CHEMISTRY 542

Answers to 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.*

$$\{ - (\hbar^2/2M)\, d^2/dz^2 + Mgz\}\Psi(z) = E\, \Psi(z)$$

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

$\Psi(z)$ must be single-valued, continuous and finite, and its first derivatives also continuous and finite. Since $V(z) = \infty$ for $z < 0$, then $\Psi(z < 0) = 0$. This means that one boundary condition is that $\Psi(z = 0) = 0$ in order for the wavefunction to be single-valued and continuous. A second boundary condition is that $\Psi(z \to \infty) = 0$, that is, we must have a finite wavefunction.

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.

Instead of splitting into two beams and arriving at the detector in two spots corresponding to m_s=+1/2 and -1/2, there will be 4 beams arriving at the detector in 4 spots corresponding to m_s=+3/2,+1/2,-1/2,-3/2

(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: $+(3/2)\hbar$, $+(1/2)\hbar$, $-(1/2)\hbar$, $-(3/2)\hbar$
S^2: $(3/2)[(3/2)+1]\, \hbar^2$

(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.*

The "10" members of the series come from nd^1, nd^2, ..., nd^{10} configurations, which arise from m_ℓ= 2, 1, 0, -1, -2 and m_s= +1/2, -1/2. Instead there will be the same m_ℓ going with 4 different m_s leading to 20 elements in each transition metal series.

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: $F(\phi)$ is not one of the eigenfunctions of L_z or .	Observed values here:
Expand $F(\phi)$ in terms of the complete orthonormal set of functions	$2\,\hbar$
$(1/\sqrt{2\pi})\exp[ik\phi]$. $F(\phi) = \sum_k c_k \Psi_k(\phi)$ and find the coefficients:	$-2\,\hbar$
$c_k = \int_0^{2\pi} \Psi_k^*(\phi)\, F(\phi)\, d\phi = \int_0^{2\pi} \Psi_k^*(\phi) A\{\cos 2\phi + 2\cos 3\phi\}\, d\phi$	$3\,\hbar$
Since we can write $\cos 2\phi = \frac{1}{2}[\exp(i2\phi) + \exp(-i2\phi)]$ and	$3\,\hbar$
$\cos 3\phi = \frac{1}{2}[\exp(i3\phi) + \exp(-i3\phi)]$, then	$3\,\hbar$
$c_k = \int_0^{2\pi} \Psi_k^*(\phi)\frac{1}{2}A\{\exp(i2\phi)+\exp(-i2\phi)+2\exp(i3\phi)+2\exp(-i3\phi)\}\, d\phi$	$3\,\hbar$
$c_k = (1/\sqrt{2\pi})^{-1}\frac{1}{2}A \int_0^{2\pi} \Psi_k^*(\phi)\{\Psi_2(\phi) + \Psi_{-2}(\phi) + 2\Psi_3(\phi) + 2\Psi_{-3}(\phi)\}\, d\phi$	$-3\,\hbar$
$c_k = (1/\sqrt{2\pi})^{-1}\frac{1}{2}A\, \{\delta_{k,2} + \delta_{k,-2} + 2\delta_{k,3} + 2\delta_{k,-3}\}$ in shorthand	$-3\,\hbar$
where $\delta_{k,2} = 1$ if k=2 or else it is zero, since it was an orthonormal set	$-3\,\hbar$
A can be obtained by integration $\int_0^{2\pi} F^*(\phi)F(\phi)\, d\phi$: $A = [5\pi]^{-1/2}$	$-3\,\hbar$
$c_k = (10)^{-1/2}\{\delta_{k,2} + \delta_{k,-2} + 2\delta_{k,3} + 2\delta_{k,-3}\}$ $c_2^2 = c_{-2}^2 = (1/10)$ $c_3^2 = c_{-3}^2 = (4/10)$	Average = $0\hbar$

(b) The energy of the system is measured

Derivation of predictions here:	Observed values here:
The average value is obtained by $\int_0^{2\pi} F^*(\phi)\, (L_z$ or $)\, F(\phi)\, d\phi$:	$2^2\, (\hbar^2/2MR^2)$
which by above algebra leads to $\sum_k c_k^2 \bullet k\hbar$ or $\sum_k c_k^2 \bullet k^2(\hbar^2/2MR^2)$	$(-2)^2(\hbar^2/2MR^2)$
The observed values should be 10% of the time the eigenvalue for	$3^2\, (\hbar^2/2MR^2)$
k=2, 10% of the time the eigenvalue for k=-2, 40% of the time the	$3^2\, (\hbar^2/2MR^2)$
eigenvalue for k=3, 40% of the time the eigenvalue for k=-3,	$3^2\, (\hbar^2/2MR^2)$
according to the probabilities given by the corresponding c_k^2	$3^2\, (\hbar^2/2MR^2)$
	$(-3)^2(\hbar^2/2MR^2)$
	$(-3)^2(\hbar^2/2MR^2)$
	$(-3)^2(\hbar^2/2MR^2)$
	$(-3)^2(\hbar^2/2MR^2)$
	Average = $8\, (\hbar^2/2MR^2)$

