CHEMISTRY 542

Make-up Exam

October 13, 2003

1. A particle of mass M is constrained to be on a line along the z axis perpendicular to the earth's surface in a gravitational field where g is the acceleration of gravity.

(a) *Write down the Schrödinger equation for this system.*

(b) *Determine the boundary conditions that must be satisfied by the wavefunction for this system.*

2. Suppose we are in a universe in which the spin quantum number for the electron is s = 3/2 instead of s = 1/2, as it is in our universe.

(a) Describe in qualitative terms what would be observed when the ground state hydrogen atom is passed through an inhomogeneous magnetic field in the hypothetical universe.

(b) What are the possible values for S_z for the electron in that universe? What is the value of S^2 for the electron in that universe?

S_z:

S^2:

(c) With s = 1/2, there are 10 *elements contained in each transition metal series* in the periodic table. *How many* would there be, if s for the electron were 3/2? *Explain.*

3. Consider a particle of mass M constrained to move on a circle of radius R where its potential energy is zero. The particle is in a physical state that is described by $F(\phi) = A\{\cos 2\phi + 2\cos 3\phi\}$. *Determine the results of the following sets of experiments on this system, that is, determine the typical outcomes of the experiments, the average values of the results:*

(a) The z component of the angular momentum of the system is measured

Derivation of predictions here:	Observed values here:
	Average=

(b) The energy of the system is measured

Derivation of predictions here:	Observed values here:
	Average=

4. The eigenvalues of a linear (one-dimensional) harmonic oscillator are known:

$\mathcal{H}(x)\, \varphi(x) = E\, \varphi(x)$ where $\mathcal{H}(x) = -(\hbar^2/2M)\, d^2/dx^2 + ½\, \kappa x^2$

where M is the mass of the oscillator, and κ is the Hooke's law force constant. That is,

$\{-(\hbar^2/2M)\, d^2/dx^2 + ½\, \kappa x^2\}\, \varphi(x) = (n + ½)\hbar\omega\, \varphi(x)$ where $n = 0, 1, 2, 3, \ldots$

A linear harmonic oscillator in its ground state is described by the normalized function

$\varphi(x) = [2\, \omega M/h]^{¼} \exp[-\omega M x^2/2\hbar]$

Now consider a three-dimensional anisotropic harmonic oscillator that has three different force constants for motion in the direction of each of the Cartesian coordinates, i.e., $V = ½\, [\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2]$

[This is akin to the vibrations of a polyatomic molecule, in which there are several vibrational coordinates, one normal mode coordinate for each normal mode of vibration.]

Write the Schrödinger equation for this system (the three-dimensional anisotropic oscillator).

Show how you would find the eigenfunctions and eigenvalues of the three-dimensional anisotropic oscillator. [The harmonic vibrations of a polyatomic molecule are found in this way.]

Write down the eigenvalue for the ground state of the three-dimensional anisotropic harmonic oscillator.

Write down the eigenfunction of the ground state of the three-dimensional anisotropic harmonic oscillator.

5. A particle of mass m in a potential well (with infinitely high walls) in the x dimension is known to be in either the $n = 2$ or $n = 3$ eigenstates with equal probability. The eigenfunctions of these states are $\psi_2(x) = (2/a)^{1/2} \sin [2\pi x/a]$ and $\psi_3(x) = (2/a)^{1/2} \sin [3\pi x/a]$, respectively.

(a) *Write an appropriate wavefunction* Ψ for the system that reflects our knowledge of the state of the system.

(c) *What energies* might be obtained if the energy of the particle is measured?

(d) *Determine the expected average* of a series of measurements of the energy of the particle.

(e) *Write the equation* that shows how the <u>expected</u> <u>mean square deviation</u> of any series of measurements of the energy of the particle can be calculated.

(f) *Carry out the solution* of (e), and then from the final result, determine the expected standard deviation of the series of measurements.

