

## 22.1.3: iii. Problems 1-10

### Q1

A particle of mass  $m$  moves in a one-dimensional box of length  $L$ , with boundaries at  $x = 0$  and  $x = L$ . Thus,  $V(x) = 0$  for  $0 \leq x \leq L$ , and  $V(x) = \infty$ . The normalized eigenfunctions of the Hamiltonian for this system are given by  $\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$ , with  $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$ , where the quantum number  $n$  can take on the values  $n=1,2,3,\dots$

- Assuming that the particle is in an eigenstate,  $\Psi_n(x)$ , calculate the probability that the particle is found somewhere in the region  $0 \leq x \leq \frac{L}{4}$ . Show how this probability depends on  $n$ .
- For what value of  $n$  is there the largest probability of finding the particle in  $0 \leq x \leq \frac{L}{4}$ ?
- Now assume that  $\Psi$  is a superposition of two eigenstates,  $\Psi = a\Psi_n + b\Psi_m$ , at time  $t = 0$ . What is  $\Psi$  at time  $t$ ? What energy expectation value does  $\Psi$  have at time  $t$  and how does this relate to its value at  $t = 0$ ?
- For an experimental measurement which is capable of distinguishing systems in state  $\Psi_n$  from those in  $\Psi_m$ , what fraction of a large number of systems each described by  $\Psi$  will be observed to be in  $\Psi_n$ ? What energies will these experimental measurements find and with what probabilities?
- For those systems originally in  $\Psi = a\Psi_n + b\Psi_m$  which were observed to be in  $\Psi_n$  at time  $t$ , what state ( $\Psi_n$ ,  $\Psi_m$ , or whatever) will they be found in if a second experimental measurement is made at a time  $t'$  later than  $t$ ?
- Suppose by some method (which need not concern us at this time) the system has been prepared in a nonstationary state (that is, it is not an eigenfunction of  $\mathbf{H}$ ). At the time of a measurement of the particle's energy, this state is specified by the normalized wavefunction  $\Psi = \sqrt{\frac{30}{L^5}} x(L-x)$  for  $0 \leq x \leq L$ , and  $\Psi = 0$  elsewhere. What is the probability that a measurement of the energy of the particle will give the value  $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$  for any given value of  $n$ ?
- What is the expectation value of  $\mathbf{H}$ , i.e. the average energy of the system, for the wavefunction  $\Psi$  given in part f?

### Q2

Show that for a system in a non-stationary state,  $\Psi = \sum_j C_j \Psi_j e^{-\frac{iE_j t}{\hbar}}$ , the average value of the energy does **not** vary with time but the expectation values of other properties **do** vary with time.

### Q3

A particle is confined to a one-dimensional box of length  $L$  having infinitely high walls and is in its lowest quantum state. Calculate:  $\langle x \rangle$ ,  $\langle x^2 \rangle$ ,  $\langle p \rangle$ , and  $\langle p^2 \rangle$ . Using the definition  $\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$ , to define the uncertainty,  $\Delta A$ , calculate  $\Delta x$  and  $\Delta p$ . Verify the Heisenberg uncertainty principle that  $\Delta x \Delta p \geq \frac{\hbar}{2}$ .

It has been claimed that as the quantum number  $n$  increases, the motion of a particle in a box becomes more classical. In this problem you will have an opportunity to convince yourself of this fact.

- For a particle of mass  $m$  moving in a one-dimensional box of length  $L$ , with ends of the box located at  $x = 0$  and  $x = L$ , the classical probability density can be shown to be independent of  $x$  and given by  $P(x)dx = \frac{dx}{L}$  regardless of the energy of the particle. Using this probability density, evaluate the probability that the particle will be found within the interval from  $x = 0$  to  $x = \frac{L}{4}$ .
- Now consider the quantum mechanical particle-in-a-box system. Evaluate the probability of finding the particle in the interval from  $x = 0$  to  $x = \frac{L}{4}$  for the system in its  $n$ th quantum state.
- Take the limit of the result you obtained in part b as  $n \rightarrow \infty$ . How does your result compare to the classical result you obtained in part a?

