Advanced Quantum Mechanics

Q1. Advanced Physical Chemistry 2000, Q9

a) Explain briefly why the *variational principle* is useful in quantum mechanics. [4]

b) Prove that for a trial wavefunction $\psi = \Sigma_n c_n \chi_n$, the expectation value of the energy,

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

satisfies the equation

$$\langle E \rangle - E_0 \geq 0,$$

where E_0 is the lowest possible eigenvalue of $\hat{H}$ (i.e. the true ground state energy), and where the non-degenerate, orthonormal functions cn satisfy the equation $\hat{H}\chi_n = E_n\chi_n$. [5]

c) Use the variational principle to show that the trial function $\psi(r) = Ne^{-\alpha r}$, with r in atomic units and normalisation constant $N = (\alpha^3/\pi)^{1/2}$, yields the following estimate for the ground state energy (also in atomic units) of a hydrogen-like atom of charge number Z.

$$\langle E \rangle = \frac{\alpha^2}{2} - \alpha Z$$

Use this expression to find the best estimate of the ground state energy of the H atom. [10]

How does the value you obtain compare with the true ground state energy of the H atom? [2]

[Note that for a spherically symmetric wavefunction the Hamiltonian for the H atom may be written (in atomic units)

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \qquad \text{with} \qquad \nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r ,$$

and that $\int_0^\infty x^n e^{-sx}\, dx = \frac{n}{s^{n+1}}$]

d) In atomic units the Hamiltonian for the He atom may be written

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}$$

where $\hat{h}_i$ is the hydrogenic Hamiltonian for electron i, as defined in part c), but with $r = r_i$, and r_{12} is the electron-electron separation.

A simple trial spatial wavefunction Ψ for the ground state of the He atom (i.e. the state of $1s^2$ configuration) can be written in terms of the normalised wavefunctions $\psi(r_1)$ and $\psi(r_2)$ of part c) as

$$\Psi = \psi(r_1)\,\psi(r_2) \equiv |1\ 2> \qquad (1)$$

Derive an equation for <E> in terms of the parameter α. [5]

[Note that $<1\ 2|\frac{1}{r_{12}}|1\ 2> = \frac{5}{8}\alpha$.]

e) Using your answer from part d), determine the best estimate of the ground state energy of the He atom in atomic units. What does the value of α you obtain suggest about the ground state wavefunction of He compared with that for the hydrogen atom? [5]

f) Explain whether a trial wavefunction of a simple product form, such as that given in equation (1), could ever be an eigenfunction of the Hamiltonian for the He atom. [5]

Q2. Advanced Physical Chemistry 2001, Q5B

The wavefunction of an electron in the 2s orbital of a hydrogen atom may be written

$$\psi = N(2-\rho)\,e^{-\rho/2}$$

where N is a normalisation constant and r ($=r/a_0$) is the distance of the electron from the nucleus, in units of the Bohr radius a_0.

a) Sketch the variation of ψ with ρ, locating the positions of any radial nodes. [3]

b) Sketch the probability of finding the electron at a distance ρ from the nucleus. [3]

c) Show that the most probable distance is given by $\rho = 5.24$. [10]

You may find the following useful: $x^3 - 8x^2 + 16x - 8 = (x-2)(x^2-6x+4)$

d) Calculate the average distance ρ of the electron from the nucleus. [8]

You may find the following useful: $\int_0^{\infty} e^{-ax}\,dx = \frac{n!}{a^{n+1}}$

e) The virial theorem states that for a particle subject to a potential energy of the form $V \propto r^s$, the mean kinetic energy <T> and the mean potential energy <V> are related by

$$\frac{1}{2}s\,<V> = <T>$$

i) Determine <V> and <T> for a 2s electron in terms of the Rydberg constant, R. [4]

ii) Determine the classical turning point of the motion of a 2s electron, using [4]

$$R = \frac{e^2}{8\pi\,\varepsilon_0 a_0} \qquad \text{and} \qquad V = -\frac{e^2}{4\pi\,\varepsilon_0 r}$$

iii) Comment on the fact that the electron can exist in regions of space where its potential energy exceeds its total energy. [2]

Q3 <u>Advanced Physical Chemistry 2002, Q7</u>

a) Write down the Hamiltonian, $\hat{H}_0(x)$, for a simple harmonic oscillator of mass m and force constant k. Give the result for the corresponding energy levels, in terms of the oscillator frequency $\omega_0 = [k/m]^{1/2}$. [4]

What is the minimum energy the oscillator may possess, and why is it non-zero? [4]

The Hamiltonian for a pair of identical coupled oscillators may be expressed as

$$\hat{H}(x) = \hat{H}_0(x_1) + \hat{H}_0(x_2) + \lambda\hat{V}$$

where the perturbation $\hat{V} = k\, x_1 x_2$, and λ is a constant ($0 \le \lambda < 1$). For a single oscillator, the only non-zero matrix elements of x_i are $\langle v_i+1|x_i|v_i\rangle = (\hbar/2m\omega_0)^{1/2}\,(v_i+1)^{1/2}$.

b) Within second-order perturbation theory, the ground state energy of the system is given approximately by

$$E = E_0 + E', \qquad \text{where} \qquad E' = -\lambda^2 \sum_{n(\neq 0)} \frac{|\langle n|\hat{V}|0\rangle|^2}{E_n - E_0}$$

Here $|0\rangle$ and $|n\rangle$ denote respectively the ground state and excited states for $\lambda = 0$, with corresponding energies E_0 and E_n. The states $|0\rangle$ and $|n\rangle$ may be expressed in product form $|v_1v_2\rangle = |v_1\rangle|v_2\rangle$, with $|v_i\rangle$ referring to a single harmonic oscillator. Show that within perturbation theory,

$$E = \hbar\,\omega_0\,(1-\tfrac{\lambda^2}{8})\,. \qquad [8]$$

c) By transforming the coordinates from x_1 and x_2 to $y_+ = (x_1+x_2)/2$ and $y_- = (x_1-x_2)/2$, show first that

$$\frac{\partial^2}{\partial x_1^{\,2}} + \frac{\partial^2}{\partial x_2^{\,2}} = \frac{1}{2}\left(\frac{\partial^2}{\partial y_+^{\,2}} + \frac{\partial^2}{\partial y_-^{\,2}}\right).$$

Using this, show that $\hat{H}$ becomes separable: $\hat{H} = \hat{H}_+(y_+) + \hat{H}_-(y_-)$, where $\hat{H}_+$ and $\hat{H}_-$ each has harmonic oscillator form. [10]

Hence obtain an exact expression for the eigenvalues of $\hat{H}$. [4]

Show that to leading order in λ^2, the ground state energy E reduces to the result obtained from second-order perturbation theory. [4]

[For small x, $(1+x)^{1/2} = 1 + \frac{1}{2}x - \frac{1}{8}x^2$.]