CHEMISTRY 542

Exam I ANSWERS

October 4, 2004

In applying the principles of Quantum Mechanics in answering each question, be sure to *state the principle you are using at each step.*

1. (a) Prove that the root mean square deviation of the value of a property S whose operator is S_{op} is given by $\{\langle S^2\rangle - \langle S\rangle^2\}^{1/2}$ for any state of the system (not necessarily an eigenfunction of S_{op}.)

The operator for the square of the deviation is $\{S_{op} - \langle S\rangle\}^2$

Find the *mean square deviation* by applying the expectation value postulate:

$\int \Psi^*\{S_{op} - \langle S\rangle\}^2\Psi d\tau = \int \Psi^*\{S_{op}^2 - 2\langle S\rangle S_{op} + \langle S\rangle^2\}\Psi d\tau$

$= \int \Psi^* S_{op}^2 \Psi d\tau - 2\langle S\rangle\int \Psi^* S_{op}\Psi d\tau + \langle S\rangle^2\int \Psi^*\Psi d\tau$ using properties of linear operators

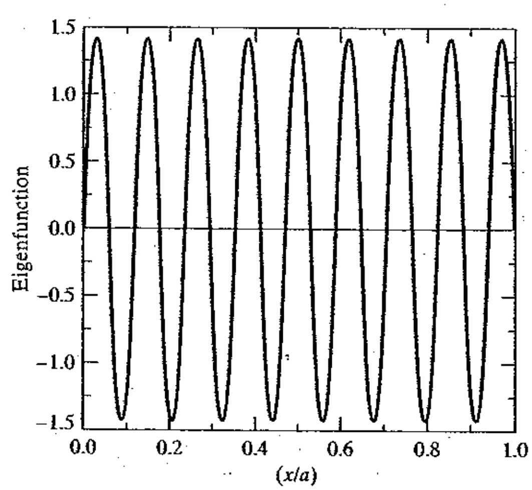
$= \langle S^2\rangle - 2\langle S\rangle\bullet\langle S\rangle + \langle S\rangle^2 \bullet 1$ using expectation value postulate and normalization

$= \langle S^2\rangle - 2\langle S\rangle^2 + \langle S\rangle^2 = \langle S^2\rangle - \langle S\rangle^2$

Therefore, the root mean square deviation is the square root of this:

$\{\langle S^2\rangle - \langle S\rangle^2\}^{1/2}$

(b) An excited state eigenfunction for a quantum particle of mass M in an infinite potential well between x = 0 and x = a is shown below, where the eigenfunction is plotted as a function of the ratio x/a within the well.



All answers are in terms of M, h, and a for the questions below about the system (b).
What is the translational energy of this particle?

The number of nodes = 16. Since the state n=1 has zero nodes, the state n=2 had one node, the graphed eigenfunction must correspond to n=17.
$E_n = n^2h^2/8Ma^2$
$E_{17} = 17^2h^2/8Ma^2$

What is the average position of the particle?

$\langle x\rangle = \int_0^a \Psi_{17}^* x \Psi_{17} dx = \int_0^a (2/a)^{1/2} \sin(17\pi x/a)\, x\, (2/a)^{1/2} \sin(17\pi x/a)\, dx$
$= (2/a) \int_0^a x \sin^2(17\pi x/a)\, dx = (2/a) \int_0^a x \sin^2(bx)\, dx$ where $b = 17\pi/a$
$= (2/a) \mid x^2/4 - (x/4b)\sin(2bx) - (1/8b^2)\cos(2bx) \mid_0^a$
Note that $\sin(2bx)$ must be zero at both limits because of the boundary conditions for Ψ at both x=0 and x=a. On the other hand the cos is 1 at both limits for the same reason. Therefore, $\langle x\rangle = (2/a) \mid x^2/4 \mid_0^a = (2/a)(a^2/4) = a/2$ for <u>any</u> of the eigenstates of energy (since n is not retained in evaluation of the integral.

What is the uncertainty in the position of the particle? That is, what is the root mean square deviation of the position of the particle?

