

Problem Set 5 Solutions

1.

- (a) Show that the speed of an electron in the n th Bohr orbit of hydrogen is $\alpha c/n$, where α is the fine structure constant, equal to $e^2/4\pi\epsilon_0\hbar c \approx 1/137$.
- (b) What would be the speed in a hydrogen-like atom with a nuclear charge of Ze ?
- (c) Let's say our threshold for worrying about relativistic effects when it amounts to a 10% correction, where $\gamma = 1.10$ (implying $v/c \approx 0.42$). For the ground state of a hydrogen-like atom, for which element do we reach this threshold?
- (d) Following the previous question, at what element is the correction 50% ($\gamma = 1.5$, $v/c \approx 0.745$).ⁱ

Solution: (a) Our main condition in deriving the Bohr model was the quantization of angular momentum (or, if you like, that the electron orbit is an integral number of wavelengths), $mvr = n\hbar$. We also figured out that the radius for the n^{th} state is $r_n = 4\pi\epsilon_0\hbar^2 n^2 / me^2$. Putting this together,

$$v = \frac{n\hbar}{mr} = \frac{n\hbar}{m} \frac{me^2}{4\pi\epsilon_0\hbar^2 n^2} = \frac{1}{n} \frac{e^2}{4\pi\epsilon_0\hbar} = \frac{1}{n} \frac{e^2}{4\pi\epsilon_0\hbar} \frac{c}{c} = \frac{\alpha c}{n} \quad (1)$$

(b) For a nuclear charge Z in a hydrogen-like atom of atomic number Z , the Coulomb force between the nucleus and electron is Z times larger. If you follow back through the Bohr model derivation, this means that the radius is decreased by a factor Z , and the velocity increased by a factor Z .

$$v = \frac{\alpha c Z}{n} \quad (2)$$

(c) If we want relativistic effects to be less than 10%, $v/c \approx 0.42$. That means

$$\frac{v}{c} = \frac{\alpha Z}{n} = 0.42 \quad \implies \quad Z = \frac{nv}{\alpha c} \approx 57 \quad (3)$$

This means, roughly speaking, that for elements of atomic number 57-58 (Lanthanum and Cerium) relativistic effects are becoming important (at least for the case where all but one electron is ionized away, but the rough conclusion holds). For understanding the details of properties like magnetism, however, we have to worry about relativity much earlier, even for light transition metals like Fe and Co. For understanding the more subtle and nuanced effects in, say, atomic spectra, even hydrogen has relativistic corrections to worry about, if your experiment is accurate enough.

ⁱThe inclusion of relativistic effects on electron orbitals has dramatic consequences for heavier elements like Hg: <http://www.rsc.org/chemistryworld/2013/06/why-mercury-liquid-relativity-evidence>

(d) The point at which relativity is a 75% correction, $v/c \approx 0.745$ - long past the point when classical physics will have failed us even *qualitatively* - comes at

$$Z = \frac{nv}{\alpha c} \approx 102 \quad (4)$$

This is Nobelium. By the time one gets into the actinides, relativity isn't just a correction, it is required for even a basic understanding of what's going on.

2. An electron is in the $n=5$ state of hydrogen. To what states can the electron make transitions, and what are the energies of the emitted photons?

Solution: From the $n=5$ state, the electron can only transition to states of lower energy, which would be to the first through fourth energy levels.ⁱⁱ The energy of the n^{th} level in the Bohr model is

$$E_n = \frac{-13.6 \text{ eV}}{n^2} \quad (5)$$

The energy of the emitted photons must be the same as the energy difference between the 5th level and the final level (which we'll just call m). The energy difference is then

$$\Delta E_{5m} = E_5 - E_m = -13.6 \text{ eV} \left(\frac{1}{5^2} - \frac{1}{m^2} \right) \quad (6)$$

Below, we tabulate the results. One emission in the visible range results.

m	Δ (eV)	spectrum range
4	$-13.6 \left(\frac{1}{25} - \frac{1}{16} \right) = 0.306$	mid infrared
3	$-13.6 \left(\frac{1}{25} - \frac{1}{9} \right) = 0.967$	near infrared
2	$-13.6 \left(\frac{1}{25} - \frac{1}{4} \right) = 2.86$	blue/violet visible
1	$-13.6 \left(\frac{1}{25} - \frac{1}{1} \right) = 13.1$	extreme UV

3. Find the directions in space where the angular probability density for the $l=2$, $m_l=0$ electron in hydrogen has its maxima and minima.

Solution: The principle quantum number n was not specified. Since $l=2$, we know $n \geq 3$. Since you only have the $n \leq 3$ wavefunctions available in your text, we may as well pick $n = 3$ for

ⁱⁱOf course, if the electron went from, say, 5 to 3, it could then go from 3 to 2 and 2 to 1, or directly from 3 to 1. Eventually, the electron in the $n=5$ state would find its way back to the lowest $n=1$ energy level. If you wanted to find all the possible ways to get there, you'd need the number of ways 5 things can be combined in pairs in which the order doesn't matter - mathematically, a combination. Here we would want $\binom{5}{2} = 5!/2!(3-2)! = 10$, so there are 10 ways to get to the ground state from $n=5$.

convenience. The $(3, 2, 0)$ wave function isⁱⁱⁱ

$$\Theta(\theta) = \sqrt{\frac{3}{8}} (3 \cos^2 \theta - 1) \quad (7)$$

The angular probability density is just the square of this

$$P(\theta) = |\Theta(\theta)|^2 = \frac{3}{8} (3 \cos^2 \theta - 1)^2 \quad (8)$$

The maxima and minima will be when $dP/d\theta = 0$. We can ignore the overall constant $3/8$ (since we'll be setting everything to zero anyway), and then just take the derivative.

$$\frac{dP}{d\theta} = -12 \sin \theta \cos \theta (3 \cos^2 \theta - 1) = 0 \quad (9)$$

We are basically done. The $\sin \cos$ pre-factor will be zero at $\{0, 90^\circ, 180^\circ\}$ and integer multiples thereof. The other roots are

$$0 = 3 \cos^2 \theta - 1 \quad \implies \quad \theta = \cos^{-1} \left(\frac{\pm 1}{\sqrt{3}} \right) \approx \{55^\circ, 155^\circ\} \quad (10)$$

Which are maxima and which are minima? Either use the second derivative test, or make a quick plot.^{iv} You can by inspection notice that the last set of roots would be zeroes of P , and since $P \geq 0$ they must be minima. You'd still need to verify what the first three roots are though.

