}{r_{12}} \right| \chi_k(1)\chi_l(2) \right\rangle \quad (2.1)$$

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle \quad (2.2)$$

chemists'

$$[ij|kl] = \left\langle \chi_i(1)\chi_j(1) \left| \frac{1}{r_{12}} \right| \chi_k(2)\chi_l(2) \right\rangle \quad (2.3)$$

For spatial orb

$$(ij|kl) = \left\langle \psi_i(1)\psi_j(1) \left| \frac{1}{r_{12}} \right| \psi_k(2)\psi_l(2) \right\rangle \quad (2.4)$$

### 2.3.3 General Rules for Matrix Elements

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

$$\langle K | \mathcal{H} | K \rangle = \sum_m^N \langle m | h | m \rangle + \frac{1}{2} \sum_m^N \sum_n^N \langle mn || mn \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_n^N ([mm|nn] - [mn|nm]) \quad (2.5)$$

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

$$\langle K | \mathcal{H} | K \rangle = \sum_m^N [m|h|m] + \sum_m^N \sum_{n>m}^N ([mm|nn] - [mn|nm]) \quad (2.6)$$

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

$$\langle K | \mathcal{H} | L \rangle = \langle m | h | p \rangle + \sum_n^N \langle mn || pn \rangle = [m|h|p] + \sum_n^N ([mp|nn] - [mn|np]) \quad (2.7)$$

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

$$\langle K | \mathcal{H} | L \rangle = \langle mn || pq \rangle = [mp|nq] - [mq|np] \quad (2.8)$$

## 2.4 Second Quantization

### 2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 \quad a_i a_j + a_j a_i = 0 \quad (2.1)$$

$$\{a_i, a_j^\dagger\} \equiv a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} \quad (2.2)$$

## 2.5 Spin-Adapted Configurations

### 2.5.1 Spin Operators

total spin

$$\hat{\mathcal{P}} = \sum_i^N \hat{\mathbf{s}}(i) \quad (2.1)$$

$$\hat{\mathcal{S}}_x = \sum_i^N \hat{\mathbf{s}}_x(i) \quad (2.2)$$

$$\hat{\mathcal{S}}_+ = \sum_i^N \hat{\mathbf{s}}_+(i) \quad (2.3)$$

$$\hat{\mathcal{S}}^2 = \hat{\mathcal{S}}_+ \hat{\mathcal{S}}_- - \hat{\mathcal{S}}_z + \hat{\mathcal{S}}_z^2 \quad (2.4)$$

$$\hat{\mathcal{S}}^2 |\Phi\rangle = S(S+1) |\Phi\rangle \quad (2.5)$$

$$\hat{\mathcal{S}}_z |\Phi\rangle = M_S |\Phi\rangle \quad (2.6)$$

$$\hat{\mathcal{S}}_z |ij \cdots k\rangle = \frac{1}{2} (N^\alpha - N^\beta) |ij \cdots k\rangle \quad (2.7)$$

### 2.5.2 Restricted Determinants and Spin-Adapted Configurations

$$|^1\Psi_1^2\rangle = \frac{1}{\sqrt{2}}(|1\bar{2}\rangle + |\bar{1}2\rangle) = \frac{1}{\sqrt{2}}(\psi_1(1)\psi_2(2)\alpha(1)\beta(2) - \psi_2(1)\psi_1(2)\alpha(1)\beta(2)) \quad (2.8)$$

### 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

$$\varepsilon_i = \langle i | h | i \rangle + \sum_b \langle ib | ib \rangle \quad (3.1)$$

$$= \langle i | h | i \rangle + \sum_b (\langle ib | ib \rangle - \langle ib | bi \rangle) \quad (3.2)$$

##### Koopmans' Theorem

$$\text{IP} = -\varepsilon_a \quad \text{EA} = -\varepsilon_r \quad (3.3)$$

Koopmans' EA is often bad.

##### 3.3.2 Brillouin's Theorem

$$\langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle = 0 \quad (3.4)$$

##### 3.3.3 The HF Hamiltonian

$$\mathcal{H}_0 = \sum_i^N f(i) \quad (3.5)$$

#### 3.4 Restricted Closed-shell HF: The Roothaan Equations

##### 3.4.1 Closed-shell HF: Restricted Spin Orbitals

$$E_0 = 2 \sum_a h_{aa} + \sum_a \sum_b (2J_{ab} - K_{ab}) \quad (3.1)$$

### 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

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1} \quad (3.2)$$

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

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \quad (3.3)$$

#### Symmetric Orthogonalization

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U} \mathbf{s}^{-1/2} \mathbf{U}^\dagger \quad (3.4)$$

(linear dependence must be removed)

#### Canonical Orthogonalization

$$\mathbf{X} = \mathbf{U} \mathbf{S}^{-1/2} = \mathbf{U} \mathbf{s}^{-1/2} \mathbf{U}^\dagger \quad (3.5)$$

