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

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February 5, 2020

Contents

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spatial mol orb – ψ – $i, j, k, ...$
spatial basis fxn – ϕ – $\mu, \nu, \lambda, ...$
spin orb – χ
occ mol orb – $a, b, c, ...$
vir mol orb – $r, s, t, ...$
exact many-elec wfn – Φ
approx many-elec wfn – Ψ
exact energy – $\mathscr{E}$
approx energy – E

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1.1

1.2

1.3

1.4 N-D Complex Vector Spaces

Suppose

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

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

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

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

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

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.

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

or

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

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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'

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\hat{\mathscr{S}}^2 |\Phi\rangle = S(S+1) |\Phi\rangle \tag{2.20}$$
$$\hat{\mathscr{S}}_z |\Phi\rangle = M_S |\Phi\rangle \tag{2.21}$$

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

2.5.2 Restricted Determinants and Spin-Adapted Configurations

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

3 The Hartree-Fock Approximation

3.1 The HF Equations

3.1.1 The Coulomb and Exchange Operators

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

$$\mathscr{K}_b(1) = \int \mathrm{d}x_2 \chi_b^*(2) r_{12}^{-1} \hat{\mathscr{P}}_{12} \chi_b(2) \tag{3.2}$$
$$= \int \mathrm{d}x_2 \chi_b^*(2) r_{12}^{-1} \chi_b(1) \hat{\mathscr{P}}_{12} \tag{3.3}$$

$$\langle \chi_a(1) \,|\, \mathscr{J}_b(1) \,|\, \chi_a(1) \rangle = J_{ab} \tag{3.4}$$
$$\langle \chi_a(1) \,|\, \mathscr{K}_b(1) \,|\, \chi_a(1) \rangle = K_{ab} \tag{3.5}$$

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

$$\varepsilon_i = \langle i \,|\, h \,|\, i \rangle + \sum_b \langle ib \,\|\, ib \rangle \tag{3.6}$$
$$= \langle i \,|\, h \,|\, i \rangle + \sum_b \left(\langle ib \,|\, ib \rangle - \langle ib \,|\, bi \rangle \right) \tag{3.7}$$

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

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

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

we have

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

Let

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

thus

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

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

def:

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

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

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

Mulliken:

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

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]

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

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

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