November 17th, 2014

Chemistry 120A 2nd Midterm

1. (36 pts) For this question, recall the binding energy levels of the Hydrogenic Hamiltonian (1-electron):

$$E_n = -m_e\, Z^2 e^4/2\hbar^2 n^2 = -E_0\, Z^2/n^2\,, \quad n = 1, 2, 3, ...$$

where Ze is the nuclear charge, m_e is the electron mass, and $E_0 = m_e\, e^4/2\hbar^2 \approx 13.7$ eV.

The eigenstates of the H-atom are $\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\, Y_{l,m}(\theta,\phi)$. In these states, the eigenvalues of the operators for square orbital angular momentum, L^2, and for the z-component of angular momentum, L_z, are $\hbar^2\, l(l+1)$ and $\hbar\, m$, respectively. The quantum number, n, can be described in terms of the radial quantum number, n_r, and the quantum of angular momentum, l, by: n = n_r + l + 1

If a Hydrogenic atom is subject to a magnetic field in the z-direction, the additional term in the Hamiltonian is $E_{\text{mag}} = +\mu_M L_z \mathcal{B}$ where μ_M is the magnitude of the orbital magnetic moment.

a) Circle those of the following that are true about the 1-electron atom. Ignore the spin of the individual electron in this problem.

i. The binding energy of an electron in any ψ_{nlm} increases as Z^2.

ii. The radial distribution function of the ψ_{310} eigenstate contains two nodes.

iii. The ψ_{200} eigenstate can be described by a vibrationally excited state of the bare (l=0) coulomb potential.

iv. The square of the total orbital angular momentum of an electron in ψ_{322} is larger than the square of its z-component by $2\hbar^2$.

v. For an electron in any ψ_{nlm}, the energy, magnitude of angular momentum, and angular momentum in the z-direction are conserved.

vi. A magnetic field applied in the z-direction would lower the energy of an electron in ψ_{311}.

b) Circle those of the following that are true for a two-electron He atom, including coulomb repulsion between the electrons and spin.

i. The spatial wave function of the ground state is described by $\Psi = \psi_{100}(r_1, \theta_1, \phi_1) \times \psi_{100}$ $(\mathrm{r}_2, \theta_2, \phi_2)$ with an effective Z less than 2.

ii. The total binding energy of two electrons in the ground state is larger than $8E_0$.

iii. The spatial wave function of an excited state of Helium can be described by $\Psi = \psi_{100}(r_1, \theta_1, \phi_1) \times \psi_{210}(\mathrm{r}_2, \theta_2, \phi_2)$.

iv. The ionization energy of pulling an electron out of the $1s2p$ configuration involving single electron orbitals ψ_{100} and ψ_{210} is close to $E_0/4$.

v. This is a legitimate slater determinant of two electrons in the ground state, where α denotes spin up and β denotes spin down.

$$\begin{vmatrix} \psi_{100}\alpha(1) & \psi_{100}\alpha(1) \\ \psi_{100}\alpha(2) & \psi_{100}\alpha(2) \end{vmatrix}$$

vi. The lowest energy state with a $1s2s$ configuration involving single electron orbitals ψ_{100} and ψ_{200} is a spin triplet.

2. (65 pts) This problem concerns the behavior of an electron moving on a ring in the presence of a small, perturbative potential $V(\phi)$ (see Figure below) that localizes the particle into different sections of the ring. The Hamiltonian for the particle in a ring is:

$$\mathcal{H}_0 = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$$

where $I = m_e R^2$ is the moment of inertia for a ring of radius R and electron of mass m_e.

The orthonormal eigen-functions for this Hamiltonian are

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm1, \pm2, ...,$$

with corresponding energy levels

$$E_m = (\hbar^2/2I)\, m^2\,, \quad m = 0, \pm1, \pm2, ...$$

With the added perturbation, the full Hamiltonian is:

$$\mathcal{H} = \mathcal{H}_0 + V(\phi)\,,$$

where

$$V(\phi) = 4\epsilon \sin^2(\phi) \;= -\epsilon(e^{i2\phi} + e^{-i2\phi} - 2)$$

and ϵ is small, positive, and has the units of energy.

In calculating matrix elements below, its useful to remember the following for the particle in a ring eigenfunctions:

$$\frac{1}{2\pi}\int_0^{2\pi} d\phi\, e^{i(m-m')\phi} = \delta_{m,m'}$$

In the following, express your answers in terms of $\hbar$, ϵ, ϕ, and I.

(a) Calculate the first order energy correction to the m=0 state due to V(ϕ).

(b) Now consider the two degenerate m= ± 1 levels of the unperturbed Hamiltonian. To find out how V(ϕ) affects them, construct a 2x2 Hamiltonian matrix using these two levels as the entire basis set (e.g., 1st order degenerate perturbation theory). What are the new energy levels?

(c) To find out how the unperturbed m= ± 1 wavefunctions get modified, solve for the eigenvectors of the 2x2 Hamiltonian matrix of part(b). State the wave function that corresponds to each new energy level in the presence of V(ϕ).

(d) For the higher energy wave function found in part (c), what is the average (expectation) value of the potential energy? Referring to the graph of $V(\phi)$ below, describe in your own words why this wave function represents the higher energy state.

(e) Which, if any, of the higher lying, degenerate states of the particle in the ring (m = ±2, ±3, ±4,...) get split by V(ϕ) within 1st order degenerate perturbation theory?

(f) Consider two electrons in the unperturbed m= ± 1 wavefunctions. Form a wavefunction of one allowed triplet state of the two electrons after the perturbation V(ϕ). To construct your answer, use the analytical form of the wavefunctions you found in part (c) with angle ϕ_1 for electron 1 and angle ϕ_2 for electron 2. Also, use α to denote spin up, and β for spin down.