We already proved $\sigma_S = \{\langle S^2\rangle - \langle S\rangle^2\}^{1/2}$ We can use this: $\sigma_x = \{\langle x^2\rangle - \langle x\rangle^2\}^{1/2}$
We already have $\langle x\rangle$, now find $\langle x^2\rangle$.
$\langle x^2\rangle = \int_0^a \Psi_{17}^* x^2 \Psi_{17} dx = \int_0^a (2/a)^{1/2} \sin(17\pi x/a)\, x^2\, (2/a)^{1/2} \sin(17\pi x/a)\, dx$
$= (2/a) \int_0^a x^2 \sin^2(17\pi x/a)\, dx = (2/a) \int_0^a x^2 \sin^2(b x)\, dx$ where $b = 17\pi/a$
$= (2/a) \mid x^3/6 - [(x^2/4b) - 1/8b^3] \bullet \sin(2bx) - (x/4b^2)\cos(2bx) \mid_0^a$ Note that $\sin(2bx)$ must be zero at both limits because of the boundary conditions for Ψ at both x=0 and x=a. On the other hand the cos is 1 at both limits for the same reason. Therefore,
$\langle x^2\rangle = (2/a)\{(a^3/6) - (a/4b^2)\} = (2/a)\{(a^3/6) - [a^3/4(17\pi)^2]\} = a^2\{1/3 - 1/2\,(17\pi)^2\}$
$\sigma_S^2 = a^2\{[2(17\pi)^2 - 3]/6(17\pi)^2\} - a/2$

What is the uncertainty in the linear momentum of the particle?

We already proved $\sigma_S = \{\langle S^2\rangle - \langle S\rangle^2\}^{1/2}$ We can use this: $\sigma_p = \{\langle p_x^2\rangle - \langle p_x\rangle^2\}^{1/2}$
$\langle p_x\rangle = 0$ because p_x can take both positive and negative values uniformly
Since $\mathcal{H} = p_x^2/2M$, $\langle p_x^2\rangle = 2M\langle E\rangle$. For the given eigenstate, $\langle E\rangle = (17)^2h^2/8Ma^2$
Therefore, $\langle p_x^2\rangle = 2M \bullet (17)^2h^2/8Ma^2 = (17)^2h^2/4a^2$
$\sigma_p = \{\langle p_x^2\rangle - \langle p_x\rangle^2\}^{1/2} = 17h/2a$

(c) A quantum particle of mass m in an infinite potential well between x = 0 and x = a is in a state described by function Ψ. Suppose the particle is twice as likely to be in its ground state than the next higher energy state.

Write down the appropriate wavefunction Ψ for this system. Normalize the wavefunction.

$\Psi = c_1\psi_1 + c_2\psi_2$ such that $c_1^2 + c_2^2 = 1$ applying superposition of states and normalization of the state function.
Given that $c_1^2 / c_2^2 = 2$.
$c_1^2 + c_2^2 = 2\,c_2^2 + c_2^2 = 1$. Thus, $3c_2^2 = 1$; $c_2^2 = (1/3)$; $c_2 = (1/\sqrt{3})$; $c_1^2 = (2/3)$; $c_1 = (2/3)^{1/2}$
$\Psi = (2/3)^{1/2}\psi_1 + (1/3)^{1/2}\psi_2 = (2/3)^{1/2}(2/a)^{1/2}\sin(1\pi x/a) + (1/3)^{1/2}(2/a)^{1/2}\sin(2\pi x/a)$

If the energy of this particle is measured, give a set of typical values that might be obtained in a series of six measurements. Only the eigenvalues can be the results of any measurement. Since $c_1^2 = (2/3)$ and $c_2^2 = (1/3)$ thus, we expect to get 2/3 of the time E_1 and 1/3 of the time, E_2.

$1h^2/8Ma^2$
$1h^2/8Ma^2$
$1h^2/8Ma^2$
$1h^2/8Ma^2$
$4h^2/8Ma^2$
$4h^2/8Ma^2$

What is the expected average of a series of 300,000 measurements?

