Approximate Methods in Quantum Chemistry
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Lecture 38: Time - Dependent Perturbation Theory - I

Hello students! Welcome to this lecture. In the previous weeks we discussed several quantum mechanical systems of varying size and complexity by using different approximate methods. In all our previous discussions, we have considered quantum mechanical systems without their time dependence. In this, and the next few lectures, we are going to address the approximate methods for time-dependent systems.

From the postulates of QM, we know that all the information of a system is there in the wave functions and we can estimate a particular property of the system by applying the corresponding QM operator on this wave function. Unlike other classical observables, time is not a property of the system (hence, no corresponding QM time operator), rather it is a variable like the coordinates. The properties of the system change with changing variable (such as, coordinates or time). In other words, the state of the system evolves in time.

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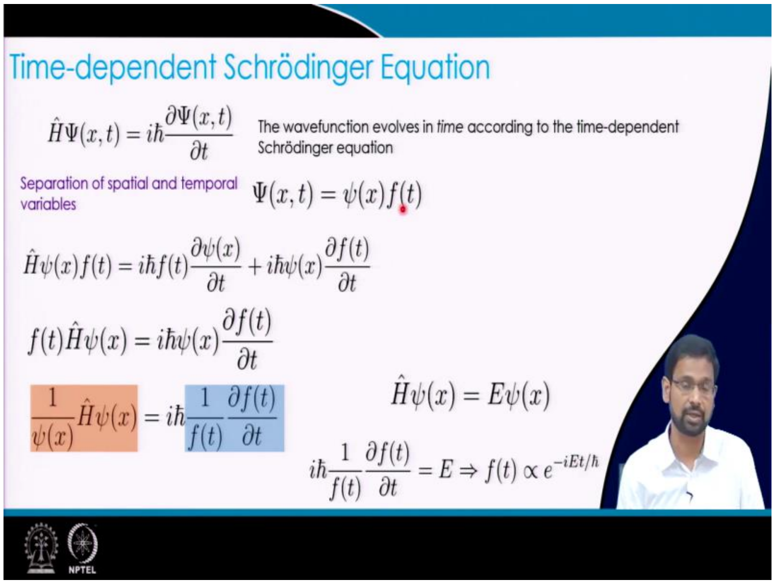

The time evolution of a QM system is given by the next postulate of QM, also known as the time-dependent Schrödinger equation (TDSE),

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

In the above expression, the wave function has both spatial (*x*) and temporal (*t*) dependence. If we consider a separation of the spatial and temporal variables and express the wave function as,

$$\Psi(x,t) = \psi(x)f(t)$$

the TDSE becomes

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

Since the space and the time are two independent variables, we can separate the two variables into two-sides of the equation to obtain

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

If both sides are equal to each other, they both must be the same constants (say, *E*). Using this for the LHS, we obtain the time-independent Schrödinger equation (TISE),

$$\hat{H}\psi(x) = E\psi(x)$$

The RHS becomes,

$$i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t} = E \Rightarrow f(t) \propto e^{-iEt/\hbar}$$

We have already spent quite some time on the spatial part of the problem, i.e., obtaining the wave function ($\psi(x)$) and the energy *E*, corresponding to the Hamiltonian. From the above exercise, we see that the temporal part of the total wave function is merely $e^{-iEt/\hbar}$, which requires the energy *E* (the solution from the TISE).

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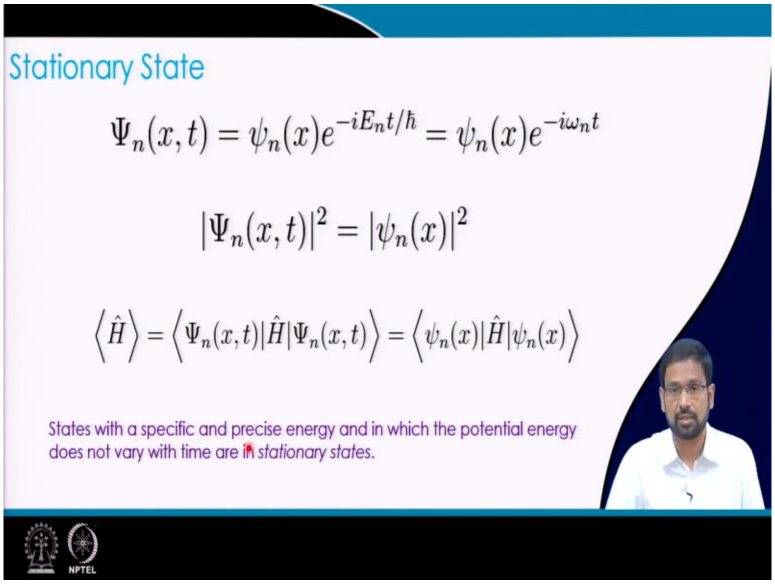

