CHEM 550/475 Homework 5 *Due Mon Nov 9 at the start of lecture*

Levine 6th Ed. (5th Ed)
6.9 (6.5) Rotational Energy Levels of CO
6.21 (6.17) <r> in H-like atom
6.28 (6.16) He without e-e repulsion
6.52 (6.47) energy spacing trends
7.31 (7.27) Lz on nonstationary state of Hydrogen atom
7.33 (7.29) E for that same problem

1) The Dirac notation equivalent of our integral for finding Fourier coefficients is the "projection operator" $P_n = |n> <n|$ (it may look strange but you already know how to "use" it). It is called the projection operator because P_n "projects out" (like casting a shadow onto an axis) the component of any arbitrary ket that lies along the basis ket $|n>$. For example, if $\psi = a|1> + b|2> + c|3>$ then
$P_1\psi = |1>(<1| a|1> + <1|b|2> + <1|c|3>)= a|1>$

Combine the definition of completeness in Levine (equation 7.39) with Levine equation 7.71 to show that $\sum_n |n><n| = 1$ (This is the usual statement of completeness for an orthonormal basis set). Note: this is really just a notational problem—all you need to do is to translate Levine's equations into Dirac notation, and using the definitions you are given to show that this new operator must return f when operating on any function f.

2) What is the *most probable* distance (in meters) of finding a 1s electron from a Uranium nucleus that has been ionized of all but 1 electron? What is the potential energy of an electron this far away from a uranium nucleus (in Joules)? The virial theorem (an important result from chapter 14 that we haven't had time to cover) tells us that 2 * <KE> of this electron will equal -<U> (or that <KE>=-<E>), the average potential energy of this electron. Use a classical estimate to calculate how fast such an electron is moving. *Comment.*

3) Following Levine, use a computer to make linear combinations of Y(1,-1), Y(1,1), Y(1,0) to generate the familiar p$_x$, p$_y$ and p$_z$ orbitals. Make 3D plots of the angular components to verify that you indeed get the angular factors from p$_x$ and p$_y$. *Why can we take linear combinations of these eigenfunctions and create new eigenfunctions of H, when we know that in general, linear combinations of eigenfunctions are not also eigenfunctions?*

4) See next page:

4) ***Rotational-Vibrational Spectra***

High-resolution IR spectrum of HBr gas
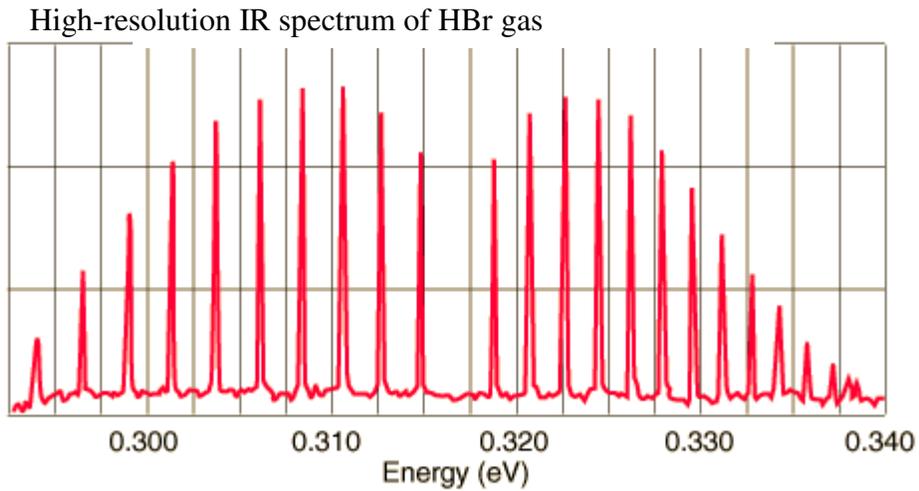
4) A) Calculate the ratio of molecules in the ground and first excited rotational states at 300K for HBr.

B) Discuss why we see a whole series of lines around the fundamental vibrational transition in the above IR spectrum.

C) Label the peaks according to the quantum numbers n and l of the initial and final states responsible for each of the 6 central lines in the spectrum above.

This data contains information about which of the following:

A) Energy of the electrons in a rotating HBr
B) Bond length
C) Bond strength
D) Isotopic distribution of H and Br