Chem 532: Problem Set #2

Due in class: Friday, Sept. 13th

(1) For an operator that does not explicitly depend on time, the time dependence of its expectation value is given by the Ehrenfest Theorem:

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

Show that the rate of change of the linear momentum is equal to the expectation value of the force, i.e., \( \frac{d \langle p_x \rangle}{dt} = \langle F_x \rangle \).

Take the hamiltonian \( H \) to be \( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \) and remember that \( F_x = -\frac{dV}{dx} \).

(2) Confirm that the operator \( l_z = \frac{\hbar}{i} \frac{d}{d\varphi} \) is hermitian. \textit{Hint:} Consider the integral 

\[ \int_0^{2\pi} \psi^*_a l_z \psi_b d\varphi \] 

and integrate by parts.

(3) If A and B are hermitian operators, prove

(a) that their product AB is hermitian only if A and B commute

(b) that \( \frac{1}{2} (AB + BA) \) is hermitian

(c) that \( A+iB \) and \( A-iB \) are not hermitian

(4) For a hydrogen atom in a \( p \) state, the possible outcomes of a measurement of \( L_z \) are \(-\hbar, 0, \) and \(+\hbar\) for \( p_{-1}, p_0, \) and \( p_1, \) respectively. In the case of a \( d \) state, the analogous outcomes are \(-2, -1, 0, +1, \) and \(+2\) in units of \( \hbar \) for \( m_l = -2 \) to \(+2, \) respectively. Suppose that at time \( t' \) a hydrogen atom is in a nonstationary state with

\[ \Psi = \frac{1}{\sqrt{6}} 2p_1 - \frac{i}{\sqrt{2}} 2p_0 - \frac{1}{\sqrt{3}} 3d_l \]

If \( L_z \) is measured at time \( t' \), give the possible outcomes and the probability of each possible outcome. What is the expectation value of \( L_z \) at time \( t' \)?
(5) Consider the normalized hydrogen atom wave functions
\[ 2p_{1} = \frac{-1}{8\sqrt{\pi}} \left( \frac{1}{a_{0}} \right)^{5/2} re^{-r/(2a_{0})} \sin \theta e^{i\phi} \]
\[ 2p_{-1} = \frac{1}{8\sqrt{\pi}} \left( \frac{1}{a_{0}} \right)^{5/2} re^{-r/(2a_{0})} \sin \theta e^{-i\phi} \]
\[ 2p_{x} = \frac{1}{\sqrt{2}} (2p_{-1} + 2p_{1}) = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_{0}} \right)^{5/2} re^{-r/(2a_{0})} \sin \theta \cos \phi \]
where \( a_{0} \) is a constant.
(a) Show that \( 2p_{x} \) and \( 2p_{1} \) are not orthogonal. (Note: \( 2p_{1} \) and \( 2p_{-1} \) are orthonormal)
(b) Use Schmidt orthogonalization to construct linear combinations that will be orthogonal and then normalize these functions.
Note: there is an easy way and a hard way to do parts a and b. \( \wedge^{+) \)

(6) In the case where the hamiltonian \( H \) is independent of time, any stationary state solution of the time dependent Schrödinger equation can be exactly expanded as
\[ \Psi = \sum_{n} c_{n} \Psi_{n} = \sum_{n} c_{n} e^{-iE_{n}t/\hbar} \psi_{n}(q) \]
where \( \psi_{n}(q) \) are solutions to the time independent Schrödinger equation with possible eigenvalues \( E_{n} \).
(a) What is the probability of obtaining a particular \( E_{n} \) in a measurement of the energy in the state \( \Psi \)?
(b) A particle in a 1-dimensional box of length \( L \) has a time-independent hamiltonian and has the wavefunction \( \Psi = \frac{1}{\sqrt{2}} \psi_{1} + \frac{1}{\sqrt{2}} \psi_{2} \) at time \( t=0 \), where \( \psi_{1} \) and \( \psi_{2} \) are the usual particle-in-a-box time-independent eigenfunctions with \( n=1 \) and \( n=2 \), respectively. What is the form of the wavefunction \( \Psi \) at time \( t=t' \)?
(c) Show that the probability density for this state at time \( t \) is equal to
\[ \frac{1}{2} \psi_{1}^{2} + \frac{1}{2} \psi_{2}^{2} + \psi_{1} \psi_{2} \cos \left[ (E_{2} - E_{1})t / \hbar \right] \]