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 $n = 0, 1, 2, 3, ...$

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

$\varphi(x) = [2\,\omega M/h]^{1/4} \exp[-\omega M x^2/2\hbar]$

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).

$$\{-(\hbar^2/2M)[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2] + ½\,[\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2]\}\Psi(x,y,z)$$
$$= E\,\Psi(x,y,z)$$

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.]

Use separation of variables:

Let $\Psi(x,y,z) = P(x)\bullet Q(y)\bullet R(z)$, substitute it into the Schr. equation:

$$\{-(\hbar^2/2M)[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2] + ½\,[\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2]\}\,P(x)\bullet Q(y)\bullet R(z)$$
$$= E\,P(x)\bullet Q(y)\bullet R(z)$$

Then divide both sides of the equation by $P(x)\bullet Q(y)\bullet R(z)$ to get

$$\frac{[-(\hbar^2/2M)\partial^2/\partial x^2 + ½\,\kappa_x x^2]\,P(x)}{P(x)} + \frac{[-(\hbar^2/2M)\partial^2/\partial y^2 + ½\,\kappa_y y^2]\,Q(y)}{Q(y)}$$
$$+ \frac{[-(\hbar^2/2M)\partial^2/\partial z^2 + ½\,\kappa_z z^2]\,R(z)}{R(z)} = E$$

Since each term involves only x or only y or only z, then each must be equal to a constant and the sum of the constants must equl the eigenvalue E

Therefore we find that we have to solve 3 equations, one in x, one in y, one in z.

$$[-(\hbar^2/2M)\partial^2/\partial x^2 + ½\,\kappa_x x^2]\,P(x) = e\,P(x)$$

and the others look just like this except in the variables y and z.
We already have the eigenfunctions and eigenvalues of the x equation:

$\varphi(x)$ and energies are $(n + \frac{1}{2})\hbar\omega$

Since the y and z equations are analogous then we know those eigenfuncitons and energies as well. We need the x, y, z subscripts to identify the various quantum numbers and harmonic frequencies which are different from each other

(since $\kappa_x \neq \kappa_y \neq \kappa_z$) :

$E = (n_x + \frac{1}{2})\hbar\omega_x + (n_y + \frac{1}{2})\hbar\omega_y + (n_z + \frac{1}{2})\hbar\omega_z$

$\Psi(x,y,z) = \varphi(x) \bullet \varphi(y) \bullet \varphi(z)$

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

$E = (n_x + \frac{1}{2})\hbar\omega_x + (n_y + \frac{1}{2})\hbar\omega_y + (n_z + \frac{1}{2})\hbar\omega_z$ are the general eigenvalues of this system where $n_x = 0,1,2,3,4 \ldots$ $n_y = 0,1,2,3,4 \ldots$ $n_z = 0,1,2,3,4 \ldots$

Ground state $E = (0+\frac{1}{2})\hbar\omega_x + (0+\frac{1}{2})\hbar\omega_y + (0+\frac{1}{2})\hbar\omega_z$

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

$\Psi(x,y,z) = \varphi(x) \bullet \varphi(y) \bullet \varphi(z)$

$= [2\omega_x M/h]^{\frac{1}{4}} \exp[-\omega_x M x^2/2\hbar] \bullet [2\omega_y M/h]^{\frac{1}{4}} \exp[-\omega_y M y^2/2\hbar]$

$\bullet [2\omega_z M/h]^{\frac{1}{4}} \exp[-\omega_z M z^2/2\hbar]$

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 <u>the state of the system</u>.

According to the conditions of the problem both states are equally probable, thus we need to have the wavefunction be a superposition of $\psi_2(x)$ and $\psi_3(x)$ with coefficients whose absolute squares are equal. $\Psi(x) = c_2\psi_2(x) + c_3\psi_3(x)$ such that $c_2^2=c_3^2=1/2$ since $c_2^2+c_3^2 = 1$ (normalization). Therefore,

$\Psi(x) = (1/\sqrt{2})\{ (2/a)^{1/2} \sin[2\pi x/a] + (2/a)^{1/2} \sin[3\pi x/a]\}$ or

$\Psi(x) = (1/\sqrt{2})\{ (2/a)^{1/2} \sin[2\pi x/a] - (2/a)^{1/2} \sin[3\pi x/a]\}$

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

The energy eigenvalues $2^2h^2/8ma^2$ and $3^2h^2/8ma^2$ only.

