

CHEM 550/475 Homework 5 Due Mon Nov 3 at 5pm

**Levine 6<sup>th</sup> Ed.** (5<sup>th</sup> Ed)

**6.9** (6.5) Rotational Energy Levels of CO

**6.21** (6.17)  $\langle r \rangle$  in H-like atom

**6.28** (6.16) He without e-e repulsion

**6.52** (6.47) energy spacing trends

**7.31** (7.27)  $L_z$  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”  $P_n = |n\rangle \langle n|$  (it may look strange but you 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  $|n\rangle$ .

For example, if  $\psi = a|1\rangle + b|2\rangle + c|3\rangle$  then

$$P_1 \psi = |1\rangle (\langle 1|a|1\rangle + \langle 1|b|2\rangle + \langle 1|c|3\rangle) = a|1\rangle$$

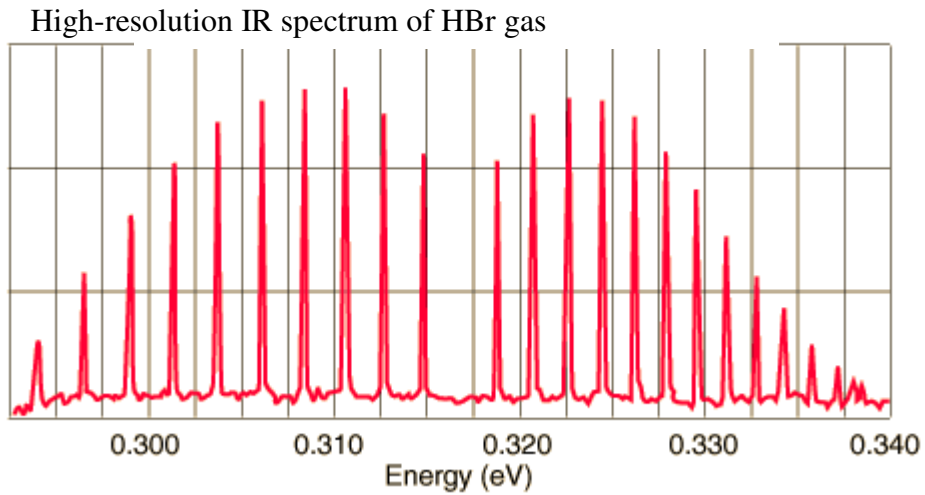
Combine the definition of completeness in Levine (equation 7.39) with Levine equation 7.71 to show that  $\sum_n |n\rangle \langle n| = 1$  (This is the usual statement of completeness for an orthonormal basis set). Note: this is really just a notational problem—all you need to do is to translate Levine’s 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  $2 * \langle KE \rangle$  of this electron will equal  $-\langle U \rangle$  (or that  $\langle KE \rangle = -\langle E \rangle$ ), the average PE 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*



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