

Time-Dependent Quantum Chemistry

A Text Book for New Physical Chemistry Students

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Preface

The purpose of this text book is to recast the theories pertaining to the time dependent quantum mechanics in a more consolidated but easily perceptible form. (to be completed)

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Chapter 2: Time-Dependent Schrödinger Equation

Highlights: Time-dependent Schrodinger Equation, Variable Separation, Stationary and Superposition States, Electronic and Vibrational Superposition States, Optical Pulse and Particle Wavepacket

Quantum mechanics governs structure and dynamics of systems at the atomic and molecular level. In quantum mechanics, the wavefunction, denoted as $\psi(x,t)$ (let us choose one dimension for obtaining a simple picture), provides a complete description of the system at any given time and gives information about a system's dynamical observables (the physical quantities which can be measured or observed, such as position, momentum, energy, etc.). The wavefunction of a quantum system evolves in time according to the time-dependent Schrödinger equation (TDSE which is a differential equation of first order in time postulated by Schrödinger for the wavefunction of a quantum particle).¹

Time-Dependent Schrödinger Equation:

The TDSE for a (nonrelativistic) single particle (speed of the particle is assumed to be much less than speed of light) in one dimension is written as

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \hat{H}\psi(x,t) \dots \text{(1)}$$

where, $i = \sqrt{-1}$, \hbar is Planck's constant divided by 2π (which is equal to 1.054572×10^{-34} J s = 0.657947×10^{-15} eV s), and \hat{H} is the Hamiltonian operator:

$$\hat{H} = \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \right) + V(x) \right]$$

in which first and second terms are respectively kinetic energy and

potential energy operators (more details of the quantum mechanical operators can be found in Chapter 3). As evident here, \hat{H} is a function of x only (it has no explicit dependence on time). The function, $\psi(x,t)$, which satisfies the above equation, is called the wavefunction.² Nature of $\psi(x,t)$ for a quantum particle is solely determined by the Hamiltonian associated with it (or in other words, the potential $V(x)$ experienced by the particle; the size and extent of the "particle" of course is a function of the potential energy term $V(x)$). $|\psi(x,t)|^2 dx$ represents the probability of finding the particle between x and $(x+dx)$. If $\psi(x,t)$ is normalized, then

one can write $\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1$. Furthermore, $|\psi(x,t)|^2$ is called the probability density for finding the particle at position x and at time t . Before we proceed further to solve the TDSE using variable separation method, we will briefly go over the meaning of a particle in classical and quantum mechanics.

Classical Versus Quantum Mechanical Picture of Motion of a Particle:

If a particle of mass m under the influence of a conservative force³ F is moving along the x -axis (our favourite one dimension is chosen to obtain a simple picture), classical mechanics gives us position of the particle at any given time, $x(t)$, using Newton's equation of motion: $m \frac{d^2x}{dt^2} = F = -\frac{dV}{dx}$, if initial condition is already given (i.e., position and velocity at $t=0$ is known). When $x(t)$ is known, we can easily figure out velocity $\left(v = \frac{dx}{dt}\right)$, momentum ($p = mv$), kinetic energy $\left(= \frac{1}{2}mv^2\right)$, or any other classical dynamical variable associated with motion of the particle for any arbitrary time. Our classical or local notion of motion of a particle is depicted in Figure 2.1(a).

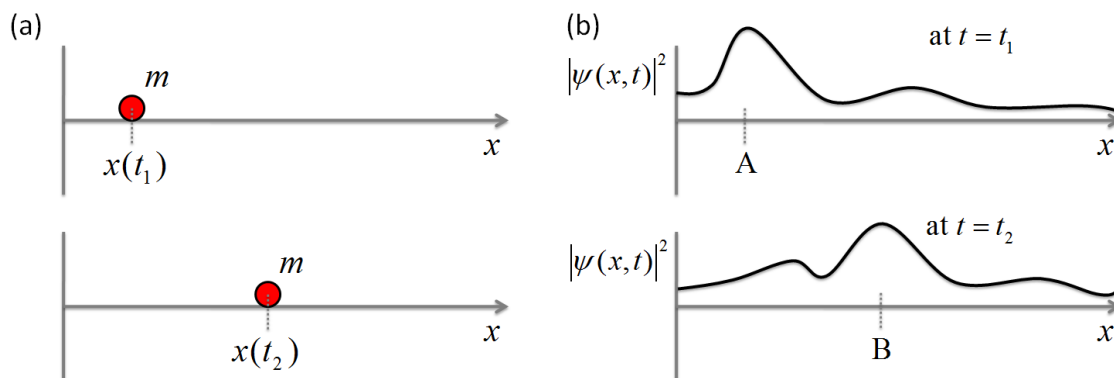


Figure 2.1: (a) Classical picture of motion of a particle. Relative positions are shown for two different times. (b) Quantum mechanical picture of motion of a particle. The probability density which represents delocalized body of a quantum particle evolves over time.

In quantum mechanics, the description of a particle is given by its wavefunction $\psi(x,t)$. We get the wavefunction by solving the time-dependent Schrödinger equation (TDSE). Given the initial condition, $\psi(x,0)$, the TDSE can determine $\psi(x,t)$ for any arbitrary time. The wavefunction, by its nature, is spread out in space (delocalized over the space) for any given time t . The global (delocalized) nature of the wavefunction of the particle at any given time contradicts our classical (or local) notion that as the wavefunction represents a particle, it must be localized at a point on the x -axis. **How can a delocalized mathematical function (wavefunction) represent a particle which is supposed to be localized?**

Quantum mechanics does not give any direct answer to the above question. Only a statistical or probabilistic answer to the above question is provided by quantum mechanics. The probability (or more specifically probability density $\rho(x,t)$) of finding the particle at point x and at time t is given by $\rho(x,t) = |\psi(x,t)|^2 = \psi^*(x,t) \cdot \psi(x,t)$. Figure 2.1(b) illustrates probability density of the moving particle at two different times. According to the definition, $|\psi(x,t)|^2 dx$ is the probability of finding the particle between x and $(x+dx)$. As $|\psi(x,t)|^2 dx$ represents the area under the graph $|\psi(x,t)|^2$ for dx interval, statistical interpretation illuminates an important fact that at $t=t_1$, the particle is more likely to be found near the point A than near the point B and at $t=t_2$, the particle is more likely to be found near the point B than near the point A. In addition, total probability of finding the particle over all space at a given time must be 1 (one). This is represented by the integral of $|\psi(x,t)|^2$:

$$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1 \dots (2)$$

When a wavefunction satisfies above condition, it is called a **normalized wavefunction**. Therefore, a physically realizable wavefunction which can represent the particle and which is a solution to the TDSE must be a normalizable wavefunction. If a wavefunction cannot be normalized, it is not acceptable as a solution to the TDSE because statistical interpretation (physically realizable interpretation) of such wavefunction fails.

Variable Separation:

The TDSE is solved by a separation of variables in position and time.⁴ This is done under the assumption that $\psi(x,t)$ can be written as

$$\psi(x,t) = \psi(x) \cdot \psi(t) \dots (3)$$

and \hat{H} does not explicitly depend on time. Substituting this trial solution into equation (1), we get

$$i\hbar \psi(x) \frac{\partial}{\partial t} \psi(t) = \psi(t) \hat{H} \psi(x)$$

$$\text{or, } i\hbar \frac{1}{\psi(t)} \frac{\partial}{\partial t} \psi(t) = \frac{1}{\psi(x)} \hat{H} \psi(x) \dots (4)$$

We immediately notice that the left hand side of equation (4) is a function of only time while the right hand side is a function of only position (as mentioned earlier \hat{H} does **not explicitly depend on time**). Therefore, both sides must be equal to a constant (say E). Then, we obtain two equations by separating the variables:

$$i\hbar \frac{\partial}{\partial t} \psi(t) = E \psi(t) \dots (5)$$

$$\text{and } \hat{H} \psi(x) = E \psi(x) \dots (6)$$

Solution to equation (5) can be given as

$$\psi(t) = \psi_0 e^{-\frac{iEt}{\hbar}} \dots (7)$$

Equation (6), on the other hand, is called the time-independent Schrödinger equation (TISE). This equation is an “eigenvalue” equation: the constant E is called the eigenvalue and $\psi(x)$ is called the eigenfunction (eigenstate). In the present context, the spectrum of a system (often used in spectroscopy) is defined as the set of energies supporting physically meaningful solutions to equation (6).

Thus, using equation (3), a solution to the TDSE can be written as

$$\psi(x,t) = \psi(x) \psi_0 e^{-\frac{iEt}{\hbar}}$$

Here, ψ_0 is just a multiplicative factor and therefore, considering the normalization condition

$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1$, without loss of any information, one can write a solution to the TDSE as

$$\psi(x, t) = \psi(x) e^{-\frac{iEt}{\hbar}} \dots (8)$$

In general, TISE (equation (6)) gives a set of solutions. Each solution is represented by $\psi_n(x)$ which is called a stationary state wavefunction, wherein n denotes the n -th state. Often, in chemistry, different spectroscopic properties of an atom or a molecule are expressed using these stationary states. Therefore, a more appropriate way of writing a solution to the TDSE is

$$\psi_n(x, t) = \psi_n(x) e^{-\frac{iE_n t}{\hbar}} \dots (9)$$

Here, $\psi_n(x)$ represents the n -th stationary state with energy E_n , and $e^{-\frac{iE_n t}{\hbar}}$ is associated **phase factor**. More details of meaning of a phase factor in a time-dependent wavefunction can be found in Chapter 3. In brief, for any complex number written in polar form ($re^{i\theta}$), phase factor is the complex exponential factor ($e^{i\theta}$). Phase factor can change the phase of the wavefunction; however, it does not change the probability density.

