

PHY801: Survey of Atomic and Condensed Matter Physics
Michigan State University

Homework 4 – Solution

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

Solution:

For the triplet 3S_1 we have $L = 0, S = 1, J = 1$. Then,

$$g_J = g_1 = 1 + \frac{1 \times 2 + 1 \times 2 - 0 \times 1}{2 \times 1 \times 2} = 2$$

and

$$\langle M \rangle = \left(\frac{N}{V} \right) 2 \times 1 \mu_B B_1(x); \quad x = \frac{2\mu_B B}{k_B T}$$

with

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

For $x \ll 1$ we obtain

$$\begin{aligned} B_1(x) &= \frac{3}{2} \left[\frac{2}{3x} + \frac{3x}{6} \right] - \frac{1}{2} \left[\frac{2}{x} + \frac{x}{6} \right] = \frac{2}{3}x; \\ \langle M \rangle &= \left(\frac{N}{V} \right) 2\mu_B \frac{2}{3} \frac{2\mu_B B}{k_B T} = n \frac{8}{3} \frac{\mu_B^2}{k_B T} B; \\ \chi &= n \frac{8}{3} \frac{\mu_B^2}{k_B T}. \end{aligned}$$

4.2. An exotic proposal to get nuclear fusion between two deuterons is 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 than for electrons.

Solution:

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

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

The deuteron molecule with electrons replaced by muons is described by the Hamiltonian

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

Now represent the results for the H_2^+ ion in Hartree units of energy and Bohr units of length. Use experimental results for the inter-nuclear distance $R_{min} = 1.06 \text{ \AA} = 2.04a_B$ and the binding energy $E_B = 2.79 \text{ eV} = 0.103 \text{ Hartree}$.

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

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

Then, R_{min} and E_B of the muonic molecular ion are given by

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

Taking $m_\mu = 207m_e$ we obtain $R_{min} = 0.00521 \text{ \AA}$ and binding energy $E_B = 579.9 \text{ eV}$. The nuclei are much closer in muonic than in electronic H_2^+ , thus making fusion much more probable.

4.3. The Schrödinger 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 units ($\hbar = m = e^2 = 1$), the normalized ground state wave function is $\psi_1(x) = e^{-|x|}$, and the corresponding energy is $E_1 = -1/2$.

- (i) Check that the above wave function and energy are correct.
- (ii) Consider a one-dimensional H_2 molecule with a δ -like both ion-electron (as above) and repulsive electron-electron interaction. The ions are fixed at a distance R . Neglect ion-ion repulsion.
 - (a) Write down the Schrödinger equation for this one-dimensional H_2 molecule.
 - (b) Construct a *gerade* molecular orbital (MO) for this molecule with the 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:

$$\begin{aligned} \int_{-\infty}^{+\infty} e^{-|x-R/2|} e^{-|x+R/2|} dx &= (1+R)e^{-R} \\ \int_{-\infty}^{+\infty} e^{-3|x-R/2|} e^{-|x+R/2|} dx &= (3e^{-R} - e^{-3R})/4 \\ (a+b)^4 &= a^4 + 4a^3b + 6a^2b^2 + 4ab^3 + b^4 \end{aligned}$$

Solution:

Part (i)

Insert the wave function to check it is an eigenstate of the Schrödinger equation with the postulated energy.

Part (ii)

(a) The Schrödinger equation of the H₂ molecule in 1-dimensional space is given by

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

with

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

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 δ -function model). If the nuclear repulsion is also short range, i.e. $\delta(R)$, then we can drop it for $R \neq 0$.

(b) The *gerade* molecular orbital (MO) is given by

$$\psi_g(x) = \frac{1}{\sqrt{2(1+S)}} [a(x) + b(x)]$$

with

$$\begin{aligned} a(x) &= e^{-|x+R/2|} , \\ b(x) &= e^{-|x-R/2|} , \\ S &= \int_{-\infty}^{+\infty} a(x)b(x)dx = \int_{-\infty}^{+\infty} e^{-|x+R/2|} e^{-|x-R/2|} dx = (1+R)e^{-R} . \end{aligned}$$

To get the values of S and in fact all integrals involving the functions $a(x)$ and $b(x)$ we should use

$$\begin{aligned} e^{-|x+R/2|} &= e^{+(x+R/2)} \text{ for } x \leq -R/2 \text{ and } e^{-|x+R/2|} = e^{-(x+R/2)} \text{ for } x \geq -R/2 \\ e^{-|x-R/2|} &= e^{+(x-R/2)} \text{ for } x \leq +R/2 \text{ and } e^{-|x-R/2|} = e^{-(x-R/2)} \text{ for } x \geq +R/2 . \end{aligned}$$

(c) The ground state energy in molecular orbital theory is given by

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

Before evaluating this integral it is convenient to write H in a different way, separating the parts from different nuclei, as

$$\begin{aligned} H &= T_1 + V_{a1} + V_{b1} + T_2 + V_{b2} + V_{a2} + V_{12} \\ &= H_{a1} + V_{b1} + H_{b2} + V_{a2} + V_{12} \\ H &= H_1 + H_2 + V_{12} . \end{aligned}$$

