

April 16th, 2014

Chemistry 120A 2nd Midterm

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

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

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.

If a Hydrogenic atom is subject to a magnetic field in the z -direction, the additional term in the Hamiltonian is $E_{\text{mag}} = +\mu_B L_z \mathcal{B}$ where $\mu_B = e\hbar/2m_e c$ is the Bohr magneton.

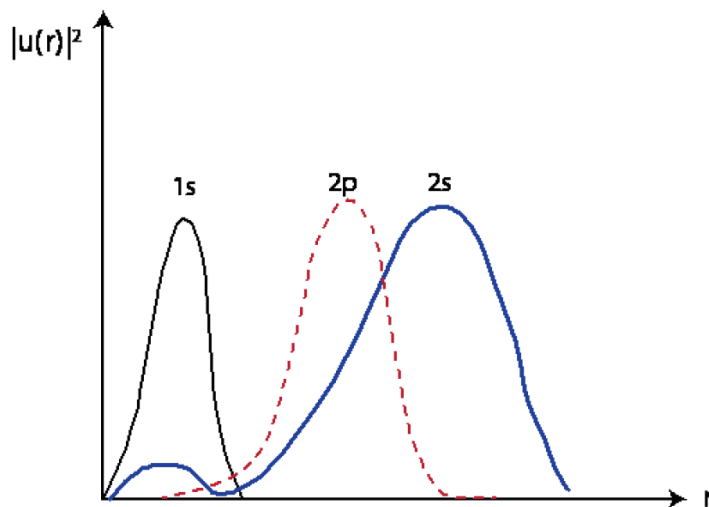


Figure 2: Radial distribution functions $u(r) = rR_{nl}(r)$

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 ionization energy of an electron in ψ_{100} increases as Z^2 .

TRUE

ii. The radial distribution function of the ψ_{300} eigenstate contains two nodes.

TRUE

iii. The ψ_{210} eigenstate can be described by a vibrationally excited state of the bare ($l=0$) coulomb potential.

FALSE: The ψ_{200} eigenstate (the $2s$ orbital) can be described by a vibrationally excited state of the bare ($l=0$) coulomb potential.

iv. The square of the orbital angular momentum of an electron in ψ_{310} is $2\hbar^2$.

TRUE

v. If a magnetic field were applied in the z -direction, ψ_{211} would no longer be an exact eigenstate of the Hamiltonian.

FALSE: The Hydrogen atom wavefunctions are eigenstates of the L_z operator, so modifying the Hamiltonian by $E_{mag} = \mu_B L_z \mathcal{B}$ does not change the exact eigenstates of the system.

vi. A magnetic field applied in the z -direction would lower the energy of an electron in ψ_{211} .

FALSE: The ψ_{211} state is RAISED in energy. The ψ_{21-1} state is LOWERED.

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 $\psi_{100}(r_1, \theta_1, \phi_1)\psi_{100}(r_2, \theta_2, \phi_2)$ with an effective Z less than 2.

TRUE

ii. The ionization energy of the ground state configuration is greater than E_0 .

TRUE

iii. The spatial wave function of an excited state of Helium can be described by $\psi_{100}(r_1, \theta_1, \phi_1)\psi_{210}(r_2, \theta_2, \phi_2)$.

FALSE: The spatial wavefunction must be either symmetric or antisymmetric with respect to exchange of electrons. This wavefunction is neither.

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

TRUE

v. The $1s2p$ configuration can be either a spin singlet or spin triplet.

TRUE

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

FALSE: The lowest energy state with a $1s2s$ configuration is the spin triplet because it has the larger s (Hund's rule).

2. (54 pts) Consider a particle in a box Hamiltonian with a bottom in the shape of a V as shown in Figure 1. This potential could arise due to an electron in the box interacting with the electric field of a point charge (i.e. proton) at a distance away. The Hamiltonian of this system is:

$$H = -\hbar^2 \nabla^2 / 2m + V(x)$$

where

$$V(x) = \lambda |x - a/2|$$

for $x > 0$ and $x < a$ and ∞ otherwise.

The eigenstates of the particle in a box are $\phi_n(x) = (\sqrt{2/a}) \sin(k_n x)$, coinciding with energy values $E_n^0 = \hbar^2 k_n^2 / 2m$, where $k_n = n\pi/a$, with $n = 1, 2, 3, \dots$

Recall that the formulas for non-degenerate perturbation theory through 2nd order are:

$$E_n = E_n^0 + V_{nn} - \sum_k V_{kn}^2 / (E_k^0 - E_n^0) \quad (1)$$

and

$$\Psi_n = \phi_n^0 - \sum_k V_{kn} \phi_k^0 / (E_k^0 - E_n^0) \quad (2)$$

where E_n^0 and ϕ_n^0 are the unperturbed energies and wave functions.