From the above discussion, we have the total wave function as,

$$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar} = \psi_n(x)e^{-i\omega_nt}$$

If we evaluate the probability density, we obtain

$$|\Psi_n(x,t)|^2 = |\psi_n(x)|^2$$

since, $\left|e^{-i\omega_nt}\right|^2 = 1$. This renders the probability density to be independent of time. Furthermore, if we evaluate the energy expectation value,

$$\left\langle \hat{H} \right\rangle = \left\langle \Psi_n(x,t)|\hat{H}|\Psi_n(x,t) \right\rangle = \left\langle \psi_n(x)|\hat{H}|\psi_n(x) \right\rangle$$

the result will remain independent of time, as shown above.

For such states, where the probability density and the energy expectation value do not change with time are called the stationary state. Stationary means something that does not change. A stationary does not mean that the particles in the system do not move. It simply says that the probability density, the energy, have precise values.

In the above discussion, the time factor *f*(*t*) used a precise value of energy E_n (the eigenvalue corresponding to the state ψ_n). Next we discuss the situation when the state is constructed as a superposition of several eigenstates, such that the energy of the state is not precise.

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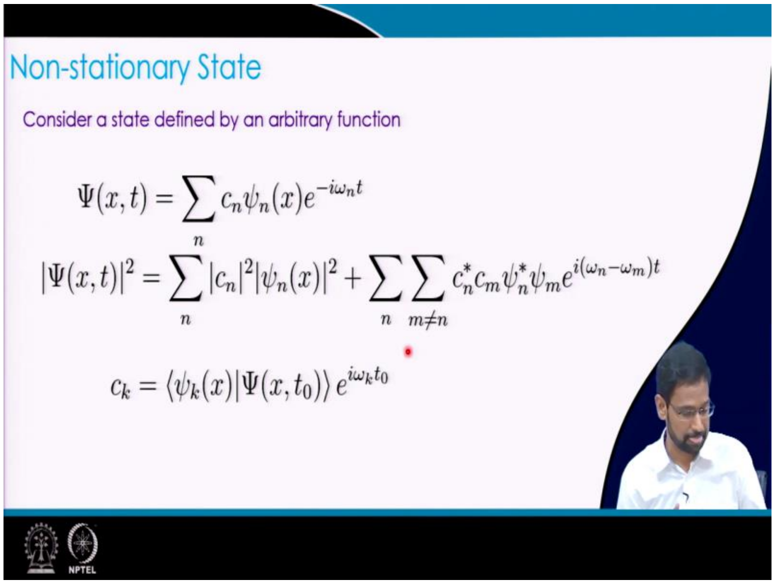

For a superposition of states, we can write down the TD-wave function as the following sum,

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-i\omega_n t}$$

Here, the coefficients of the expansion can be obtained as,

$$c_k = \langle \psi_k(x) | \Psi(x,t_0) \rangle \, e^{i\omega_k t_0}$$

Where t_0 represents the initial time and hence the coefficients do not change with time. Since the coefficients reflect the composition of the states, it means that the composition of the state would remain unchanged with time.

For this state, if we evaluate the proability density, we obtain

$$|\Psi(x,t)|^2 = \sum_n |c_n|^2 |\psi_n(x)|^2 + \sum_n \sum_{m \neq n} c_n^* c_m \psi_n^* \psi_m e^{i(\omega_n - \omega_m)t}$$

The 2nd term in the above expression shows the time-dependence in the probability density. Hence, the state $\Psi(x,t)$, is a non-stationary state. Similarly, we can also show that the expectation value of different operators would also change with time. Note, the non-stationary states appear when the state of the system does not have a precise energy.