Then,

$$E_0 = \langle H_1 \rangle + \langle H_2 \rangle + \langle V_{12} \rangle .$$

Because of symmetry between electron 1 and 2, we have $\langle H_1 \rangle = \langle H_2 \rangle$. So, only $\langle H_1 \rangle$ needs to be evaluated.

$$\begin{aligned} \langle H_1 \rangle &= \frac{1}{2(1+S)} \int_{-\infty}^{+\infty} [a(x_1) + b(x_1)] (H_a + V_{b1}) [a(x_1) + b(x_1)] dx_1 \\ &= \frac{1}{2(1+S)} [\langle a|H_1|a \rangle + \langle a|H_1|b \rangle + \langle b|H_1|a \rangle + \langle b|H_1|b \rangle] . \end{aligned}$$

We then evaluate

$$\begin{aligned}\langle a|H_1|a \rangle &= \int_{-\infty}^{+\infty} a(x_1)(H_{a1} + V_{b1})a(x_1)dx_1 = -\frac{1}{2} + \int_{-\infty}^{+\infty} a(x_1)(V_{b1})a(x_1)dx_1 \\ &= -\frac{1}{2} - \int_{-\infty}^{+\infty} e^{-2|x_1+R/2|}\delta(x_1 - R/2)dx_1 = -\frac{1}{2} - e^{-2R} .\end{aligned}$$

Similarly,

$$\begin{aligned}\langle b|H_1|b \rangle &= \int_{-\infty}^{+\infty} b(x_1)(H_{a1} + V_{b1})b(x_1)dx_1 = \int_{-\infty}^{+\infty} b(x_1)(T_1 + V_{a1} + V_{b1})b(x_1)dx_1 \\ &= \int_{-\infty}^{+\infty} b(x_1)(T_1 + V_{b1} + V_{a1})b(x_1)dx_1 = -\frac{1}{2} + \int_{-\infty}^{+\infty} b(x_1)(V_{a1})b(x_1)dx_1 = -\frac{1}{2} - e^{-2R} .\end{aligned}$$

The overlap terms in the energy are

$$\begin{aligned}\langle b|H_1|a \rangle &= \int_{-\infty}^{+\infty} dx_1 b(x_1)(H_{a1} + V_{b1})a(x_1) = -\frac{1}{2} \int_{-\infty}^{+\infty} dx_1 b(x_1)a(x_1) + \int_{-\infty}^{+\infty} dx_1 b(x_1)(V_{b1})a(x_1) \\ &= -\frac{S}{2} - \int_{-\infty}^{+\infty} dx_1 e^{-|x_1-R/2|}\delta(x_1 - R/2)e^{-|x_1+R/2|} = -\frac{S}{2} - e^{-R} = \langle a|H_1|b \rangle .\end{aligned}$$

Combining all four terms we get

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

Finally, the only remaining term is the electron-electron repulsion term

$$\begin{aligned}\langle V_{12} \rangle &= \frac{1}{4(1+S)^2} \int \int dx_1 dx_2 (a(x_1) + b(x_1)) (a(x_2) + b(x_2)) [\delta(x_1 - x_2)] (a(x_1) + b(x_1)) (a(x_2) + b(x_2)) \\ &= \frac{1}{4(1+S)^2} \int dx_1 [a(x_1) + b(x_1)]^4 = \frac{1}{4(1+S)^2} \int dx_1 [a^4 + 4a^3b + 6a^2b^2 + 4ab^3 + b^4] .\end{aligned}$$

We then get, similar to the calculation of normalization,

$$\int_{-\infty}^{+\infty} a^4(x)dx = \int_{-\infty}^{+\infty} b^4(x)dx = \frac{1}{2} .$$

Then, similar to the calculation of S , we get

$$\begin{aligned}\int_{-\infty}^{+\infty} a^2(x)b^2(x)dx &= \frac{(1+2R)e^{-2R}}{2} , \\ \int_{-\infty}^{+\infty} a^3(x)b(x)dx &= \int_{-\infty}^{+\infty} a(x)b^3(x)dx = \frac{3e^{-R} - e^{-3R}}{4} .\end{aligned}$$

Finally,

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

Putting all the terms together we get the FAMOUS ground state energy in the MO approximation, which is also referred to as the Hund-Mullikan (HM) approximation, as

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

(d) In contrast, if we use the Heitler-London approximation,

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

we get

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

(e) HM is always higher than HL. When $R \rightarrow \infty$, $\langle V_{12} \rangle^{HL} \rightarrow 0$, whereas $\langle V_{12} \rangle^{HM} \rightarrow +\frac{1}{4}$. Still some electron-electron repulsive energy is present in the Hund-Mullikan model. In the $R \rightarrow \infty$ limit, the energy does not approach the sum of two hydrogen atoms, which should be equal to -1 Hartree.