:Guiding Questions:

2.1: One key method of solving the TDSE discussed above is “variable separation”. We have seen that the TDSE is separable when \hat{H} is independent of time. \hat{H} is Hamiltonian operator which includes the kinetic $\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right)$ and the potential ($V(x)$) energy terms. By construction, the kinetic energy term does not depend on time; however, the potential energy term V can be a function of both time and space. Therefore, the TDSE is separable when V is independent of time (only depends on space). This argument is not entirely correct. Variable separation method can also be employed when V is a function **only of time** everywhere in space. If $V(t)$ is expressed as $V_0 \cos(\omega_0 t)$, find out an expression for $\psi(x, t)$.

2.2: For a certain one-dimensional particle of mass m , the wavefunction is given by $\psi(x, t) = Ae^{-\frac{amx^2}{\hbar}} e^{-iat}$, where, A and a are real positive constants. Find out the potential energy for which the above wavefunction satisfies the TDSE.

Stationary and Superposition States:

:Metaphor:

(a)

$$\psi(x,t) = \psi(x) e^{-\frac{iE_1 t}{\hbar}}$$

(b)

$$\psi(x,t) = a_1 \psi_1(x) e^{-\frac{iE_1 t}{\hbar}} + a_2 \psi_2(x) e^{-\frac{iE_2 t}{\hbar}}$$

An octopus can change skin colour. Let us assume that an octopus localized in the $(x_1 - x_2)$ space changes colour periodically. Then the octopus represents a stationary state wavefunction of a particle. A wavefunction of a stationary state contains time-dependent phase factor which changes the phase of the wavefunction periodically (equivalent to change of colour); however, the particle does not move due to presence of its own time-dependent phase factor. Only a superposition state of the particle allows the particle to evolve in time.

Given a solution to TDSE, as illustrated above, one can find out the probability density of the particle for the n -th stationary state:

$$|\psi_n(x,t)|^2 = \psi_n^*(x,t) \cdot \psi_n(x,t) = \psi_n^*(x) e^{\frac{iE_n t}{\hbar}} \cdot \psi_n(x) e^{-\frac{iE_n t}{\hbar}} = \psi_n^*(x) \cdot \psi_n(x) = |\psi_n(x)|^2$$

We immediately realize that the probability density is independent of time! If the probability density does not change with time, there is no time-dependence or in other words, there is no effective motion of the particle. This is why this state is called a stationary state.

If we want to describe motion of a quantum particle, we have to describe the quantum system not by a particular solution (stationary state) given in equation (9), rather by a linear combination of particular solutions (stationary states). We may note here that any linear combination of particular solutions is also a solution to the TDSE. When a linear combination of particular solutions (stationary states), each with its own characteristic time-dependent phase factor, is used to describe a quantum system, we obtain time-dependence in the probability density. Such a state is called superposition state.⁵

For example, let us assume that a particle can be represented by following wavefunction:

$$\psi(x,t) = a_1 \psi_1(x) e^{-\frac{iE_1 t}{\hbar}} + a_2 \psi_2(x) e^{-\frac{iE_2 t}{\hbar}}$$

Then the probability density for finding the particle is given by

$$|\psi(x,t)|^2 = |a_1|^2 |\psi_1(x)|^2 + |a_2|^2 |\psi_2(x)|^2 + a_1 a_2^* \psi_1(x) \psi_2^*(x) e^{-\frac{i(E_1 - E_2)t}{\hbar}} + c.c.$$

The above equation has three important terms. The first one from pure $\psi_1(x)$, the second one from pure $\psi_2(x)$, and the third one from an interference term between two states. The interference term is a result of having a superposition of eigenstates with different energies – called a wavepacket. All the time-dependence of $\psi(x,t)$ is contained in this interference term. Therefore, a wavepacket, which originates from a superposition of stationary states having different energies, is required in order to have a time-dependence in the probability density and in other observables, such as average position or average momentum of the particle.

Thus, the general solution to the TDSE can be given by

$$\psi(x,t) = \sum_{n=1}^{\infty} a_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}} \quad (\text{if stationary states have discrete spectrum/energy states})$$

$$\text{or, } \psi(x,t) = \int_0^{\infty} a_E \psi_E(x) e^{-\frac{iEt}{\hbar}} dE \quad (\text{if stationary states have continuous spectrum})$$

Here, a_E is amplitude and $e^{-\frac{iEt}{\hbar}}$ is phase factor. Therefore, to observe quantum dynamics, a wavepacket must be constructed with characteristic amplitudes and phase factors.

:Guiding Question:

2.3: If ψ_m and ψ_n , respectively represented by $\psi_m(x,t) = \psi_m(x) e^{-\frac{iE_m t}{\hbar}}$ and $\psi_n(x,t) = \psi_n(x) e^{-\frac{iE_n t}{\hbar}}$, are solutions to the TDSE, show that following wavefunction also satisfies the TDSE.

$$\psi(x,t) = a_m \psi_m(x) e^{-\frac{iE_m t}{\hbar}} + a_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}}$$

Simple Examples:

(a) Electronic Superposition State:

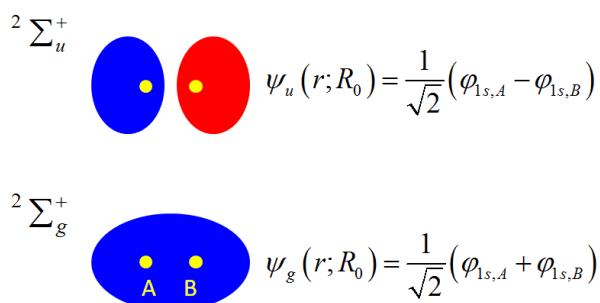


Figure 2.2: Electronic wavefunctions of the ground ${}^2\Sigma_g^+$ and first electronically excited ${}^2\Sigma_u^+$ states of H_2^+ . We may note here that each molecular orbital (${}^2\Sigma_g^+$ or ${}^2\Sigma_u^+$) is expressed as a linear combination of atomic orbitals (LCAO). LCAO, by its nature of construction, carries the sense of “superposition”; however, LCAO is not considered a “superposition” scheme because corresponding (time-dependent) phase factor associated with each atomic orbital are not considered in LCAO. So, to be precise, a “superposition” scheme involves adding states with their corresponding (time-dependent) phase factor.

One of the simplest examples of an electronic superposition state which can be easily realized is perhaps a superposition state created by the two lowest-lying $^2\Sigma_g^+$ and $^2\Sigma_u^+$ electronic states of H_2^+ .⁶ The electronic wavefunctions of these two states (they are depicted in Figure 2.2) can be written as

$$\psi_g(r, t; R_0) = \psi_g(r; R_0) e^{-\frac{iE_g t}{\hbar}}$$

$$\text{and } \psi_u(r, t; R_0) = \psi_u(r; R_0) e^{-\frac{iE_u t}{\hbar}}$$

Here, we have assumed that the nuclear positions are fixed at the equilibrium geometry (R_0) of the ground electronic state.

Thus, the total electronic wavefunction of the superposition state can be expressed as

$$\begin{aligned} \psi(r, t; R_0) &= \psi_g(r, t; R_0) + \psi_u(r, t; R_0) \\ &= \psi_g(r; R_0) e^{-\frac{iE_g t}{\hbar}} + \psi_u(r; R_0) e^{-\frac{iE_u t}{\hbar}} \end{aligned}$$

Finally, the time-dependent electron density is given by

$$\begin{aligned} |\psi(r, t; R_0)|^2 &= [\psi^*(r, t; R_0) \cdot \psi(r, t; R_0)] \\ &= \left[\psi_g^*(r; R_0) e^{\frac{iE_g t}{\hbar}} + \psi_u^*(r; R_0) e^{\frac{iE_u t}{\hbar}} \right] \cdot \left[\psi_g(r; R_0) e^{-\frac{iE_g t}{\hbar}} + \psi_u(r; R_0) e^{-\frac{iE_u t}{\hbar}} \right] \\ &= |\psi_g(r; R_0)|^2 + |\psi_u(r; R_0)|^2 + \psi_g(r; R_0) \psi_u^*(r; R_0) e^{\frac{i(E_u - E_g)t}{\hbar}} + c.c. \\ &= |\psi_g(r; R_0)|^2 + |\psi_u(r; R_0)|^2 + 2\psi_g(r; R_0) \psi_u(r; R_0) \cos\left[\frac{(E_u - E_g)t}{\hbar}\right] \end{aligned}$$

because, $\psi_g(r; R_0)$ and $\psi_u(r; R_0)$ are real and are given, respectively, by

$$\psi_g(r; R_0) = \frac{1}{\sqrt{2}}(\phi_{1s,A} + \phi_{1s,B})$$

$$\text{and } \psi_u(r; R_0) = \frac{1}{\sqrt{2}}(\phi_{1s,A} - \phi_{1s,B}).$$

Here, $\phi_{1s,A}$ and $\phi_{1s,B}$ refer to the 1s orbitals of two hydrogen atoms denoted as A and B, respectively:

$$|\psi(r, t; R_0)|^2 = |\psi_g(r; R_0)|^2 + |\psi_u(r; R_0)|^2 + 2\psi_g(r; R_0)\psi_u(r; R_0)\cos\left[\frac{\Delta E_{ug}t}{\hbar}\right] \dots (10)$$

in which, ΔE_{ug} represents the energy separation between $^2\Sigma_g^+$ and $^2\Sigma_u^+$ electronic states of H_2^+ . The above equation shows that time-dependent electron density oscillates with a period of $\frac{\hbar}{\Delta E_{ug}}$.