Anyway: a plot quickly leads us to identify

$$\begin{array}{ll} \{0, 90^\circ, 180^\circ\} & \text{maxima} \\ \{55^\circ, 125^\circ\} & \text{minima} \end{array}$$

4. What is the probability of finding an $n=2, l=1$ electron between a_o and $2a_o$?

Solution: Now our first problem is that m wasn't specified, and we can have $m = \{0, \pm 1\}$. Does m make a difference in finding the probability? Should either φ or θ make any difference in a quantity which is only a function of the radius?

The answer is no, but one can't just guess that. There is really only one way to find out. As it turns out, we can do all three possibilities with almost no extra work. The relevant wave functions

ⁱⁱⁱIn lecture, I used $P(\theta)$ for the angular wave function depending on θ . I'll try to make the solutions consistent with the text.

^{iv}In addition to Wolfram Alpha, try typing `plot of y=(3(cos(x))^2-1)^2` in google.

are, in full,

$$\psi_{210}(r, \theta, \varphi) = \frac{1}{\sqrt{3} (2a_o)^{3/2} a_o} r e^{-r/2a_o} \sqrt{\frac{3}{2}} \cos \theta \frac{1}{\sqrt{2\pi}} \quad (11)$$

$$\psi_{21\pm 1}(r, \theta, \varphi) = \frac{1}{\sqrt{3} (2a_o)^{3/2} a_o} r e^{-r/2a_o} \left(\mp \frac{\sqrt{3}}{2} \sin \theta \right) \frac{1}{\sqrt{2\pi}} e^{\pm i\varphi} \quad (12)$$

We first notice that the $e^{\pm i\varphi}$ factor in the second equation will go away when we find $|\psi_{21\pm 1}|$, so it is irrelevant for finding probability. Similarly, the \mp sign on the sine term will go away. The only real difference between the two functions is sine in place of cosine, and a factor of $\sqrt{2}$ overall. As it turns out, the two differences will cancel each other out, and the probability is independent of m .

First, we need to find the probability density, $|\psi|^2 dV$. The volume element in spherical coordinates is $r^2 \sin \theta dr d\theta d\varphi$, with $\theta \in \{0, \pi\}$ and $\varphi \in \{0, 2\pi\}$. Noting this, we can just square the wave functions above and set up the integrals. Since we're worried about radii from a_o to $2a_o$, that sets the limits for r . For φ and θ , we integrate over the full range of each variable.

$$P_{210} = \int_0^{2\pi} \frac{1}{2\pi} d\varphi \int_0^\pi \frac{3}{2} \cos^2 \theta \sin \theta d\theta \int_{a_o}^{2a_o} \frac{1}{24a_o^3} \frac{r^2}{a_o^2} e^{-r/a_o} r^2 dr \quad (13)$$

$$P_{21\pm 1} = \int_0^{2\pi} \frac{1}{2\pi} d\varphi \int_0^\pi \frac{3}{4} \sin^2 \theta \sin \theta d\theta \int_{a_o}^{2a_o} \frac{1}{24a_o^3} \frac{r^2}{a_o^2} e^{-r/a_o} r^2 dr \quad (14)$$

Now, the φ integral is just going to give us a factor 2π in each, no problem. What about the θ integrals? The integrands are different, but so are the pre-factors. Curious.

$$P_{210} : \int_0^\pi \frac{3}{2} \cos^2 \theta \sin \theta d\theta = \frac{3}{2} \cdot \frac{2}{3} = 1 \quad (15)$$

$$P_{21\pm 1} : \int_0^\pi \frac{3}{4} \sin^2 \theta \sin \theta d\theta = \frac{4}{3} \cdot \frac{3}{4} = 1 \quad (16)$$

There is no θ or ϕ dependence, and this must be the case: since we asked a question that didn't depend on either angle, and then integrated over the whole range of both angles, it couldn't come out any differently. The angular functions are normalized, so it had to be the case that when we integrated over their whole range the result is unity.

So: with sufficiently clever (and documented) reasoning, you could have started at this point right here, recognizing that m doesn't matter at all and you can just work with the radial functions. Specifically, $P_{210} = P_{21\pm 1} \equiv P_{21}$, so one can just use the radial function.

$$P_{21} = \int_{a_0}^{2a_0} \frac{1}{24a_0^3} \frac{r^2}{a_0^2} e^{-r/a_0} r^2 dr = \frac{1}{24a_0^5} \int_1^2 a_0 \cdot a_0^4 u^4 e^{-u} du \quad (\text{let } u = r/a_0, du = dr/a_0) \quad (17)$$

$$P_{21} = \frac{1}{24} \int_1^2 u^4 e^{-u} du = \frac{1}{24} \left(\frac{65e - 168}{e^2} \right) \approx 0.049 \quad (18)$$

The expectation value of the radius in the $n = 2, l = 1$ state is $5a_0$, so it is not crazy that the probability of finding the electron much closer to the nucleus than this is rather small. If you look at the plot on pg. 208 in your textbook, you can see that the answer is reasonable. You can also see that the answer does *definitely* depend on l , if not m , since the radial function is different for $l=0$ and $l=\pm 1$.

