Chem 361
Quantum Chemistry

Midterm Exam
November 15, 2004

Name ANGEL A

Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.

This close book exam, and you are responsible to be sure that your exam has no missing pages (5 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

If therefore angels are not composed of matter and form, as was said above, it follows that it would be impossible to have two angels of the same species
... The motion of an angel can be continuous or discontinuous as it wishes .
And thus an angel can be at one instant in one place, and at another instant in another place, not existing at any intermediate time.
- Thonas Aquinas (1268)

Honor Statement

I have neither give nor received aid in this examination.

Full signature Angel Aquino

Problem 1(30 points)
Show that

$$\left[\hat{L}_x,\hat{L}_y\right]=i\hbar\hat{L}_z$$

$$\hat{L}_z = -i\hbar\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] \qquad \hat{L}_x = -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

$$\hat{L}_y = -i\hbar\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]$$

$$\hat{L}_x\hat{L}_y f = (-i\hbar)^2\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]\left[z\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial z}\right] =$$

$$= (-i\hbar^2)\left[y\frac{\partial f}{\partial x} + \cancel{yz\frac{\partial^2 f}{\partial z\partial x}} - \cancel{z^2\frac{\partial^2 f}{\partial y\partial x}} + \cancel{zx\frac{\partial^2 f}{\partial y\partial z}} - \cancel{yx\frac{\partial^2 f}{\partial z^2}}\right]$$

$$\hat{L}_y\hat{L}_x f = (-i\hbar)\left[z\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial z}\right]\left[y\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial y}\right]$$

$$= (-i\hbar)\left[\cancel{zy\frac{\partial^2 f}{\partial x\partial z}} - \cancel{z^2\frac{\partial^2 f}{\partial x\partial y}} - \cancel{xy\frac{\partial^2 f}{\partial z^2}} + x\frac{\partial f}{\partial y} + \cancel{xz\frac{\partial^2 f}{\partial z\partial y}}\right]$$

$$\hat{L}_x\hat{L}_y f - \hat{L}_y\hat{L}_x f = (-i\hbar)^2\left(y\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial y}\right) = i\hbar(-i\hbar)\left(x\frac{\partial f}{\partial y} - y\frac{\partial f}{\partial x}\right)$$

$$\boxed{\left[\hat{L}_x,\hat{L}_y\right]f = i\hbar\hat{L}_z f}$$

Problem 2 (20 points)
The following reaction might occur in the interior of a star:

$$He^{++} + H \rightarrow He^{+} + H^{+}$$

Assuming that all the species are in their ground state, calculate the electronic energy change in eV. Does the reaction need or generate energy? Explain your answer.

H → HYDROGEN ATOM $Z = 1$
He^+ → HYDROGEN LIKE $Z = 2$

$$\left.\begin{array}{l} \\ \\ \end{array}\right\} E_n = -\frac{Z^2}{2n^2}\,\text{hartree}$$

HYDROGEN $Z = 1$ $n = 1$ $E_g^{H} = -\frac{1}{2}\,\text{hartree}$

He^+ $Z = 2$ $n = 1$ $E_g^{He^+} = -2\,\text{hartree}$

$$\Delta E = E_g^{He^+} - E_g^{H} = -2\,\text{hartree} + \frac{1}{2}\,\text{hartree} = -\frac{3}{2}\,\text{hartree}$$

$$= -\frac{3}{2}\,27.21\,\text{eV} = -40.82\,\text{eV} < 0$$

Rxn GENERATES 40,82 eV of ENERGY

Problem 3 (30 points)

The Hamiltonian for a hydrogen atom in an external magnetic field where the field is in the z directions is given by:

$$\hat{H} = \hat{H}_o + \frac{\beta_e B}{\hbar}\hat{L}_z$$

where $\hat{H}_0$ is the Hamiltonian operator of a hydrogen atom in the absence of the magnetic field. Thus the wave functions of the Schrödinger equation for the hydrogen atom in a magnetic field are the same as those for the hydrogen atom in the absence of the field In this case the energy associated with the wave function is:

