

$$\boxed{E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)}$$

$$= \frac{\hbar^2 \pi^2}{2mL^2} \left(n_x^2 + \frac{n_y^2}{4} + \frac{n_z^2}{4} \right)$$

Lowest state: $n_x = n_y = n_z = 1 \Rightarrow \boxed{E = \frac{3}{2} \left(\frac{\hbar^2 \pi^2}{2mL^2} \right)}$

Now, we can increase any n . Taking $n_x = 1, n_y = 2, n_z = 1$ gives $\boxed{E = \frac{9}{4} \left(\frac{\hbar^2 \pi^2}{2mL^2} \right)}$

This is degenerate, since $n_x = n_y = 1, n_z = 2$ gives the same E .

Now take $n_x = 1, n_y = n_z = 2 \Rightarrow \boxed{E = 3 \left(\frac{\hbar^2 \pi^2}{2mL^2} \right)}$

Next: $n_x = 1, n_y = 3, n_z = 1 \Rightarrow \boxed{E = \frac{7}{2} \left(\frac{\hbar^2 \pi^2}{2mL^2} \right)}$

degenerate: $n_x = n_y = 1, n_z = 3$ gives same E .

Next: $n_x = 2, n_y = n_z = 1 \Rightarrow \boxed{E = \frac{9}{2} \left(\frac{\hbar^2 \pi^2}{2mL^2} \right)}$

Finally, $n_x = 2, n_y = 2, n_z = 1 \Rightarrow \boxed{E = \frac{21}{4} \left(\frac{\hbar^2 \pi^2}{2mL^2} \right)}$

degenerate, with $n_x = n_z = 2, n_y = 1$.

$$2) \quad E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\Rightarrow E_{111} = \frac{3\hbar^2 \pi^2}{2mL^2} = \boxed{28.2 \text{ eV}}$$

b) $n_x = 2, n_y = n_z = 1$ (or $n_x = n_y = 1, n_z = 2$
or $n_x = n_z = 1, n_y = 2$)

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (4 + 1 + 1) = \frac{6\hbar^2 \pi^2}{2mL^2} = \boxed{56.4 \text{ eV}}$$

#3.) A particle of mass m moves in a three dimensional box with sides L . If the particle is in the third excited level, corresponding to $n^2=11$, find

a.) The energy of a particle.

From #1.) we know that

$$E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right]$$

In this case, $L_1 = L_2 = L_3 = L$

$$E = \frac{\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$$

$$= \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad \text{where } n^2 = n_1^2 + n_2^2 + n_3^2$$

They tell us $n^2=11$, so

$$E = \frac{11 \pi^2 \hbar^2}{2mL^2}$$

b.) the combinations of n_1 , n_2 , and n_3 that would give this energy.

We need

$$n_1^2 + n_2^2 + n_3^2 = 11$$

#3.) continued

That will work for

$$\begin{array}{l} n_1 = 3, n_2 = n_3 = 1 \\ n_1 = n_2 = 1, n_3 = 3 \\ n_1 = n_3, n_2 = 3 \end{array}$$

c.) The wave functions for these states

Again, from #1.),

$$\psi(x,y,z) = \sqrt{\frac{8}{L_1 L_2 L_3}} \sin\left(\frac{n_1 \pi x}{L_1}\right) \sin\left(\frac{n_2 \pi y}{L_2}\right) \sin\left(\frac{n_3 \pi z}{L_3}\right)$$

For $L_1 = L_2 = L_3 = L$

$$= \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \sin\left(\frac{n_3 \pi z}{L}\right)$$

So our states are

$$\psi_{311} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{3\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

$$\psi_{131} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{3\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

$$\psi_{113} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{3\pi z}{L}\right)$$

#6.) continued

which have solutions

$$\psi_1(x) = A e^{ik_1 x} + B e^{-ik_1 x}$$

$$\psi_2(y) = C e^{ik_2 y} + D e^{-ik_2 y}$$

$$\psi_3(y) = E e^{ik_3 y} + F e^{-ik_3 y}$$

$$\phi(t) = e^{-i \frac{E}{\hbar} t}$$

(we usually use $\pm ikx$ instead of sines + cosines for free particles. Same thing, though)

Energy and momentum squared are sharp. To prove, act on $\psi(\vec{r}, t)$ with $\hat{E} = i\hbar \frac{\partial}{\partial t}$ and $\hat{p}^2 = -\hbar^2 \nabla^2$

#7.) For a particle confined to a cubic box of dimension L , show that the normalizing factor is $A = (2/L)^{3/2}$, the same value for all the stationary states. How is this result changed if the box has edge lengths L_1, L_2 , and L_3 , all of which are different?