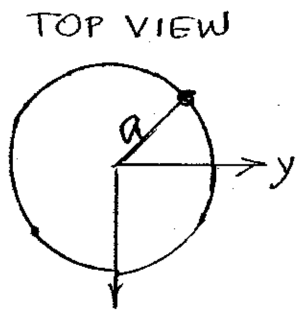
Using the expectation value postulate, $\langle E\rangle = \int_0^a \Psi^*\mathcal{H}\,\Psi dx = \int_0^a \Psi^*[-(\hbar^2/2M)(d^2/dx^2)]\,\Psi dx$

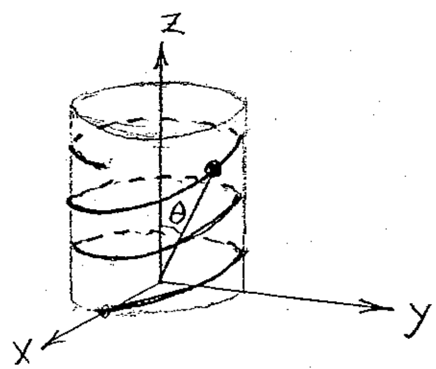
When we substitute $\Psi = c_1\psi_1 + c_2\psi_2$, where ψ_1 and ψ_2 are respectively the first and second eigenfunctions of energy, and are individually normalized, then
$\langle E\rangle = c_1^2E_1 + c_2^2 E_2$ will result from the integration.
$\langle E\rangle = \{(2/3)1^2 + (1/3)2^2\}(h^2/8Ma^2) = 2(h^2/8Ma^2)$.

2. The helix is a very important structure for biochemistry. At least some parts of important biological macromolecules have helical structure. In Problem Set 1 you could interpret the variation of the wavelength of the three bands in the ultraviolet spectrum of series of compounds containing aromatic rings by using the simple model of a particle on a circle.
It turns out that many qualitative aspects of the optical rotation spectra of helical systems can be interpreted entirely by using only the electron on a helix model system. Let us see how to start. We have solved several Schrödinger equations in only one variable, for a particle on a circle, as well as a particle on a line along the x axis. Now let us consider the case which is sort of a combination of the two, that is, we take the line and wrap it on the outside of a right circular cylinder to form a helix.

A particle of mass M is constrained to move along a right-handed helix consisting of t turns (shown below). The radius of the helix is a and the pitch of the helix (the distance between successive turns) is $b2\pi$. The position of the electron anywhere on the helix is given by:

$$x = a\cos\theta \qquad y = a\sin\theta \qquad z = b\theta$$





Since there are t turns, at the bottom end of the helix $\theta = 0°$
and at the top end of the helix $\theta = t(2\pi)$.
For a free particle constrained to move on this helix of t turns, we specify that V(x,y,z) = constant = 0 <u>on the helix</u> and V = ∞ everywhere else. Obviously a complicated V!
The kinetic energy of this single particle is of course, still given by

$$\text{K.E.} = p_x^2/2M + p_y^2/2M + p_z^2/2M$$

We replace the individual components of linear momentum by the corresponding <u>quantum mechanical operators</u>,

$(p_x)_{op} = (\hbar/i)\partial/\partial x$	$(p_y)_{op} = (\hbar/i)\partial/\partial y$	$(p_z)_{op} = (\hbar/i)\partial/\partial z$

Therefore, in terms of x,y and z, the <u>Hamiltonian operator</u> for this particle is

$$\mathcal{H} = -(\hbar^2/2M)(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V(x,y,z)$$

As we have already found in other simple systems such as the particle on a circle, it is possible to make use of a change in coordinate system to simplify the form of the Schrödinger equation that needs to be solved. For the particle on a circle, we changed coordinates from the set (x,y) into the set (R,ϕ). Since the radius R of the circle is a constant we solved a Schrödinger equation in ϕ only.

