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

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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

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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

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

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

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

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

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

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

For spatial orb

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

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

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

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

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