Some Aspects
of

Electronic Structure Theory

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Master CourseQuantumchemistry 2008

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

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

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

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

$$= \frac{c_1^2\langle \phi_1 | H | \phi_1 \rangle + c_1c_2\langle \phi_1 | H | \phi_2 \rangle + c_2c_1\langle \phi_2 | H | \phi_1 \rangle + c_2^2\langle \phi_2 | H | \phi_2 \rangle}{c_1^2\langle \phi_1 | \phi_1 \rangle + c_1c_2\langle \phi_1 | \phi_2 \rangle + c_2c_1\langle \phi_2 | \phi_1 \rangle + c_2^2\langle \phi_2 | \phi_2 \rangle}$$

Variation-2-Energy

$$E = \frac{c_1^2\langle\phi_1|H|\phi_1\rangle + c_1c_2\langle\phi_1|H|\phi_2\rangle + c_2c_1\langle\phi_2|H|\phi_1\rangle + c_2^2\langle\phi_2|H|\phi_2\rangle}{c_1^2\langle\phi_1|\phi_1\rangle + c_1c_2\langle\phi_1|\phi_2\rangle + c_2c_1\langle\phi_2|\phi_1\rangle + c_2^2\langle\phi_2|\phi_2\rangle}$$

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

$$E = \frac{c_1^2H_{11} + 2c_1c_2H_{12} + c_2^2H_{22}}{c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}}$$

H,S Matrix elements
c coefficients

Variational calculus : E >= E_{exact} => determine c using dE/dc=0

Variation-3 (diff.)

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

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

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

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

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

Secular Equations/Determinant

Secular Equations

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

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⇔matrix

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

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

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

$$\hat{H}\Psi = E\Psi \Rightarrow \mathbf{HC} = E\mathbf{C}$$

Operator

(wave)function

number

matrix

vector

number

Spin

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

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

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

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

Spin orbital

$$\psi = \psi\alpha$$

$$\overline{\psi} = \psi\beta$$

$$\left[H, S^2\right] = \left[H, S_z\right] = 0$$

Antisymmetry

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

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

Fermions (electrons) : $\boxed{\Psi(1,2) = -\Psi(2,1)}$

(Slater) Determinant

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

- 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

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

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

Building block

$$\Psi^{(K)} = \sum_{i}^{N} c_i^{(K)} \Phi_i \qquad \boldsymbol{CI}$$

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