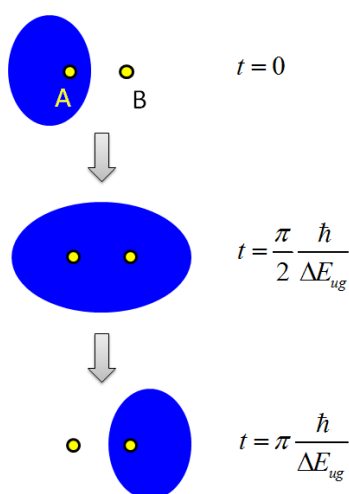


Figure 2.3: Time-dependent electron density following the preparation of the electronic superposition state.

For H_2^+ , ΔE_{ug} is 11.83967 eV^7 at the equilibrium geometry of the ground electronic state and therefore, oscillation time period of the time-dependent electron density is calculated to be 348 attosecond (where, 1 attosecond = 1×10^{-18} second). But how does this electron density change after creating the superposition state?

We know that a cosine function can take any value between +1 and -1. To visualize the temporal evolution of the electron density of the superposition state, we may consider +1, 0 and -1 values.

(a) $\cos\left[\frac{\Delta E_{ug} t}{\hbar}\right] = +1$ or, at $t = 0$:

$$\begin{aligned} |\psi(r, t; R_0)|^2 &= \left| \frac{1}{\sqrt{2}}(\varphi_{1s,A} + \varphi_{1s,B}) \right|^2 + \left| \frac{1}{\sqrt{2}}(\varphi_{1s,A} - \varphi_{1s,B}) \right|^2 + 2 \frac{1}{\sqrt{2}}(\varphi_{1s,A} + \varphi_{1s,B}) \frac{1}{\sqrt{2}}(\varphi_{1s,A} - \varphi_{1s,B}) \\ &= \frac{1}{2} [\varphi_{1s,A}^2 + \varphi_{1s,B}^2 + 2\varphi_{1s,A}\varphi_{1s,B} + \varphi_{1s,A}^2 + \varphi_{1s,B}^2 - 2\varphi_{1s,A}\varphi_{1s,B}] + \varphi_{1s,A}^2 - \varphi_{1s,B}^2 \\ &= \varphi_{1s,A}^2 + \varphi_{1s,B}^2 + \varphi_{1s,A}^2 - \varphi_{1s,B}^2 \\ &= 2\varphi_{1s,A}^2 \end{aligned}$$

Thus, at $t = 0$, when the superposition state is just created, the total electron density will be localized at one hydrogen atom (atom A , as depicted in Figure 2.3).

(b) $\cos\left[\frac{\Delta E_{ug} t}{\hbar}\right] = 0$ or, at $t = \frac{\pi \hbar}{2 \Delta E_{ug}}$:

$$\begin{aligned} |\psi(r, t; R_0)|^2 &= \left| \frac{1}{\sqrt{2}}(\varphi_{1s,A} + \varphi_{1s,B}) \right|^2 + \left| \frac{1}{\sqrt{2}}(\varphi_{1s,A} - \varphi_{1s,B}) \right|^2 \\ &= \frac{1}{2} [\varphi_{1s,A}^2 + \varphi_{1s,B}^2 + 2\varphi_{1s,A}\varphi_{1s,B} + \varphi_{1s,A}^2 + \varphi_{1s,B}^2 - 2\varphi_{1s,A}\varphi_{1s,B}] \\ &= \varphi_{1s,A}^2 + \varphi_{1s,B}^2 \end{aligned}$$

Thus, at $t = \frac{\pi \hbar}{2 \Delta E_{ug}}$ after the superposition state is created, the total electron density will be delocalized over the both hydrogen atoms (as depicted in Figure 2.3).

(c) $\cos\left[\frac{\Delta E_{ug} t}{\hbar}\right] = -1$ or, at $t = \pi \frac{\hbar}{\Delta E_{ug}}$:

$$\begin{aligned} |\psi(r, t; R_0)|^2 &= \left| \frac{1}{\sqrt{2}}(\varphi_{1s,A} + \varphi_{1s,B}) \right|^2 + \left| \frac{1}{\sqrt{2}}(\varphi_{1s,A} - \varphi_{1s,B}) \right|^2 - 2 \frac{1}{\sqrt{2}}(\varphi_{1s,A} + \varphi_{1s,B}) \frac{1}{\sqrt{2}}(\varphi_{1s,A} - \varphi_{1s,B}) \\ &= \frac{1}{2} [\varphi_{1s,A}^2 + \varphi_{1s,B}^2 + 2\varphi_{1s,A}\varphi_{1s,B} + \varphi_{1s,A}^2 + \varphi_{1s,B}^2 - 2\varphi_{1s,A}\varphi_{1s,B}] - \varphi_{1s,A}^2 + \varphi_{1s,B}^2 \\ &= \varphi_{1s,A}^2 + \varphi_{1s,B}^2 - \varphi_{1s,A}^2 + \varphi_{1s,B}^2 \\ &= 2\varphi_{1s,B}^2 \end{aligned}$$

Thus, at $t = \pi \frac{\hbar}{\Delta E_{ug}}$ after the superposition state is created, the total electron density will be again localized at another hydrogen atom (atom B , as depicted in Figure 2.3)

:Guiding Question:

2.4: Effect of Vibration on an Electronic Superposition State: In the above analysis of electronic superposition state, we have assumed that H_2^+ ion has only frozen equilibrium geometry (R_0). But this is clearly an oversimplified assumption because ground vibrational state wavefunction, even under quantum harmonic oscillator approximation, exhibits a spatial distribution. How does this affect the time-evolution of an electronic superposition state?

Hint: Consider Born-Oppenheimer total wavefunction as

$$\psi(x,t) = \chi(R) \left[\psi_g(x) e^{-\frac{iE_g t}{\hbar}} + \psi_u(x) e^{-\frac{iE_u t}{\hbar}} \right]$$

First and second terms on the right-hand side are respectively nuclear and electronic parts of the total wavefunction.

(b) Vibrational Superposition State:

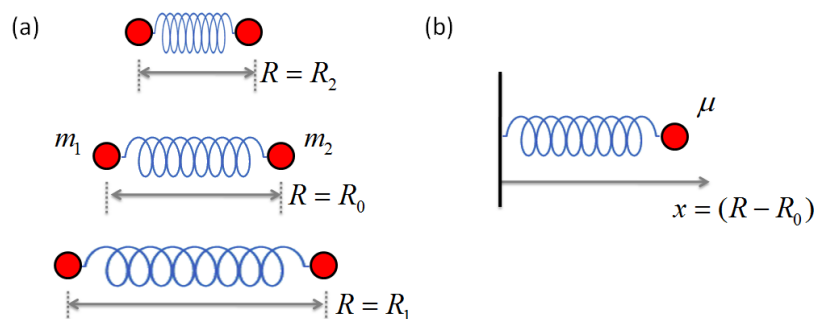


Figure 2.4: (a) Vibrational motion of a diatomic molecule is represented by a spring with two masses; (b) Reduced mass connected to the wall by a spring.

One of the simplest examples of vibrational superposition state can perhaps be realized from a superposition of the ground and the first excited state of a diatomic quantum harmonic oscillator. A quantum harmonic oscillator is a good model for a vibrating diatomic molecule. Under this model, a diatomic molecule can be represented by a spring, as shown in Figure 2.4(a). In this figure, m_1 and m_2 are masses of two atoms. Equilibrium bond distance is R_0 and R represents instantaneous bond length during the vibration. Therefore, if $x(=R-R_0) > 0$, the spring is stretched and if $x < 0$, the spring is compressed.

Considering the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$, and based on the relative coordinate $x = (R - R_0)$, the above two-body problem can be conveniently reduced to a one-body problem as given in Figure 2.4(b). The vibration of the one-body system is governed by $\omega = \sqrt{\frac{k}{\mu}}$ where, k is the force constant, representing a measure of stiffness of the spring (a small value of k implies a weak bond and a large value of k implies a strong bond), and ω represents the frequency of the vibration (in radian per seconds).