5. Find the most probable radius **and** the expected value of the radial position $\langle r \rangle$ of an electron in the $2p$ state.

$$\psi_{2p} = \frac{1}{\sqrt{3}} \frac{r}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \quad (19)$$

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10}$ m is the Bohr radius.

Solution: The most likely distance corresponds to the distance at which the probability of finding the electron is maximum. This is distinct from the expected value of the radius $\langle r \rangle$. For a 3D wavefunction in spherical coordinates (r, θ, φ) , the probability of finding an electron at a distance r in the interval $[r, r + dr]$ is the squared magnitude of the wavefunction times the volume of a spherical shell of thickness dr and radius r , $4\pi r^2$. However, the wave function above is only the radial function ($R(r)$), the θ and φ dependence has been neglected. That means to be formally correct, the probability is

$$P(r) dr = |\psi|^2 \cdot r^2 dr \quad \text{or} \quad P(r) = |\psi|^2 \cdot r^2 \quad (20)$$

That is, the factor 4π comes from integrating over θ and φ in the case when we have a wavefunction which is *independent* of the angular coordinates. The $2p$ state does have an angular dependence, so either we need to use the full wavefunction with the θ and φ dependence included, or we need to use the probability density as given above. We will do the latter. Given ψ_{2p} above, that gives us

$$P(r) = \left| \frac{1}{\sqrt{3}} \frac{r}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \right|^2 \cdot r^2 = \frac{r^4}{24a_0^5} e^{-r/a_0} \quad (21)$$

The most probable radius is when $P(r)$ takes a maximum value, which must occur when $dP/dr = 0$ and $d^2P/dr^2 < 0$. Thus:

$$\frac{dP}{dr} = 0 = \left(\frac{1}{24a_o^5} \right) \frac{d}{dr} \left(r^4 e^{-r/a_o} \right) = \left(\frac{1}{24a_o^5} \right) \left(4r^3 e^{-r/a_o} - \frac{r^4}{a_o} e^{-r/a_o} \right) \quad (22)$$

$$0 = \left(\frac{r^3}{24a_o^5} e^{-r/a_o} \right) \left(4 - \frac{r}{a_o} \right) \quad (23)$$

$$\implies r = \{0, 4a_o, \infty\} \quad (24)$$

One can either apply the second derivative test or make a quick plot of $P(r)$ to verify that $r=4a_o$ is the sole maximum of the probability distribution, and hence the most probable radius, while $r=0$ and $r=\infty$ are minima.

The expectation value is

$$\langle r \rangle = \int rP(r) dr = \int_0^{\infty} \frac{r^5}{24a_o^5} e^{-r/a_o} dr = \frac{a_o}{24} \int_0^{\infty} u^4 e^{-u} du = \frac{a_o}{24} \cdot 5! = 5a_o \quad (25)$$

6. (a) How many different sets of quantum numbers (n, l, m_l, m_s) are possible for an electron on the $4f$ level? **(b)** Suppose a certain atom has three electrons in the $4f$ level. What is the maximum possible value of the total m_s of the three electrons? **(c)** What is the maximum possible total m_l of three $4f$ electrons? **(d)** Suppose an atom has ten electrons in the $4f$ level. What is the maximum possible value of the total m_s of the ten $4f$ electrons? **(e)** What is the maximum possible total m_l of ten $4f$ electrons?

Solution: 14, +3/2, +8, +2, +10

7. Energetics of diatomic systems An approximate expression for the potential energy of two ions as a function of their separation is (treating the problem one dimensionally),

$$V = -\frac{ke^2}{x} + \frac{b}{x^9} \quad (26)$$

The first term is the usual Coulomb interaction, while the second term is introduced to account for the repulsive effect of the two ions at small distances. **(a)** What is the equilibrium spacing x_o ? **(b)** Find b as a function of the equilibrium spacing x_o . **(c)** For NaCl, with an equilibrium spacing of $r_o = 0.236$ nm, calculate the frequency of small oscillations about $x = x_o$. *Hint: do a Taylor expansion of the potential energy to make it look like a harmonic oscillator for small $x = x_o$.*

Solution: The equilibrium spacing will be characterized by the net force between the ions being zero, or equivalently, the potential energy being zero:

$$F(r_o) = -\left.\frac{dU}{dr}\right|_{r=r_o} = 0 = \frac{ke^2}{r_o^2} - \frac{9b}{r_o^{10}} \quad (27)$$

$$ke^2 r_o^8 = 9b \quad (28)$$

$$b = \frac{1}{9} ke^2 r_o^8 \quad (29)$$

Substituting this result back into our potential energy expression, we can find the potential energy at equilibrium, how much energy is gained by the system of ions condensing into a crystal. First, the potential energy as a function of spacing:

$$PE = U(r) = -\frac{ke^2}{r} + \frac{ke^2 r_o^8}{9r^9} \quad (30)$$

Evaluating at equilibrium, $r_o = 0.279$ nm,

$$U(r_o) = -\frac{ke^2}{r_o} + \frac{ke^2}{9r_o} = -\frac{8ke^2}{9r_o} \approx -5.42 \text{ eV} \quad (31)$$

The frequency of small oscillations can be found by Taylor expanding the potential about equilibrium for small displacements from equilibrium:

$$U(r - r_o) \approx U(r_o) + U'(r_o)(r - r_o) + \frac{1}{2}U''(r_o)(r - r_o)^2 \quad (32)$$

