量子化学作业 第三章 （2017-2018 学期）

3-3. In each case, show that $f(x)$ is an eigenfunction of the operator given. Find the eigenvalue.

$\hat{A}$	$f(x)$
$(a)\dfrac{d^2}{dx^2}$	$\cos\omega x$
$(b)\dfrac{d}{dt}$	$e^{i\omega t}$
$(c)\dfrac{d^2}{dx^2}+2\dfrac{d}{dx}+3$	$e^{\alpha x}$
$(d)\dfrac{\partial}{\partial y}$	x^2e^{6y}

3- 5. Write out the operator $\hat{A}^2$ for $\hat{A}=$

$$(a)\frac{d^2}{dx^2} \qquad (\mathrm{b})\frac{d}{dx}+x \qquad (\mathrm{c})\frac{d^2}{dx^2}-2x\frac{d}{dx}+1$$

Hint: Be sure to include $f(x)$ before carrying out the operations.

3-9. In Section 3.5, we applied the equations for a particle in a box to the TC electrons in butadiene. This simple 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 $2.8 \times 10^4 cm^{-1}$. (Remember that hexatriene has six π electrons.)

3-10. Prove that if $\psi(x)$ is a solution to the Schrodinger equation, then any constant times of $\psi(x)$ is also a solution.

3-13. What are the units, if any, for the wave function of a particle in a one-dimensional box?

3-15. Show that

$$< x >= \frac{a}{2}$$

for all the states of a particle in a box. Is this result physically reasonable?

3-18. A classical particle in a box has an equi-likelihood of being found anywhere within the region $0 \le x \le a$. Consequently, its probability distribution is

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

Show that $< x > \, = a/2$ and $< x^2 > \, = a^2/3$ for this system. Now show that $< x^2 >$ (Equation 3.32) and σ_x (Equation 3.33) for a quantum-mechanical particle in a box take on the classical values as $n \to \infty$. This result is an example of the *correspondence principle.*

3-21. Using the trigonometric identity

$$\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$$

show that the particle-in-a-box wave functions (Equations 3.27) satisfy the relation

$$\int_0^a \psi_n^*(x)\psi_m(x)dx = 0 \qquad m \neq n$$

(The asterisk in this case is superfluous because the functions are real.) If a set of functions satisfies the above integral condition, we say that the set is orthogonal and, in particular, that $\psi_m(x)$ is *orthogonal* to $\psi_n(x)$. If, in addition, the functions are normalized, then we say that the set is *orthonormal*.

3-25. In going from Equation 3.34 to 3.35, we multiplied Equation 3.34 from the left by $\psi(x)$ and then integrated over all values of x to obtain Equation 3.35. Does it make any difference whether we multiplied from the left or the right?

3-26. Calculate $<x>$ and $<x^2>$ for the $n=2$ state of a particle in a one-dimensional box of length a. Show that

$$\sigma_x = \frac{a}{4\pi}\left(\frac{4\pi^2}{3} - 2\right)^{1/2}$$

3-31. Show that $<\mathbf{p}>=0$ for the ground state of a particle in a three-dimensional box with sides of length a, b, and c.

3-33. The Schrodinger equation for a particle of mass m constrained to move on a circle of radius a is

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

where $I=ma^2$ is the moment of inertia and θ is the angle that describes the position of the particle around the ring. Show by direct substitution that the solutions to this equation are

$$\psi(\theta)=Ae^{in\theta}$$

where $n=\pm(2IE)^{1/2}/\hbar$. Argue that the appropriate boundary condition is $\psi(x)=\psi(x+2\pi)$ and use this condition to show that

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

Show that the normalization constant A is $(2\pi)^{1/2}$. Discuss how you might use these results for a free-electron model of benzene.

C-10. Using Equation C.16, prove that $\mathbf{u} \times \mathbf{v}$ is given by Equation C. 17.

C-11. Show that $l = |\mathbf{l}| = mvr$ for circular motion.

