

Physics 4410
Quantum Mechanics and Atomic Physics II
Professor William T. Ford

Homework #4

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1 Problem #1

- (a) If we operate under the first order approximation such that individual electrons occupy one-particle hydrogenic states (nlm). This coupled with the fact that electrons are fermions and must obey the *Pauli Exclusion Principle* we can write the electron configurations for all the elements up to neon.

For hydrogen and helium we have the lowest energy level $n = 1$ which results in $l = 0$. So for this orbital we can have 2 electrons, one of each spin. So the electron configuration is

$$\begin{aligned}\text{H} &: (1s) \\ \text{He} &: (1s)^2\end{aligned}$$

Now for the next elements we must move to the next energy level $n = 2$. At this level we have $l = 1, 0$. Again for the $l = 0$ level we can hold 2 electrons which corresponds to the next two elements

$$\begin{aligned}\text{Li} &: (1s)^2(2s) \\ \text{Be} &: (1s)^2(2s)^2\end{aligned}$$

Now for the $n = 2$ $l = 1$ we are allowed three different m states given by $m = 1, 0, -1$ so we are allowed a total of six electrons in this level when we account for spin. Therefore in this level we can get all the electrons we need to get up to neon

$$\begin{aligned}\text{B} &: (1s)^2(2s)^2(2p) \\ \text{C} &: (1s)^2(2s)^2(2p)^2 \\ \text{N} &: (1s)^2(2s)^2(2p)^3 \\ \text{O} &: (1s)^2(2s)^2(2p)^4 \\ \text{F} &: (1s)^2(2s)^2(2p)^5 \\ \text{Ne} &: (1s)^2(2s)^2(2p)^6\end{aligned}$$

- (b) The total angular momenta for the elements we covered in part (a) follows from the l state. For the first four elements (H, He, Li, and Be) the orbital angular momentum is $l = 0$ due to the fact that every electron is in a s sub-shell. So the total angular momentum is just the total spin, which for an even number of electrons is $S = 0$ and for an odd number of electrons is $S = 1/2$. So we have

$$\begin{aligned}\text{H} &: {}^2S_{1/2} \\ \text{He} &: {}^1S_0 \\ \text{Li} &: {}^2S_{1/2} \\ \text{Be} &: {}^1S_0\end{aligned}$$

Note the S denotes the orbital angular momentum $l = 0$. Now for the next elements the total angular momentum becomes more complicated. For Boron the total spin of the valance electron is $S = 1/2$ and the orbital angular momentum is $l = 1$. These angular momentum can combine to yield $J = 1/2, 3/2$. This results in

$$\text{B} : {}^2P_{3/2}, {}^2P_{1/2}$$

For carbon again we have $l = 1$ but this time we have two electrons in with this angular momentum each with the possible value $m = 1, 0, -1$. Therefore the addition of these angular

momenta results in a possible $L = 2, 1, 0$ and again the total spin of two electrons can be $S = 1, 0$. This results in the possible total angular momenta given by

$$C : {}^1S_0, {}^3S_1, {}^1P_1, {}^3P_{2,1,0}, {}^1D_2, {}^3D_{3,2,1}$$

For nitrogen we still have $l = 1$ now with three electrons. This implies that the total orbital angular momentum is $L = 3, 2, 1, 0$. And with three electrons we can have a possible total spin of $S = 3/2, 1/2$. So the possible total angular momenta is given by

$$N : {}^2S_{1/2}, {}^4S_{3/2}, {}^2P_{3/2,1/2}, {}^4P_{5/2,3/2,1/2}, {}^2D_{5/2,3/2}, {}^4D_{7/2,5/2,3/2,1/2}, {}^2F_{7/2,5/2}, {}^4F_{9/2,7/2,5/2,3/2}$$

