BCHM 485 Solutions to select practice problems from Exam #2 of previous years

Below are my solutions to Exam #2 practice problems. I strongly suggest that you try solving these problems yourself *first*, *before* looking at my solutions.

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Problem 1. Consider quantum-mechanical rotations in three dimensions (aka 3D rigid rotor or particle on a sphere) corresponding to the quantum number $l = 3$. Calculate and list all values of the angle between the vector of the angular momentum and the z axis.

The orbital angular momentum of the electron is characterized by the quantum number $l = 1$. This means that the length of the orbital angular momentum vector is $\left|\vec{l}\right| = \sqrt{l(l+1)}\,\hbar = \sqrt{12}\,\hbar$. For a given value of the quantum number m_l, the z-projection of the angular momentum is $l_z = m_l\hbar$. Thus the tilt angle from the z-axis is defined by the following equation: $\cos\theta = \frac{m_l}{\sqrt{12}}$. As the m_l values range from -3 to +3 (7 total), the corresponding θ angle values are: 150°, 125.26°, 106.78°, 90°, 73.22°, 54.74°, and 30°.

Problem 2. Consider an excited state of hydrogen atom with electron in the 3p orbital with m_l=1. Answer the following questions. You don't need to provide fully numerical answers – they can be expressed via a combination of numerical factors and physical constants, like e, $\hbar$, ε_o, a_o, etc

A. Write the expression for the probability density to find the electron at a given point (r,θ,ϕ) in the 3D space. (You may leave the numerical factors as they are: no need to reduce or calculate them.)

$$P = \left|\Psi_{3,1,1}\right|^2 = \left(R_{3,1}(r)\right)^2 \left|\mathrm{Y}_{1,1}(\theta,\phi)\right|^2 = \left(\frac{1}{81\sqrt{\pi}}\right)^2 (1/a_o)^3 \left(6-\frac{r}{a_o}\right)^2 \left(\frac{r}{a_o}\right)^2 e^{-2r/3a_o}\sin^2\theta$$

B. In which point(s) in the 3D space within the atom you are unlikely to find the electron?

We need to find a point(s) in space where the probability density $P = 0$. As is clear from the answer to A, P depends on both the distance r and the angle θ, i.e. on two independent variables, because, as a consequence of the separation of variables, it's a product of the angular part, $P_{\text{ang}} \propto \sin^2\theta$, and the radial part, let's call it P_{rad}: $P_{\text{rad}} \propto \left(6-\frac{r}{a_o}\right)^2 \left(\frac{r}{a_o}\right)^2 e^{-2r/3a_o}$. The probability density equals zero when either radial or angular part or both equal zero. The radial part equals zero at r=0 (i.e. at the nucleus) and at $r=6a_o$, which corresponds to all points on a sphere of radius $6a_o$ (which in this case is a nodal sphere). The angular part equals zero when $\sin^2\theta = 0$, i.e. at $\theta = 0°$ and $\theta = 180°$ (independent of the angle ϕ). This corresponds to all points on the z axis (which automatically also includes the point with r=0, i.e. the nucleus).

Thus the answer is: all points on a sphere of radius $6a_o$ and all points on the z-axis (i.e. all points with x=y=0).

C. At what distance from the nucleus you are most likely to find the electron? (If you have problems finding the answer analytically through derivative, you can try to answer this question by graphing the corresponding probability)

Since the question is about *distance*, not just point(s) in the 3D space, we need to use the radial probability distribution function that gives the probability to find the electron at a distance r from the nucleus, $W(r) = \left(R_{3,1}(r)\right)^2 r^2 = \frac{8}{81^2\times 3}\frac{r^4}{a_o^5}\left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o} \propto u^4(6-u)^2 e^{-2u/3}$ where for convenience of subsequent handling this expression I defined a new variable: $u = \frac{r}{a_o}$. (Let's ignore the numerical coefficient in the expression for *W*(*r*) because it's not important for finding a max of this function.) The most likely distance corresponds to the maximum of *W*(*r*), so we need to solve the equation: $\frac{d}{dr}W(r) = 0$. I calculated the derivative below step by step, so you can follow my

$$\frac{d}{du}W \Rightarrow \frac{d}{du}\left[u^4(6-u)^2 e^{-2u/3}\right] = 4u^3(6-u)^2 e^{-2u/3} - 2u^4(6-u)e^{-2u/3} - \frac{2}{3}u^4(6-u)^2 e^{-2u/3} =$$