### Q5

According to the rules of quantum mechanics as we have developed them, if  $\Psi$  is the state function, and  $\phi_n$  are the eigenfunctions of a linear, Hermitian operator,  $\mathbf{A}$ , with eigenvalues  $a_n$ ,  $\mathbf{A}\phi_n = a_n\phi_n$ , then we can expand  $\Psi$  in terms of the complete set of

eigenfunctions of  $\mathbf{A}$  according to  $\Psi = \sum_n c_n \phi_n$ , where  $c_n = \int \phi_n^* \Psi d\tau$ . Furthermore, the probability of making a measurement of the property corresponding to  $\mathbf{A}$  and obtaining a value  $a_n$  is given by  $|c_n|^2$ , provided both  $\Psi$  and  $\phi_n$  are properly normalized. Thus,  $P(a_n) = |c_n|^2$ . These rules are perfectly valid for operators which take on a discrete set of eigenvalues, but must be generalized for operators which can have a continuum of eigenvalues. An example of this latter type of operator is the momentum

operator,  $\mathbf{p}(-x)$ , which has eigenfunctions given by  $\phi_p(x) = A e^{\frac{ipx}{\hbar}}$  where  $p$  is the eigenvalue of the  $\mathbf{p}_x$  operator and  $A$  is a normalization constant. Here  $p$  can take on any value, so we have a continuous spectrum of eigenvalues of  $\mathbf{p}_x$ . The obvious generalization to the equation for  $\Psi$  is to convert the sum over discrete states to an integral over the continuous spectrum of states:

$$\Psi(x) = \int_{-\infty}^{+\infty} C(p) \phi_p(x) dp = \int_{-\infty}^{+\infty} C(p) A e^{\frac{ipx}{\hbar}} dp$$

The interpretation of  $C(p)$  is now the desired generalization of the equation for the probability  $P(p)dp = |C(p)|^2 dp$ . This equation states that the probability of measuring the momentum and finding it in the range from  $p$  to  $p+dp$  is given by  $|C(p)|^2 dp$ .

Accordingly, the probability of measuring  $p$  and finding it in the range from  $p_1$  to  $p_2$  is given by  $\int_{p_1}^{p_2} P(p) dp = \int_{p_1}^{p_2} C(p)^* C(p) dp$ .

$C(p)$  is thus the probability amplitude for finding the particle with momentum between  $p$  and  $p+dp$ . This is the **momentum representation** of the wavefunction. Clearly we must require  $C(p)$  to be normalized, so that  $\int_{-\infty}^{+\infty} C(p)^* C(p) dp = 1$ . With this

restriction we can derive the normalization constant  $A = \frac{1}{\sqrt{\pi\hbar}}$ , giving a direct relationship between the wavefunction in coordinate space,  $\Psi(x)$ , and the wavefunction in momentum space,  $C(p)$ :

$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} C(p) e^{\frac{ipx}{\hbar}} dp,$$

and by the Fourier integral theorem:

$$C(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x) e^{\frac{ipx}{\hbar}} dx.$$

Lets use these ideas to solve some problems focusing our attention on the harmonic oscillator; a particle of mass  $m$  moving in a one-dimensional potential described by  $V(x) = \frac{kx^2}{2}$ .

- Write down the Schrödinger equation in the coordinate representation.
- Now lets proceed by attempting to write the Schrödinger equation in the momentum representation. Identifying the kinetic energy operator  $\mathbf{T}$ , in the momentum representation is quite straitforward  $\mathbf{T} = \frac{\mathbf{p}^2}{2m} = -\text{Error!}$ . Writing the potential,  $V(x)$ , in the momentum representation is not quite as straightforward. The relationship between position and momentum is realized in their commutation relation  $[\mathbf{x}, \mathbf{p}] = i\hbar$ , or  $(\mathbf{x}\mathbf{p} - \mathbf{p}\mathbf{x}) = i\hbar$ . This commutation relation is easily verified in the coordinate representation leaving  $\mathbf{x}$  untouched ( $\mathbf{x} = x$ ) and using the above definition for  $\mathbf{p}$ . In the momentum representation we want to leave  $\mathbf{p}$  untouched ( $\mathbf{p} = p$ ) and define the operator  $\mathbf{x}$  in such a manner that the commutation relation is still satisfied. Write the operator  $\mathbf{x}$  in the momentum representation. Write the full Hamiltonian in the momentum representation and hence the Schrödinger equation in the momentum representation.
- Verify that  $\Psi$  as given below is an eigenfunction of the Hamiltonian in the coordinate representation. What is the energy of the system when it is in this state? Determine the normalization constant  $C$ , and write down the normalized ground state wavefunction in coordinate space.