The time-independent Schrödinger equation (TISE) for the reduced one-body problem is given by, $\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \right) + \frac{1}{2} kx^2 \right] \psi(x) = E \psi(x)$. When this second order differential equation is solved, well-behaved wavefunctions are obtained for the energy values $E_v = \hbar \left(\frac{k}{\mu} \right)^{1/2} \left(v + \frac{1}{2} \right)$, where $v = 0, 1, 2, 3, \dots$. The wavefunctions corresponding to these E_v are non-degenerate states expressed by *Hermite polynomials*. Details of this solution and expressions of Hermite polynomials can be found in most of the standard quantum chemistry text books.⁸ Here, we are only interested in ground $\psi_0(x)$ and first excited $\psi_1(x)$ vibrational states of the quantum harmonic oscillator. They are given by (as depicted in Figure 2.5)

$$\psi_0(x) = \left(\frac{\alpha}{\pi} \right)^{1/4} \exp\left(\frac{-\alpha x^2}{2} \right) \text{ and } \psi_1(x) = \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2} \right)$$

$$\text{where, } \alpha = \sqrt{\frac{k\mu}{\hbar^2}}.$$

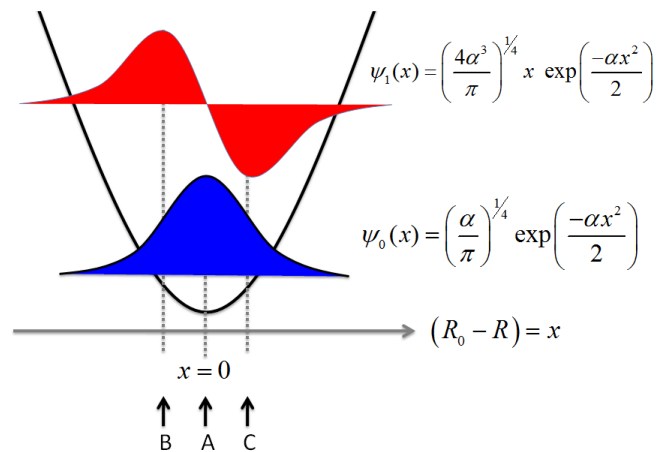


Figure 2.5: Vibrational wavefunctions of the ground and the first excited states of a diatomic molecule.

Then the superposition state created by the ground and the first excited states of a diatomic quantum harmonic oscillator can be written as

$$\begin{aligned}\psi(x,t) &= \psi_0(x) e^{\frac{-iE_0t}{\hbar}} + \psi_1(x) e^{\frac{-iE_1t}{\hbar}} \\ &= \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right) e^{\frac{-iE_0t}{\hbar}} + \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right) e^{\frac{-iE_1t}{\hbar}}\end{aligned}$$

Finally, the probability density of the vibrational superposition state is given by

$$\begin{aligned}|\psi(x,t)|^2 &= |\psi_0(x)|^2 + |\psi_1(x)|^2 + 2\psi_0(x)\psi_1(x)\cos\left(\frac{\Delta E_{10}t}{\hbar}\right) \\ &= \left(\frac{\alpha}{\pi}\right)^{1/2} \exp(-\alpha x^2) + \left(\frac{4\alpha^3}{\pi}\right)^{1/2} x^2 \exp(-\alpha x^2) \\ &\quad + 2\left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{4\alpha^3}{\pi}\right)^{1/4} \exp(-\alpha x^2) x \cos\left(\frac{\Delta E_{10}t}{\hbar}\right)\end{aligned}$$

As we have considered earlier, to visualize the temporal evolution of the vibrational superposition state, we may consider +1, 0 and -1 values of the cosine function.

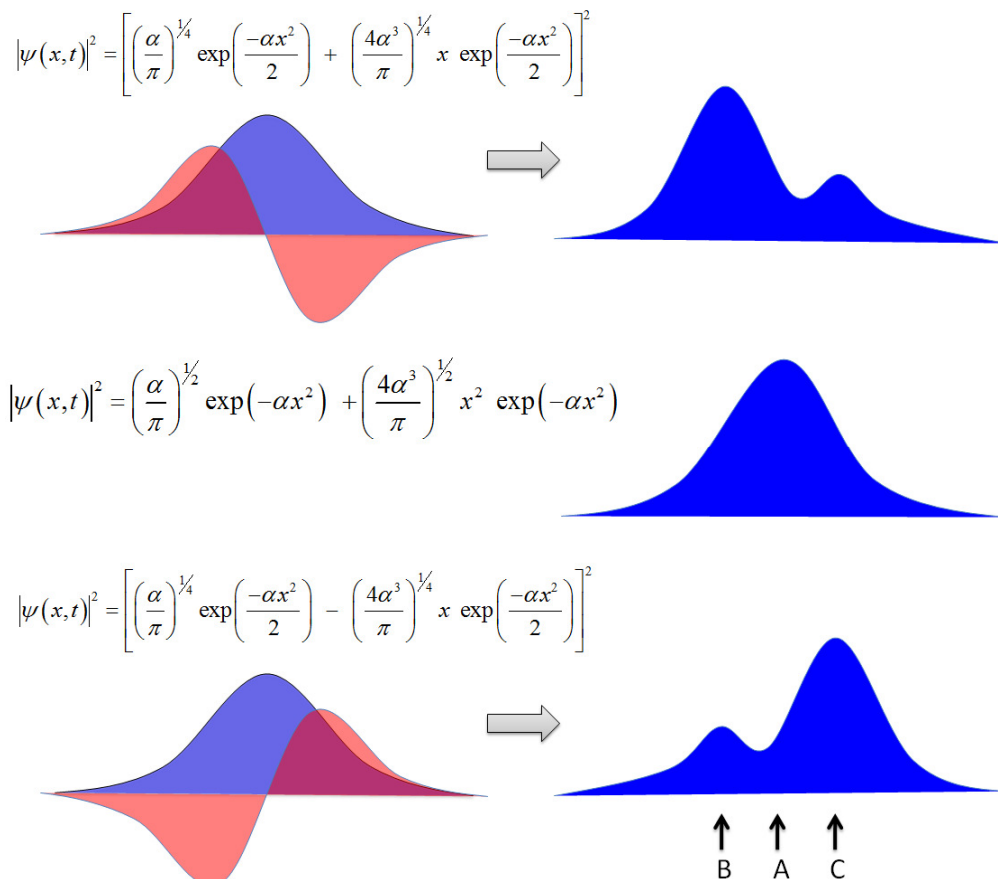


Figure 2.6: Time-dependent density of the vibrational superposition state following its preparation.

(a) $\cos\left(\frac{\Delta E_{10}t}{\hbar}\right) = +1$ or, at $t=0$:

$$\begin{aligned} |\psi(x,t)|^2 &= \left(\frac{\alpha}{\pi} \right)^{1/2} \exp(-\alpha x^2) + \left(\frac{4\alpha^3}{\pi} \right)^{1/2} x^2 \exp(-\alpha x^2) + 2 \left(\frac{\alpha}{\pi} \right)^{1/4} \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x \exp(-\alpha x^2) \\ &= \left[\left(\frac{\alpha}{\pi} \right)^{1/4} \exp\left(\frac{-\alpha x^2}{2} \right) + \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2} \right) \right]^2 \end{aligned}$$

Thus, at $t=0$, when the superposition state is just created, maximum of the probability density appears at position B (as shown in Figure 2.6).

(b) $\cos\left(\frac{\Delta E_{12}t}{\hbar}\right) = 0$ or, at $t = \frac{\pi}{2} \frac{\hbar}{\Delta E_{10}}$:

$$|\psi(x,t)|^2 = \left(\frac{\alpha}{\pi}\right)^{1/2} \exp(-\alpha x^2) + \left(\frac{4\alpha^3}{\pi}\right)^{1/2} x^2 \exp(-\alpha x^2)$$

Thus, at $t = \frac{\pi}{2} \frac{\hbar}{\Delta E_{10}}$ after the superposition state is created, maximum of the probability density appears at position A (as shown in Figure 2.6).

(c) $\cos\left[\frac{\Delta E_{10}t}{\hbar}\right] = -1$ or, at $t = \pi \frac{\hbar}{\Delta E_{10}}$:

$$|\psi(x,t)|^2 = \left[\left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right) - \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right) \right]^2$$

Thus, at $t = \pi \frac{\hbar}{\Delta E_{10}}$ after the superposition state is created, maximum of the probability density appears at position C (as shown in Figure 2.6).

:Guiding Question:

2.5: Consider the superposition of the ground and the second excited states of the quantum harmonic oscillator. Show how the time-dependent probability density would oscillate for this vibrational superposition state?

Hint: Use following wavefunctions for the ground and the second excited vibrational states of a quantum harmonic oscillator:

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right) \text{ and } \psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) \exp\left(\frac{-\alpha x^2}{2}\right), \text{ where, } \alpha = \sqrt{\frac{k\mu}{\hbar^2}}.$$

Exercises:

2.6: For a certain one-dimensional particle of mass m , the wavefunction is given by $\psi(x,t) = Ae^{-\frac{iamx}{\hbar}} e^{-iat}$, where, A and a are real positive constants. Find out the potential energy for which the above wavefunction satisfies the TDSE.

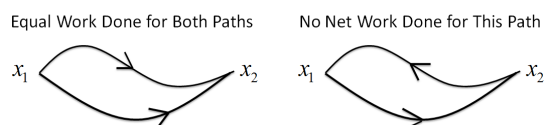
2.7: For a certain one-dimensional particle of mass m , the wavefunction is given by $\psi(x,t) = Ae^{-ikx} e^{-\frac{iEt}{\hbar}}$, where, $k = \sqrt{\frac{2mE}{\hbar^2}}$ and E is the total energy of the particle. Find out the potential energy for which the above wavefunction satisfies the TDSE.