For the *particle on the helix*, instead of having the operators and the eigenfunctions in terms of three variables (x,y,z), we can use a transformation to the new coordinates (a,b,θ) defined above: $x = a\cos\theta$ $\quad y = a\sin\theta$ $\quad z = b\,\theta$

By varying a, b, and θ one could sweep all of 3-D space, but for the helix, a and b are constants. Thus, our operators and eigenfunctions can be written in terms of only one variable, θ. In other words, to locate the particle on the helix, we only need to know the value of θ. We express the derivatives with respect to x,y,z in terms of the derivatives with respect to a, b, and θ, and since a and b are constants for the helix, we afterwards leave out all derivatives $\partial^n/\partial a^n$, $\partial^n/\partial b^n$ from the Hamiltonian, that is, we can do the following:

$$\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \Rightarrow (a^2+b^2)^{-1}\,\partial^2/\partial\theta^2 \quad \text{for } a \text{ and } b \text{ are constants}$$

Thus, in terms of θ, the <u>Schrödinger equation</u> to be solved is (write the equation explicitly in terms of a, b, and θ):

$\{ - (\hbar^2/2M)\bullet (a^2+b^2)^{-1}\,\partial^2/\partial\theta^2 + 0 \}\,\Psi(\theta) = E\,\Psi(\theta)$

Examine the above Schrödinger equation for this system, and figure out what kind of function will satisfy this equation. Remember that this system is similar in some way to the particle on a line along the x axis from 0 to L, except that here the line is wound around the outside surface of a right circular cylinder.

Try $\Psi(\theta)$ of the form: $\quad A\sin(k\theta) + B\cos(k\theta)$

Substitute it into the Schrödinger equation and <u>establish whether it can satisfy the equation</u>.

$(\partial/\partial\theta)\sin(k\theta) = k\cos(k\theta)$; $\qquad (\partial/\partial\theta)\cos(k\theta) = -k\sin(k\theta)$

$(\partial^2/\partial\theta^2)\sin(k\theta) = -k^2\sin(k\theta)$; $\qquad (\partial^2/\partial\theta^2)\cos(k\theta) = -k^2\cos(k\theta)$

Substitute $\Psi(\theta) = A\sin(k\theta) + B\cos(k\theta)$ into the Schrödinger equation:

$\{ - (\hbar^2/2M)\bullet (a^2+b^2)^{-1}\,\partial^2/\partial\theta^2 \}\,[A\sin(k\theta) + B\cos(k\theta)] =\mathbf{?}\ E\,[A\sin(k\theta) + B\cos(k\theta)]$

$\text{LHS} = - (\hbar^2/2M)\bullet (a^2+b^2)^{-1}\,[A(-k^2)\sin(k\theta) + B(-k^2)\cos(k\theta)]$

$\quad = - (\hbar^2/2M)\bullet (a^2+b^2)^{-1}\,(-k^2)\,[A\sin(k\theta) + B\cos(k\theta)]$

$\text{RHS} = E\,[A\sin(k\theta) + B\cos(k\theta)]$ $\qquad$ YES! it satisfies the equation.

Note that this gives us $E = - (\hbar^2/2M)\bullet (a^2+b^2)^{-1}\,(-k^2)$

What are the conditions that a function describing the state of this physical system (the single particle of mass M on the helix) has to meet in order to be an acceptable description? Hint: The particle is not allowed to exist beyond either end of the helix.

In general	Explicitly, for this system*
State function has to be (a) finite	Since sin is between 1 and -1, cos is between 1 and -1, the function is finite.
(b) continuous	Since particle cannot exist beyond θ =0 end of the helix, Ψ=0 at $\theta < 0$ (negative values of θ). To be continuous, $\Psi(\theta=0)$ must= 0; [A sin(k•0) + Bcos(k•0)]=0. Since for any k sin(k•0)=0, we only have to set B=0 to make $\Psi(\theta=0) = 0$ Therefore, $\Psi(\theta)$ = A sin(kθ).
	Since particle cannot exist beyond θ =t2π end of the helix, Ψ=0 at $\theta >$ t2π. To be continuous, $\Psi(\theta= t2\pi)$ must= 0; $\Psi(\theta= t2\pi)$ = A sin(k•t2π) must = 0. This can only happen if (k•t2π) itself is (integer•π); call the integer n 2kt =1,2,3,4 ..., n ; or k = n/2t so that $\Psi(\theta)$ = A sin(nθ/2t).
(c) single-valued	This is satisfied, $\Psi(\theta)$ = A sin(nθ/2t) has only one value for any point on the helix; and from above, we have also made it single valued at θ=0 and at θ= t2π

*That is, apply each of the requirements of acceptable state functions in mathematical terms specific to this system (in terms of the constants *a*, *b*, *t*, and the variable θ).