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

$$\tilde{\mathbf{X}} = \dots \quad (3.6)$$

thus

$$\phi'_\mu = \sum_\nu^K \phi_\nu \tilde{X}_{\nu\mu} \quad \mu = 1, 2, \dots, K - m \quad (3.7)$$

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

$$\phi' = \phi \mathbf{X} \quad (3.8)$$

$$\psi = \phi \mathbf{C} \quad (3.9)$$

we have

$$\psi = \phi' \mathbf{X}^{-1} \mathbf{C} \quad (3.10)$$

Let

$$\mathbf{C}' = \mathbf{X}^{-1} \mathbf{C} \quad \text{or} \quad \mathbf{C} = \mathbf{X} \mathbf{C}' \quad (3.11)$$

thus

$$\mathbf{F} \mathbf{X} \mathbf{C}' = \mathbf{S} \mathbf{X} \mathbf{C}' \varepsilon \quad (3.12)$$

$$(\mathbf{X}^\dagger \mathbf{F} \mathbf{X}) \mathbf{C}' = (\mathbf{X}^\dagger \mathbf{S} \mathbf{X}) \mathbf{C}' \varepsilon = \mathbf{C}' \varepsilon \quad (3.13)$$

def:

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \quad (3.14)$$

### 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

$$N = \sum_\mu \sum_\nu P_{\mu\nu} S_{\mu\nu} = \text{tr } \mathbf{P} \mathbf{S} \quad (3.15)$$

Mulliken:

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{P} \mathbf{S})_{\mu\mu} \quad (3.16)$$

Löwin:

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2})_{\mu\mu} \quad (3.17)$$



## 3.5 Model Calculations on H<sub>2</sub> and HeH<sup>+</sup>

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

$$\alpha = \alpha_{(\zeta=1.0)} \times \zeta^2 \quad (3.1)$$

### 3.5.2 STO-3G H<sub>2</sub>

### 3.5.3 An SCF Calculation on STO-3G HeH<sup>+</sup>

## 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

$$f^\alpha(1) = h(1) + \sum_a^{N_\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N_\beta} J_a^\beta(1) \quad (3.1)$$

$$E_0 = \sum_a h_{aa} + \frac{1}{2} \sum_a^{N_\alpha} \sum_b^{N_\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2} \sum_a^{N_\beta} \sum_b^{N_\beta} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N_\alpha} \sum_b^{N_\beta} J_{ab}^{\alpha\beta} \quad (3.2)$$

### 3.8.2 Introduction of a Basis: The Pople-Nesbet Equations

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S} \mathbf{C}^\alpha \boldsymbol{\epsilon}^\alpha \quad (3.3)$$

$$\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S} \mathbf{C}^\beta \boldsymbol{\epsilon}^\beta \quad (3.4)$$

### 3.8.3 Unrestricted Density Matrices

spin density

$$\rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \quad (3.5)$$

$$\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta \quad (3.6)$$

### 3.8.4 Expression for the Fock Matrices

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda} \sum_{\sigma} [P_{\lambda\sigma}^T(\mu\nu|\sigma\lambda) - P_{\lambda\sigma}^{\alpha}(\mu\lambda|\sigma\nu)] \quad (3.7)$$

$$F_{\mu\nu}^{\beta} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda} \sum_{\sigma} [P_{\lambda\sigma}^T(\mu\nu|\sigma\lambda) - P_{\lambda\sigma}^{\beta}(\mu\lambda|\sigma\nu)] \quad (3.8)$$

### 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

$$\sum_{c<d, t<u} c_{cd}^{tu} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle = E_{\text{corr}} \quad (4.1)$$

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c<d, t<u} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle = c_{ab}^{rs} E_{\text{corr}} \quad (4.2)$$

def

$$B_{rasb} = \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle \quad (4.3)$$

$$D_{rasb,tcud} = \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle \quad (4.4)$$

$$c_{rasb} = c_{ab}^{rs} \quad (4.5)$$

thus

$$\begin{pmatrix} 0 & \mathbf{B}^{\dagger} \\ \mathbf{B} & \mathbf{D} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix} \quad (4.6)$$

then diagonalize.

Another way:

$$E_{\text{corr}} = -\mathbf{B}^{\dagger} (\mathbf{D} - E_{\text{corr}} \mathbf{1})^{-1} \mathbf{B} \quad (4.7)$$

solve it iteratively.

### 4.3 Some Illustrative Calculations

### 4.4 Natural Orbitals and the 1-Particle Reduced DM

reduced density function

$$\rho(\mathbf{x}_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) \Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \quad (4.1)$$

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

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) \Phi(\mathbf{x}'_1, \cdots, \mathbf{x}_N) \quad (4.2)$$

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_{ij} \chi_i(\mathbf{x}_1) \gamma_{ij} \chi_j^*(\mathbf{x}'_1) \quad (4.3)$$

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

$$\eta_i = \sum_k \chi_k U_{ki} \quad (4.4)$$

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_{kl} \eta_k(\mathbf{x}_1) (\mathbf{U}^\dagger \gamma \mathbf{U})_{kl} \eta_l^*(\mathbf{x}'_1) \quad (4.5)$$

def

$$\lambda = \mathbf{U}^\dagger \gamma \mathbf{U} \quad (4.6)$$

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

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_i \lambda_i \eta_i(\mathbf{x}_1) \eta_i^*(\mathbf{x}'_1) \quad (4.7)$$

$\lambda_i$  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  $H_2$

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

delocalized MOs:

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

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

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

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

### 5.1.2 Some Illustrative Calculations

IEPA is not variational.