Let's do it for L_1, L_2 and L_3 all different first, and then take them all equal to L as a special case.

From #1, we know our wavefunctions look like

$$\psi(x, y, z) = A \sin\left(\frac{n_1 \pi x}{L_1}\right) \sin\left(\frac{n_2 \pi y}{L_2}\right) \sin\left(\frac{n_3 \pi z}{L_3}\right)$$

7.) continued

To normalize this, we know that the probability to find the particle somewhere in the box is 100%. But the box is 3-D, so we have to use a volume integral:

$$P = \int_V |\psi(x,y,z)|^2 dV$$
$$= A^2 \int_0^{L_1} dx \sin^2\left(\frac{n_1 \pi x}{L_1}\right) \int_0^{L_2} dy \sin^2\left(\frac{n_2 \pi y}{L_2}\right) \int_0^{L_3} dz \sin^2\left(\frac{n_3 \pi z}{L_3}\right)$$

Each one of these is exactly the integral we had to do for 1-D box normalization:

$$\int_0^L \sin^2\left(\frac{n \pi x}{L}\right) dx = \frac{L}{2}$$

Right? So we get

$$A^2 \left(\frac{L_1}{2}\right) \left(\frac{L_2}{2}\right) \left(\frac{L_3}{2}\right) = \frac{A^2 L_1 L_2 L_3}{2^3} = 1$$

$$\text{So } A = \sqrt{\frac{8}{L_1 L_2 L_3}}$$

For $L_1 = L_2 = L_3 = L$

$$A = \sqrt{\frac{8}{L^3}} = \left(\frac{2}{L}\right)^{3/2}$$

#8.) continued

For ground, $n_1 = n_2 = n_3 = 1$, and $L = 10 \text{ fm}$

$$\Rightarrow \boxed{E_{\text{min}} = 107.4 \text{ MeV}}$$

#10.) Consider an electron for which $n=4$, $l=3$, and $m_l=3$.

Calculate the numerical value of

a.) the orbital angular momentum

Equation 7.14 says

$$\begin{aligned} |\vec{L}| &= \sqrt{l(l+1)} \hbar \\ &= \sqrt{3(3+1)} \hbar \end{aligned}$$

$$\boxed{|\vec{L}| = \sqrt{12} \hbar}$$

b.) the z component of the angular momentum

7.14 also says

$$L_z = m_l \hbar$$

$$\boxed{L_z = 3 \hbar}$$

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a) $n=1: l=0, m_l=0$

$n=2: l=0, m_l=0$

$l=1, m_l=-1, 0, 1.$

b) $E_n = -\frac{ke^2}{2a_0} \left[\frac{Z^2}{n^2} \right] = -13.6 \frac{Z^2}{n^2}$

So for $n=1$, $E_1 = -122.4 \text{ eV}$
 $n=2$, $E_2 = -30.6 \text{ eV}$ ($Z=3$ for Lithium)

These don't depend on l or m_l , just n

#12) continued

We are only interested in the probability for the particle to be located between r and $r+dr$, for all angles θ and ϕ . So integrate over all θ and ϕ .

$$P = \int_0^{2\pi} \int_0^{\pi} |\psi(r)|^2 r^2 \sin\theta \, d\theta \, d\phi \, dr$$
$$= |\psi(r)|^2 r^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta$$

$$\therefore \boxed{P = 4\pi |\psi(r)|^2 r^2 \, dr} \quad \blacksquare$$

#16.) In obtaining the results for hydrogen-like atoms in Section 7.5, the atomic nucleus was assumed to be immobile due to its much larger mass compared with that of the electron. If this assumption is relaxed, the results remain valid if the electron mass is replaced everywhere by the reduced mass μ of the electron nucleus combination:

$$\mu = \frac{m_e M}{m_e + M}$$

Here M is the nuclear mass.

a.) Making this replacement in equation 7.38, show that a more general expression for the allowed energies of a one-electron atom with atomic number Z is

#16.) continued

$$E_n = -\frac{\mu k^2 e^4}{2\hbar^2} \left(\frac{Z^2}{n^2} \right)$$

Equation 7.38 is

$$E_n = -\frac{ke^2}{2a_0} \left(\frac{Z^2}{n^2} \right)$$

where

$$a_0 = \frac{\hbar^2}{m_e k e^2}$$

replace m_e with μ

$$a_0 = \frac{\hbar^2}{\mu k e^2}$$

So

$$E_n = -\frac{ke^2}{2} \left(\frac{\mu k e^2}{\hbar^2} \right) \left(\frac{Z^2}{n^2} \right)$$

$$E_n = -\frac{\mu k^2 e^4}{2\hbar^2} \left(\frac{Z^2}{n^2} \right)$$

b.) The wave length for the $n=3$ to $n=2$ transition of the hydrogen atom is 656.3 nm (visible red light). What is the wavelength of the same transition in singly ionized helium? In positronium?