derivation: $= \frac{2}{3}e^{-2u/3}u^3(6-u)\left[6(6-u)-3u-u(6-u)\right] = \frac{2}{3}e^{-2u/3}u^3(6-u)\left[36-15u+u^2\right] =$

$$= \frac{2}{3}e^{-2u/3}u^3(6-u)(u-3)(u-12) = 0$$

Of the possible solutions to this equation only $u = 3$ and $u = 12$ correspond to maxima of *W*, and of these two only the latter corresponds to a global maximum – you can verify this by calculating *W(u)* at these *u*-values. So, recalling that $u = \frac{r}{a_o}$, the most likely distance equals $12a_0$.

Note: because $W(r) = \left(R_{3,1}(r)\right)^2 r^2 = \left[R_{3,1}(r)r\right]^2$, you could simplify finding the maximum of *W(r)* analytically through zero of the derivative by searching for maxima of $F(r) = R_{3,1}(r)r \Rightarrow u^2(6-u)e^{-u/3}$, which is a bit simpler function to deal with in terms of derivatives.

D. Determine the average distance of the electron from the nucleus.

So, what you need here is to calculate the mean value of the distance (<*r*>) of the electron from the nucleus. You can simply plug *r* into the expectation value equation from the 4th postulate and evaluate the corresponding integrals. Because *r* does not depend on the angles, the integrals over the angular parts of the wave function in the numerator and denominator cancel each other, and so do the numerical factors.

$$\langle r\rangle_{3p} = \frac{\int \Psi^* r \Psi dv}{\int \Psi^* \Psi dv} = \frac{\int_0^\infty \left[R_{3,1}(r)\right]^2 r^3 dr}{\int_0^\infty \left[R_{3,1}(r)\right]^2 r^2 dr} = \frac{\int_0^\infty r^5 \left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o} dr}{\int_0^\infty r^4 \left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o} dr} = a_o \frac{\int_0^\infty u^5 (6-u)^2 e^{-2u/3} du}{\int_0^\infty u^4 (6-u)^2 e^{-2u/3} du} =$$

$$= a_o \frac{\int_0^\infty \left(36u^5 - 12u^6 + u^7\right) e^{-2u/3} du}{\int_0^\infty \left(36u^4 - 12u^5 + u^6\right) e^{-2u/3} du} = a_o \frac{36\frac{5!}{(2/3)^6} - 12\frac{6!}{(2/3)^7} + \frac{7!}{(2/3)^8}}{36\frac{4!}{(2/3)^5} - 12\frac{5!}{(2/3)^6} + \frac{6!}{(2/3)^7}} =$$

$$= a_o \frac{3}{2}\frac{36\cdot 5! - 12\cdot 6!\frac{3}{2} + 7!\frac{9}{4}}{36\cdot 4! - 12\cdot 5!\frac{3}{2} + 6!\frac{9}{4}} = a_o \frac{3}{2}\frac{2700}{324} = 12.5a_o$$

Here I defined a new variable: $u = \frac{r}{a_o}$ and used the table integral $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$ where $a = 2/3$.

An alternative (and somewhat simpler) way to get the answer is to use the expression for the radial distribution function $W(r)=\left(R_{3,1}(r)\right)^2 r^2=\frac{8}{81^2\times 3}\frac{r^4}{a_o{}^5}\left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o}$ (which gives the probability to find the electron at a given distance r from the nucleus) and calculate the average distance as the following integral (make sure you use the correct normalization factor):

$$\langle r\rangle_{3p}=\int_0^\infty rW(r)dr=\int_0^\infty r\left[R_{3,1}(r)\right]^2 r^2dr=\frac{8}{3\times 81^2}\int_0^\infty\frac{r^5}{a_o{}^5}\left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o}dr=$$

$$=\frac{8}{3\times 81^2}a_0\int_0^\infty u^5\,(6-u)^2\,e^{-2u/3}du=\frac{8}{3\times 81^2}a_0\int_0^\infty\left(36u^5-12u^6+u^7\right)e^{-2u/3}du=$$

$$=\frac{8}{3\times 81^2}a_0\left(36\frac{5!}{(2/3)^6}-12\frac{6!}{(2/3)^7}+\frac{7!}{(2/3)^8}\right)=\frac{8}{3\times 81^2}a_0\left(\frac{3}{2}\right)^6 2700=12.5a_0$$

E. Calculate the average potential energy of the electron in this orbital and compare it with the total energy in this state. Does the relationship (<*V*> = 2*E*) we derived in class for the 1s and in your HW#3 for 2p orbital still hold?

