Michigan State University Fall 2008
Chemistry 991

Practice Exam

I.. (48 points)

A. Can all wavefunctions be normalized? If not, why not.

Clearly not. If we have plane waves, they do not vanish at infinity sufficiently fast to converge their integrals.

B. Provide the analogy of Newton's equations of motion in Quantum Mechanics.

Newton's eoms hold for the expectation values of the corresponding quantities; i. e., the time derivative of the expectation value of the momentum equals the expectation value of the force.

C. For a potential barrier of the form $V(x) = \begin{Bmatrix} V_0 & for\,|x|<L \\ 0 & for\,|x|>L \end{Bmatrix}$ ($V_0 > 0$) indicate the general nature of the wavefunctions in the two space ranges when $E > V_0$.

For $E > V_0$, inside the barrier region $|x| < L$ the solutions must be oscillating, so a linear combo of $\exp(\pm i\kappa x)$, with $\kappa \sim \sqrt{E - V_0}$. Outside, a linear combo of oscillations, $\exp(\pm ikx)$, with $k \sim \sqrt{E}$.

D. If a matrix A with elements A_{nm} is Hermitian what does that require of the matrix elements?

$A_{nm} = (A_{mn})^*$

E. Write the orthonormality and completeness (closure) relations.

orthonormality $\int dx\psi_n^*(x)\psi_m(x) = \delta_{nm}$

completeness $\sum_n \psi_n^*(x)\psi_n^*(x') = \delta(x - x')$

F. If we have a Gaussian wavefunction in coordinate space with width parameter σ, what does that imply about the corresponding momentum space wavefunction? What does that say about the Heisenberg uncertainty principle?

The corresponding *k*-space wavefunction is also a Gaussian but with width parameter $1/\sigma$. Uncertainty principle says $\Delta x \Delta p \geq \hbar$. If $\Delta x = \sigma$ and $\Delta p = \hbar \Delta k$, then $\Delta x \Delta p = \sigma(\hbar/\sigma) = \hbar$, so agrees.

H. Define the term "stationary state" and state the condition that leads to it.

One that is independent of time. It comes about from only one quantum state being populated.

II. (27 points)

A. Evaluate the probability current

$$j(x,t)=\frac{\hbar}{2mi}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)$$

for the wavefunction
$\psi(x,t)=\left[Ae^{ipx/\hbar}+Be^{-ipx/\hbar}\right]e^{-ip^2t/2m\hbar}$.

B. Interpret the answer.

A. The complex conjugate of ψ is $\psi^*(x,t)=\left(A^*e^{-ipx/\hbar}+B^*e^{+ipx/\hbar}\right)e^{ip^2t/2m\hbar}$; so a direct calculation yields

$$j(x,t)=\frac{\hbar}{2mi}\left[\begin{array}{l}\left(A^*e^{-ipx/\hbar}+B^*e^{+ipx/\hbar}\right)\left(\frac{ip}{\hbar}Ae^{+ipx/\hbar}-\frac{ip}{\hbar}Be^{-ipx/\hbar}\right)\\ -\left(-\frac{ip}{\hbar}A^*e^{-ipx/\hbar}+\frac{ip}{\hbar}B^*e^{+ipx/\hbar}\right)\left(Ae^{+ipx/\hbar}+Be^{-ipx/\hbar}\right)\end{array}\right]$$

$$=\frac{pi}{2mi}\left[\left(|A|^2-A^*Be^{-2ipx/\hbar}+AB^*e^{+2ipx/\hbar}-|B|^2\right)-\left(-|A|^2-A^*Be^{-2ipx/\hbar}+AB^*e^{+2ipx/\hbar}+|B|^2\right)\right]$$

$$=\frac{p}{m}\left(|A|^2-|B|^2\right).$$

B. The wave function $\psi(x,t)$ expresses a superposition of two currents of particles moving in opposite directions. Each of the currents is constant and time-independent in its magnitude. The term $e^{-ip^2t/2m\hbar}$ implies that the particles are of energy $p^2/2m$. The amplitudes of the currents are *A* and *B*.

III. (25 points)

Show that the expectation value

$$\left\langle \psi(x,t) \middle| \hat{H}^{\ell} \middle| \psi(x,t) \right\rangle$$

equals

$$\sum_n |a_n|^2 E_n^l, \text{where } a_n \equiv a_n(0)$$

by expanding the wavefunction in an energy basis.

Write $\psi(x,t) = \sum_n a_n(t)\psi_n(x)$, where

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \qquad \text{(energy basis).}$$

Substitute in

$$I \equiv \left\langle x(x,t) \middle| \hat{H}^{\ell} \middle| \psi(x,t) \right\rangle = \int dx \psi^*(x,t) \hat{H}^{\ell} \psi(x,t)$$
$$= \sum_n \sum_{n'} a_n^*(t) \int dx \psi_n^*(x) \hat{H}^{\ell} \psi_{n'}(x).$$

Now,

$$\hat{H}^{\ell}\psi_{n'}(x) = \hat{H}^{\ell-1}\hat{H}\psi_{n'}(x) = \hat{H}^{\ell-1}E_{n'}\psi_{n'}(x)$$
$$= E_{n'}\hat{H}^{\ell-1}\psi_{n'}(x) = \ldots = E_n^{\ell}\psi_{n'}(x).$$

Thus,

$$I = \sum_n \sum_{n'} a_n^*(t) a_{n'}(t) E_{n'}^{\ell} \int dx \psi_n^*(x) \psi_{n'}(x)$$
$$= \sum_n \sum_{n'} a_n^*(t) a_{n'}(t) E_{n'}^{\ell} \; \delta_{nn'} \qquad \text{(orthonormality)}$$
$$= \sum_n E_n^{\ell} a_n^*(t) a_n(t).$$

But,

$$a_n^*(t) = e^{iE_n t/\hbar} a_n(0) \qquad a_n(t) = e^{-iE_n t/\hbar} a_n(0), \text{ so}$$
$$I = \sum_n E_n^{\ell} |a_n(0)|^2.$$