The first term in the expansion is just the potential energy at equilibrium which we found above. The second term, linear in displacement, must vanish at equilibrium (which is exactly the condition we enforced to find b , after all). The third term is quadratic in displacement, just as it would be for a simple harmonic oscillator, $U = \frac{1}{2}k(r - r_o)^2$. Thus, the coefficient of the quadratic term must be $\frac{1}{2}k$, which means the frequency of small oscillations is $\omega = \sqrt{k/\mu}$, where μ is the reduced mass of the system:

$$\mu = \frac{m_{\text{Na}}m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} \approx 13.95 \text{ u} = 2.32 \times 10^{-26} \text{ kg} \quad (33)$$

That is, the diatomic molecule looks like two masses coupled by a spring.

$$\frac{1}{2}k = \frac{1}{2}U''(r_o) \quad (34)$$

$$k = U''(r_o) = -\frac{2ke^2}{r_o^3} \frac{90b}{r_o^{11}} = \frac{8ke^2}{r_o^3} \approx 140 \text{ N/m} \quad (35)$$

$$\omega = \sqrt{\frac{k}{\mu}} = 2\pi f \quad (36)$$

The frequency of oscillation f is then

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \approx 1.24 \times 10^{13} \text{ Hz} \approx 414 \text{ cm}^{-1} \quad (37)$$

A reliable experimental value is about 365 cm^{-1} , in good agreement with our simple model.^v

8. A collection of hydrogen atoms is placed in a magnetic field of 3.50 T. Ignoring the effects of electron spin, find the wavelengths of the three normal Zeeman components of **(a)** the $3d$ to $2p$ transition, **(b)** the $3s$ to $2p$ transition.

Solution: In a magnetic field B , the energy levels for a given l state will split according to their value of m_l . If the original energy of the level is E_l , then the original level will be split symmetrically into $2l + 1$ sub-levels, with adjacent levels shifted by $\mu_B B$:

$$E_{l,m_l} = E_l + m_l \mu_B B \quad (38)$$

This is shown schematically below for $l=2$ and $l=1$ levels. The $3d$ ($l=2$) level has possible m_l values of $m_l = \{-2, -1, 0, 1, 2\}$, and thus in a magnetic field B what was a single level is now 5 individual levels. For the $2p$ ($l=1$) level, we have m_l values of only $m_l = \{-1, 0, 1\}$, and the original level becomes a triplet upon applying a magnetic field.

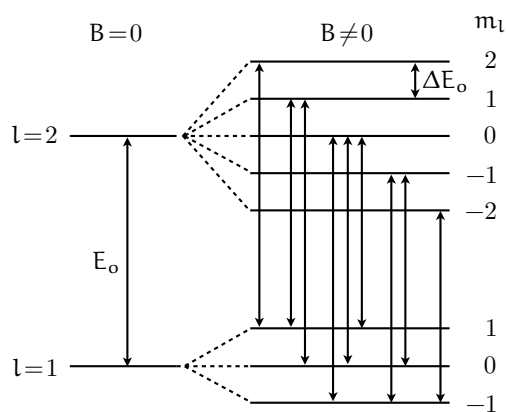


Figure 1: Allowed transitions from $l=2$ to $l=1$ with a magnetic field applied.

Before calculating anything, we can apply the dipole selection rules, which states that m_l can change by only $\{0, \pm 1\}$. This means that, for example, from the $l=2$, $m_l=1$ sub-level an electron may “jump” to the any of the $l=1$, $m_l=\{2, 1, 0\}$ sub-levels. On the other hand, from $l=2$, $m_l=2$ sub-level an electron may only jump to the $l=1$, $m_l=1$ sub-level. Following these rules, we see from the figure above that there are only 9 possible transitions allowed. Further, noting that the levels are equally spaced, we have in fact only three different transition energies.

^vSee <http://scitation.aip.org/content/aip/journal/jpcrd/36/2/10.1063/1.2436891>.

The spacing between the levels ΔE is the Zeeman energy given above, $\Delta E = \mu_B B$. From our schematic above, it is clear that the only possible transition energies in a magnetic field are the original transition energy (no change in m_l), or the original transition energy plus or minus ΔE (m_l changes by ± 1). The original transition energy E and the corresponding wavelength λ is readily found from our knowledge of the hydrogen atom

$$E = E_3 - E_2 = -13.6 \text{ eV} \left(\frac{1}{3^2} - \frac{1}{2^2} \right) = 1.89 \text{ eV} \quad \implies \quad \lambda = \frac{hc}{E} = 656 \text{ nm} \quad (39)$$

(In the calculation of λ we use Thus, the new transition energies must be

$$E \mapsto \{E - \Delta E, E, E + \Delta E\} = \{E - \mu_B B, E, E + \mu_B B\} \quad (40)$$

That is, the original transition energy plus two new ones. We can easily convert these two new energies into two new wavelengths by the energy-wavelength relationship $E = hc/\lambda$. However, this does require some numerical precision (i.e., carrying at least 7-8 digits in your calculations, and knowing the requisite constants to commensurate precision), and it is somewhat easier to simply calculate the change in energy by itself. You can do this with propagation of uncertainty, if you aren't familiar with it we will just quote the result:

$$|\Delta\lambda| = \left| \frac{d\lambda}{dE} \right| \Delta E = \frac{hc}{E^2} \Delta E = \frac{\lambda^2}{hc} \Delta E \quad (41)$$

Since we know the energy changes by ΔE and the base energy is E ,

$$|\Delta\lambda| = \frac{\lambda^2 \Delta E_o}{hc} = \frac{\lambda^2 \mu_B B}{hc} \approx 0.07 \text{ nm} \quad (42)$$

The shift in energy of ΔE_o implies a shift in wavelength of $\Delta\lambda \approx 0.070 \text{ nm}$, meaning the new transitions must be at the original wavelength $\lambda = 656 \text{ nm}$ plus or minus $\Delta\lambda = 0.07 \text{ nm}$.

9. Consider a hydrogen atom and a singly-ionized helium atom (i.e., Bohr-like). Which atom has the lower ground state energy, and how big is the difference? Justify your answer with an explicit calculation, even if it is just an order-of-magnitude estimate.