#(6.) continued

For He, $\mu \approx m_e$, so

$$\Delta E = E_3 - E_2 = \frac{m_e k^2 e^4 Z^2}{2\hbar^2} \left(\frac{1}{4} - \frac{1}{9} \right)$$

$$\therefore \Delta E_{\text{He}} = 4\Delta E_{\text{H}}$$

$$\Delta E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E}$$

$$\lambda_{\text{He}} = \frac{hc}{\Delta E_{\text{He}}} = \frac{hc}{4\Delta E_{\text{H}}} = \frac{\lambda_{\text{H}}}{4}$$

$$\boxed{\lambda_{\text{He}} = 164.1 \text{ nm}}$$

For positronium, $Z=1$ and $M=m_e$

$$\therefore \mu = \frac{m_e^2}{2m_e} = \frac{m_e}{2}$$

$$\Rightarrow \Delta E_{\text{positronium}} = \frac{1}{2} \Delta E_{\text{H}}$$

$$\boxed{\lambda_{\text{positronium}} = 2\lambda_{\text{H}} = 1312.6 \text{ nm}}$$

#20.) Prove that the n^{th} energy level of an atom has degeneracy equal to n^2 .

Remember that degeneracy means that different states have the same energy. For a hydrogen-like atom the energy is

$$E_n = (-13.6 \text{ eV}) \frac{Z^2}{n^2}$$

So the only quantum number the energy depends on is n . But for every n , there's a buttload of other states, corresponding to different l and m_l values. And all of these will be degenerate. So our job is to count how many possible l and m_l values there are for a given n .

We know that for a given n ,

$$l = 0, \dots, n-1$$

So for the n^{th} level, there are n possible l values. But for each l , we have more states given by all the different m_l s.

$$m_l = -l, \dots, 0, \dots, l$$

Or $2l+1$ possible m_l values for a given l . So for

$$l=0,$$

$$m_l = 0$$

so there's only one state.

For $l=1$

$$m_l = -1, 0, 1$$

so there's three states

20.) continued

Similarly, for $l=2$, there will be 5 states, and so on. So for a given n , we need to find all the l 's, see how many states each l gives us, and add them all up to find the total number of states:

$$\text{total \# of states} = \sum_{l=0}^{n-1} (2l+1)$$

So somehow we need to evaluate this sum for general n . Now watch how clever your TA is.

We can write this sum out like

$$\text{tot. \# of states} = 1 + 3 + 5 + 7 + \dots + 2(n-2)+1 + 2(n-1)+1$$

right? This is

$$\text{tot \# of states} = 1 + 3 + 5 + 7 + \dots + 2n-3 + 2n-1$$

Now watch this! It doesn't matter what order you add them in, so write the sum backwards

$$\text{tot \# of states} = 2n-1 + 2n-3 + \dots + 7 + 5 + 3 + 1$$

Now add the sum written forwards!

$$\begin{aligned} \text{total \# of states} &= 2n-1 + 2n-3 + \dots + 7 + 5 + 3 + 1 \\ + \text{total \# of states} &= 1 + 3 + \dots + 2n-7 + 2n-5 + 2n-3 + 2n-1 \end{aligned}$$

$$2(\text{total \# of states}) = 2n + 2n + \dots + 2n + 2n + 2n + 2n$$

There's n of those terms, so

$$2(\text{total \# of states}) = (2n)n = 2n^2$$

#20) continued

So

$$\text{total \# of states} = n^2 = \text{degeneracy!}$$

Slick, no? (Actually, I think this should be $2n^2$ due to spin degeneracy)

Actually, I ain't all that clever. I stole that trick from Gauss. The story behind it is pretty cool. When Gauss was a little kid in grade school (about 8 or 9 years old or something), one day his class was being bad, so the teacher decided to punish them. He figured a good punishment would be to have them add all the integers from 1 to 100, cuz he figured it would take all day for them to do it and it would be painful and all that. But about 5 seconds after he told them to do it, Gauss yelled out "5050!" He came up with that trick when he was 9 years old, for God's sake! Supa-Genius.