You can simply plug $\hat{V}=-\frac{e^2}{4\pi\varepsilon_o}\frac{1}{r}$ into the expectation value equation from the 4th postulate and evaluate the corresponding integrals, as we did in class for the 1s electron. Let's first put the numerical factor $-\frac{e^2}{4\pi\varepsilon_o}$ aside and calculate the average value of $\frac{1}{r}$. Because $\frac{1}{r}$ does not depend on the angles, the integrals over the angular parts of the wave function in the numerator and denominator cancel each other, and so do the numerical factors (the normalization coefficient and a_o) in the wave function.

$$\left\langle\frac{1}{r}\right\rangle=\frac{\int\Psi^*\frac{1}{r}\Psi dv}{\int\Psi^*\Psi dv}=\frac{\int_0^\infty\left[R_{3,1}(r)\right]^2 r\,dr}{\int_0^\infty\left[R_{3,1}(r)\right]^2 r^2dr}=\frac{\int_0^\infty r^3\left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o}dr}{\int_0^\infty r^4\left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o}dr}=\frac{1}{a_o}\frac{\int_0^\infty u^3(6-u)^2e^{-2u/3}du}{\int_0^\infty u^4(6-u)^2e^{-2u/3}du}=$$

$$=\frac{1}{a_o}\frac{\int_0^\infty\left(36u^3-12u^4+u^5\right)e^{-2u/3}du}{\int_0^\infty\left(36u^4-12u^5+u^6\right)e^{-2u/3}du}=\frac{1}{a_o}\frac{36\frac{3!}{(2/3)^4}-12\frac{4!}{(2/3)^5}+\frac{5!}{(2/3)^6}}{36\frac{4!}{(2/3)^5}-12\frac{5!}{(2/3)^6}+\frac{6!}{(2/3)^7}}=$$

$$=\frac{1}{a_o}\frac{2}{3}\frac{36\cdot 3!-12\cdot 4!\frac{3}{2}+5!\frac{9}{4}}{36\cdot 4!-12\cdot 5!\frac{3}{2}+6!\frac{9}{4}}=\frac{1}{a_o}\frac{2}{3}\frac{54}{324}=\frac{1}{a_o}0.1111=\frac{1}{9a_o}$$

Here, as in Q.C, I introduced a new variable, $u=\frac{r}{a_o}$, and used the table integral $\int_0^\infty x^m e^{-ax}dx=\frac{m!}{a^{m+1}}$ where a=2/3 and different values of m. Now all we need it to bring back the numerical factor $-\frac{e^2}{4\pi\varepsilon_o}$

to get: $\langle V\rangle = -\frac{e^2}{4\pi\varepsilon_o}\left\langle\frac{1}{r}\right\rangle = -\frac{e^2}{4\pi\varepsilon_o}\frac{1}{9a_o}$ and convert this expression into a form that can be compared with the expression for the total energy of the electron in this state. From the definition of a_o, $a_o = \frac{\hbar^2}{m_e}\frac{4\pi\varepsilon_o}{e^2}$, we get $\frac{e^2}{4\pi\varepsilon_o} = \frac{\hbar^2}{m_e}\frac{1}{a_o}$, and substituting it into the equation for the average potential energy, we finally obtain: $\langle V\rangle = -\frac{e^2}{4\pi\varepsilon_o}\left\langle\frac{1}{r}\right\rangle = -\frac{\hbar^2}{m_e a_o{}^2}\frac{1}{9} = 2E_{n=3}$. Therefore we conclude that the relationship ($\langle V\rangle = 2E$) we derived in class for the 1s orbital still holds.

A similar relationship holds for other states of electron, see for example, Example Problem 9.2 in the textbook.