List of possibly useful integrals that will be provided with each exam

$\int \sin(ax)dx = -(1/a)\cos(ax)$

$\int \cos(ax)dx = (1/a)\sin(ax)$

$\int \sin^2(ax)dx = ½\, x - (1/4a)\sin(2ax)$

$\int \cos^2(ax)dx = ½\, x + (1/4a)\sin(2ax)$

$\int \sin(ax)\sin(bx)dx = [1/2(a-b)]\sin[(a-b)x)] - [1/2(a+b)]\sin[(a+b)x)],\quad a^2 \neq b^2$

$\int \cos(ax)\cos(bx)dx = [1/2(a-b)]\sin[(a-b)x)] + [1/2(a+b)]\sin[(a+b)x)],\quad a^2 \neq b^2$

$\int x\sin(ax)dx = (1/a^2)\sin(ax) - (x/a)\cos(ax)$

$\int x\cos(ax)dx = (1/a^2)\cos(ax) + (x/a)\sin(ax)$

$\int x^2\cos(ax)dx = [(a^2x^2 - 2)/a^3]\sin(ax) + 2x\cos(ax)/a^2$

$\int x^2\sin(ax)dx = -[(a^2x^2 - 2)/a^3]\cos(ax) + 2x\sin(ax)/a^2$

$\int x\sin^2(ax)dx = x^2/4 - x\sin(2ax)/4a - \cos(2ax)/8a^2$

$\int x^2\sin^2(ax)dx = x^3/6 - [x^2/4a - 1/8a^3]\sin(2ax) - x\cos(2ax)/4a^2$

$\int x\cos^2(ax)dx = x^2/4 + x\sin(2ax)/4a + \cos(2ax)/8a^2$

$\int x^2\cos^2(ax)dx = x^3/6 + [x^2/4a - 1/8a^3]\sin(2ax) + x\cos(2ax)/4a^2$

$\int x\exp(ax)dx = \exp(ax)\,(ax-1)/a^2$

$\int x\exp(-ax)dx = \exp(-ax)\,(-ax-1)/a^2$

$\int x^2\exp(ax)dx = \exp(ax)\,[x^2/a - 2x/a^2 + 2/a^3]$

$\int x^m\exp(ax)dx = \exp(ax)\sum_{r=0 \text{ to } m} (-1)^r\, m!x^{m-r}/(m-r)!a^{r+1}$

$\int_0^\infty x^n\exp(-ax)dx = n!/a^{n+1}\qquad a > 0$, n positive integer

$\int_0^\infty x^2\exp(-ax^2)dx = (1/4a)(\pi/a)^{½}\qquad a > 0$

$\int_0^\infty x^{2n}\exp(-ax^2)dx = (1\cdot3\cdot5\cdot\ldots\cdot(2n-1)/(2^{n+1}a^n)(\pi/a)^{½}\qquad a > 0$

$\int_0^\infty x^{2n+1}\exp(-ax^2)dx = n!/2a^{n+1}\qquad a > 0$, n positive integer

$\int_0^\infty \exp(-a^2x^2)dx = (1/2a)\,(\pi)^{½}\qquad a > 0$

$\int_0^\infty \exp(-ax)\cos(bx)dx = a/(a^2+b^2)\qquad a > 0$

$\int_0^\infty \exp(-ax)\sin(bx)dx = b/(a^2+b^2)\qquad a > 0$

$\int_0^\infty x\exp(-ax)\sin(bx)dx = 2ab/(a^2+b^2)^2\qquad a > 0$

$\int_0^\infty x\exp(-ax)\cos(bx)dx = (a^2-b^2)/(a^2+b^2)^2\qquad a > 0$

$\int_0^\infty \exp(-a^2x^2)\cos(bx)dx = [(\pi)^{½}/2a]\cdot\exp[-b^2/4a^2]\qquad ab \neq 0$

ADDITIONAL INFORMATION

$a_0 = (\hbar^2/m_e e^2)$ the "Bohr radius", 0.529177×10^{-10} m
$(e^2/2a_0) = 13.6057$ eV one rydberg, a unit of energy = (1/2) hartree
c = frequency•wavelength = 2.997924×10^{10} cm sec^{-1} the speed of light
1 eV = 8065.6 cm^{-1}

Slater's rules for finding the screening :

1. For an electron in the same 1s orbital as the electron of interest $s_{1s} = 0.30$
2. For electrons with $n > 1$ and $\ell = 0, 1$

$$s_{n\ell} = 0.35k_{same} + 0.85k_{in} + 1.00k_{inner}$$

where
k_{same} = number of other electrons in the <u>same shell</u> as the screened electron of interest
k_{in} = number of electrons in the shell with principal quantum number n-1
k_{inner} = number of electrons in the shell with principal quantum number n-2

3. For d electrons, for example, 3d

$$s_{3d} = 0.35k_{3d} + 1.00k_{in}$$

where
k_{3d} = number of 3d electrons
k_{in} = number of electrons with $n \leq 3$ and $\ell < 2$