PHY 491
Home Work Assignment #4
September 26-October 3, 2011

4.1

Consider an atom whose ground state is ${}^3S_1$. What is the value of Lande g-factor? Find the magnetization **M** as a function of magnetic field B (oriented along the z axis), temperature *T*, and concentration $n = N/V$. Show that in the limit of very high temperature $\mu_B B << k_B T$, the susceptibility is given by $\chi = 8n\mu_B^2 / 3k_B T$.

For the triplet ${}^3S_1$, $L = 0,\ S = 1,\ J = 1$

$$g_J = 1 + \frac{1x2 + 1x2 - 0x1}{2x1x2} = 2$$

$$< M >= \left(\frac{N}{V}\right) 2\mu_B 1 B_1(x);\ x = \frac{2\mu_B B}{k_B T}$$

$$B_1(x) = \frac{3}{2}\coth\left(\frac{3x}{2}\right) - \frac{1}{2}\coth\left(\frac{x}{2}\right)$$

$$When\ x << 1;\ B_1(x) = \frac{3}{2}\left[\frac{2}{3x} + \frac{3}{2}\frac{x}{3}\right] - \frac{1}{2}\left[\frac{2}{x} + \frac{1}{2}\frac{x}{3}\right] = \frac{2}{3}x$$

$$< M >= \left(\frac{N}{V}\right) 2\mu_B \frac{2}{3}\frac{2\mu_B B}{k_B T} = n\frac{8\mu_B^2}{3k_B T}B$$

$$\chi = n\frac{8\mu_B^2}{3k_B T}$$

4.2

An exotic proposal to get nuclear fusion between two deuterons is to to use the idea of muon catalysis. One constructs a “Hydrogen molecule ion”, only with deuterons instead of protons and a muon in place of an electron. Use your knowledge of the H_2^+ ion to predict the equilibrium separation between the deuterons in the muonic molecule. Explain why the chance of getting fusion is better for muons rather than electrons.

The electron in the H_2^+ ion is described by the Hamiltonian

$$-\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{e^2}{\left|\vec{r} - \vec{R}/2\right|} - \frac{e^2}{\left|\vec{r} + \vec{R}/2\right|} \equiv H_e$$

The deuteron molecule with electron replaced by a muon is described by the Hamiltonian

$$-\frac{\hbar^2}{2m_\mu}\nabla_r^2 - \frac{e^2}{\left|\vec{r} - \vec{R}/2\right|} - \frac{e^2}{\left|\vec{r} + \vec{R}/2\right|} \equiv H_\mu$$

Now represent the results for the H_2^+ ion in Hartree units of energy and Bohr unit for the length. Use experimental results for $R_{\min}$ and binding energy E_B.

$$R_{\min} = 1.06A^o = 2.04a_B; E_B = 2.79eV = 0.103\,Hartree$$

For the Deuteron problem we have to find the new length and energy scales.

$$a_B^* = \frac{\hbar^2}{2m_\mu e^2} = \frac{m_e}{m_\mu}a_B;\ Hartree^* = \frac{e^2}{a_B^*} = \frac{m_\mu}{m_e}Hartree$$

For this the $R_{\min}$ and E_B are given in the "atomic units" by

$$R_{\min} = 2.04a_B^* = \frac{m_e}{m_\mu}2.04a_B =; E_B = 0.103\,Hartree^* = \frac{m_\mu}{m_e}0.103Hartree$$

Taking $m_\mu = 207m_e$ we have

$$R_{\min} = 0.0051A^o;\ E_B = 579.9eV$$

4.3

The schrodinger equation for one electron in an attractive one-dimensional delta-function potential of the form $V(x) = -e^2\delta(x)$ is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - e^2\delta(x)\psi(x) = E\psi(x)$$

In atomic unit $(\hbar = m = e^2 = 1)$, the normalized ground state wave function is $\psi_1(x) = e^{-|x|}$, with energy $E_1 = -1/2$

(i) Check that the above wave function and energy are correct.

(ii) Consider a one-dimensional H_2 molecule with a $\delta-$like both ion-electron (as above) and repulsive electron-electron interaction. The ions are fixed at a distance *R*, and neglect ion-ion repulsion.