$$\Psi(x) = C e^{\left(-\sqrt{mk} \frac{x^2}{2\hbar}\right)}.$$

d. Now consider  $\Psi$  in the momentum representation. Assuming that an eigenfunction of the Hamiltonian may be found of the form  $\Psi(p) = Ce^{-\alpha p^2}$ , substitute this form of  $\Psi$  into the Schrödinger equation in the momentum representation to find the value of  $\alpha$  which makes this an eigenfunction of  $\mathbf{H}$  having the same energy as  $\Psi(x)$  had. Show that this  $\Psi(p)$  is the proper fourier transform of  $\Psi(x)$ . The following integral may be useful:

$$\int_{-\infty}^{+\infty} e^{-\beta x^2} \cos(bx) dx = \sqrt{\frac{\pi}{\beta}} e^{-\frac{b^2}{4\beta}}.$$

since this Hamiltonian has no degenerate states, you may conclude that  $\Psi(x)$  and  $\Psi(p)$  represent the same state of the system if they have the same energy.

## Q6

The energy states and wavefunctions for a particle in a 3-dimensional box whose lengths are  $L_1, L_2$ , and  $L_3$  are given by

$$E(n_1, n_2, n_3) = \frac{h^2}{8m} \left[ \left( \frac{n_1}{L_1} \right)^2 + \left( \frac{n_2}{L_2} \right)^2 + \left( \frac{n_3}{L_3} \right)^2 \right] \text{ and}$$

$$\Psi(n_1, n_2, n_3) = \sqrt{\frac{2}{L_1}} \sqrt{\frac{2}{L_2}} \sqrt{\frac{2}{L_3}} \sin \left( \frac{n_2 \pi y}{L_2} \right) \sin \left( \frac{n_3 \pi z}{L_3} \right).$$

These wavefunctions and energy levels are sometimes used to model the motion of electrons in a central metal atom (or ion) which is surrounded by six ligands.

- Show that the lowest energy **level** is nondegenerate and the second energy **level** is triply degenerate if  $L_1 = L_2 = L_3$ . What values of  $n_1, n_2$ , and  $n_3$  characterize the **states** belonging to the triply degenerate level?
- For a box of volume  $V = L_1 L_2 L_3$ , show that for three electrons in the box (two in the nondegenerate lowest "orbital", and one in the next), a lower **total** energy will result if the box undergoes a rectangular distortion ( $L_1 = L_2 \neq L_3$ ). **which preserves the total volume** than if the box remains undistorted (hint: if  $V$  is fixed and  $L_1 = L_2$ , then  $L_3 = \frac{V}{L_1^2}$  and  $L_1$  is the only "variable").
- Show that the degree of distortion (ratio of  $L_3$  to  $L_1$ ) which will minimize the total energy is  $L_3 = \sqrt{2} L_1$ . How does this problem relate to Jahn-Teller distortions? Why (in terms of the property of the central atom or ion) do we do the calculation with fixed volume?
- By how much (in eV) will distortion lower the energy (from its value for a cube,  $L_1 = L_2 = L_3$ ) if  $V = 8 \text{ \AA}^3$  and  $\frac{h^2}{8m} = 6.01 \times 10^{-27} \text{ erg cm}^2$ .  $1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg}$

## Q7

The wavefunction  $\Psi = Ae^{-a|x|}$  is an exact eigenfunction of some one-dimensional Schrödinger equation in which  $x$  varies from  $-\infty$  to  $+\infty$ . The value of  $a$  is:  $a = (2\text{\AA})^{-1}$ . For now, the potential  $V(x)$  in the Hamiltonian  $\left( \text{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right)$  for which  $\Psi(x)$  is an eigenfunction is unknown.

- Find a value of  $A$  which makes  $\Psi(x)$  normalized. Is this value unique? What units does  $\Psi(x)$  have?
- Sketch the wavefunction for positive and negative values of  $x$ , being careful to show the behavior of its slope near  $x = 0$ . Recall that  $|x|$  is defined as:

$$|x| = \begin{cases} x & \text{if } x > 0 \\ -x & \text{if } x < 0 \end{cases}$$

- Show that the derivative of  $\Psi(x)$  undergoes a discontinuity of magnitude  $2\sqrt{a}$  as  $x$  goes through  $x = 0$ . What does this fact tell you about the potential  $V(x)$ ?
- Calculate the expectation value of  $|x|$  for the above normalized wavefunction (obtain a numerical value and give its units). What does this expectation value give a measure of?