Solution: For a hydrogen-like system (i.e., nucleus plus one electron) with Z protons in the nucleus, the net attractive energy of the proton and electron will scale as Z . That's one reason already that the helium atom will be more stable, the electron is simply more attracted to the nucleus. A second factor of Z comes in through the quantization of angular momentum, but the conclusion does not change. If you work out the Bohr model energy levels from the start with a nuclear

charge of $+Ze$ rather than just $+e$, you'll find the energies scale as Z^2 .^{vi} The higher Z is, the more negative the electron energies are, and the more stable the atom.

We can estimate the difference as being a factor of $Z_{\text{He}}^2 = 4$ compared to the hydrogen ground state energy, or $-13.6 \text{ eV} \cdot 4 \approx -54.4 \text{ eV}$, which is a very good estimate.

10. The wave function for the ground state of hydrogen ($n=1$) is

$$\psi_1 = \frac{1}{\sqrt{\pi a_o^3}} e^{-r/a_o} \quad (43)$$

where a_o is the Bohr radius.

- (a) What is the *most probable* value of r for the ground state?
 (b) What is the total probability of finding the electron at a distance greater than this radius?

Solution: (a) Just like the last problem.

$$P(r) = 4\pi r^2 |\psi|^2 = \frac{4r^2}{a_o^3} e^{-2r/a_o} \quad (44)$$

$$\frac{dP}{dr} = \frac{4}{a_o^3} e^{-2r/a_o} \left(2r - \frac{2r^2}{a_o} \right) \quad (45)$$

$$\implies r = a_o \quad (46)$$

Again, a quick plot shows $r = a_o$ is a maximum in the probability distribution, so a_o is the most probable radius. We have again ignored the trivial solutions of $r=0$ and $r \rightarrow \infty$.

(b) The odds of the electron being at a distance larger than this is found by integrating $P(r) dV$ from a_o outward to ∞ .

$$P(r > a_o) = \int_{a_o}^{\infty} |\psi|^2 \cdot 4\pi r^2 dr = \int_{a_o}^{\infty} \frac{4r^2}{a_o^3} e^{-2r/a_o} dr \quad (47)$$

The substitution $u = 2r/a_o$, $du = 2 dr/a_o$ makes this into a known integral. The limits then become 2 and ∞

$$P(r > a_o) = \int_2^{\infty} \frac{u^2}{a_o} e^{-u} \frac{a_o}{2} du = \frac{1}{2} \int_2^{\infty} u^2 e^{-u} du = \frac{1}{2} (-e^{-u}) (u^2 + 2u + 2) \Big|_2^{\infty} \quad (48)$$

$$= \frac{1}{2} e^{-2} (10) = \frac{5}{e^2} \approx 0.677 \quad (49)$$

^{vi}See http://en.wikipedia.org/wiki/Bohr_model#Electron_energy_levels

The probability distribution is rather asymmetric - there is approximately a 2 in 3 chance of finding the particle farther from the nucleus than the most probable radius.

11. A phenomenological expression for the potential energy of a bond as a function of spacing is given by

$$U(r) = \frac{A}{r^n} - \frac{B}{r^m} \quad (50)$$

For a stable bond, $m < n$. Show that the molecule will break up when the atoms are pulled apart to a distance

$$r_b = \left(\frac{n+1}{m+1} \right)^{1/(n-m)} r_o \quad (51)$$

where r_o is the equilibrium spacing between the atoms. Be sure to note your criteria for breaking used to derive the above result.

Solution: The potential $U(r)$ has an associated force, the molecule's restoring force:

$$F(r) = -\frac{dU}{dr} \quad (52)$$

The molecule will break when its maximum restoring force is reached, when $dF/dr = -d^2U/dr^2 = 0$. Equilibrium is when $F = -dU/dr = 0$. At the equilibrium spacing r_o , the force is zero, or equivalently, the potential is at a minimum.

$$F(r_o) = -\frac{dU}{dr} \Big|_{r_o} = \frac{nA}{r_o^{n+1}} - \frac{mB}{r_o^{m+1}} = 0 \quad (53)$$

$$\frac{nA}{mB} = \frac{r_o^{n+1}}{r_o^{m+1}} = r_o^{n-m} \quad (54)$$

$$r_o = \left(\frac{nA}{mB} \right)^{\frac{1}{n-m}} \quad (55)$$

Is this really a minimum for U ? We can check with the second derivative test: if $d^2U/dr^2 = -dF/dr > 0$ at r_o , have a maximum. We will need dF/dr shortly anyway. You didn't really need to do this on your homework, but it is instructive:

$$-\frac{dF}{dr} = \frac{d^2U}{dr^2} = \frac{n(n+1)A}{r^{n+2}} - \frac{m(m+1)B}{r^{m+2}} \quad (56)$$

$$\left. \frac{d^2U}{dr^2} \right|_{r_o} = n(n+1)A \left(\frac{mB}{nA} \right)^{\frac{n+2}{n-m}} - m(m+1)B \left(\frac{mB}{nA} \right)^{\frac{m+2}{n-m}} \quad (57)$$

$$= \left(\frac{mB}{nA} \right)^2 \left[n(n+1)A \left(\frac{mB}{nA} \right)^{\frac{n}{n-m}} - m(m+1)B \left(\frac{mB}{nA} \right)^{\frac{m}{n-m}} \right] \quad (58)$$

$$= \left(\frac{mB}{nA} \right)^2 \left(\frac{mB}{nA} \right)^{\frac{n}{n-m}} \left[n(n+1)A - m(m+1)B \left(\frac{mB}{nA} \right)^{\frac{m-n}{n-m}} \right] \quad (59)$$

$$= \left(\frac{mB}{nA} \right)^2 \left(\frac{mB}{nA} \right)^{\frac{n}{n-m}} \left[n(n+1)A - m(m+1)B \left(\frac{nA}{mB} \right) \right] \quad (60)$$

$$= \left(\frac{mB}{nA} \right)^{\frac{n+2}{n-m}} \left[n(n+1)A - n(m+1)A \right] \quad (61)$$

$$= nA \left(\frac{mB}{nA} \right)^{\frac{n+2}{n-m}} \left[n-m \right] > 0 \quad (62)$$

Clearly, the only way this expression will be positive is if $n > m$, which means stable bonds have $n > m$ as the problem states. This means that the repulsive force has a higher index than the attractive force, and it is of shorter range.