2.8: If we assume that $\psi(x,t)$ is a linear combination of the first two lowest-lying states of a particle in a one-dimensional box. Calculate the probability density associated with $\psi(x,t)$. Pictorially depict how does the probability density periodically move from one side of the box to the other side of the box as a function of time?

2.9: The TDSE given by $i\hbar \frac{\partial}{\partial t} \psi(x,t) = \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \right) + V(x) \right] \psi(x,t)$ represents a single particle of mass m experiencing a time-independent potential. If suddenly an additional constant potential V_0 starts acting on the particle, what changes do you expect on the wavefunction and the probability density?

References:

1. Theory-minded curious readers are referred to (a) E. Schrödinger, *Collected Papers on Wave Mechanics*, Chelsea Publishing Company, New York, Third (Augmented) English Edition, 1982; (b) J. S. Briggs and J. M. Rost, *On the Derivation of the Time-Dependent Equation of Schrödinger*, *Foundations of Physics*, 31, 693-712 (2001).
2. General discussion on the wavefunction and its statistical or probabilistic interpretations can be found in most of the standard quantum chemistry books. The same has been documented in Chapter 3 of this book from a time-dependent perspective. Curious new physical chemistry students are referred to four lovely text books: (a) I. N. Levine, *Quantum Chemistry, Chapter 7: Theorems of Quantum Mechanics*, Seventh Edition, Pearson Education, Inc. New Jersey, 2014; (b) D. J. Griffiths, *Introduction to Quantum Mechanics, Chapter 1: The Wave Function*, Second Edition, Pearson Education, Inc., New Jersey, 2005; (c) P. Atkins and R. Freidman, *Molecular Quantum Mechanics, Chapter 1: The Foundations of Quantum Mechanics*, Oxford University Press, Fifth Edition, 2011; and (d) D. A. McQuarrie, *Quantum Chemistry, Chapter 4: The Postulates and General Principles of Quantum Mechanics*, University Science Books, Second Edition, 2008.
3. In classical mechanics the conservative force is defined as the force for which the work done in moving a particle between two points is independent of the path taken between two points.



Thus the energy of the particle subjected to a conservative force depends only on its position, not on the path taken by the particle to reach that position. This energy is called potential energy – an energy that depends on the position of the particle. For an infinitesimal displacement dx , if the potential energy change is dV , then under the conservative force, $\text{Energy} = \text{Force} \times \text{Displacement}$; or, $dV = -F \times dx$; or, $F = -\frac{dV}{dx}$. Here negative sign comes from the

fact that potential energy increases when displacement increases, but the force is active on the opposite direction to reduce the potential energy. Curious readers are further referred to H. Goldstein, C. Poole, J. Safko, *Classical Mechanics*, Third Edition, Pearson, 2001.

4. General discussion of variable separation method can be found in most of the standard quantum chemistry books. To name a few lovely books: (a) I. N. Levine, *Quantum Chemistry, Chapter 1: The Schrödinger Equation*, Seventh Edition, Pearson Education, Inc. New Jersey, 2014; (b) D. A. McQuarrie, *Quantum Chemistry, Chapter 4: The Postulates and General Principles of Quantum Mechanics*, University Science Books, Second Edition, 2008.
5. One of the oldest quantum chemistry books where superposition state has been mentioned in the context of quantum dynamics is perhaps by H. Eyring, J. Walter, G. E. Kimball, *Quantum Chemistry, Chapter XVII: The Quantum Mechanical Theory of Reaction Rates*, John Wiley and Sons, Inc. New York, 1944; Curious readers are also referred to two relatively new books: (a) D. J. Tannor, *Introduction to Quantum Mechanics A Time-Dependent Approach, Chapter 1: The Time-Dependent Schrödinger Equation*, University Science Books, Sausalito (CA), 2007; (b) D. A. McQuarrie, *Quantum Chemistry, Chapter 4: The Postulates and General Principles of Quantum Mechanics*, University Science Books, Second Edition, 2008.
6. In the context of electronic superposition state leading to the attosecond phenomena, readers are referred to a few interesting recent articles: (a) F. Remele and R. D. Levine, *An Electronic Time Scale in Chemistry*, *Proc. Natl. Acad. Sci. (USA)*, 103, 6793-6798 (2006); and (b) S. Chandra and A. Bhattacharya, *Attochemistry of Ionized Halogen, Chalcogen, Pnictogen and Tetrel Bonded Clusters*, *J. Phys. Chemistry, A*, 120, 10057-10071 (2016); (c) H. J. Wörner, C. A. Arrell, N. Banerji, A. Cannizzo, M. Chergui, A. K. Das, P. Hamm, U. Keller, P. M. Kraus, E. Liberatore, P. Lopez-Tarifa, M. Lucchini, M. Meuwly, C. Milne, J.-E. Moser, U. Rothlisberger, G. Smolentsev, J. Teuscher, J. A. van Bokhoven, and O. Wenger, *Charge migration and charge transfer in molecular systems*, *Struc. Dyn.* 4, 061508 (2017); (d) E. Goulielmakis, Z.-H. Loh, A. Wirth, R. Santra, N. Rohringer, V. S. Yakovlev, S. Zherebtsov, T. Pfeifer, A. M. Azzeer, M. F. Kling, S. R. Leone, F. Krausz, *Real-time observation of valence electron motion*, *Nature*, 466, 739-743 (2010); (e) F. Calegari, D. Ayuso, A. Trabatttoni, L. Belshaw, S. De Camillis, S. Anumula, F. Frassetto, L. Poletto, A. Palacios, P. Decleva, J. B. Greenwood, F. Martín, M. Nisoli, *Ultrafast Electron Dynamics in Phenylalanine Initiated by Attosecond Pulses*, *Science*, 346, 336-339 (2014).

7. M. Beyer and F. Merkt, *Structure and dynamics of H_2^+ near the dissociation threshold: A combined experimental and computational investigation*, J. Mol. Spectrosc. 330, 147 (2016).
8. See, for example, D. A. McQuarrie, *Quantum Chemistry, Chapter 5: The Harmonic Oscillator and Vibrational Spectroscopy*, University Science Books, Second Edition, 2008.

Chapter 2A: Answers

2.1: One can write down the TDSE, $i\hbar \frac{\partial}{\partial t} \psi(x,t) = \hat{H}\psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(t) \right] \psi(x,t)$. One can now use variable separation method and insert $\psi(x,t) = \psi(x) \cdot \psi(t)$ into the above equation. Rearranging the time- and space-dependent terms (as we did before) one can write,

$$i\hbar \frac{1}{\psi(t)} \frac{\partial}{\partial t} \psi(t) - V(t) = \frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] \psi(x) = E \text{ (constant)}$$

and as a result, we get two equations (space and time-dependent, respectively). We will carefully look at time-dependent equation, $i\hbar \frac{1}{\psi(t)} \frac{\partial}{\partial t} \psi(t) - V(t) = E$.

As $V(t) = V_0 \cos(\omega_0 t)$, one can rewrite the time-dependent equation as follows,

$$\frac{\partial \psi(t)}{\partial t} + \frac{-(V(t) + E)}{i\hbar} \psi(t) = 0 \dots (3)$$

The above equation has a form of first order differential equation, $\frac{\partial y}{\partial t} + P(x)y = Q(x)$, which

can be solved using the integrating factor $e^{\int P(x)dx}$. Comparing the equation (3) and the standard form given above, one can determine the appropriate integrating factor which can be used to multiply both sides of equation (3) to obtain the solution. The integrating factor for the

present problem taking the time limit $[0, t]$ is $e^{\int_0^t \frac{-(V(t)+E)}{i\hbar} dt} = e^{\frac{-1}{i\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t + Et \right)}$.

Thus, one can rewrite the equation (3) as

$$e^{\frac{-1}{i\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t + Et \right)} \frac{\partial \psi(t)}{\partial t} + \frac{-(V(t) + E)}{i\hbar} \psi(t) e^{\frac{-1}{i\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t + Et \right)} = 0$$

$$\text{or, } \frac{\partial}{\partial t} \left[\psi(t) e^{\frac{-1}{i\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t + Et \right)} \right] = 0$$

$$\text{or, } \psi(t) e^{\frac{-1}{i\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t + Et \right)} - \psi(0) = 0 \text{ taking time limit as } [0, t]$$

$$\text{or, } \psi(t) = \psi(0) e^{\frac{1}{i\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t + Et \right)}.$$

Therefore, total wavefunction (which depends both on space and time) can be written as

$$\psi(x, t) = \psi(x) \cdot \psi(t) = \psi(x) \psi(0) e^{\frac{1}{i\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t + Et \right)} = \psi(x) \psi(0) e^{\frac{-iEt}{\hbar}} e^{\frac{-i}{\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t \right)}$$

Compare the above solution with the earlier form wherein V was assumed to be independent of time, $\psi(x, t) = \psi(x) e^{\frac{-iEt}{\hbar}}$. Thus, we notice that due to presence of a purely time-dependent potential, a phase factor is introduced to the total wavefunction. As in the end, $|\psi(x, t)|^2$ represents the probability density, this state represented by the wavefunction

$\psi(x, t) = \psi(x) \psi(0) e^{\frac{-iEt}{\hbar}} e^{\frac{-i}{\hbar} \left(\frac{V_0}{\omega_0} \sin \omega_0 t \right)}$ illustrates a stationary state (probability density is time-independent).