- e. The potential  $V(x)$  appearing in the Schrödinger equation for which  $\Psi = Ae^{-a|x|}$  is an exact solution is given by  $V(x) = \frac{\hbar^2 a}{m} \delta(x)$ . Using this potential, compute the expectation value of the Hamiltonian  $\left( \mathbf{H} = -\frac{\hbar}{2m} \frac{d^2}{dx^2} + V(x) \right)$  for your normalized wavefunction. Is  $V(x)$  an attractive or repulsive potential? Does your wavefunction correspond to a bound state? Is  $\langle H \rangle$  use  $\frac{\hbar^2}{2m} = 6.06 \times 10^{-28} \text{ erg cm}^2$  and  $1\text{eV} = 1.6 \times 10^{-12} \text{ erg}$ .
- f. Transform the wavefunction,  $\Psi = Ae^{-a|x|}$ , from coordinate space to momentum space.
- g. What is the ratio of the probability of observing a momentum equal to  $2a\hbar$  to the probability of observing a momentum equal to  $-a\hbar$ ?

## Q8

The  $\pi$ -orbitals of benzene,  $C_6H_6$ , may be modeled very crudely using the wavefunctions and energies of a particle on a ring. Let's first treat the particle on a ring problem and then extend it to the benzene system.

- a. Suppose that a particle of mass  $m$  is constrained to move on a circle (of radius  $r$ ) in the  $xy$  plane. Further assume that the particle's potential energy is constant (zero is a good choice). Write down the Schrödinger equation in the normal cartesian coordinate representation. Transform this Schrödinger equation to cylindrical coordinates where  $x = r\cos(\phi)$ ,  $y = r\sin(\phi)$ , and  $z = z$  ( $z = 0$  in this case). Taking  $r$  to be held constant, write down the general solution,  $\Phi(\phi)$ , to this Schrödinger equation. The "boundary" conditions for this problem require that  $\Phi(\phi) = \Phi(\phi + 2\pi)$ . Apply this boundary condition to the general solution. This results in the quantization of the energy levels of this system. Write down the final expression for the normalized wavefunction and quantized energies. What is the physical significance of these quantum numbers which can have both positive and negative values? Draw an energy diagram representing the first five energy levels.
- b. Treat the six  $\pi$ -electrons of benzene as particles free to move on a ring of radius  $1.40 \text{ \AA}$ , and calculate the energy of the lowest electronic transition. Make sure the Pauli principle is satisfied! What wavelength does this transition correspond to? Suggest some reasons why this differs from the wavelength of the lowest observed transition in benzene, which is  $2600 \text{ \AA}$ .

## Q9

A diatomic molecule constrained to rotate on a flat surface can be modeled as a planar rigid rotor (with eigenfunctions,  $\Phi(\phi)$ , analogous to those of the particle on a ring) with fixed bond length  $r$ . At  $t = 0$ , the rotational (orientational) probability distribution is observed to be described by a wavefunction  $\Psi(\phi, 0) = \sqrt{\frac{4}{3\pi}} \cos^2 \phi$ . What values, and with what probabilities, of the rotational angular momentum,  $\left( -i\hbar \frac{\partial}{\partial \phi} \right)$ , could be observed in this system? Explain whether these probabilities would be time dependent as  $\Psi(\phi, 0)$  evolves into  $\Psi(\phi, t)$ .

## Q10

A particle of mass  $m$  moves in a potential given by  $V(x, y, z) = \frac{k}{2}(x^2 + y^2 + z^2) = \text{frac}{k}{2}r^2$ .

- a. Write down the time-independent Schrödinger equation for this system.
- b. Make the substitution  $\Psi(x, y, z) = X(x)Y(y)Z(z)$  and separate the variables for this system.
- c. What are the solutions to the resulting equations for  $X(x)$ ,  $Y(y)$ , and  $Z(z)$ ?
- d. What is the general expression for the quantized energy levels of this system, in terms of the quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$ , which correspond to  $X(x)$ ,  $Y(y)$ , and  $Z(z)$ ?
- e. What is the degree of degeneracy of a state of energy

$$E = 5.5\hbar\sqrt{\frac{k}{m}} \text{ for this system?}$$

- f. An alternative solution may be found by making the substitution  $\Psi(r, \theta, \phi) = F(r)G(\theta, \phi)$ . In this substitution, what are the solutions for  $G(\theta, \phi)$ ?
- g. Write down the differential equation for  $F(r)$  which is obtained when the substitution  $\Psi(r, \theta, \phi) = F(r)G(\theta, \phi)$  is made. Do not solve this equation.

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