Student Name____

Michigan State University

Chemistry 991 Fall 2008

Exam 2 KEY

17 November

I. (48 points)

A. What would be the problem with defining $\hat{x}\hat{p}$ as a quantum mechanical observable? How would you define an operator based on this one that would correspond to a quantum mechanical observable?

The operator would not be Hermitian; therefore, it cannot represent an observable.

To make it Hermitian, symmetrize it to $\left(\hat{x}\hat{p}+\hat{p}\hat{x}\right)/2$

B. What is the requirement on the operators that represent observables that lets them be simultaneously specified?

The operators representing the observables must commute.

C. Which complete set of functions would you use to expand some function $f\left(\theta,\varphi\right)$ on the unit sphere? How would you write this expansion? How are the coefficients defined?

Use the spherical harmonics.

$$f\left(\theta,\varphi\right)=\sum_{l,m} f_l^m Y_l^m\left(\theta,\varphi\right)$$

where the $f_l^m=\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\varphi Y{*}_l^m\left(\theta,\varphi\right) f\left(\theta,\varphi\right)$

D. When separating variables in three dimensions with a central potential, why are the corresponding energies independent of the ‘m’ quantum number?

The rotational symmetry of the problem is responsible.

E. Why is the matrix element $\langle \psi_E | a^+ a | \psi_E \rangle$ necessarily non-negative, where a and a^+ are lowering and raising operators and $|\psi_E\rangle$ is an eigenstate of the harmonic oscillator Hamiltonian?

It can be written as $\langle a\psi_E | a\psi_E \rangle$ using the adjoint character of these operators, and this is the scalar product of the same vector, that is necessarily non-negative.

F. What is the implication of the expression $Ha\psi_E = (E-1)a\psi_E$?

It states that $a\psi_E$ is an eigenstate of H with eigenvalue *E-1*. Thus, a can be viewed as a lowering operator.

G. For a time-independent operator, the time evolution of the expectation value of an operator *A* is

$$\frac{d}{dt}\langle \psi | A | \psi \rangle = \frac{i}{\hbar}\langle \psi | [H, A] | \psi \rangle$$

Show that this implies conservation of energy.

Set $A = H$. Since $[H, H] = 0$, $d\frac{\langle \psi | H | \psi \rangle}{dt} = 0$, so energy is conserved.

H. In solving the radial part of the Schrodinger equation for its bound states, by the series solution method, what (physical and mathematical) property is eventually responsible for obtaining a series with a finite number of terms?

The mathematical requirement is that the wavefunction is finite at infinity, and that reflects the physical requirement that the wavefunction be normalizable.

II. (26 points)

Show that the matrix elements x_{kn} and p_{kn} of the position and momentum operators for stationary states (thus using wavefunctions $|\psi_k\rangle$ for an energy representation) satisfy $\frac{(E_n - E_k)}{i\hbar} x_{kn} = \frac{1}{m} p_{kn}$ by considering matrix elements of the commutator $[\hat{H}, \hat{x}]$, where $\hat{H} = \hat{T} + \hat{V}$.

The identities $[\hat{x}, f(\hat{p})] = i\hbar \frac{df(\hat{p})}{d\hat{p}}$ and $[\hat{p}, f(\hat{x})] = -i\hbar \frac{df(\hat{x})}{d\hat{x}}$ may prove useful.

With $H = \frac{\hat{p}^2}{2m} + V(\hat{x})$, we consider $[H, \hat{x}]$:

$$[H, \hat{x}] = \left[\frac{\hat{p}^2}{2m}, \hat{x}\right] + [V, \hat{x}] = \frac{\hbar}{i}\frac{\hat{p}}{m} + 0.$$

Taking matrix elements, using $|\psi_k\rangle, |\psi_n\rangle$,

$$\langle\psi_k|[H, \hat{x}]|\psi_n\rangle = \frac{\hbar}{im}\langle\psi_k|\hat{p}|\psi_n\rangle.$$

This is

$$\{\langle\psi_k|H\rangle\}\hat{x}|\psi_n\rangle - \langle\psi_k|\hat{x}H|\psi_n\rangle = \frac{\hbar}{im} p_{kn},$$

using the definition of matrix element of an operator.

Now, $H|\psi_k\rangle = E_k|\psi_k\rangle \qquad H|\psi_n\rangle = E_n|\psi_n\rangle$,

so (remembering *H* is Hermitian so its eigenvalues are real),

$$E_k\langle\psi_k|\hat{x}|\psi_n\rangle - E_n\langle\psi_k|\hat{x}|\psi_n\rangle = \frac{\hbar}{im} p_{kn}.$$

We rearrange to

$$\frac{(E_n - E_k)}{i\hbar} x_{kn} = \frac{1}{m} p_{kn}.$$

III. (26 points)

A. Show that $\left[L^2, L_z\right] = 0$.

Recall that [AB,C] = [A,C]B + A[B,C].

$$\left[L^2, L_z\right] = \left[\left(L_x^2 + L_y^2 + L_z^2\right), L_z\right] = \left[L_x^2, L_z\right] + \left[L_y^2, L_z\right]$$

$$\text{Set}\left[L_x^2, L_z\right] = \left[L_x, L_z\right]L_x + L_x\left[L_x, L_z\right]$$

$$\left[L_y^2, L_z\right] = \left[L_y, L_z\right]L_y + L_y\left[L_y, L_z\right]$$

$$\left[L_y, L_z\right] = i\hbar L_x \qquad (x, y, z)(y, z, x)(z, x, y)$$

$$\left[L_x, L_z\right] = -i\hbar L_y$$

$$\left[L^2, L_z\right] = -i\hbar L_y L_x - i\hbar L_x L_y + i\hbar L_x L_y + i\hbar L_y L_x = 0.$$

B. Evaluate the expectation value of $L_z, L_x,$ and L_y in the L_z basis (where $L_z\left|m\right\rangle = \hbar m\left|m\right\rangle$).

(It's easiest to express $L_x = \left(L_+ + L_-\right)/2$ and $L_y = \left(L_+ - L_-\right)/2i$, in terms of raising $\left(L_+\right)$ and lowering $\left(L_-\right)$ operators.)

The expectation values are

$$\left\langle m\right|L_z\left|m\right\rangle = \hbar m\left\langle m|m\right\rangle = \hbar m$$

$$\left\langle m\right|L_x\left|m\right\rangle = \left\langle m\right|\left(L_+ + L_-\right)\left|m\right\rangle/2 = 0,$$

because $L_\pm$ are raising/lowering operators and give ~ $\left\langle m|m \pm 1\right\rangle = 0$ by orthogonality similar for L_y.