What about breaking the molecule? For distances smaller than r_o , the force is repulsive, while for distances greater than r_o it is attractive – in either case, it serves to try and restore the equilibrium position. However, the competition between the shorter-range repulsive force and longer-range attractive force means that there is a critical distortion of the molecule for $r > r_o$ at which the force is maximum, and any stronger force (or larger displacement) will separate the constituents to an arbitrarily large distance – the molecule will be broken.

We have the force between the molecular constituents above:

$$F(r) = \frac{nA}{r^{n+1}} - \frac{mB}{r^{m+1}} \quad (63)$$

so we can readily calculate the maximum force with which the bond may try to restore its equilibrium. The force above is the force with which the molecule will respond if we push or pull on it. The maximum force will occur when $dF/dr=0$, at a radius r_b

$$\left. \frac{dF}{dr} \right|_{r_b} = \frac{n(n+1)A}{r_b^{n+2}} - \frac{m(m+1)B}{r_b^{m+2}} = 0 \quad (64)$$

$$\frac{n(n+1)A}{m(m+1)B} = \frac{r_b^{n+2}}{r_b^{m+2}} = r_b^{n-m} \quad (65)$$

$$r_b = \left(\frac{n(n+1)}{m(m+1)B} \right)^{\frac{1}{n-m}} = \left(\frac{nA}{mB} \right)^{\frac{1}{n-m}} \left(\frac{n+1}{m+1} \right)^{\frac{1}{n-m}} \quad (66)$$

Now, how do we know this is the *maximum* force, and not a minimum force? We grind through another derivative . . . we must have $d^2F/dr^2 > 0$ for a maximum:

$$\begin{aligned} \frac{d^2F}{dr^2} &= \frac{n(n+1)(n+2)A}{r^{n+3}} - \frac{m(m+1)(m+2)B}{r^{m+3}} = r^{n+3} \left[n(n+1)(n+2)A - \frac{m(m+1)(m+2)B}{r^{m-n}} \right] \\ \left. \frac{d^2F}{dr^2} \right|_{r_b} &= r_o^{n+3} \left(\frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[n(n+1)(n+2)A - m(m+1)(m+2)B r_o^{n-m} \left(\frac{n+1}{m+1} \right)^{\frac{n-m}{n-m}} \right] \end{aligned} \quad (67)$$

$$= r_o^{n+3} \left(\frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[n(n+1)(n+2)A - m(n+1)(m+2)B r_o^{n-m} \right] \quad (68)$$

$$= r_o^{n+3} \left(\frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[n(n+1)(n+2)A - m(n+1)(m+2)B \left(\frac{nA}{mB} \right) \right] \quad (68)$$

$$= r_o^{n+3} \left(\frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[n(n+1)(n+2)A - n(n+1)(m+2)A \right] \quad (69)$$

$$= An(n+1)r_o^{n+3} \left(\frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[n-m \right] > 0 \quad (70)$$

For the second to last line, we noted that $r_o^{n-m} = nA/mB$. Once again, if $n > m$, the second derivative is positive, and thus the force is maximum at r_b . Applying a force sufficiently strong to stretch the bond to a separation r_b will serve to break it. Incidentally, the maximum force required is

$$\begin{aligned} F(r_b) &= \frac{nA}{r_o^{n+1}} \left(\frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} - \frac{mB}{r_o^{m+1}} \left(\frac{n+1}{m+1} \right)^{\frac{m+1}{m-n}} = \left(\frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left[\frac{nA}{r_o^{n+1}} - \frac{mB}{r_o^{m+1}} \left(\frac{n+1}{m+1} \right) \right] \\ &= \left(\frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left[nA \left(\frac{nA}{mB} \right)^{\frac{n+1}{m-n}} - mB \left(\frac{nA}{mB} \right)^{\frac{m+1}{m-n}} \left(\frac{n+1}{m+1} \right) \right] \end{aligned} \quad (71)$$

$$= \left(\frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left(\frac{nA}{mB} \right)^{\frac{n+1}{m-n}} \left[nA - nA \left(\frac{n+1}{m+1} \right) \right] \quad (72)$$

$$= nA \left(\frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left(\frac{nA}{mB} \right)^{\frac{n+1}{m-n}} \left(\frac{m-n}{m+1} \right) = \frac{nA}{r_b^{n+1}} \left(\frac{m-n}{m+1} \right) \quad (73)$$

12. Explain why each of the following sets of quantum numbers (n, l, m_l, m_s) is not permitted for hydrogen:

$$\begin{aligned} & (2, 2, -1, +\frac{1}{2}) \\ & (3, 1, +2, -\frac{1}{2}) \\ & (4, 1, +1, -\frac{3}{2}) \\ & (2, -1, +1, +\frac{1}{2}) \end{aligned}$$

Solution: Let's look at them one by one:

$$(2, 2, -1, +\frac{1}{2}) \tag{74}$$

From this we gather $n=2$, which means that l is restricted to the set $\{0, 1\}$. Since this set claims $l=2$, it is clearly invalid.

$$(3, 1, +2, -\frac{1}{2}) \tag{75}$$

Here we have $n=2$ and $l=1$. This restricts m_l to the set $\{-1, 0, 1\}$, so the listed value of $m_l=+2$ is invalid.

$$(4, 1, +1, -\frac{3}{2}) \tag{76}$$

We need only look at the value of m_s . The electron spin quantum number can be only $+\frac{1}{2}$ or $-\frac{1}{2}$, not $-\frac{3}{2}$.

$$(2, -1, +1, +\frac{1}{2}) \tag{77}$$

Here we have $n=2$. The value of l is restricted to zero *positive* integers less than n , so the claim of $l=-1$ makes this set invalid.