Calculate the energy eigenvalues of this system in terms of the constants *a*, *b*, *t*

We already found that $E = -(\hbar^2/2M)\bullet(a^2+b^2)^{-1}(-k^2)$. Now that continuous condition has found for us that k = n/2t, substitution of this gives

$E = +(\hbar^2/2M)\bullet(a^2+b^2)^{-1}(n/2t)^2$

$E = +n^2\hbar^2/[8M(a^2+b^2)t^2]$

Specify the conditions that must be satisfied by the quantities appearing in your expression for the energy eigenvalue.

n must be an integer: n=1,2,3,...
n cannot be zero because this would make sin and there fore the wavefunction zero for all values of θ.

Normalize the function that satisfies the above conditions: $\Psi(\theta) = A \sin(n\theta/2t)$

$$\int_{\theta=0}^{\theta=t2\pi} A^2\sin^2(n\theta/2t)\, d\theta = 1; \qquad A^2\left[\frac{\theta}{2} - \frac{(\sin(n\theta/t))}{4\left(\frac{n}{2t}\right)}\right]_{\theta=0}^{\theta=t2\pi} = 1\ ; \qquad A^2[\, t2\pi/2] = 1\ ; \quad A = \{t\pi\}^{½}$$

Summarize: Explicitly write the 3 lowest energy eigenvalues and corresponding normalized eigenfunctions below:

quantum number	Energy eigenvalue	Eigenfunction $\Psi(\theta) = \{t\pi\}^{½} \bullet \sin(n\theta/2t)$
n=1	$1^2\hbar^2/[8M(a^2+b^2)t^2]$	$\Psi(\theta) = \{t\pi\}^{½} \bullet \sin(1\theta/2t)$
n=2	$2^2\hbar^2/[8M(a^2+b^2)t^2]$	$\Psi(\theta) = \{t\pi\}^{½} \bullet \sin(2\theta/2t)$
n=3	$3^2\hbar^2/[8M(a^2+b^2)t^2]$	$\Psi(\theta) = \{t\pi\}^{½} \bullet \sin(3\theta/2t)$

In this coordinate system, the z component of linear momentum is

$$(p_z)_{op} = (\hbar/\boldsymbol{i})\, b\, (a^2+b^2)^{-1}\, \partial/\partial\theta$$

For the system of a particle on a helix, determine whether $(p_z)_{op}$ commutes with $\mathcal{H}$

$[(p_z)_{op}, \mathcal{H}] = [(\hbar/\boldsymbol{i})\, b\, (a^2+b^2)^{-1}\, \partial/\partial\theta,\ -(\hbar^2/2M)\bullet (a^2+b^2)^{-1}\, \partial^2/\partial\theta^2] = 0$. YES they commute

What are the constraints, if any, on simultaneously measuring the energy and the z component of linear momentum for this system? Explain.

none. Heisenberg uncertainty principle states
$\sigma\, p_z \bullet \sigma_{\mathcal{H}} \geq ½ \langle [p_z, \mathcal{H}]/i \rangle$. Since $[p_z, \mathcal{H}] = 0$ the product of standard deviations in measurements of p_z and E is ≥ 0. There are no theoretical limits.

Calculate the expected average value of the outcomes of measurements of p_z on this system in its lowest energy state.

$$\langle p_z \rangle = \int_{\theta=0}^{\theta=t2\pi} \{t\pi\}^{½} \bullet \sin(1\theta/2t)\, (\hbar/\boldsymbol{i})\, b\, (a^2+b^2)^{-1}\, \partial/\partial\theta\, \{t\pi\}^{½} \bullet \sin(1\theta/2t)\, d\theta$$

$$= \{t\pi\}\bullet(\hbar/\boldsymbol{i})\, b\, (a^2+b^2)^{-1} \int_{\theta=0}^{\theta=t2\pi} \sin(\theta/2t)\, d/d\theta[\, \sin(\theta/2t)]$$

This is of the form $\int_{x=\sin(0)}^{x=\sin\pi} x\,dx = \left.\frac{x^2}{2}\right]_0^0 = 0$

$\langle p_z \rangle = 0$