2.2: As $\psi(x, t) = A e^{-\frac{amx^2}{\hbar}} e^{-iat}$, we get $\frac{\partial \psi(x, t)}{\partial t} = (-ia) \psi(x, t)$

and $\frac{\partial \psi(x, t)}{\partial x} = \left(-\frac{am}{\hbar} 2x\right) \psi(x, t)$ or,

$$\begin{aligned} \frac{\partial^2 \psi(x, t)}{\partial x^2} &= \left(-\frac{am}{\hbar} 2x\right)^2 \psi(x, t) - \frac{2am}{\hbar} \psi(x, t) \\ &= -\frac{2am}{\hbar} \left[1 - \frac{2am}{\hbar} x^2\right] \psi(x, t) \end{aligned}$$

From the TDSE, we get

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \right) + V \right] \psi(x, t)$$

Or,

Chapter 3: General Principles of Time-Dependent Quantum Mechanics

Highlights: Time-Dependent Behaviour of the Probability Density and the Expectation Value

In this chapter, we will revise a set of postulates¹ and their consequences based on which different time-dependent quantum descriptions of physical or chemical systems are formulated. Readers are referred to a lovely text book Quantum Mechanics by Cohen-Tannoudji *et al.*, wherein several postulates of quantum mechanics are discussed in adequate details.² For our present interest in developing the subject *time-dependent quantum chemistry*, we will go over the general postulates of quantum mechanics from a time-dependent point of view. In particular, as quoted by Cohen-Tannoudji *et al.*, the following questions are relevant in the present context:

(a) *How is the state of a quantum system at a given time described mathematically?*

(b) *How can the state of a quantum system at any arbitrary time t be found if the state at time $t = 0$ is known?*

(c) *How can we predict the results of the time-dependent experimental measurement of various dynamical quantities using the time-dependent quantum mechanics?*

We will see that the content presented in this chapter provides an answer to the above questions.

General Characteristics of a Wavefunction:

We have already noted in Chapter 2 that, in quantum mechanics, a complete description of motion of a particle is given by its wavefunction $\psi(x,t)$ obtained by solving the time-dependent Schrödinger equation (TDSE): $i\hbar \frac{\partial}{\partial t} \psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x,t)$, if the initial wavefunction $\psi(x,0)$ is given.³ Exact form the wavefunction depends on the potential $V(x)$ experienced by the particle.

We have also noted that a wavefunction, by its nature, is always delocalized over the entire space (over the entire x -axis) for any given time t . However, the statistical interpretation of the wavefunction illuminates the fact that the probability (more technically probability density $\rho(x,t)$) for finding the particle at point x and at time t is given by $\rho(x,t) = |\psi(x,t)|^2 = \psi^*(x,t) \cdot \psi(x,t)$ and this is why the particle is more likely to be found near a point on the x -axis where $|\psi(x,t)|^2$ is maximum. In addition, a wavefunction, which can be considered as an acceptable solution to the TDSE of a particular system, must be a **normalized wavefunction** to maintain unit probability density over all space. The total probability of finding the particle over all space must be equal to 1 (because we have only one particle).

We will pause here and ask a number of questions relevant to the time-dependent behaviour of a wavefunction in the light of the above discussion:

(a) How do we normalize a wavefunction at $t = 0$?

(b) If a wavefunction is normalized at $t = 0$, does it remain normalized for all later times?

Normalizing a Wavefunction: One can normalize a wavefunction using the normalization condition

$$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1 \quad \dots (1)$$

Let us take an example to illustrate this point. Assume that the wavefunction of a particle at $t = 0$ has following Gaussian form:

$$\psi(x,0) = A e^{-ax^2}; \text{ where, } A \text{ and } a \text{ are real and positive constants.}$$

Then, the probability density is given by

$$\rho(x,0) = A^2 e^{-2ax^2}$$

Now employing the normalization condition we get,

$$\int_{-\infty}^{+\infty} A^2 e^{-2ax^2} dx = 1$$

$$\text{And, } A^2 \sqrt{\frac{\pi}{2a}} = 1, \text{ using the standard Gaussian integral, } \int_{-\infty}^{+\infty} e^{-ax^2+bx+c} dx = \sqrt{\frac{\pi}{a}} e^{\left(\frac{b^2}{4a}+c\right)}$$

And, $A = \left(\frac{2a}{\pi}\right)^{1/4}$ which is normalization constant.

Thus, the normalized Gaussian wavefunction at $t = 0$ has following form,

$$\psi(x, 0) = \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}$$

Therefore, it is obvious from the above analysis that, even if a wavefunction is not normalized (i.e., the integral in equation 1 equals some constant), we can make it normalized by using normalization condition. Here, we must note that **if a wavefunction cannot be normalized, it is not acceptable as a solution to the TDSE because the statistical interpretation (which is the only physically realizable interpretation) of such wavefunction fails.** In fact, $\psi(x, t)$ will be considered as physically acceptable wavefunction (a physically acceptable wavefunction is also called a well-behaved wavefunction) if and only if

- (a) $\psi^* \psi$ must be single-valued,
- (b) Not infinite over a finite range,
- (c) Continuous everywhere,
- (d) Possesses continuous first derivative,
- and (e) Normalizable.

Time-Dependence of Normalization Constant: Our next concern pertaining to the time-dependent behaviour of a wavefunction is that even if a wavefunction is normalized at $t = 0$, does it remain normalized for all later times? This question can be rephrased as, “Can normalization constant A be a function of time?” To find an answer to this question we will consider the time-derivative of the probability density:

$$\frac{\partial}{\partial t} |\psi(x, t)|^2 = \frac{\partial}{\partial t} [\psi^*(x, t) \cdot \psi(x, t)] = \frac{\partial \psi^*(x, t)}{\partial t} \psi(x, t) + \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial t} \dots (2)$$

(following the product rule for the derivative operator)

From the TDSE, on the other hand, we get,

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x, t)$$

$$\text{And, } \frac{\partial \psi(x, t)}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} - \frac{iV}{\hbar} \psi(x, t) \dots (3)$$

And taking complex conjugate of the above equation, we get

$$\frac{\partial \psi^*(x,t)}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \psi^*(x,t)}{\partial x^2} + \frac{iV}{\hbar} \psi^*(x,t) \dots (4)$$

Inserting equation (3) and (4) into equation (2), we get

$$\begin{aligned} \frac{\partial}{\partial t} |\psi(x,t)|^2 &= \left[-\frac{i\hbar}{2m} \frac{\partial^2 \psi^*(x,t)}{\partial x^2} + \frac{iV}{\hbar} \psi^*(x,t) \right] \psi(x,t) + \psi^*(x,t) \left[\frac{i\hbar}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} - \frac{iV}{\hbar} \psi(x,t) \right] \\ &= \frac{i\hbar}{2m} \left[\psi^*(x,t) \frac{\partial^2 \psi(x,t)}{\partial x^2} - \frac{\partial^2 \psi^*(x,t)}{\partial x^2} \psi(x,t) \right] \\ &= \frac{i\hbar}{2m} \frac{\partial}{\partial x} \left[\psi^*(x,t) \frac{\partial \psi(x,t)}{\partial x} - \frac{\partial \psi^*(x,t)}{\partial x} \psi(x,t) \right] \end{aligned}$$

Integrating both sides in the limit $[-\infty, +\infty]$, we get

$$\int_{-\infty}^{+\infty} \frac{\partial}{\partial t} |\psi(x,t)|^2 dx = \frac{i\hbar}{2m} \left[\psi^*(x,t) \frac{\partial \psi(x,t)}{\partial x} - \frac{\partial \psi^*(x,t)}{\partial x} \psi(x,t) \right]_{-\infty}^{+\infty} = 0$$

$$\text{And, } \frac{d}{dt} \left[\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx \right] = 0 \dots (5)$$

because ψ or ψ^* is zero at $x = \pm\infty$
(an important characteristic of a well-behaved wavefunction).

Here we note that a total derivative $\frac{d}{dt}$ is used for the above integral which is a function only of t , and a partial derivative $\frac{\partial}{\partial t}$ is used for integrand which is a function of both x and t . Equation (5) illuminates an important fact that once $\psi(x,t)$ is normalized, it remains normalized at any later time. Or in other words, total probability density does not change over time. This is a remarkable property of the TDSE that it automatically preserves the normalization of the wavefunction.

:Guiding Questions:

3.1: In variable separation method (see Chapter 2), we have seen that E is a constant. Prove that E must be a *real* constant for a normalizable wavefunction.

Hints: use $\frac{d}{dt} \left[\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx \right] = 0$

3.2: For a moment, if we assume that $\frac{d}{dt} \left[\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx \right] = A^2 |\psi(x)|^2 e^{\frac{2Et}{\hbar}}$ is true for a system.

Find out meaning of this time-dependent total electron density.