(a) Write down the Schrodinger equation for this one-dimensional H_2 molecule.
(b) Construct a *gerade* molecular orbital (MO) for this molecule with correct normalization coefficient
(c) Calculate the ground state energy for the molecule using this MO.
(d) Construct a Heitler-London (HL) wave function for the molecule and calculate the energy.
(e) Compare the energies obtained using the two approaches and discuss the physics.

Use:

$$\int_{-\infty}^{+\infty} e^{-|x-R/2|}e^{-|x+R/2|}dx = (1+R)e^{-R}$$

$$\int_{-\infty}^{+\infty} e^{-3|x-R/2|}e^{-|x+R/2|}dx = (3e^{-R}-e^{-3R})/4$$

$$(a+b)^4 = a^4+4a^3b+6a^2b^2+4ab^3+b^4$$

(1) Schrodinger equation in atomic units ($e^2 = m = \hbar = 1$)

$$H\psi(x_1,x_2) = E\psi(x_1,x_2)$$

$$H = \left[-\frac{1}{2}\frac{d^2}{dx_1^2}-\frac{1}{2}\frac{d^2}{dx_2^2}-\delta(x_1-R/2)-\delta(x_1+R/2)-\delta(x_2-R/2)-\delta(x_2+R/2)+\delta(x_1-x_2)\right]$$

The first two terms are the kinetic energies, the next four terms are the attractive energies between the two electrons and two nuclei and the last term is the repulsive energy of two electrons (a short range delta function model). If the nuclear repulsion is also short range i.e. $\delta(R)$, then for $R \neq 0$, we can drop it.

(2) Gerade molecular orbital (MO)

$$\psi_g(x) = \frac{1}{\sqrt{2(1+S)}}[a(x)+b(x)]; \quad a(x) = e^{-|x+R/2|}, b(x) = e^{-|x-R/2|}$$

$$S = \int_{-\infty}^{+\infty} a(x)b(x)dx = \int_{-\infty}^{+\infty} e^{-|x+R/2|}e^{-|x-R/2|}dx = (1+R)e^{-R}$$

To get the value of S and in fact all integrals involving the functions $a(x)\, and\, b(x)$
We should use:

$$e^{-|x+R/2|} = e^{+(x+R/2)}\ for\ x \le -R/2\ and\ e^{-|x+R/2|} = e^{-(x+R/2)}\ for\ x \ge -R/2$$

$$e^{-|x-R/2|} = e^{+(x-R/2)}\ for\ x \le R/2\ and\ e^{-|x-R/2|} = e^{-(x-R/2)}\ for\ x \ge R/2$$

(3) Ground State in MO theory

$$E_0 = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} dx_1 dx_2 \psi_g(x_1)\psi_g(x_2) H \psi_g(x_1)\psi_g(x_2) \equiv \langle H \rangle$$

Before doing this it is convenient to write H in a different way separating the parts from different nuclei.

$$H = T_1 + V_{a1} + V_{b1} + T_2 + V_{b2} + V_{a2} + V_{12}$$
$$= H_{a1} + V_{b1} + H_{b2} + V_{a2} + V_{12} \qquad 1$$
$$H = H_1 + H_2 + V_{12}$$

$$E_0 = < H_1 > + < H_2 > + < V_{12} >$$

Because of symmetry between 1 and 2 we have $< H_1 > = < H_2 >$. So we calculate one of them.

$$< H_1 > = \frac{1}{2(1+S)} \int_{-\infty}^{+\infty} [a(x_1) + b(x_1)](H_{a1} + V_{b1})[a(x_1) + b(x_1)]dx_1$$
$$= \frac{1}{2(1+S)} \left[\langle a|H_1|a\rangle + \langle a|H_1|b\rangle + \langle b|H_1|a\rangle + \langle b|H_1|b\rangle \right]$$
$$\langle a|H_1|a\rangle = \int_{-\infty}^{+\infty} a(x_1)(H_{a1} + V_{b1})a(x_1)dx_1 = -\frac{1}{2} + \int_{-\infty}^{+\infty} a(x_1)(V_{b1})a(x_1)dx_1 = -\frac{1}{2} + \int_{-\infty}^{+\infty} e^{-2|x_1 + R/2|}\delta(x_1 - R/2)dx_1$$
$$= -\frac{1}{2} - e^{-2R}$$
$$\textit{Similarly } \langle b|H_1|b\rangle = \int_{-\infty}^{+\infty} b(x_1)(H_{a1} + V_{b1})b(x_1)dx_1 = \int_{-\infty}^{+\infty} b(x_1)(T_1 + V_{a1} + V_{b1})b(x_1)dx_1 = \int_{-\infty}^{+\infty} b(x_1)(T_1 + V_{b1} + V_{a1})b(x_1)dx_1$$
$$= -\frac{1}{2} + \int_{-\infty}^{+\infty} b(x_1)(V_{a1})b(x_1)dx_1 = -\frac{1}{2} - e^{-2R}$$

