

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

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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

$$\mathbf{\Omega} = \mathbf{U}^\dagger \mathbf{O} \mathbf{U} \quad (1.8)$$

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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

$$|\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix} \quad (2.1)$$

It can be further shortened to

$$|\chi_i\chi_j\cdots\chi_k\rangle \quad (2.2)$$