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

Postulate 3 says the expected average is $\langle E\rangle = \int_0^a \Psi^*(x)\hat{H}\Psi(x)dx$, since we have already normalized $\Psi(x)$.

$\langle E\rangle = \int_0^a (1/\sqrt{2})\{\psi_2(x) + \psi_3(x)\}^*\hat{H} (1/\sqrt{2})\{ \psi_2(x) + \psi_3(x)\}dx$

$= (1/2)\int_0^a\{\psi_2^*\hat{H} \psi_2dx+\psi_2^*\hat{H} \psi_3dx+\psi_3^*\hat{H} \psi_2dx+\psi_3^*\hat{H}\psi_3dx\}$

$= (1/2)\{E_2 \int_0^a\psi_2^*\psi_2dx + E_3 \int_0^a\psi_2^*\psi_3dx+ E_2 \int_0^a\psi_3^*\psi_2dx+ E_3 \int_0^a\psi_3^*\psi_3dx\}$

$\langle E\rangle = (1/2)\{E_2+ E_3\} = (1/2)\{ 2^2+ 3^2\}h^2/8ma^2$

For the - combination the results are the same as above:

$\langle E\rangle = \int_0^a (1/\sqrt{2})\{\psi_2(x) - \psi_3(x)\}^*\hat{H} (1/\sqrt{2})\{ \psi_2(x) - \psi_3(x)\}dx$

$= (1/2)\{E_2 \int_0^a\psi_2^*\psi_2dx - E_3 \int_0^a\psi_2^*\psi_3dx- E_2 \int_0^a\psi_3^*\psi_2dx+ E_3 \int_0^a\psi_3^*\psi_3dx\}$

$\langle E\rangle = (1/2)\{E_2+ E_3\} = (1/2)\{ 2^2+ 3^2\}h^2/8ma^2$

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

The operator for the square of the deviation in measurements of energy is

$Op = (\hat{H} - \langle E \rangle)^2$

Postulate 3 gives the average, thus the mean square deviation

$= \int_0^a (1/\sqrt{2})\{\psi_2(x) + \psi_3(x)\}^* (\hat{H} - \langle E \rangle)^2 (1/\sqrt{2})\{\psi_2(x) + \psi_3(x)\}dx$

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

mean square dev $= \int_0^a (1/\sqrt{2})\{\psi_2(x) + \psi_3(x)\}^* (\hat{H} - \langle E \rangle)^2 (1/\sqrt{2})\{\psi_2(x) + \psi_3(x)\}dx$

$= \int_0^a (1/\sqrt{2})\{\psi_2(x) + \psi_3(x)\}^* (\hat{H}^2 - 2\langle E \rangle \hat{H} + \langle E \rangle^2) (1/\sqrt{2})\{\psi_2(x) + \psi_3(x)\}dx$

Note that $\hat{H}^2\psi_2(x) = \hat{H}E_2\psi_2(x) = E_2\hat{H}\psi_2(x) = E_2^2\psi_2(x)$

and $\langle E \rangle \hat{H}\psi_2(x) = \langle E \rangle E_2\psi_2(x)$ and $\langle E \rangle^2\psi_2(x) = \langle E \rangle^2\psi_2(x)$ since $\langle E \rangle^2$ is a number.

mean square dev =

$(1/2)\int_0^a\{\psi_2 + \psi_3\}^* (E_2^2\psi_2 + E_3^2\psi_3 - 2\langle E \rangle E_2\psi_2 - 2\langle E \rangle E_3\psi_3 + \langle E \rangle^2\psi_2 + \langle E \rangle^2\psi_3\}dx$

$= (1/2)\{E_2^2 + E_3^2 - 2\langle E \rangle(E_2 + E_3) + 2\langle E \rangle^2\} = (1/2)\{E_2^2 + E_3^2 - 4\langle E \rangle^2 + 2\langle E \rangle^2\}$

$= (1/2)\{E_2^2 + E_3^2\} - \langle E \rangle^2 = [(1/2)\{2^4 + 3^4\} - \{(2^2+3^2)/2\}^2]\{h^2/8ma^2\}^2$

$= [25/4]\{h^2/8ma^2\}^2$

standard deviation is the square root of this $= (5/2)(h^2/8ma^2)$