2 Problem #2

- (a) According the *Hund's first rule* the state with the highest total spin has the lowest energy. This implies that the 1S helium has higher total energy than the 3S helium.
- (b) Due to *Hund's first rule* the ground state of carbon has a maximal spin which for two electrons is $S = 1$. This is a symmetric state. So when we apply *Hund's second rule* we need to pick the highest total orbital angular momentum consistent with overall antisymmetrization. Due to the fact that the spin is symmetric the orbital must be antisymmetric which is the $L = 1$ state. This implies that the carbon atom is in the 3P state.
- (c) As we found in problem #1 Boron can have two different total angular momenta ${}^2P_{3/2}, {}^2P_{1/2}$. To determine which is the ground state we must apply *Hund's third rule* which states that if a subshell is no more than half filled then the lowest energy level has $J = |L - S|$ this implies that the ground state of Boron is

$${}^2P_{1/2}$$

- (d) We can also find the ground state of carbon by applying all three Hund's rules. By taking maximal spin we can eliminate

$$\cancel{{}^1S_0}, {}^3S_1, \cancel{{}^1P_1}, {}^3P_{2,1,0}, \cancel{{}^1D_2}, {}^3D_{3,2,1}$$

which leaves us with

$${}^3S_1, {}^3P_{2,1,0}, {}^3D_{3,2,1}$$

now we apply *Hund's second rule* we find that the highest orbital angular momentum that preserves the antisymmetrization is

$${}^3P_{2,1,0}$$

now we have a subshell that is less than half filled so we want $J = |L - S|$ which yields the ground state

$3P_0$

For Nitrogen we again want a maximal spin which in this case is $S = 3/2$ so we are left with the states

$${}^4S_{3/2}, {}^4P_{5/2,3/2,1/2}, {}^4D_{7/2,5/2,3/2,1/2}, {}^4F_{9/2,7/2,5/2,3/2}$$

and now we can note that for $S = 3/2$ we have a symmetric spin state. Therefore we need to find a antisymmetric orbital state. This implies that each possible $m = 1, 0, -1$ state must be occupied, by Pauli exclusion. So that yields the total orbital angular momentum $L = 1 + 0 - 1 = 0$ which results in the S orbital angular momentum leaving

$${}^4S_{3/2}$$

as the ground state of Nitrogen.

3 Problem #3

Given an infinite potential well of width L with a perturbation added to it in the form of the potential

$$V(x) = V_0(x/L)$$

we have the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$ where \hat{H}_1 is the perturbation given. We can calculate the shift in energy to the n th state by using

$$E_n^{(1)} = \langle n_0 | \hat{H}_1 | n_0 \rangle \quad (3.1)$$

where $|n_0\rangle$ is the eigenstates of the unperturbed Hamiltonian known to be

$$|n_0\rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

with the corresponding energy

$$E_n^{(0)} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$

So we apply equation 3.1 to get

$$\begin{aligned} E_n^{(1)} &= \langle n_0 | \hat{H}_1 | n_0 \rangle \\ &= \frac{V_0}{L} \frac{2}{L} \int_0^L x \sin^2\left(\frac{n\pi}{L}x\right) dx \\ &= \frac{2V_0}{L^2} \int_0^L x \sin^2\left(\frac{n\pi}{L}x\right) dx \\ &= \frac{2V_0}{L^2} \left(\frac{x^2}{4} - \frac{x \sin\left(\frac{2n\pi}{L}x\right)}{4n\pi/L} - \frac{\cos\left(\frac{2n\pi}{L}x\right)}{8(n\pi/L)^2} \right) \Bigg|_0^L \\ &= \frac{2V_0}{L^2} \left(\frac{L^2}{4} - \frac{L \sin\left(\frac{2n\pi}{L}L\right)}{4n\pi/L} - \frac{\cos\left(\frac{2n\pi}{L}L\right)}{8(n\pi/L)^2} - \frac{0^2}{4} + \frac{0 \sin\left(\frac{2n\pi}{L}0\right)}{4n\pi/L} + \frac{\cos\left(\frac{2n\pi}{L}0\right)}{8(n\pi/L)^2} \right) \\ &= \frac{2V_0}{L^2} \left(\frac{L^2}{4} - \frac{L \sin(2n\pi)}{4n\pi/L} - \frac{\cos(2n\pi)}{8(n\pi/L)^2} + \frac{L^2}{8(n\pi)^2} \right) \\ &= \frac{2V_0}{L^2} \left(\frac{L^2}{4} - \frac{L^2}{8(n\pi)^2} + \frac{L^2}{8(n\pi)^2} \right) \\ &= \frac{V_0}{2} \end{aligned}$$