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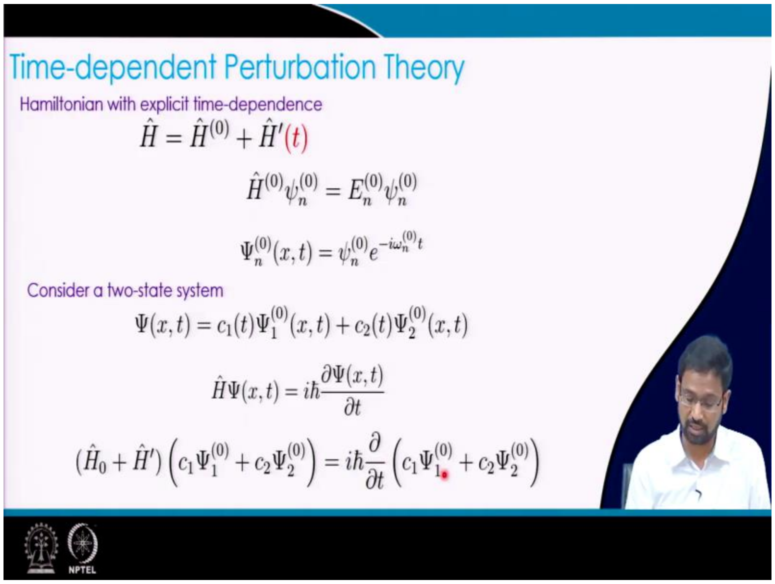

In the previous examples (either a pure eigenstate or a superposition of states), we maintained that the Hamiltonian is time-independent. However, in many cases we can have explicit time-dependence in the Hamiltoinanian. In such cases, we can treat the time-dependent part of the Hamltonian as a perturbation to the rest of the (time-independent) Hamiltonian, i.e.,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'(t)$$

Here, we assume that we know the solution of the time-independent part of the problem, i.e.,

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

and the total wave function can be written as,

$$\Psi_n^{(0)}(x,t) = \psi_n^{(0)}e^{-i\omega_n^{(0)}t}$$

Before we apply the perturbation theory to this problem, let us consider a 2-state problem where the state of the system is given by,

$$\Psi(x,t) = c_1(t)\Psi_1^{(0)}(x,t) + c_2(t)\Psi_2^{(0)}(x,t)$$

where, $\Psi_i^{(0)}(x,t)$ is the i^{th} unperturbed state and the coefficients $C_i(t)$ are the time-dependent amplitudes describing the overall wave function. Using TDSE for the above state, i.e.,

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

we obtain,

$$(\hat{H}_0 + \hat{H}')\left(c_1\Psi_1^{(0)} + c_2\Psi_2^{(0)}\right) = i\hbar\frac{\partial}{\partial t}\left(c_1\Psi_1^{(0)} + c_2\Psi_2^{(0)}\right)$$

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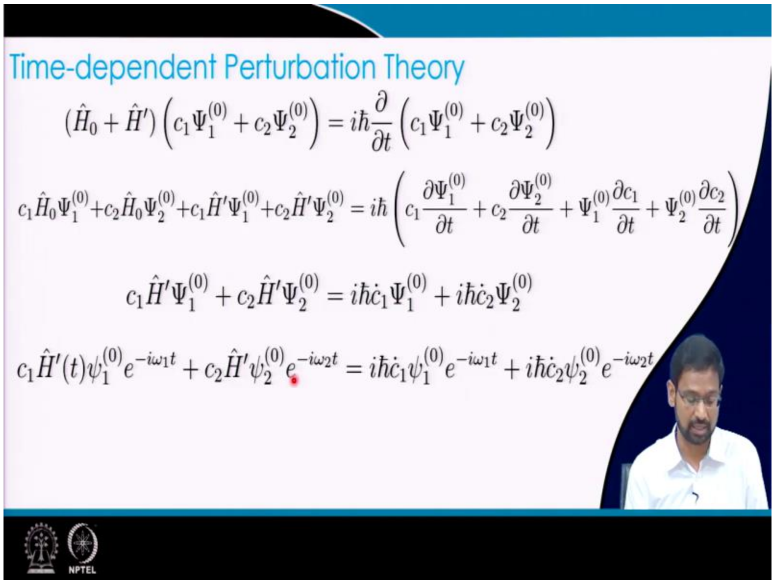

Rearranging the previous equation,

$$c_1\hat{H}_0\Psi_1^{(0)} + c_2\hat{H}_0\Psi_2^{(0)} + c_1\hat{H}'\Psi_1^{(0)} + c_2\hat{H}'\Psi_2^{(0)} = i\hbar\left(c_1\frac{\partial\Psi_1^{(0)}}{\partial t} + c_2\frac{\partial\Psi_2^{(0)}}{\partial t} + \Psi_1^{(0)}\frac{\partial c_1}{\partial t} + \Psi_2^{(0)}\frac{\partial c_2}{\partial t}\right)$$