As in Q.C, a somewhat simpler, alternative way to get the answer is to use the expression for the radial distribution function, $W(r) = \left(R_{3,1}(r)\right)^2 r^2 = \frac{8}{81^2\times 3}\frac{r^4}{a_o{}^5}\left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o}$ (which gives the probability to find the electron at a given distance r from the nucleus) and calculate the average value of $1/r$ as the following integral:

$$\left\langle\frac{1}{r}\right\rangle = \int_0^\infty \frac{1}{r}W(r)dr = \int_0^\infty \frac{1}{r}\left[R_{3,1}(r)\right]^2 r^2 dr = \frac{8}{3\times 81^2}\frac{1}{a_o^3}\int_0^\infty \frac{r^2}{a_o{}^2}\frac{r^2}{r}\left(6-\frac{r}{a_o}\right)^2 e^{-2r/3a_o}dr =$$

$$= \frac{8}{3\times 81^2}\frac{1}{a_o}\int_0^\infty u^3\,(6-u)^2\,e^{-2u/3}du = \frac{8}{3\times 81^2}\frac{1}{a_o}\int_0^\infty \left(36u^3 - 12u^4 + u^5\right)e^{-2u/3}du =$$

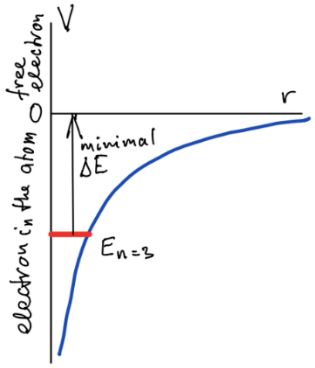
$$= \frac{8}{3\times 81^2}\frac{1}{a_o}\left(36\frac{3!}{(2/3)^4} - 12\frac{4!}{(2/3)^5} + \frac{5!}{(2/3)^6}\right) = \frac{8}{3\times 81^2}\frac{1}{a_o}\left(\frac{3}{2}\right)^4 54 = \frac{1}{9a_o}$$

F. Calculate the angle between the vector of the orbital angular momentum of the electron and the z-axis.

The orbital angular momentum of the electron is characterized by the quantum number $l = 1$. This means that the length of the orbital angular momentum vector is $\left|\vec{l}\right| = \sqrt{l(l+1)}\,\hbar = \sqrt{2}\,\hbar$. The z-projection of the angular momentum is $l_z = m_l\,\hbar = \hbar$. Thus the tilt angle from the z-axis is defined by the following equation: $\cos\theta = \frac{m_l}{\sqrt{l(l+1)}} = \frac{1}{\sqrt{2}}$. Therefore the θ angle is 45°.

G. What is the smallest quantum of energy required for this electron to leave the atom?

The energy of the 3p orbital is $E_{n=3} = -\frac{m_e e^4}{8\varepsilon_o^2 h^2\, 9} = -\frac{\hbar^2}{2m_e a_o^2\, 9}$. In order to leave the atom (ionization), electron needs enough energy to overcome the potential energy (the Coulomb interaction) that keeps it inside the atom. The maximal value of the Coulomb interaction equals zero, at $r\to\infty$. Therefore the minimal quantum of energy the electron needs in order to leave the atom is $\Delta E = 0 - E_{n=3} = \frac{m_e e^4}{8\varepsilon_o^2 h^2\, 9} = \frac{\hbar^2}{2m_e a_o^2\, 9} \approx 2.42\times10^{-19}$ J (see the drawing below). Less than this value will not be enough to ionize the atom, while a greater quantum of energy should suffice, too.



Problem 3. Consider a gas of iodine (I_2) molecules at standard temperature and pressure (0°C and 1 atm (101.325 kPa)). The rotational constant for molecular iodine is 0.03737 cm^{-1}, the force constant is 172 N/m. The atomic mass of iodine is 127 a.m.u. Answer the following six questions. *Show your calculations*.

A. Calculate the molecular partition function for vibrations of molecular iodine at these conditions. *Explain your assumptions.*

Assuming the vibrational states of I_2 can be described by the harmonic oscillator model, we can use the expression for partition function of H.O.: $q_{vib} = q_{HO} = (1 - e^{-h\nu\beta})^{-1}$. Using the information provided, we get: μ = 127/2 amu= 63.5 amu= 1.0541 10^{-25} kg; $\nu = \nu_{HO} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = 6.429\times10^{12}$ s^{-1}, hence $q_{vibr} = q_{HO}$ = 1.4771. Note that because $\frac{h\nu}{k_B T} = 1.1301$, the high-T approximation is not valid in this case.

B. What fraction of iodine molecules on average occupy the first excited vibrational energy level at this temperature? *Explain your assumptions and support with calculations if needed.*

The first excited vibrational level of HO has the energy $\varepsilon = \varepsilon_{n=1} = h\nu$ (remember, we set the energy of the ground state to 0?) and no degeneracy. Thus the fractional population of this energy level is $p_{n=1} = \frac{e^{-h\nu\beta}}{q_{vib}} = e^{-h\nu\beta}\left(1 - e^{-h\nu\beta}\right) = 0.2187$. Thus, approx. 22% of I_2 molecules occupy the first excited vibrational energy level.

