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

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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

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

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

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

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

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

1.4.1 Change of Basis

$$|\alpha\rangle = \sum_i |i\rangle\,\langle i|\alpha\rangle = \sum_i |i\rangle\,U_{i\alpha} \tag{1.5}$$

$$|i\rangle = \sum_\alpha |\alpha\rangle\,\langle i|\alpha\rangle = \sum_\alpha |\alpha\rangle\,U^*_{i\alpha} \tag{1.6}$$

If i, α are all orthonormal, $\mathbf{U}$ must be unitary.

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

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

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

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

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