The first two terms of the LHS and RHS are equal (from the TDSE for state $\Psi_1^{(0)}$ and $\Psi_2^{(0)}$ and the unperturbed Hamiltonian H_0), which leaves us with

$$c_1\hat{H}'\Psi_1^{(0)} + c_2\hat{H}'\Psi_2^{(0)} = i\hbar\dot{c}_1\Psi_1^{(0)} + i\hbar\dot{c}_2\Psi_2^{(0)}$$

Expressing the total wave function $\Psi_i^{(0)}(x,t)$ in terms of its time-independent part and the time factor ($f(t)$), we obtain

$$c_1\hat{H}'(t)\psi_1^{(0)}e^{-i\omega_1 t} + c_2\hat{H}'\psi_2^{(0)}e^{-i\omega_2 t} = i\hbar\dot{c}_1\psi_1^{(0)}e^{-i\omega_1 t} + i\hbar\dot{c}_2\psi_2^{(0)}e^{-i\omega_2 t}$$

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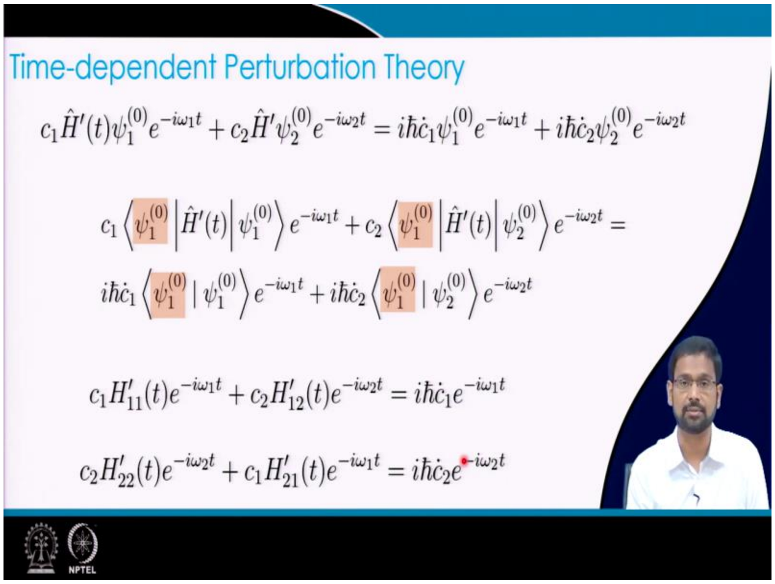

By multiplying $\langle\psi_1^{(0)}|$, in both LHS and RHS of the above equation, we get

$$c_1\left\langle\psi_1^{(0)}\middle|\hat{H}'(t)\middle|\psi_1^{(0)}\right\rangle e^{-i\omega_1 t} + c_2\left\langle\psi_1^{(0)}\middle|\hat{H}'(t)\middle|\psi_2^{(0)}\right\rangle e^{-i\omega_2 t} =$$

$$i\hbar\dot{c}_1\left\langle\psi_1^{(0)} \mid \psi_1^{(0)}\right\rangle e^{-i\omega_1 t} + i\hbar\dot{c}_2\left\langle\psi_1^{(0)} \mid \psi_2^{(0)}\right\rangle e^{-i\omega_2 t}$$

Given the orthonormality of $\psi_i^{(0)}$, the above relation simplifies to

$$c_1H'_{11}(t)e^{-i\omega_1 t} + c_2H'_{12}(t)e^{-i\omega_2 t} = i\hbar\dot{c}_1e^{-i\omega_1 t}$$

Where the Hamiltonian matrix elements $H'_{11}(t) = \left\langle\psi_1^{(0)}\middle|\hat{H}'(t)\middle|\psi_1^{(0)}\right\rangle$

Similarly, if we multiply $\langle\psi_2^{(0)}|$ we would obtain,

$$c_2H'_{22}(t)e^{-i\omega_2 t} + c_1H'_{21}(t)e^{-i\omega_1 t} = i\hbar\dot{c}_2e^{-i\omega_2 t}$$

In the next lecture, we will learn how we solve the above set of equations for a 2-state problem.

Thank you for your attention.