You are given the following integrals to write answers in terms of the given parameters (E_n^0 , a , and λ).

$$\int_0^a |x - a/2| (2/a) \sin[k_1 x] \sin[k_1 x] dx = a/7 \quad (3)$$

$$\int_0^a |x - a/2| (2/a) \sin[k_3 x] \sin[k_3 x] dx = a/5 \quad (4)$$

$$\int_0^a |x - a/2| (2/a) \sin[k_1 x] \sin[k_3 x] dx = a/9 \quad (5)$$

- (a) Use the first ($n=1$) and third ($n=3$) lowest lying states of the particle in a box potential to construct the Hamiltonian matrix that describes the system with the V-shaped bottom.

$$\hat{H} = \begin{bmatrix} H_{1,1} & H_{1,3} \\ H_{3,1} & H_{3,3} \end{bmatrix} = \begin{bmatrix} E_1^0 + V_{1,1} & V_{1,3} \\ V_{3,1} & E_3^0 + V_{3,3} \end{bmatrix}$$

Using the integrals provided, this can be simplified to:

$$\hat{H} = \begin{bmatrix} E_1^0 + \frac{a}{7} & \frac{a}{9} \\ \frac{a}{9} & E_3^0 + \frac{a}{5} \end{bmatrix}$$

- (b) Using non-degenerate perturbation theory through second order, what are the new energies and new wave functions associated with the original $n=1$ and $n=3$ states? Draw a level diagram describing the old energies and how they split as a result of the perturbation.

Use equation (1) to find the energies:

$$E_1 = E_1^0 + V_{1,1} - \frac{V_{3,1}^2}{E_3^0 - E_1^0} = E_1^0 + \frac{a}{7} - \frac{a^2}{81} \frac{1}{E_3^0 - E_1^0}$$

$$E_3 = E_3^0 + V_{3,3} - \frac{V_{1,3}^2}{E_1^0 - E_3^0} = E_3^0 + \frac{a}{5} + \frac{a^2}{81} \frac{1}{E_3^0 - E_1^0}$$

Use equation (2) to find the new wavefunctions:

$$\Psi_1 = \phi_1^0 - \frac{V_{3,1}}{E_3^0 - E_1^0} \phi_3^0 = \phi_1^0 - \frac{a}{9} \frac{1}{E_3^0 - E_1^0} \phi_3^0$$

$$\Psi_3 = \phi_3^0 - \frac{V_{1,3}}{E_1^0 - E_3^0} \phi_1^0 = \phi_3^0 + \frac{a}{9} \frac{1}{E_3^0 - E_1^0} \phi_1^0$$

- (c) We did not consider the second ($n=2$) lowest lying state of the particle in the box in order to calculate the change in the $n=1$ and $n=3$ energies. State which matrix elements we are neglecting in doing so. What does ignoring the $n=2$ state imply about these matrix elements?

We are ignoring the $H_{1,2}$, $H_{2,1}$, $H_{2,2}$, $H_{2,3}$, and $H_{3,2}$ terms. These could also be called the $V_{1,2}$, $V_{2,1}$, $V_{2,3}$, $V_{3,2}$, and $E_2^0 + V_{2,2}$ terms. Ignoring these terms implies that they do not affect the new energies or wavefunctions of the $n=1$ and $n=3$ states. Note that $V_{1,2} = V_{2,1} = V_{2,3} = V_{3,2} = 0$, but $V_{2,2} \neq 0$

- (d) We could have included higher lying states of the unperturbed system ($n=4, 5, 6, \dots$) to make a better approximation of the new ground state wave function. Find the general rule for which unperturbed states would contribute.

Examining the symmetry of the unperturbed wavefunctions and potential in the $[0, a]$ interval,

$$\begin{array}{ll} n = \text{odd} & \phi_n^0 \text{ is even} \\ n = \text{even} & \phi_n^0 \text{ is odd} \\ V(x) & \text{even} \end{array}$$

Recalling that (odd)·(odd) = even, (odd)·(even) = odd and that integrating an odd function over $[0, a]$ is zero, we see that

$$V_{m,n} = \begin{cases} 0 & m \text{ even, } n \text{ odd} \\ \text{nonzero} & m \text{ even, } n \text{ even} \\ \text{nonzero} & m \text{ odd, } n \text{ odd} \end{cases}$$

- (e) Now consider the wavefunction of two fermion particles (i.e. electrons) in the box with a V-shaped bottom. Construct the wavefunction that describes its ground state, including spin. You can use the solutions for the single particle found in part (b). For spin up, use the symbol α , and for spin down, use the symbol β . What is the energy of this state, ignoring any coulomb repulsions between the two electrons?

We can use a Slater determinant to solve for the wavefunction of this two-electron ground state. For one electron at x_1 and the other at x_2 :

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \Psi_1(x_1)\alpha(1) & \Psi_1(x_1)\beta(1) \\ \Psi_1(x_2)\alpha(2) & \Psi_1(x_2)\beta(2) \end{vmatrix}$$

Which is equivalent to:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} = \Psi_1(x_1)\Psi_1(x_2) * [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

If we ignore Coulomb repulsion, the energy of the total system should just be the sum of the energies of the two electrons separately:

$$E_{tot} = E_1(1) + E_1(2) = 2E_1 = 2E_1^0 + \frac{2a}{7} - \frac{2a^2}{81} \frac{1}{E_3^0 - E_1^0}$$

Figure 1