Note we used an integral table to find

$$\int x \sin^2(ax) = \frac{x^2}{4} - \frac{x \sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2}$$

We see that by adding this perturbation we shifted every energy level up by a factor of $V_0/2$

4 Problem #4

For an infinite square well of width b with the perturbation

$$\hat{H}_1 = \epsilon \sin\left(\frac{\pi}{b}x\right)$$

we can apply equation 3.1 with

$$|n_0\rangle = \sqrt{\frac{2}{b}} \sin\left(\frac{n\pi}{b}x\right)$$

to calculate the shift in energy to first order in ϵ . Note we used mathematica to calculate the integral.

$$\begin{aligned} E_n^{(1)} &= \langle n_0 | \hat{H}_1 | n_0 \rangle \\ &= \frac{2\epsilon}{b} \int_0^b \sin\left(\frac{\pi}{b}x\right) \sin^2\left(\frac{n\pi}{b}x\right) dx \\ &= -\frac{2\epsilon}{b} \left(\frac{b \left[(8n^2 - 2) \cos\left(\frac{\pi}{b}x\right) + (2n + 1) \cos\left(\frac{\pi(2n-1)}{b}x\right) + (1 - 2n) \cos\left(\frac{\pi(2n+1)}{b}x\right) \right]}{4\pi(4n^2 - 1)} \right) \Bigg|_0^b \\ &= -\frac{2\epsilon}{4\pi(4n^2 - 1)} \left((8n^2 - 2) \cos(\pi) + (2n + 1) \cos(\pi(2n - 1)) + (1 - 2n) \cos(\pi(2n + 1)) \right. \\ &\quad \left. - (8n^2 - 2) - (2n + 1) - (1 - 2n) \right) \\ &= -\frac{2\epsilon}{4\pi(4n^2 - 1)} \left(-(8n^2 - 2) + (2n + 1) \cos(\pi(2n - 1)) + (1 - 2n) \cos(\pi(2n + 1)) - 8n^2 \right) \\ &= -\frac{2\epsilon}{4\pi(4n^2 - 1)} \left(-16n^2 + 2 + (2n + 1) \cos(\pi(2n - 1)) + (1 - 2n) \cos(\pi(2n + 1)) \right) \end{aligned}$$

Note the value for $\cos(\pi(2n \pm 1))$ depends of if n is even or odd. For n even we have $\cos(\pi(2n \pm 1)) = -1$ which yields

$$\begin{aligned} E_{n \rightarrow \text{even}}^{(1)} &= -\frac{2\epsilon}{4\pi(4n^2 - 1)} (-16n^2 + 2 - 2n - 1 - 1 + 2n) \\ &= -\frac{2\epsilon}{4\pi(4n^2 - 1)} (-16n^2) \\ &= \frac{8\epsilon n^2}{\pi(4n^2 - 1)} \end{aligned}$$

And for n odd we have $\cos(\pi(2n \pm 1)) = 1$ which yields

$$\begin{aligned} E_{n \rightarrow \text{odd}}^{(1)} &= -\frac{2\epsilon}{4\pi(4n^2 - 1)} (-16n^2 + 2 + 2n + 1 + 1 - 2n) \\ &= -\frac{2\epsilon}{4\pi(4n^2 - 1)} (-16n^2 + 4) \\ &= \frac{2\epsilon(16n^2 - 4)}{4\pi(4n^2 - 1)} \\ &= \frac{2\epsilon(4n^2 - 1)}{\pi(4n^2 - 1)} \\ &= \frac{2\epsilon}{\pi} \end{aligned}$$