

Notes of Modern Quantum Chemistry, Szabo & Ostlund

hebrewsnabla

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Contents

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

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

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'

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

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

chemists'

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

For spatial orb

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

2.3.3 General Rules for Matrix Elements

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

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

or (Since $[mm \mid mm] - [mm \mid mm] = 0$)

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

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

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

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

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

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

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