C-12. Show that

$$\frac{d}{dt}(\mathbf{u} \cdot \mathbf{v}) = \frac{d\mathbf{u}}{dt}\mathbf{v} + \mathbf{u}\frac{d\mathbf{v}}{dt}$$

and

$$\frac{d}{dt}(\mathbf{u} \times \mathbf{v}) = \frac{d\mathbf{u}}{dt} \times \mathbf{v} + \mathbf{u} \times \frac{d\mathbf{v}}{dt}$$

C-13. Using the results of Problem C- 12, prove that

$$\mathbf{u}\times\frac{d^2\mathbf{u}}{dt^2}=\frac{d}{dt}(\mathbf{u}\times\frac{d\mathbf{u}}{dt})$$

（以下题目选做）

3-35. The quantized energies of a particle in a box result from the boundary conditions, or from tl1e fact that the particle is restricted to .a finite region. In this problem, we investigate the quantum-mechanical problem of a free particle, one that is not restricted to a finite region. The potential energy $V(x)$ is equal to zero and the Schrodinger equation is

$$\frac{d^2\psi}{dx^2}+\frac{2mE}{\hbar^2}\psi(x)=0 \qquad -\infty<x<\infty$$

Note that the particle can lie anywhere along the x axis in this problem. Show that the two solutions of this Schrodinger equation are

$$\psi_1(x)=A_1e^{i(2mE)^{1/2}x/\hbar}=A_1e^{ikx}$$

And

$$\psi_2(x)=A_2e^{-i(2mE)^{1/2}x/\hbar}=A_2e^{-ikx}$$

Where

$$k=\frac{(2mE)^{1/2}}{\hbar}$$

Show that if E is allowed to take on negative values, then the wave functions become unbounded for large x . Therefore, we will require that the energy, E , be a positive quantity.

To get a physical interpretation of the states that $\psi_1(x)$ and $\psi_2(x)$ describe, operate on $\psi_1(x)$ and $\psi_2(x)$ with the momentum operator $\hat{P}$ (Equation 3.11), and show that

$$\hat{P}\psi_1 = -i\hbar\frac{d\psi_1}{dx} = \hbar k\psi_1$$

And

$$\hat{P}\psi_2 = -i\hbar\frac{d\psi_2}{dx} = -\hbar k\psi_2$$

Notice that these are eigenvalue equations. Our interpretation of these two equations is that ψ_1 describes a free particle with fixed momentum $\hbar k$ and that ψ_2 describes a particle with fixed momentum $-\hbar k$. Thus, ψ_1 describes a particle moving to the right and ψ_2 describes a particle moving to the left, both with a fixed momentum. Notice also that there are no restrictions on k , and so the particle can have any value of momentum. Now show that

$$E = \frac{\hbar^2 k^2}{2m}$$

Notice that the energy is not quantized; the energy of the particle can have any positive value in this case because no boundaries are associated with this problem.

Last, show that $\psi_1^*(x)\psi_1(x) = A_1^*A_1 = |A_1|^2 = \text{constant}$, and that $\psi_2^*(x)\psi_2(x) = A_2^*A_2 = |A_2|^2 = \text{constant}$. Discuss this result in terms of the probabilistic interpretation of $\psi^*\psi$. Also discuss the application of the uncertainty principle to this problem. What are σ_x and σ_p ?

(Hint: Refer to the given reference book, < Quantum Chemistry>, Levine)

3-39. We can use the following wave function to illustrate some fundamental symmetry properties of wave functions:

$$\psi_n = \begin{cases} \dfrac{1}{a^{1/2}} \sin \dfrac{n\pi x}{2a} & n \text{ even} \\ \dfrac{1}{a^{1/2}} \cos \dfrac{n\pi x}{2a} & n \text{ odd} \end{cases} \qquad (-a < x < a)$$

Show that the wave functions are alternately symmetric and antisymmetric or even and odd with respect to the operation $x \to -x$, which is a reflection through the $x = 0$ line. This symmetry property of the wave function is a consequence of the symmetry of the Hamiltonian operator, as we shall now show. The Schrodinger equation may be written as

$$\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$$

Reflection through the $x = 0$ line gives $x \to -x$, and so,

$$\hat{H}(-x)\psi_n(-x) = E_n\psi_n(-x)$$

Now show that if the potential energy $V(x)$ is even, then $\hat{H}(x) = \hat{H}(-x)$ (i.e., that $\hat{H}$ is symmetric), and so show that

$$\hat{H}(x)\psi_n(-x) = E_n\psi_n(-x)$$

Thus, we see that $\psi_n(-x)$ is also an eigenfunction of $\hat{H}$ belonging to the same eigenvalue E_n. Now, if there is only one eigenfunction associated with each eigenvalue (we call this a nondegenerate case), then argue that $\psi_n(x)$ and $\psi_n(-x)$ must differ by a multiplicative constant [i.e., that $\psi_n(-x) = c\psi_n(x)$]. By applying the inversion operation again to this equation, show that $c = \pm 1$ and that all the wave functions must be either even or odd with respect to reflection through the $x = 0$ line because the Hamiltonian operator is symmetric. Thus, we see that the symmetry of the Hamiltonian operator influences the symmetry of the wave functions.