13. List the excited states (in spectroscopic notation) to which the $4p$ state can make downward transitions.

Solution: Ignoring spin, the relevant selection rule is $\Delta l = \pm 1$. For the $4p$ state, $l = 1$, so we can move to states that are lower in energy (such that we have a downward transition) that have $l = \{0, 1\}$, i.e., s and d states. Given $n=4$, we are left with transitions to $3d$, $3s$, $2s$, and $1s$.

In our simplest model of the hydrogen atom, the $4s$ state would have the same energy as the $4p$

state, and no transition is possible. However, you now know that spin-orbit coupling makes the $4s$ state slightly lower in energy than the $4p$ state, so a downward transition $4p \rightarrow 4s$ is also in principle possible. In this case we would have to worry about spin conservation and whether the transition requires a spin flip, and it becomes a bit complicated. Let's just say it is unlikely. (No points off if you missed this one, since it is a subtlety.)

14. Splitting of Hydrogen lines. The electron's intrinsic magnetic moment $\vec{\mu}_s$ and intrinsic spin angular momentum \vec{S} are proportional to each other; their relationship can be written as

$$\vec{\mu}_s = -g_s \frac{e}{2m} \vec{S} = -g_s \mu_B \frac{\vec{S}}{\hbar} \quad (78)$$

with $g_s \approx 2$. The energy of the electron in a effective magnetic field \vec{B} is $E = -\vec{\mu}_s \cdot \vec{B}$.

In hydrogen, transitions occur between two spin-orbit-split $2p$ states and a single $1s$ state, leading to two emission lines. If the emission wavelength in the absence of spin-orbit coupling is 656.47 nm, and the spin-orbit splitting is 0.016 nm, estimate the strength of the effective magnetic field produced by the electron's orbital motion (i.e., the effective field due to the spin-orbit interaction) which results in this wavelength difference.

Solution: We can make use of the result below to relate the energy and wavelength differences, viz.:

$$|\Delta\lambda| = \left| \frac{d\lambda}{dE} \right| \Delta E = \frac{hc}{E^2} \Delta E = \frac{\lambda^2}{hc} \Delta E \quad (79)$$

Given a wavelength difference, we can find the energy difference. In a magnetic field, electrons take on two different energy states depending on whether their spins are parallel or antiparallel to the field, with their difference in energy being $2\mu_s B$. Given $g_s = 2$, $\mu_s = \mu_B$, and the energy difference in a magnetic field is $\Delta E = 2\mu_B B$. Thus,

$$\Delta E = 2\mu_B B = \frac{hc\Delta\lambda}{\lambda^2} \quad (80)$$

Solving for B , and using the numbers given,

$$B = \frac{hc\Delta\lambda}{2\mu_B\lambda^2} \approx 0.4 \text{ T} \quad (81)$$

15. Multiplicity of atomic magnetic moments. Calculate the magnetic moments that are possible for the $n = 4$ level of Hydrogen, making use of the quantization of angular momentum. You may neglect the existence of spin. Compare this with the Bohr prediction for $n = 4$.

Solution: If $n=4$, then we have possible values for l of $l=\{0, 1, 2, 3\}$. This gives us the magnetic moments possible:

$$\mu = -\mu_B \sqrt{l(l+1)} \quad (82)$$

$$\mu = \{0, \sqrt{2}, \sqrt{6}, 2\sqrt{3}\} \mu_B \quad (83)$$

By comparison, the Bohr model would predict for level n a magnetic moment of $n\mu_B$, or $4\mu_B$ in this case.

16. Transitions in a magnetic field. Transitions occur in an atom between $l=2$ and $l=1$ states in a magnetic field of 2.0 T, obeying the selection rules $\Delta m_l = 0, \pm 1$. If the wavelength before the field was turned on was 680.0 nm, determine the wavelengths that are observed. You may find the following relationship useful:

$$|\Delta\lambda| = \left| \frac{d\lambda}{dE} \right| \Delta E = \frac{hc}{E^2} \Delta E = \frac{\lambda^2}{hc} \Delta E \quad (84)$$

Recall that the Zeeman effect changes the energy of a single-electron atom in a magnetic field by

$$\Delta E = m_l \left(\frac{e\hbar}{2m_e} \right) B \quad \text{with} \quad m_l = -l, -(l-1), \dots, 0, \dots, l-1, l \quad (85)$$

For convenience, note that $e\hbar/2m_e = \mu_B \approx 57.9 \mu\text{eV/T}$, and neglect the existence of spin.

Solution: In a magnetic field B , the energy levels for a given l state will split according to their value of m_l . If the original energy of the level is E_l , then the original level will be split symmetrically into $2l+1$ sub-levels, with adjacent levels shifted by $\mu_B B$:

$$E_{l,m_l} = E_l + m_l \mu_B B \quad (86)$$

This is shown schematically below for $l=2$ and $l=1$ levels. The $l=2$ level has possible m_l values of $m_l = \{-2, -1, 0, 1, 2\}$, and thus in a magnetic field B what was a single level is now 5 individual levels. For $l=1$, we have m_l values of only $m_l = \{-1, 0, 1\}$, and the original level becomes a triplet upon applying a magnetic field.

