Chemistry 651

Hour exam 1

9 May 2006

1. If we use a Gaussian wavefunction for the hydrogen atom, we find the ground state energy to be
$$E(a) = \tfrac{3}{2}a - \sqrt{8a/\pi} \tag{1}$$
where a is a variational parameter. By means of the variational theorem: 1) derive a value for a; 2) derive the minimum in $E(a)$; and 3) compare $E(a)$ to the true ground state energy.

2. Suppose we are given the exact Hamiltonian and we conjecture that the wavefunction function can be represented by a sum of three terms,
$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 \tag{2}$$
where c_i are to be determined and the $\{\phi_i\}$ are orthonormal. If the Hamiltonian matrix is
$$H_{ii} = \alpha \qquad \forall i \qquad H_{12} = H_{21} = \beta \tag{3}$$
and all the remaining H_{ij} vanish, what are the three variationally determined wavefunctions, and their corresponding energies.

3. Polarizibility of the H-atom revisited. This time we will use perturbation theory to derive α, as defined by
$$\langle\mu\rangle = \alpha \cdot \mathbf{E} \tag{4}$$
The dipole moment operator is $\mu = \mathbf{r}$ and the applied perturbation is
$$H^{(1)} = -\mu \cdot \mathbf{E} = -zE \tag{5}$$
Calculate α using only two hydrogenic basis functions, $1s$ and $2p_z$. Derive α on the basis of the induced polarization of the 1s orbital by the electric field along z. Using the notation we discussed in class,
$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} \qquad \psi_n^{(1)} = -\sum_{m\neq n} \psi_m^{(0)} \frac{\langle\psi_m^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} \tag{6}$$
$$E_n = E_n^{(0)} + E_n^{(1)} \qquad E_n^{(1)} = \langle\psi^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle \tag{7}$$
Write the polarizability in terms of matrix elements of the $1s$ and $2p_z$ functions. Recall that $E_n^{(0)} = -\frac{1}{2n^2}$.

4. Prove that the Pauli exclusion principle is a direct consequence of the antisymmetrization of products of one electron functions. Illustrate this by one example of your choice.

5. In the HF treatment of the Li atom, we found that the energy had contributions from so-called Coulomb and exchange integrals. Write one coulomb and a corresponding exchange integral that would arise.

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1. Gaussian wf $\Rightarrow$ $E(a) = \frac{3}{2}a - \sqrt{\frac{8a}{\pi}}$

$$\frac{\partial E}{\partial a} = 0 = \frac{3}{2} - \frac{1}{2}\sqrt{\frac{8}{\pi a}} \Rightarrow a = \frac{8}{9\pi}$$

$$E(a) = \frac{3}{2}\cdot\frac{8}{9\pi} - \sqrt{\frac{8\cdot 8}{9\cdot\pi^2}} = -\frac{4}{3\pi} \quad \text{approx } E$$

$E_{exact} = -\frac{1}{2}$, $E_{approx} \sim -0.4$

2.

$$|H - E| = \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & 0 \\ 0 & 0 & \alpha \end{vmatrix} = 0$$

$$(\alpha - E)^2 - \beta^2 = 0 \Rightarrow \alpha - E = \pm\beta$$

$E = \alpha \pm \beta$ and of course $E = \alpha$

eigenvectors ...

eigenvalue $\alpha + \beta$

$(\alpha - E)C_1 + \beta C_2 = 0$

$-\beta C_1 + \beta C_2 = 0 \Rightarrow C_1 = C_2$

$\psi_a = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$ $\quad E_a = \alpha + \beta$

likewise $\psi_b = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$ $\quad E_b = \alpha - \beta$

and $\psi_c = \phi_3$ $\quad E_c = \alpha$

3. $\langle \mu \rangle \equiv \alpha \cdot E$

$\mu = \langle \psi | r | \psi \rangle$

but $\psi = \psi_{1s}^{(0)} - \psi_{2p_z}^{(0)} \dfrac{\langle 2p_z | H^{(1)} | 1s \rangle}{E_{2p_z}^{0} - E_{1s}^{0}}$

$E_{1s} = -1/2n^2 = -1/2; \quad E_{2p_z} = -\dfrac{1}{2(2^2)} = -\dfrac{1}{8}$

$E_{2p_z}^{0} - E_{1s}^{0} = -\dfrac{1}{8} + \dfrac{1}{2} = \dfrac{3}{8}$

$\therefore \quad \psi = |1s\rangle - \dfrac{8}{3} |2p_z\rangle \langle 2p_z | H^{(1)} | 1s \rangle$

and

$\langle \psi | z | \psi \rangle = -2 \cdot \dfrac{8}{3} \langle 1s | z | 2p_z \rangle \langle 2p_z | \underbrace{H^{(1)}}_{-zE} | 1s \rangle$

$= \dfrac{16}{3} \langle 1s | z | 2p_z \rangle^2 E$

$\therefore \quad \alpha = \dfrac{16}{3} \langle 1s | z | 2p_z \rangle^2$

4. Pauli exclusion principle : if any two electrons have the same set of quantum #'s, its wavefunction vanishes.

$$wf = |\phi_1 \phi_2 \cdots \phi_n|$$

So, consider a two dimensional Hilbert space

$$wf = \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix}$$

if $\phi_1 = \phi_2$ the determinant vanishes.

No two e^- can have identical wf's.

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5. $$E_{HF}(Li) \sim 2\epsilon^0_{1s} + \epsilon^0_{2s} + J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}$$

$$J_{1s,2s} = \int d1\,d2\ \phi_{1s}(1)\phi_{1s}(1)\frac{1}{r_{12}}\phi_{2s}(2)\phi_{2s}(2)$$

$$K_{1s,2s} = \int d1\,d2\ \phi_{1s}(1)\phi_{2s}(1)\frac{1}{r_{12}}\phi_{1s}(2)\phi_{2s}(2)$$