$$E_n = E_n^o + \beta_e B m$$

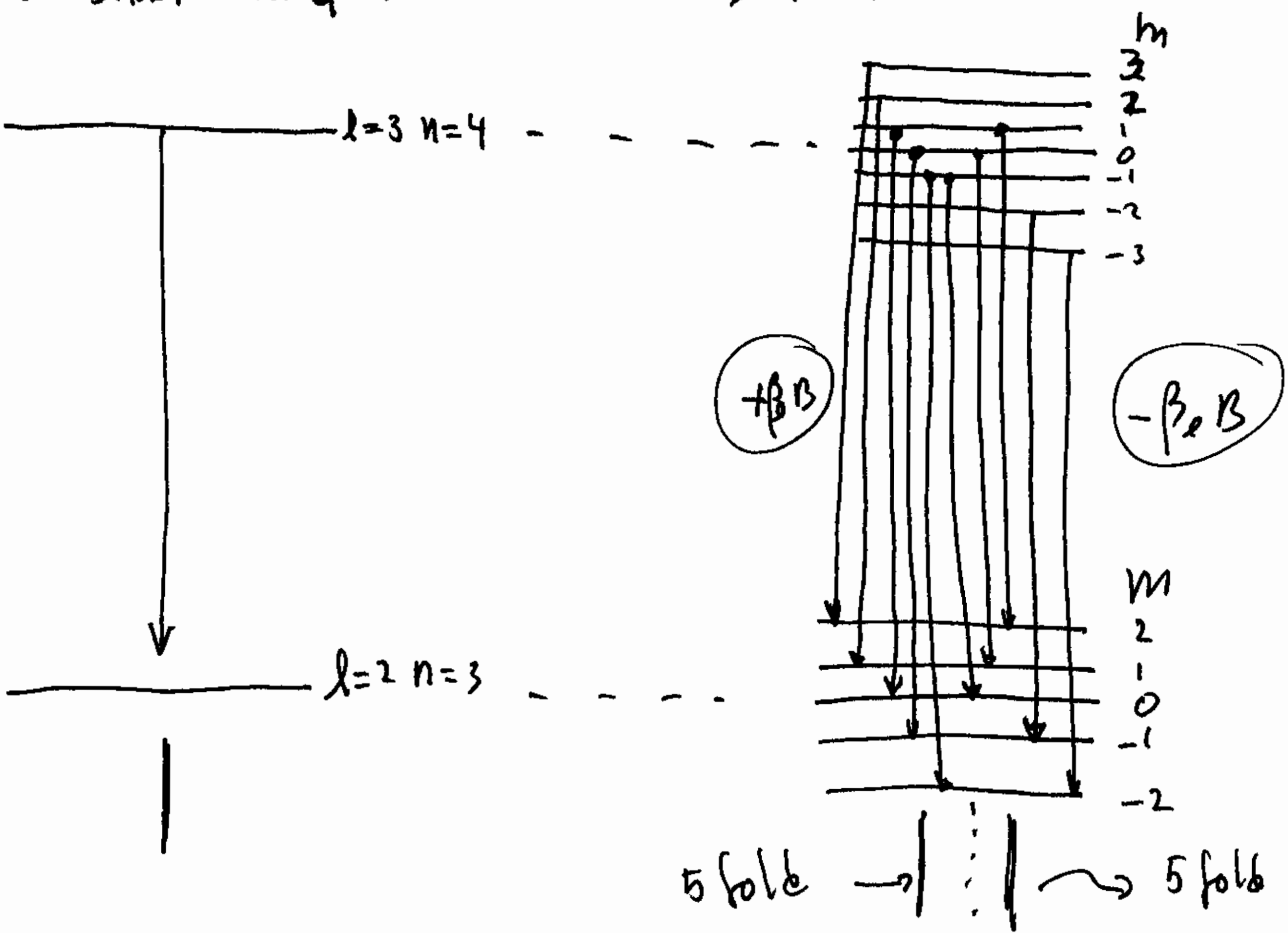
where E_n^o is the energy in the absence of the magnetic field and m is the magnetic quantum number.

For this system, consider the transition between the $\ell = 2$ and $\ell = 3$ states of atomic hydrogen. also we know that for light whose electric field vector is perpendicular to the direction of the external magnetic filed, the selection rule is

$$\Delta m = \pm 1$$

For this case, describe all of the possible allowed transitions. FOR $\ell = 3 \Rightarrow n = 4$ AT LEAST

CONSIDER $n = 4$ $\ell = 3$ ⟶ $n = 3$ $\ell = 2$



Problem 4 (20 points)
Using the same form of an optimized variational wavefunction

$$\Psi(r_1, r_2) = A\, e^{-\alpha(r_1 + r_2)},$$

estimate the ground state energy of Li^+. Explain in detail your answer.

Hint: You do not need to calculate any integral, but you need to use what you know about He.

FOR He AND He-LIKE ATOMS (ENERGY IN HARTREES).

$$E_\psi = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha \qquad \begin{array}{l} Z = 2 \ \text{He} \\ Z = 3 \ Li^+ \end{array}$$

$$\frac{dE_\psi}{d\alpha} = 2\alpha_c - 2Z + \frac{5}{8} = 0$$

$$\boxed{\alpha_c = Z - \frac{5}{16} = 3 - \frac{5}{16} = \frac{43}{16}} \text{ FOR } Li^+$$

$$E_\psi(Li^+) = \left(\frac{43}{16}\right)^2 - 2(3)\frac{43}{16} + \frac{5}{8}\,\frac{43}{16}$$

$$= \frac{43}{16}\left[\frac{43}{16} - 6 + \frac{5}{8}\right] = \frac{43}{16}\left[\frac{43 - 96 + 10}{16}\right] = -\left(\frac{43}{16}\right)^2$$

GROUND STATE ENERGY FOR Li^+

$$\boxed{E_g(Li^+) = -7.22 \text{ hartree}} \ \boxed{= -196.46 \text{ eV}}$$