CHEMISTRY 542

First Exam

October 6, 2003

1. Find the wavefunctions and energy levels of the stationary states of a particle of mass M in a uniform gravitational field g for the case when the region of motion of the particle is limits from below by a perfectly reflecting plane. Hint: This is a one-dimensional problem subject to $V(z) = \infty$ for $z \leq 0$ and $V(z) = Mgz$ for $z \geq 0$ since the motion in the xy plane is free.

(a) Write the Schrödinger equation that has to be solved for $\Psi(z)$.

(b) What are the boundary conditions?

(c) Quite often, in quantum mechanics a change of variable leads to a Schrödinger equation that is more easily solvable. If we use a change of variable

$$q = [2M^2 g/\hbar^2]^{1/3}\,[z - (E/Mg)]$$

we get the following simple form of the equation to be solved:

$$d^2\Psi(q)/dq^2 - q\Psi(q) = 0$$

Assume that a friend of yours who is a mathematician gives you the functions which are the solutions to this differential equation (they are called Airy functions) and that you have been given the roots of the Airy functions, that is the values of q at which the function $\Psi(q)$ goes to zero, are $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \ldots$all of which are negative numbers.

Question: What are the eigenvalues of energy E for the particle of mass M in a uniform gravitational field g for the case when the region of motion of the particle is limited from below by a perfectly reflecting plane?

(d) A limiting case is the semi-classical limit. The semi-classical limit is the asymptotic expression for the Airy function:

$$\Phi(q) \approx |q|^{-1/4}\ \sin\{\,(2/3)|q|^{3/2} + \pi/4\}$$

Question: What are the eigenvalues of energy in the semi-classical limit?

2. Let the functions α and β represent the complete orthonormal set of one-electron spin functions, that is, they are respectively the eigenfunctions of the angular momentum operator S_z with corresponding eigenvalues $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. Furthermore, using S_+ and S_- operators, it is possible to find the following results:
$S_x\alpha = \frac{1}{2}\hbar\beta$ $\quad S_x\beta = \frac{1}{2}\hbar\alpha$ $\qquad S_y\alpha = i\frac{1}{2}\hbar\beta$ $\qquad S_y\beta = -i\frac{1}{2}\hbar\alpha$

The magnetic dipole moment of a particle is directly proportional to its intrinsic angular momentum. In the Stern-Gerlach experiment, a beam of particles is sent through an inhomogeneous magnetic field which splits the beam into several beams each having particles with a different component of magnetic dipole moment in the field direction. For example, a beam of ground state Na atoms is split into two beams, corresponding to the two possible orientations of the spin of the valence electron.
Question: If we set up a Stern-Gerlach apparatus with the field in the z direction and then allow the $+\frac{1}{2}\hbar$ beam (electrons in the spin eigenfunction α) from this apparatus to enter a second Stern-Gerlach apparatus that has the field in the x direction, derive the relative beam intensities for $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, respectively. That is, find the results of measuring S_x in a system that is in a state described by the function α.
Hint: First, find the eigenfunctions of S_x in terms of the complete orthonormal set of functions α and β. What are the eigenvalues of S_x? Then, find the average value of the results of measuring S_x in a system that is in a state described by the function α. What then are the relative beam intensities for $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$ from the second Stern-Gerlach apparatus?

3. For a one-electron atom the spin-orbit interaction term in the Hamiltonian is

$$\xi(r)\,\boldsymbol{\ell}\bullet\mathbf{s}/\hbar^2$$

where ℓ and **s** are the orbital and spin angular momentum vector operators, respectively, and

$$\xi(r) = \hbar^2\,\{(1/2m^2c^2)(1/r)(\partial V/\partial r)\}$$

m is the mass of the electron and c is the speed of light, V and r are the potential energy and the distance of the electron from the nucleus, respectively.
For a state of the one-electron atom characterized by quantum numbers l, s, j, m_j, What are the possible values of j? Derive the interaction energy E_{SO}, given that

$$\int\xi(r)R_{nl}^2(r)r^2dr = \alpha^2 Z\,\langle a_0^3/r^3\rangle_{nl}(e^2/2a_0),$$

where the symbols have their standard meanings, including Z= the number of protons in the nucleus and α, in this instance, is the so-called fine structure constant, a dimensionless quantity, $\alpha = 1/137.03604$.

E_{SO} in <u>many-electron atoms</u> can be treated approximately by the above equations, provided Z_{eff} is used for the valence electron, the core having zero angular momentum. Apply your equation for E_{SO} to the Na atom and calculate the splitting of the yellow D line of sodium. [The experimental value is 17.2 cm^{-1}.]

This relation for E_{SO} can be used to find empirical values of the average $\langle a_0^3/r^3\rangle_{nl}$ for the valence shell of atoms from the hyperfine splitting of the transitions from the SO state, for example $({}^2P_{3/2}, {}^2P_{1/2}) \rightarrow {}^2S_{1/2}$ (ground) in the case of alkali atoms. In these designations of the states of atoms, the superscript is 2S+1, and the subscript is the j quantum number, while the P or S are the symbols for the orbital angular momentum L =1 or 0, of course. For atoms of the representative elements in the Periodic Table, the hyperfine splitting provides $\langle a_0^3/r^3\rangle_{nl}$. Barnes and Smith, Phys. Rev. 93, 95 (1954) found that $Z_{eff} = Z\text{-}n$ worked well enough for this purpose. Derive the equation they used

$$\Delta E_{SO} = \alpha^2 Z_{eff} \langle a_0^3/r^3\rangle_{nl}(e^2/2a_0)(l+½)$$

and verify the following values of $\langle a_0^3/r^3\rangle_{np}$, a dimensionless quantity. Note that $(e^2/2a_0) = 13.606$ eV x 8065.5 cm^{-1}/eV= 109,737.3 cm^{-1}

	Configuration	State	cm^{-1}	$\langle a_0^3/r^3\rangle_{np}$
Na	3p	${}^2P$	17.2	0.244
Mg	3s3p	${}^3P$	60.8	0.77
Al	3p	${}^2P$	112.0	1.28
Si	$3p^2$	${}^3P$	223.3	2.31
P	$3p^3$			by interpoln.
S	$3p^4$	${}^3P$	573.6	5.02
Cl	$3p^5$	${}^2P$	881.0	7.16

These quantities are significant in that they were predicted to be a factor in the magnitudes of NMR shieldings and were later found to correlate with the NMR chemical shift ranges of the nuclei of representative elements, i.e., large $\langle a_0^3/r^3\rangle_{np}$ means large chemical shift range for the nucleus.