Before calculating anything, we can apply the dipole selection rules, which states that m_l can change by only $0, \pm 1$. This means that, for example, from the $l=2, m_l=1$ level an electron may “jump” to the any of the $l=1, m_l = \{2, 1, 0\}$ levels. On the other hand, from $l=2, m_l=2$ level an electron may only jump to the $l=1, m_l=1$ level. Following these rules, we see from the figure above that there are only 9 possible transitions allowed. Further, noting that the levels are equally spaced, we have in fact only three different transition energies.

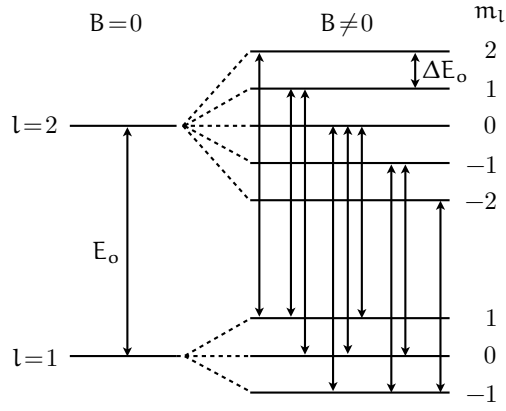


Figure 2: Allowed transitions from $l=2$ to $l=1$ with a magnetic field applied.

The spacing between the levels ΔE_o is the Zeeman energy given above, $\Delta E_o = \mu_B B$. From our schematic above, it is clear that the only possible transition energies in a magnetic field are the original transition energy (no change in m_l), or the original transition energy plus or minus ΔE_o (m_l changes by ± 1). The original transition energy E_o is readily found from the given wavelength $\lambda = 500$ nm:

$$E_o = \frac{hc}{\lambda} \approx 1.82 \text{ eV} \quad (87)$$

Thus, the new transition energies must be

$$E_o \mapsto \{E_o - \Delta E_o, E_o, E_o + \Delta E_o\} = \{E_o - \mu_B B, E_o, E_o + \mu_B B\} \quad (88)$$

That is, the original transition energy plus two new ones. We can easily convert these two new energies into two new wavelengths by the energy-wavelength relationship $E = hc/\lambda$. However, this does require some numerical precision (i.e., carrying at least 7-8 digits in your calculations, and knowing the requisite constants to commensurate precision), and it is somewhat easier to simply calculate the change in energy by itself. Since we know the energy changes by $\pm \Delta E_o$, using the formula given we have

$$|\Delta \lambda| = \frac{\lambda^2 \Delta E_o}{hc} = \frac{\lambda^2 \mu_B B}{hc} \approx 0.043 \text{ nm} \quad (89)$$

The shift in energy of ΔE_o implies a shift in wavelength of $\Delta \lambda \approx 0.043$ nm, meaning the new transitions must be at the original wavelength λ plus or minus $\Delta \lambda$:

$$\lambda \mapsto \{\lambda - \Delta \lambda, \lambda, \lambda + \Delta \lambda\} = \{679.957, 680.000, 680.043\} \text{ nm} \quad (90)$$

17. By considering the visible spectrum of hydrogen and He^+ , show how you could determine spectroscopically if a sample of hydrogen was contaminated with helium. (Hint: look for differences in the visible emission lines, $\lambda \approx 390 \sim 750$ nm. A difference of 10 nm is easily measured.)

Solution: We know the energies in a hydrogen atom are just $E_n = (-13.6 \text{ eV})/n^2$ for a given level n . For the He^+ ion, the only real difference is the extra positive charge in the nucleus. If we have Z positive charges in the nucleus, the energies become $E_n = (-13.6 \text{ eV}) Z^2/n^2$. For $Z = 2$, we just end up multiplying all the energies by a factor 4. The questions are: does this lead to any new radiative transitions, are they in the visible range, and are they well-separated enough? We can just list the energy levels for the two systems and see what we come up with.

We already know that the visible transitions in Hydrogen occur when excited states relax to the $n = 2$ level. Thus, we can probably find a new transition for He^+ by just considering the first few higher levels above $n = 2$. We only need one new spectral line to be able to find He^+ , so we may as well just consider a few transitions at first and see if we get lucky.

	H	He^+
n	E_n (eV)	E_n (eV)
1	-13.6	$-13.6 \cdot 4$
2	$-13.6 \cdot \frac{1}{4}$	-13.6
3	$-13.6 \cdot \frac{1}{9}$	$-13.6 \cdot \frac{4}{9}$
4	$-13.6 \cdot \frac{1}{16}$	$-13.6 \cdot \frac{1}{4}$
5	$-13.6 \cdot \frac{1}{25}$	$-13.6 \cdot \frac{4}{25}$

We see a couple of things already. The $n = 2$ state for He^+ happens to accidentally have the same energy as the $n = 1$ state for H, likewise for the $n = 4$ state for He^+ and the $n = 2$ state for H. That means that we can't just pick transitions at random, some of them will accidentally have the same energy. In particular, the even numbers will always match up with an existing H transition.

However, the $n = 3$ state for He^+ has the curious fraction $4/9$ in it, which can't possibly occur for H. Transitions into the $n = 3$ state should yield unique energies. Let's compute the visible transitions in hydrogen H, since there are only a few, and see if some He^+ transitions stick out in the in-between wavelengths:

H transition	λ_H (nm)	He^+ transition	λ_{He^+} (nm)
$3 \rightarrow 2$	656	$4 \rightarrow 3$	469
$4 \rightarrow 2$	486	$3 \rightarrow 2$	164
$5 \rightarrow 2$	434		
$6 \rightarrow 2$	410		

Already with just the $4 \rightarrow 3$ transition in He^+ , we have an expected emission (or absorption) at

469 nm, a full 17 nm from the nearest H line, and well in the visible range to boot (a nice pretty blue). Should be easy to pick out!