Fall 2011 CHEM 760: Introductory Quantum Chemistry

Homework 2

1. Show that $(\cos ax)(\cos by)(\cos cz)$ is an eigenfunction of the operator

   $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

   which is called the Laplacian operator.

2. We just learned that if φ_n is an eigenfunction for the time-independent Schrödinger equation, then

   $$\Psi_n(x,t) = \varphi_{n(x)} e^{-iE_n t/\hbar}$$

   Show that if $\varphi_{n(x)}$ and $\varphi_{m(x)}$ are both stationary states of $\hat{H}$, then the state

   $$\Psi(x,t) = c_n \varphi_{n(x)} e^{-iE_n t/\hbar} + c_m \varphi_{m(x)} e^{-iE_m t/\hbar}$$

   satisfies the time-dependent Schrödinger equation.

3. Show that the probability associated with the sate ψ_n for a particle in a one-dimensional box of length a obeys the following relationships:

   $$Prob\left(0 \le x \le \frac{a}{4}\right) = Prob\left(\frac{3a}{4} \le x \le a\right) = \begin{cases} \frac{1}{4},\ n\ even \\ \frac{1}{4} - \frac{(-1)^{\frac{n-1}{2}}}{2\pi n},\ n\ odd \end{cases}$$

   $$Prob\left(\frac{a}{4} \le x \le \frac{a}{2}\right) = Prob\left(\frac{a}{2} \le x \le \frac{3a}{4}\right) = \begin{cases} \frac{1}{4},\ n\ even \\ \frac{1}{4} + \frac{(-1)^{\frac{n-1}{2}}}{2\pi n},\ n\ odd \end{cases}$$

4. What are the units, if any, for the wave function of a particle in a one-dimensional box?
5. We just discussed in class the values of $\langle x \rangle$, $\langle x^2 \rangle$ and σ_x for a quantum-mechanical particle in a box. For comparison, a classical particle in a box has an equal-likehood of being found anywhere within the region of $0 \le x \le a$. Consequently, its probability distribution is

   $$p(x)dx = \frac{1}{a}dx, 0 \le x \le a$$

   a) Calculate $\langle x \rangle$, $\langle x^2 \rangle$ and σ_x for the classical particle.
   b) Show that in the limit as $n \to \infty$, the quantum mechanical results are taken on the classical values.
6. Show that the particle-in-box wave functions satisfies the orthonormal relation

   $$\int_0^a \psi_m^*(x)\psi_n(x)dx = \delta_{mn}$$

   Hint: Using the trigonometric identity $sin\alpha sin\beta = \frac{1}{2}\cos(\alpha - \beta) - \frac{1}{2}\cos(\alpha + \beta)$
7. The Schrödinger equation for a particle of mass *m* constrained to move on a ring of radius *a* is

   $$-\frac{\hbar}{2I}\frac{d^2\psi}{d\theta^2} = E\psi(\theta),\ 0 \le \theta \le 2\pi$$

where $I = ma^2$ is the moment of inertia and θ is the angle that describes the position of the particle around the ring.

a) Show that the eigenfunctions to this equation are

$\psi(\theta) = Ae^{in\theta}$, where $n = \pm(2IE)^{1/2}/\hbar$

b) Argue that the appropriate condition is $\psi(\theta) = \psi(\theta + 2\pi)$ and use this condition to show that

$E_n = \frac{n^2\hbar^2}{2I}, n = 0, \pm1, \pm2, \ldots$

c) Calculate the normalization constant A.

8. In class we applied the equation for a particle in a box to the π electrons in butadiene. This model is called the free-electron model. Using the same argument, show that the length of hexatriene can be estimated to be 867 pm. Show that the first electronic transition is predicted to occur at 2.8×10^4 cm^{-1}.

9. What are the degeneracies of the first four energy levels for a particle in a three-dimensional box with a = b = 1.5c?