C. Calculate the molecular partition function for rotations of molecular iodine at these conditions. *Explain your assumptions and support with calculations if needed.*

Assume that rotations of the chlorine molecule can be described using the 3-D rigid rotor model (particle on a sphere). Also *assume* high-temperature approximation ($k_B T >> hcB$), where

T = 273.15 K. The latter assumption is justifiable because $\frac{k_B T}{hcB}$ = 5074.4 >> 1. ← *this should be part of the reasoning explanation and has to be checked…* (note that 1cm^{-1} = 100 m^{-1})

Then the rotational molecular partition function is $q_{rot} = \frac{1}{hcB\beta\sigma} = \frac{k_B T}{2hcB}$, where the symmetry number σ = 2 for a homonuclear diatomic molecule, like I_2. Substituting the above result into this equation gives: $q_{rot} = \frac{k_B T}{2hcB}$ = 5074.4 /2 = 2537.2.

D. What fraction of iodine molecules on average occupy the first excited rotational energy level at this temperature? *Explain your assumptions and support with calculations if needed.*

The first excited rotational level of the molecule (assuming a 3D rigid rotor model) has the energy $\varepsilon = \varepsilon_{l=1} = hcBl(l+1) = 2hcB$ (remember: the rotational constant is $B = \frac{\hbar^2}{2Ihc}$) and its degeneracy is $g_{l=1} = 2l + 1 = 3$. Thus the fractional population of this energy level is

$p_{l=1} = \frac{g_{l=1} e^{-2hcB\beta}}{\sigma q_{rot}} = \frac{3e^{-2hcB\beta}}{1/hcB\beta} = \frac{3e^{-2hcB\beta}}{k_B T} hcB = 5.9 \times 10^{-4}$, where I used q_{rot} from Q. C. Thus, approx. 0.06% of I_2 molecules occupy the first excited vibrational energy level. Note that I included the symmetry number σ=2 in the denominator, because q_{rot} was also scaled/divided by σ.

E. Calculate the contribution from rotational motion to the entropy of 1 mole of iodine molecules at these conditions. *Explain your assumptions.*

The general equation relating the entropy in question to the rotational partition function is $S = \frac{E}{T} + k_B \ln Q_{rot} = -N\frac{\partial}{\partial\beta}\ln q_{rot} + Nk_B \ln q_{rot}$. (Note that because the molecules can be considered distinguishable, $Q = q^N$.) Using the expression for the molecular partition function from Question C and taking into account that it's 1 mole of molecules, i.e. $N_A \times k_B = R$, we get

$$S = -\frac{N_A}{T}\frac{\partial}{\partial\beta}\ln q_{rot} + N_A k_B \ln q_{rot} = N_A k_B + N_A k_B \ln\left(\frac{k_B T}{2hcB}\right) = R + R\ln\left(\frac{k_B T}{2hcB}\right) = R\left[1 + \ln\left(\frac{k_B T}{2hcB}\right)\right]$$

= 8.308×(1 + 7.8388) J = 8.308 J + 65.122 J = 73.429 J

Note that because the high-T approximation is valid, and rotation of a di-atomic molecule is characterized by 2 degrees of freedom, you could have saved time by simply replacing E here with $2 \times \frac{1}{2} k_B T \times N_A = RT$ without calculating the derivative of lnq_{rot}. Remember, we discussed this in class?

F. Calculate the molecular partition function for translational motion of iodine molecule at these conditions. *Explain your assumptions.* (Because this question is about the molecular partition function, you can treat the molecules as distinguishable.)

The molecular partition function for translational motion is $q_{transl} = \frac{V}{\Lambda^3}$, where $V = 22.4$ L = 22.4×10^{-3} m^3 is the volume of 1 mole of ideal gas at standard conditions, and $\Lambda = \frac{h}{\sqrt{2\pi m_{I_2} k_B T}}$ is the thermal de Broglie wavelength for the iodine molecule: $\Lambda = 6.63\times10^{-12}$ m = 0.0663 Å at these conditions.

Thus, $q_{transl} = 7.68\times10^{31}$. *Note:* the value of q_{transl} is <u>huge</u> compared to q_{vibr} and q_{rot}.