IEPA is not invariant to unitary transformations.

works bad for Ne and  $N_2$ .

## 5.2 Coupled-pair Theories

Ignore single, triple, etc.

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{a<b, r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{a<b<c<d, r<s<t<u} c_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle + \dots \quad (5.1)$$

then

$$\sum_{c<d, t<u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} = E_{\text{corr}} \quad (5.2)$$

$$\begin{aligned} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c<d, t<u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} + \sum_{c<d, t<u} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{abcd}^{rstu} \rangle c_{abcd}^{rstu} &= E_{\text{corr}} c_{ab}^{rs} \\ \dots & \end{aligned} \quad (5.3)$$

How to truncate/decouple?

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

### 5.2.1 The Coupled-cluster Approximation

Suppose

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} * c_{cd}^{tu} = \dots \quad (5.4)$$

thus

$$\begin{aligned} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c<d, t<u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \\ + \sum_{c<d, t<u} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{abcd}^{rstu} \rangle (c_{ab}^{rs} * c_{cd}^{tu}) = \left( \sum_{c<d, t<u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs} \end{aligned} \quad (5.5)$$

after some tricks

$$\begin{aligned} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c<d, t<u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \\ + \sum_{c<d, t<u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle (c_{ab}^{rs} c_{cd}^{tu} - \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle) = \left( \sum_{c<d, t<u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs} \end{aligned} \quad (5.6)$$

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} - \sum_{c < d, t < u} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = 0 \quad (5.7)$$

along with (5.2), 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  $\langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = 0$  in (5.7)

$$E_{\text{corr}}(\text{L-CCA}) = -\mathbf{B}^\dagger \mathbf{D}^{-1} \mathbf{B} \quad (5.8)$$

L-CCA is size-consistent. L-CCA is unitary invariant.

CEPA: set  $\langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = c_{ab}^{rs} c_{cd}^{tu}$

$$e_{ab} = \sum_{t < u} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{tu} \rangle c_{ab}^{tu} \quad (5.9)$$

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{c < d, t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} = e_{ab} c_{ab}^{rs} \quad (5.10)$$

$$E_{\text{corr}}(\text{CEPA}) = \sum_{a < b} e_{ab} \quad (5.11)$$

## 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  $\rightarrow \prod_{\text{dot}} \langle in, in \parallel out, out \rangle$
- 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?

RS perturbation theory is size-consistent

## 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

$$G_0(\mathbf{x}, \mathbf{x}', E) = \sum_i \frac{\chi_i(\mathbf{x})\chi_i^*(\mathbf{x}')}{E - \varepsilon_i} \quad (7.1)$$

$$[G_0(E)]_{ij} = \frac{\delta_{ij}}{E - \varepsilon_i} \quad (7.2)$$

i.e.

$$\mathbf{G}_0(E) = (E\mathbf{1} - \boldsymbol{\varepsilon})^{-1} \quad (7.3)$$

#### 7.2.1 The Self-Energy

Dyson equation

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\boldsymbol{\Sigma}(E)\mathbf{G}(E) \quad (7.4)$$

### 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

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

where

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

## 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

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

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

$$\mathbf{U}_k = -\alpha_{k-1} \mathbf{G}_{k-1} \mathbf{f}_{k-1} - \mathbf{G}_{k-1} (\mathbf{f}_k - \mathbf{f}_{k-1}) = -\mathbf{G}_{k-1} [\mathbf{f}_k + \mathbf{f}_{k-1} (\alpha_{k-1} - 1)] \quad (\text{C.2})$$

$$a_k^{-1} = \mathbf{U}_k^\dagger \mathbf{d}_k = \mathbf{U}_k^\dagger (\mathbf{f}_k - \mathbf{f}_{k-1}) \quad (\text{C.3})$$

$$T_k = \mathbf{U}_k^\dagger \mathbf{U}_k \quad (\text{C.4})$$

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

$$\mathbf{G}_k = \mathbf{G}_{k-1} + a_k \mathbf{U}_k \mathbf{U}_k^\dagger \quad (\text{C.5})$$

$$\alpha_k = 1 \quad (\text{C.6})$$

- 3.

$$\mathbf{q}_k = -\alpha_{k-1} \mathbf{G}_{k-1} \mathbf{f}_{k-1} \quad (\text{C.7})$$

$$(\text{C.8})$$

### C.6 Transition States

### C.7 Constrained Variation

## D Molecular Integrals for $\text{H}_2$ as a Function of Bond Length