#22.) Suppose that a hydrogen atom is in the $2s$ state. Taking $r=a_0$, calculate values for

a.) $\psi_{2s}(a_0)$

For the hydrogen atom, the states are in the form

$$\psi_{nl}(a_0) = R_{nl}(r) Y_l^{m_l}(\theta, \phi)$$

where the $R_{nl}(r)$ are Laguerre polynomials and the $Y_l^{m_l}(\theta, \phi)$ are the spherical harmonics,

#22.) continued

$$\begin{aligned} P_{2s}(a_0) &= 4\pi |\psi_{2s}(a_0)|^2 a_0^2 \\ &= 3.43 \times 10^{10} \text{ m}^{-1} \end{aligned}$$

#23.) The radial part of the wavefunction for the hydrogen atom in the $2p$ state is given by

$$R_{2p}(r) = A r e^{-r/2a_0}$$

where A is a constant and a_0 is the Bohr radius. Using this expression, calculate the average value of r for an electron in this state.

We need to calculate $\langle r \rangle$ for this thing. That'll be

$$\begin{aligned} \langle r \rangle &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{n,l,m_l}^* r \psi_{n,l,m_l} r^2 \sin\theta dr d\theta d\phi \\ &= \int_0^\infty dr r^3 |R_{n,l}(r)|^2 \int_0^\pi d\theta \sin\theta |\Theta(\theta)|^2 \int_0^{2\pi} d\phi |\Phi(\phi)|^2 \end{aligned}$$

The integrals of θ and ϕ will both be equal to one since $\Theta(\theta)$ and $\Phi(\phi)$ are individually normalized. So we're left with

$$\begin{aligned} \langle r \rangle &= \int_0^\infty r^3 |R_{n,l}(r)|^2 dr \\ &= A^2 \int_0^\infty r^5 e^{-r/a_0} dr \end{aligned}$$

You can go look this mother up, or if you like pain, you can integrate by parts 5 times! Not for me!

#23) continued

Look it up and get

$$\langle r \rangle = A^2 a_0^6 5! = 5a_0 = 2.645 \text{ \AA}$$

#25.) Calculate the average potential and kinetic energies for the electron in the ground state of hydrogen.

The potential energy is

$$U(r) = -\frac{ke^2}{r}$$

So the average is (again, we only gotta worry about the radial integral)

$$\langle U(r) \rangle = \int_0^{\infty} \psi_{1s}^*(r, \theta, \phi) \left(-\frac{ke^2}{r}\right) \psi_{1s}(r, \theta, \phi) r^2 dr$$

$$= -\frac{4ke^2}{a_0^3} \int_0^{\infty} r e^{-2r/a_0} dr$$

You can integrate by parts to get

$$\langle U(r) \rangle = -\frac{ke^2}{a_0} = -27.2 \text{ eV}$$

To get $\langle K \rangle$,

$$\langle K \rangle + \langle U(r) \rangle = \langle E \rangle = -13.6 \text{ eV}$$

$$\therefore \langle K \rangle = 13.6 \text{ eV}$$

26 | Most probable: Where $P(r)$ is @ a max.

But $P(r) = |rR(r)|^2$ so to find a max of $P(r)$ we can find crit pts of $rR(r)$.

$$n=2, l=0: rR(r) = C \left(2r - \frac{r^2}{a_0} \right) e^{-r/2a_0}$$

$$\text{So } \frac{d(rR)}{dr} = C e^{-r/2a_0} \left[-\frac{1}{2a_0} \left(2r - \frac{r^2}{a_0} \right) + \left(2 - \frac{2r}{a_0} \right) \right]$$

$$= C e^{-r/2a_0} \left[\frac{1}{2a_0} \left(\frac{r^2}{a_0} - 4r \right) + 2 \right] = 0$$

$$\Rightarrow \left(\frac{r}{a_0} \right) = \frac{3 \pm \sqrt{9-4}}{1} = 3 \pm \sqrt{5}$$

$$\text{So } r = (3 \pm \sqrt{5}) a_0$$

which gives the biggest? Graph or plug in - it's the

$$\boxed{r = (3 + \sqrt{5}) a_0} \quad \text{This is larger than } 4a_0$$

$$\text{For } 2p, n=2 \text{ \& } l=1 \Rightarrow R(r) = C \frac{r}{a_0} e^{-r/2a_0}$$

$$\text{So } \frac{d}{dr}(rR) = C \left[2 \left(\frac{r}{a_0} \right) - \frac{r^2}{2a_0^2} \right] e^{-r/2a_0}$$

$\Rightarrow r=0$ or $r=4a_0$. The $4a_0$ gives the larger prob,

so $\boxed{r=4a_0}$ which agrees w/ Bohr.