3.3: Write down the complex conjugate of the following equations:

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x,t) \text{ and } \hat{H}\psi(x) = E\psi(x)$$

3.4: Determine whether following wavefunctions at $t=0$ are physically acceptable solution to the TDSE:

(a) $\psi(x,0) = Ae^{-x}$ over the interval $(0, +\infty)$, (b) $\psi(x,0) = Ae^{-x}$ over the interval $(-\infty, +\infty)$, (c) $\psi(x,0) = Ae^{ikx}$ over the interval $(0, +\infty)$, (d) $\psi(x,0) = Ae^{ikx}$ over the interval $(-\infty, +\infty)$.

The analysis given above leads us to two important postulates of time-dependent quantum mechanics in the context of motion of a quantum particle:

Postulate 1 and its Consequences: *The state of a quantum particle is completely defined by its (position- and time-dependent) wavefunction, $\psi(x,t)$. At time t , $\psi^*(x,t) \cdot \psi(x,t) dx = \rho(x,t) dx$ gives the probability of finding a particle in the dx interval between x and $(x+dx)$ positions. Only a well-behaved wavefunction represents a physically realizable state of the particle. A well-behaved wavefunction must be normalizable, its first derivative must be continuous and finite. Once a wavefunction is normalized, it remains normalized at any later time.*

Postulate 2 and its Consequences: *The wavefunction of a particle evolves in time according to the time-dependent Schrödinger equation: $i\hbar \frac{\partial}{\partial t} \psi(x,t) = \hat{H}\psi(x,t)$. We have already used this*

postulate in Chapter 1 and have seen some of the consequences, rendering two important concepts – stationary and superposition states. A stationary state represents a state wherein the probability density remains independent of time and a superposition state represents a state wherein the probability density exhibits time-dependent change.

In addition to above two postulates, we have already become familiar with another important postulate of quantum mechanics, without perhaps noticing it. So far, we have not given any formal introduction to the quantum mechanical operators. Our familiar \hat{H} is an operator corresponding to the total energy (classical observable) which appears in the TDSE.

Postulate 3 and its Consequences: For every observable in classical mechanics, there corresponds a linear and Hermitian operator in quantum mechanics. Table I lists some examples of the quantum mechanical operators and their classical observables.

Table I: Classical mechanical observables and corresponding quantum mechanical operators

Quantum Mechanical Operator (one dimensional)			Classical Observable
Name	Symbol	Operation	
Hamiltonian	\hat{H}	$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \right) + V(x) \right]$	Total Energy, E
Potential Energy	\hat{V}	Multiply by $V(x)$	Potential Energy, $V(x)$
Kinetic Energy	\hat{K}_x	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \right)$	Kinetic Energy, K_x
Momentum	\hat{P}_x	$-i\hbar \left(\frac{\partial}{\partial x} \right)$	Momentum, p_x
Position	\hat{X}	Multiply by x	Position, x

:Guiding Questions:

TO BE ADDED

Expectation Value and its Time-Evolution:

In quantum mechanics, perhaps the most important introductory question is, “How can a delocalized mathematical function (wavefunction) represent a particle which is supposed to be localized (according to our classical or general consensus)?” We have understood that quantum mechanics only provides a probabilistic answer to this question in terms of the probability density $\rho(x,t)$ for finding the particle at point x and at time t . Here we will further illuminate this point.

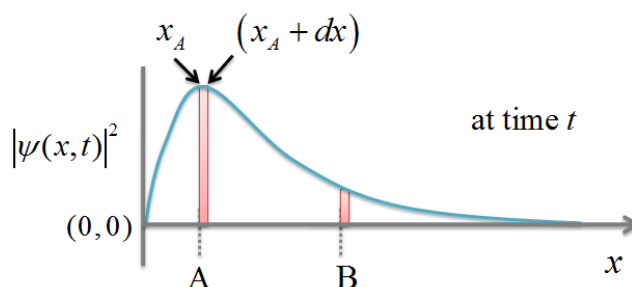


Figure 3.1: A typical example of probability distribution of a particle in one dimension.

We have mentioned earlier that a quantum "particle" with shape and size is defined by its wave function, $\psi(x,t)$, which of course depends on the potential energy term in the Hamiltonian. We have already realized that the wavefunction $\psi(x,t)$ itself can be a complex function; but, the probability density $\rho(x,t) = |\psi(x,t)|^2 = \psi^*(x,t) \cdot \psi(x,t)$ (where $\psi^*(x,t)$ is a complex conjugate of $\psi(x,t)$) must always be real. Figure 3.1 illustrates a typical example of the probability density $\rho(x,t)$ distribution for a particle at time t . As $\rho(x,t)dx = |\psi(x,t)|^2 dx = \psi^*(x,t) \cdot \psi(x,t)dx$ represents the area under the graph $|\psi(x,t)|^2$ for dx interval, one can easily conclude that the particle is more likely to be found near the point A than near the point B on the x -axis (shaded area near point A is larger than that near the

point B). But what does this probability density $\rho(x,t)$ distribution imply with regard to the experimental measurement?

To address the above question, let us consider a large collection (a box) of identical hydrogen atoms. Each atom contains one electron and the time-independent Schrödinger equation for each atom renders wavefunctions of the electron, which are expressed as products of a spherical harmonic function and a radial function, and which depend on three quantum numbers (n , l , and m_l).⁴ These wavefunctions are called atomic orbitals. Each atomic orbital exhibits specific size and shape describing a (three-dimensional) spatial distribution of the electron in the hydrogen atom. For example, the wavefunction with $n=1$, $l=0$ and $m_l=0$ is called the $1s$ orbital of the electron. Similarly, hydrogen atom has three $2p$ orbitals (namely $2p_x$, $2p_y$ and $2p_z$). We may recall that the probability density $\rho(x,t)$ distribution, as given in Figure 3.1, very closely resembles the radial probability distribution of the electron in the $2p_x$ orbital of a hydrogen atom, assuming that the nucleus remains at the $(0,0)$ position. Therefore, arguably, Figure 3.1 schematically depicts the probability for finding the electron in the $2p_x$ orbital of a hydrogen atom at a distance x from the nucleus.

Now imagine the above-mentioned box contains a large collection of identical hydrogen atoms. Each atom has an electron which is present in the $2p_x$ orbital. For the experiment, we first take out one hydrogen atom from the box and then perform a very precise and accurate experimental measurement to find out the position of the electron in the hydrogen atom (with respect to the nucleus). Definitely, experimentally we will get a specific position (say position A) for the $2p_x$ electron. Thereafter, we take out another hydrogen atom and repeat the position measurement process. In the second measurement, it is not necessary that we will find the electron at position A ; we may rather find the electron at a different position (say position B). However, if we continue the probe for the large number of identical hydrogen atom samples, we will notice that frequency (or probability) of finding the position A is larger than that of position B . In fact, repeated experimental measurement should finally render the same distribution which is predicted by quantum mechanics, if infinitely large collection of identical hydrogen atom samples is used. Therefore, probability density distribution directly connects quantum mechanical prediction to the possible experimental outcomes.

One can very easily determine the average position of the electron (or the particle in general) from a repeated measurement. This average position should match the expectation value of position which can be computed using following equation for a given normalized wavefunction,

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t) x \psi(x,t) dx$$

Thus, for a given wavefunction, **the expectation value of a physical or dynamical quantity provides a way to compute the average of repeated experimental measurements.** This argument takes us to the fourth postulate of time-dependent quantum chemistry.

Postulate 4: *If a quantum mechanical system is described by a normalized wavefunction $\psi(x,t)$ then the average value of an observable corresponding to the operator \hat{A} is given by*

$$\langle A \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t) \hat{A} \psi(x,t) dx, \text{ similarly, } \langle A^2 \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t) \hat{A}^2 \psi(x,t) dx \text{ and finally the variance}$$

of the measurement is given by $\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2$.

From a time domain perspective, an obvious question arises here: How does the expectation value of position $\langle x \rangle$ change as time progresses? We will illuminate this question below.

The expectation value of x is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t) x \psi(x,t) dx$$

Taking the first derivative with respect to time, we get

$$\frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \frac{\partial \psi^*(x,t)}{\partial t} x \psi(x,t) dx + \int_{-\infty}^{+\infty} \psi^*(x,t) x \frac{\partial \psi(x,t)}{\partial t} dx \dots (6)$$

We note here that on the left we have total derivative $\frac{d}{dt}$ and on the right hand side we have partial derivative $\frac{\partial}{\partial t}$. Now from the TDSE, we know

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \hat{H} \psi(x,t)$$

$$\text{and, } \frac{\partial}{\partial t} \psi(x,t) = \frac{1}{i\hbar} \hat{H} \psi(x,t) \dots (7)$$

And taking complex conjugate of the TDSE, we get

$$\frac{\partial}{\partial t} \psi^*(x,t) = -\frac{1}{i\hbar} [\hat{H}\psi(x,t)]^* \dots (8)$$

Inserting equations (7) and (8) into equation (6), we get

$$\frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} -\frac{1}{i\hbar} [\hat{H}\psi(x,t)]^* x \psi(x,t) dx + \int_{-\infty}^{+\infty} \psi^*(x,t) x \frac{1}{i\hbar} \hat{H}\psi(x,t) dx \dots (9)$$

As \hat{H} is a Hermitian operator, one can write $\int_{-\infty}^{+\infty} f^* \hat{H} g dx = \int_{-\infty}^{+\infty} g (\hat{H} f)^* dx$