The overlap terms in the energy are:

$$\langle b|H_1|a\rangle = \int dx_1 b(x_1)(H_{a1} + V_{b1})a(x_1) = -\frac{1}{2}\int dx_1 b(x_1)a(x_1) + \int dx_1 b(x_1)(V_{b1})a(x_1)$$
$$= -\frac{S}{2} - \int dx_1 e^{-|x_1 - R/2|}\delta(x_1 - R/2)e^{|x_1 - R/2|} = -\frac{S}{2} - e^{-R}$$
$$= \langle a|H_1|b\rangle$$

Putting together all the four terms we get

$$\langle H_1\rangle = -\frac{1}{2(1+S)}\left[1 + S + 2e^{-R} + 2e^{-2R}\right] = \langle H_2\rangle$$

Finally we are left with the electron=electron repulsion term

$$\langle V_{12}\rangle = \frac{1}{4(1+S)^2}\int\int dx_1 dx_2 (a(x_1)+b(x_1))(a(x_2)+b(x_2))[\delta(x_1-x_2)](a(x_1)+b(x_1))(a(x_2)+b(x_2))$$

$$= \frac{1}{4(1+S)^2}\int dx_1 [a(x_1)+b(x_1)]^4 = \frac{1}{4(1+S)^2}\int dx_1 \left[a^4+b^4+6a^2b^2+4a^3b+4ab^3\right]$$

$$\int_{-\infty}^{+\infty} a^4(x)dx = \int_{-\infty}^{+\infty} b^4(x)dx = \frac{1}{2}\ (similar\ \ to\, calculatio\, n\ \ of\ \ normalizat\ ion)$$

$$\int_{-\infty}^{+\infty} a^2(x)b^2(x)dx = \frac{(1+2R)e^{-2R}}{2}\ (similar\ \ to\ \ calculatio\, n\ \ of\ \ S)$$

$$\int_{-\infty}^{+\infty} a^3(x)b(x)dx = \int_{-\infty}^{+\infty} a(x)b^3(x)dx = \frac{3e^{-R}-e^{-3R}}{4}$$

$$\langle V_{12}\rangle = \frac{1}{4(1+S)^2}\left[1+6e^{-R}+3(1+2R)e^{-2R}-2e^{-3R}\right]$$

Putting all the terms together we get the FAMOUS ground state energy in MO approximation (also referred to as Hund Millikan (HM) approximation

$$E_g^{HM} = -1-\frac{2\left(e^{-R}+e^{-2R}\right)}{(1+S)}+\frac{1}{4(1+S)^2}\left[1+6e^{-R}+3(1+2R)e^{-2R}-2e^{-3R}\right]$$

Part 4.

In contrast if we use the Hetler-London approximation

$$\psi^{HL}(x_1,x_2) = N[a(x_1)b(x_2)+b(x_1)a(x_2)]$$

We get

$$E_g^{HL} = -1-\frac{2\left(e^{-R}+Se^{-2R}\right)}{\left(1+S^2\right)}+\frac{(1+2R)e^{-2R}}{\left(1+S^2\right)}$$

Part 5

Compare HM and HL.

HM is always higher than HL. When $R\to\infty$, $\langle V_{12}\rangle^{HL}\to 0$ whereas $\langle V_{12}\rangle^{HM}\to +\frac{1}{4}$.

Still some electron-electron repulsive energy is present in the Hund-Mullikan model. In this limit the energy does not approach the sum of two hydrogen atoms which should be equal to -1.