#27.) Compute the probability that a 2s electron of hydrogen will be found inside the Bohr radius for this state, $4a_0$. Compare this with the probability of finding a 2p electron in the same region.

We need to look up $\psi_{2s}(r, \theta, \phi)$

$$\psi_{2s}(r, \theta, \phi) = \left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} Y_0^0(\theta, \phi)$$

Again the $\theta + \phi$ integrals will give 1, so

$$\begin{aligned} P_{2s}(r) &= \int_0^{4a_0} |R_{n,\ell}(r)|^2 r^2 dr \\ &= \left(\frac{1}{2a_0}\right)^3 \int_0^{4a_0} \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} r^2 dr \\ &= \frac{1}{8a_0} \int_0^{4a_0} \left(4 - \frac{4r}{a_0} + \frac{r^2}{a_0^2}\right) \frac{r^2}{a_0^2} e^{-r/a_0} dr \end{aligned}$$

$$\text{Let } u = \frac{r}{a_0} \quad \text{when } r=0, u=0 \\ r=4a_0, u=4$$

$$du = \frac{dr}{a_0}$$

$$= \frac{1}{8} \int_0^4 (4u^2 - 4u^3 + u^4) e^{-u} du$$

Good God! Need to integrate each of those terms by parts repeatedly to get

$$\begin{aligned} &= \frac{1}{8} \left[(4u^3 - 4u^2 - u^4) + (12u^2 - 4u^3 - 8u) + (24u - 12u^2 - 8) \right. \\ &\quad \left. + (24 - 24u) - 24 \right] e^{-u} \Big|_0^4 \end{aligned}$$

#27) continued

Putting in limits

$$\boxed{P_{2s}(r) = 0.176}$$

Do the same thing again for $R_{2,1}(r)$

$$R_{2,1}(r) = \left(\frac{1}{2a_0}\right)^{3/2} \frac{r}{\sqrt{3}a_0} e^{-r/2a_0}$$

and you'll wind up with

$$\boxed{P_{2p}(r) = 0.371}$$

#30) Calculate the uncertainty product $\Delta r \Delta p$ for the 1s electron of a hydrogen-like atom with atomic number Z .

To find uncertainties, remember

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

Δp is easiest. $\langle p \rangle = 0$ due to symmetry, and we can find $\langle p^2 \rangle$ using

$$\langle K \rangle = \frac{\langle p^2 \rangle}{2m} = |\langle E \rangle| = \frac{Z^2 \hbar^2}{2m a_0^2}$$

$$\therefore \langle p^2 \rangle = \left(\frac{Z\hbar}{a_0}\right)^2 \Rightarrow \Delta p = \frac{Z\hbar}{a_0}$$

#30.) continued

Now comes the painful part. We have to find $\langle r \rangle$ and $\langle r^2 \rangle$. Poop.

$$\begin{aligned}\langle r \rangle &= \int_0^{\infty} R_{1,1}^*(r) r R_{1,1}(r) r^2 dr \\ &= \left(\frac{Z}{a_0}\right)^3 4 \int_0^{\infty} r^3 e^{-2Zr/a_0} dr\end{aligned}$$

Integrate by parts, of course

$$= \frac{3a_0}{2Z}$$

$$\langle r^2 \rangle = \left(\frac{Z}{a_0}\right)^3 4 \int_0^{\infty} r^4 e^{-2Zr/a_0} dr$$

Again, integrate by parts (4 times!)

$$= \frac{3a_0^2}{Z^2}$$

So

$$\begin{aligned}\Delta r &= \sqrt{\langle r^2 \rangle - \langle r \rangle^2} = \sqrt{\frac{3a_0^2}{Z^2} - \frac{9a_0^2}{4Z^2}} \\ &= \sqrt{\frac{3a_0^2}{4Z^2}} = \sqrt{\frac{3}{4}} \frac{a_0}{Z}\end{aligned}$$

$$\therefore \Delta r \Delta p = \sqrt{\frac{3}{4}} \frac{a_0}{Z} \left(\frac{Z\hbar}{a_0}\right) = \sqrt{\frac{3}{4}} \hbar$$