This is why we can write

$$-\frac{1}{i\hbar} \int_{-\infty}^{+\infty} [\hat{H}\psi(x,t)]^* x \psi(x,t) dx = -\frac{1}{i\hbar} \int_{-\infty}^{+\infty} \psi^*(x,t) \hat{H} x \psi(x,t) dx \dots (10)$$

Inserting equation (10) into equation (9) we get

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \frac{1}{i\hbar} \left[\int_{-\infty}^{+\infty} \psi^*(x,t) x \hat{H} \psi(x,t) dx - \int_{-\infty}^{+\infty} \psi^*(x,t) \hat{H} x \psi(x,t) dx \right] \\ &= \frac{1}{i\hbar} \left[\int_{-\infty}^{+\infty} \psi^*(x,t) [x\hat{H} - \hat{H}x] \psi(x,t) dx \right] \\ \text{or, } \frac{d\langle x \rangle}{dt} &= \frac{i}{\hbar} \left[\int_{-\infty}^{+\infty} \psi^*(x,t) [\hat{H}x - x\hat{H}] \psi(x,t) dx \right] \dots (11) \end{aligned}$$

As \hat{H} is expressed as $\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right]$, we can write

$$[\hat{H}x - x\hat{H}] \psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] x \psi(x,t) - x \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x,t)$$

As $\frac{d^2}{dx^2}(x \psi) = \frac{d}{dx} \left[x \frac{d\psi}{dx} + \psi \right] = x \frac{d^2\psi}{dx^2} + \frac{d\psi}{dx} + \frac{d\psi}{dx} = x \frac{d^2\psi}{dx^2} + 2 \frac{d\psi}{dx}$, one can write,

$$\begin{aligned}
\left[\hat{H}x - x\hat{H} \right] \psi(x,t) &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] x \psi(x,t) - x \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x,t) \\
&= -\frac{\hbar^2}{2m} \cdot 2 \frac{d\psi}{dx} - \frac{\hbar^2}{2m} \cdot x \frac{d^2\psi}{dx^2} + Vx\psi + \frac{\hbar^2}{2m} \cdot x \frac{d^2\psi}{dx^2} - Vx\psi \\
&= -\frac{\hbar^2}{m} \frac{d\psi}{dx}
\end{aligned}$$

The above equation can be further rewritten in terms of momentum operator. As

$\hat{P}_x \psi = -i\hbar \frac{d\psi}{dx}$, one can write $\frac{d\psi}{dx} = -\frac{1}{i\hbar} \hat{P}_x \psi$. Therefore, we can write,

$$\left[\hat{H}x - x\hat{H} \right] \psi(x,t) = -\frac{\hbar^2}{m} \left(-\frac{1}{i\hbar} \hat{P}_x \psi(x,t) \right) = -\frac{i\hbar}{m} \hat{P}_x \psi(x,t) \dots (12)$$

Inserting equation (12) into equation (11), we get

$$\frac{d\langle x \rangle}{dt} = \frac{i}{\hbar} \left[\int_{-\infty}^{+\infty} \psi^*(x,t) \left(-\frac{i\hbar}{m} \right) \hat{P}_x \psi(x,t) dx \right] = \frac{1}{m} \int_{-\infty}^{+\infty} \psi^*(x,t) \hat{P}_x \psi(x,t) dx = \frac{\langle P_x \rangle}{m}$$

$$\text{or, } m \frac{d\langle x \rangle}{dt} = \langle P_x \rangle \dots (13)$$

The above equation represents quantum mechanical equivalent of the classical mechanical description of linear momentum ($mv = P$). In general, if an operator \hat{A} does not have explicit time-dependence, the time evolution of its expectation value can be described by

$$\begin{aligned}
\frac{d\langle A \rangle}{dt} &= \frac{i}{\hbar} \left[\int_{-\infty}^{+\infty} \psi^* \left(\hat{H}\hat{A} - \hat{A}\hat{H} \right) \psi dx \right] \\
\text{or, } i\hbar \frac{d\langle A \rangle}{dt} &= \int_{-\infty}^{+\infty} \psi^* \left(\hat{H}\hat{A} - \hat{A}\hat{H} \right) \psi dx
\end{aligned}$$

Ehrenfest Theorem:

Ehrenfest theorem provides a relationship between the expectation values $\langle x \rangle$ and $\langle P \rangle$, and the classical values x and P , respectively. Thus this theorem shows the connection between quantum and classical dynamics.

As we did before, we can write for expectation value of momentum,

$$\langle P_x \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t) \hat{P}_x \psi(x,t) dx$$

$$\text{or, } \frac{d\langle P_x \rangle}{dt} = \frac{i}{\hbar} \int_{-\infty}^{+\infty} \psi^* [\hat{H}\hat{P}_x - \hat{P}_x\hat{H}] \psi dx \dots (14)$$

Given $\hat{H} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right]$ and $\hat{P}_x = -i\hbar \left(\frac{d}{dx} \right)$, we can write,

$$\begin{aligned} \hat{H}\hat{P}_x \psi &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \left(-i\hbar \frac{d}{dx} \right) \psi(x,t) \\ &= -\frac{i\hbar^3}{2m} \frac{d^3\psi}{dx^3} - i\hbar V \frac{d\psi}{dx} \end{aligned}$$

and

$$\begin{aligned} \hat{P}_x\hat{H} \psi &= \left(-i\hbar \frac{d}{dx} \right) \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x,t) \\ &= \frac{i\hbar^3}{2m} \frac{d^3\psi}{dx^3} - i\hbar V \frac{d\psi}{dx} - i\hbar \frac{dV}{dx} \psi \end{aligned}$$

$$\text{Thus, } [\hat{H}\hat{P}_x - \hat{P}_x\hat{H}] \psi = i\hbar \frac{dV}{dx} \psi \dots (15)$$

Inserting equation (15) into equation (14), we get

$$\begin{aligned} \frac{d\langle P_x \rangle}{dt} &= \frac{i}{\hbar} \int_{-\infty}^{+\infty} \psi^* i\hbar \frac{dV}{dx} \psi dx = - \int_{-\infty}^{+\infty} \psi^* \frac{dV}{dx} \psi dx \\ \text{or, } \frac{d\langle P_x \rangle}{dt} &= - \left\langle \frac{dV}{dx} \right\rangle \dots (16) \end{aligned}$$

This equation is called Ehrenfest theorem⁵ which is nothing but the quantum mechanical equivalent of classical mechanical Newton's law: $F = m f$

Key Mathematical Representations of Quantum Mechanics:

The wavefunction and the operator are two key constituents of quantum mechanics. The wavefunction represents the state of a system and when the operator acts the wavefunction, we get the experimental observables. We have already understood that all well-behaved wavefunctions must be square normalizable.

Exercise:

(1) The time-independent wavefunction $\psi(x)$ can be always taken to be real. Even if $\psi(x, t)$ is complex, one can express $\phi(x) = \psi(x) + \psi^*(x)$ to obtain a real solution where $\psi(x)$ and $\psi^*(x)$ both satisfy TISE. Prove this argument.

(2) Prove that if $\psi(x, t)$ is a solution to the TDSE, $A\psi(x, t)$ is also a solution to the TDSE.

Important Note: $\psi(x, t)$ is necessarily complex due to the presence of the phase factor; however, $\psi(x)$ and E are always real.

(2) Determine whether following wavefunctions at $t=0$ are physically acceptable solution to the TDSE:

(a) $\psi(x, 0) = \sin^{-1}(x)$ over the interval $(-1, +1)$, (b) $\psi(x, 0) = Ae^{-|x|}$ over the interval $(-\infty, +\infty)$.

References and Notes:

1. Quantum mechanical postulates are statements that are assumed to be true and to be starting point for further reasoning and arguments. The ultimate test of the fidelity of the postulates must be obtained by comparing the results predicted by quantum mechanics with experimental data.
2. C. Cohen-Tannoudji, B. Diu, and F. Laloe, *Quantum Mechanics, Volume One, Chapter III: The Postulates of Quantum Mechanics*, English Translation, Hermann and John Willey and Sons, 1977.
3. In Mathematics language, this is called initial value problem (an ordinary differential equation with an initial condition).
4. Refer to any standard quantum chemistry text book for hydrogen atom problem.
- 5.

3(2):

Chapter 3A: Answers

Answers

Ans: Using variable separation method, we have obtained following form of the wavefunction:

$$\psi(x,t) = A \psi(x) e^{-\frac{iEt}{\hbar}} \dots (a)$$

Where, A is normalization constant. If E is a complex quantity, one can express this as a general form of a complex number: $E = (\mathcal{E}_0 + i\mathcal{E})$. Then one can rewrite equation (1) as,

$$\psi(x,t) = A \psi(x) e^{-\frac{i(\mathcal{E}_0 + i\mathcal{E})t}{\hbar}} = A \psi(x) e^{-\frac{i\mathcal{E}_0 t}{\hbar}} e^{+\frac{\mathcal{E}t}{\hbar}} \dots (b)$$

We have seen that $\psi(x,t)$ remains normalized at all time. Mathematically, it is expressed as

$\frac{d}{dt} \left[\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx \right] = 0$. This mandates one fact that the integral $\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx$ must be always

independent of time. However,

