

Notes of Modern Quantum Chemistry, Szabo & Ostlund

hebrewsnabla

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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

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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),

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

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

def

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

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

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

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