

Some Aspects
of
Electronic Structure Theory

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What Universe are we in:

- For now time independent
- Electronic Structure
- Born Oppenheimer
- Relativity?
- The Answer is 42
- The Question ??

$$H = \sum_i h(i) + \sum_{i < j} \frac{1}{r_{ij}} + \text{Nuclear Repulsion}$$

1-electron

2-electron

Contents

- Hartree Fock, DFT, MCSCF and CI; Wavefunctions
- Orbital Optimisation; Brillouin Theorem
- Perturbation Theory; General + applied to correlation
- Size Consistency; CCSD and CEPA
- Relativity
- Valence Bond Theory
- **Special requests**
- **Fun**
- Quantumchemistry at 2nd year level is assumed.

Ask questions

Anything I say or should say is part of the exam

Variational Theory-1-Energy

$$\psi = c_1\phi_1 + c_2\phi_2$$

$$\begin{aligned} E &= \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle c_1\phi_1 + c_2\phi_2 | H | c_1\phi_1 + c_2\phi_2 \rangle}{\langle c_1\phi_1 + c_2\phi_2 | c_1\phi_1 + c_2\phi_2 \rangle} \\ &= \frac{\langle c_1\phi_1 | H | c_1\phi_1 \rangle + \langle c_1\phi_1 | H | c_2\phi_2 \rangle + \langle c_2\phi_2 | H | c_1\phi_1 \rangle + \langle c_2\phi_2 | H | c_2\phi_2 \rangle}{\langle c_1\phi_1 | c_1\phi_1 \rangle + \langle c_1\phi_1 | c_2\phi_2 \rangle + \langle c_2\phi_2 | c_1\phi_1 \rangle + \langle c_2\phi_2 | c_2\phi_2 \rangle} \\ &= \frac{c_1^2 \langle \phi_1 | H | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | H | \phi_2 \rangle + c_2 c_1 \langle \phi_2 | H | \phi_1 \rangle + c_2^2 \langle \phi_2 | H | \phi_2 \rangle}{c_1^2 \langle \phi_1 | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | \phi_2 \rangle + c_2 c_1 \langle \phi_2 | \phi_1 \rangle + c_2^2 \langle \phi_2 | \phi_2 \rangle} \end{aligned}$$

Variation-2-Energy

$$E = \frac{c_1^2 \langle \phi_1 | H | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | H | \phi_2 \rangle + c_2 c_1 \langle \phi_2 | H | \phi_1 \rangle + c_2^2 \langle \phi_2 | H | \phi_2 \rangle}{c_1^2 \langle \phi_1 | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | \phi_2 \rangle + c_2 c_1 \langle \phi_2 | \phi_1 \rangle + c_2^2 \langle \phi_2 | \phi_2 \rangle}$$

$$\langle \phi_i | H | \phi_j \rangle = H_{ij} = H_{ji} \quad \langle \phi_i | \phi_j \rangle = S_{ij} = S_{ji}$$

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

H,S Matrix elements

c coefficients

Variational calculus : $E \geq E_{\text{exact}} \Rightarrow$ determine c using $dE/dc=0$

Variation-3 (diff.)

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}} = \frac{t}{n}$$

$$\left(\frac{t}{n}\right)^\diamond = \frac{t^\diamond n - n^\diamond t}{n^2} = \frac{t^\diamond - n^\diamond \frac{t}{n}}{n} = \frac{t^\diamond - n^\diamond E}{n}$$

$$\frac{\partial E}{\partial c_1} = 0 = t^\diamond - n^\diamond E$$

$$= 2c_1 H_{11} + 2c_2 H_{12} - E(2c_1 S_{11} + 2c_2 S_{12}) = 0$$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

Secular Equations/Determinant

Secular Equations

$$c_1 (H_{11} - ES_{11}) + c_2 (H_{12} - ES_{12}) = 0$$
$$c_1 (H_{21} - ES_{21}) + c_2 (H_{22} - ES_{22}) = 0$$

only solution when secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

- *Solve this to determine energies*
- *Use energies in equations to obtain coefficients*
- *Normalise wave functions*

Variation-4 operator \Leftrightarrow matrix

Assume orthonormality $S_{ij} = \delta_{ij}$

$$c_1(H_{11} - E) + c_2(H_{12}) = 0$$

$$c_1(H_{21}) + c_2(H_{22} - E) = 0$$

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \Rightarrow \mathbf{H}c = Ec$$

Operator \hat{H} Ψ = number E Ψ \Rightarrow matrix \mathbf{H} \mathbf{C} = vector \mathbf{E} \mathbf{C} number

(wave)function number matrix vector number

Spin

$$\vec{s} = (s_x, s_y, s_z) \quad s^2 = (\vec{s} \cdot \vec{s}) = s_x^2 + s_y^2 + s_z^2$$

$$\hat{s}_x \alpha = +\frac{1}{2} \hbar \beta \quad \hat{s}_y \alpha = +i \frac{1}{2} \hbar \beta \quad \hat{s}_z \alpha = \frac{1}{2} \hbar \alpha$$

$$\hat{s}_x \beta = +\frac{1}{2} \hbar \alpha \quad \hat{s}_y \beta = -i \frac{1}{2} \hbar \alpha \quad \hat{s}_z \beta = -\frac{1}{2} \hbar \beta$$

$$s^2 \alpha = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 \alpha = \frac{3}{4} \hbar^2 \alpha \quad s^2 \beta = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 \beta = \frac{3}{4} \hbar^2 \beta$$

Spin orbital

$$\psi = \psi \alpha$$

$$\bar{\psi} = \psi \beta$$

$$[H, S^2] = [H, S_z] = 0$$

Antisymmetry

particles indistinguishable : $\Psi^2(1,2) = \Psi^2(2,1)$

Bosons : $\Psi(1,2) = +\Psi(2,1)$

Fermions (**electrons**) : $\Psi(1,2) = -\Psi(2,1)$

(Slater) Determinant

$$\Psi(1,2) = |a\bar{b}| = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1) & \bar{b}(1) \\ a(2) & \bar{b}(2) \end{vmatrix} = \frac{1}{\sqrt{2}} (a(1)\bar{b}(2) - \bar{b}(1)a(2))$$


- Pauli principle
- Hunds rule
- energy depends on spinstate (e.g. Singlet/triplet)

- Show antisymmetry
- Show Pauli principle
- Derive general normalisation constant
- Is this eigenfunction of S^2 and S_z

Antisymmetry-2

$$\hat{A} = \frac{1}{\sqrt{n!}} \sum_P (-1)^P \hat{P}$$

$$\Phi = \hat{A}(a(1)b(2)c(3)\dots) = |abc\dots|$$

 Building
block

$$\Psi^{(K)} = \sum_i^N c_i^{(K)} \Phi_i \quad CI$$

Variational-calculus : $E^{(K)} \geq E^{(K)}(\text{Exact})$