Quantum dynamics….with the dynamics

2-level system (oscillations forever)

- Consider a two-state system : $\Psi(r,t) = c_1(t)\phi_1(r) + c_2(t)\phi_2(r)$

- $\phi_1(r)$ and $\phi_2(r)$ are orthonormal states, that is $<\phi_1|\phi_1> = <\phi_2|\phi_2> = 1$ and $<\phi_1|\phi_2> = <\phi_2|\phi_1> = 0$ (Recall that $<\phi_1|\phi_1> = \int \phi_1^*(r)\,\phi_1(r)\,dr = 1$, with ϕ_1^* complex conjugate of ϕ_1)

- In addition, the states $|\phi_1>$ and $|\phi_2>$ are eigenstates of the Hamiltonian, that is: $H|\phi_1> = E_1|\phi_1>$ and $H|\phi_2> = E_2|\phi_2>$

- The time-dependent Schrödinger equation (TDSE) reads:

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

$$i\hbar\frac{\partial\left[c_1(t)\phi_1 + c_2(t)\phi_2\right]}{\partial t} = H(r,t)\left[c_1(t)\phi_1 + c_2(t)\phi_2\right]$$

We can determine an expression for the time-evolution of each time-dependent coefficients, $c_1(t)$ or $c_2(t)$ by multiplying the TDSE by the complex conjugate of the corresponding stationary-state and integrating (in Dirac notation this amounts to multiplying by the bra ($<\phi_1|$ to obtain $c_1(t)$ for instance). Doing so for $c_1(t)$ in Dirac notation we get:

$$i\hbar\left[\frac{\partial c_1(t)}{\partial t}<\phi_1|\phi_1> + \frac{\partial c_2(t)}{\partial t}<\phi_2|\phi_1>\right] = c_1(t)<\phi_1|H(r,t)|\phi_1> + c_2(t)<\phi_1|H(r,t)|\phi_2>$$

$$i\hbar\frac{\partial c_1(t)}{\partial t} = c_1(t)<\phi_1|H(r,t)|\phi_1> + c_2(t)<\phi_1|H(r,t)|\phi_2>$$

We do the same procedure with $<\phi_2|$ to obtain an expression for $\dot{c}_2(t)$

$$i\hbar\frac{\partial c_2(t)}{\partial t} = c_2(t)<\phi_2|H(r,t)|\phi_2> + c_2(t)<\phi_2|H(r,t)|\phi_1>$$

We can write this system of equations in matrix form:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} E_1(t) & V_{12}(t) \\ V_{21}(t) & E_2(t) \end{pmatrix}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$$

We take the case where the Hamiltonian matrix is independent of time, t and we can write:

$i\hbar\frac{\partial \mathbf{c}}{\partial t} = \mathbf{Hc}$ and $\mathbf{c}(t) = \exp\left(\frac{-i}{\hbar}\mathbf{H}t\right)\mathbf{c}(0)$

where $\mathbf{c}$ is a column vector and $\mathbf{H}$ a matrix.

We can clearly see if there is no interaction energy between states ($V_{21}(t) = V_{12}(t) = 0$), then the transition probability for a given state will be constant ($|c|^2 = cst$), the state remains in a stationary state and does not oscillate.

A brief note on the unitary evolution operator:

The wavefunction is a time-dependent quantity. We can define an evolution operator $\hat{U}(t, t_0)$ that propagates the wavefunction in time:

$|\Psi(r,t) > = \hat{U}(t, t_0)|\Psi(r, t_0) >$

This operator must satisfy certain properties, namely:

- Unitarity:

If the wavefunction is normalized at t_0 it must remain normalized at a later date t, hence, the operator $\hat{U}$ should not change the norm of the wavefunction. As a result, we have:

$$< \Psi(r,t)|\Psi(r,t) > = < \Psi(r,t_0)|\hat{U}^\dagger(t,t_o)\hat{U}(t,t_0)|\Psi(r,t_0) > = 1.$$

For the above relation to hold, $\hat{U}^\dagger(t,t_o)\hat{U}(t,t_0) = \mathbf{1}$, where $\mathbf{1}$ is the identity operator. This implies that $\hat{U}^\dagger(t,t_o) = \hat{U}^{-1}(t,t_0)$.

- Continuity

$|\Psi(r,t) > = \hat{U}(t,t)|\Psi(r,t) >$, which implies that $\hat{U}(t,t) = \mathbf{1}$. The operator acting on the wavefunction at a time t, when the wavefunction is already at time t gives the wavefunction back again, hence the operator acts as an identity operator.

- Composition

We can propagate the wavefunction to two consecutive points in time, either by applying $\hat{U}$ once or two times consecutively:

$$|\Psi(r,t_2) > = \hat{U}(t_2,t_0)|\Psi(r,t_0) >$$

or

$$|\Psi(r,t_2) > = \hat{U}(t_2,t_1)\hat{U}(t_1,t_0)|\Psi(r,t_0) >$$

Hence we have:

$$\hat{U}(t_2, t_0) = \hat{U}(t_2, t_1)\hat{U}(t_1, t_0)$$

In order to obtain an expression for $\hat{U}$, we can insert it into the TDSE:

$$i\hbar\frac{\partial|\Psi(r,t)>}{\partial t} = H(r,t)|\Psi(r,t)>$$

with $t_0 = 0$

$$i\hbar\frac{\partial\hat{U}(t)}{\partial t}|\Psi(r,t=0)> = H(r,t)\hat{U}(t)|\Psi(r,t=0)>$$

$$i\hbar\frac{\partial\hat{U}(t)}{\partial t} = H(r,t)\hat{U}(t)$$

$$\hat{U}(t) = \exp\left(\frac{-i}{\hbar}\int_0^t H(r,t')\,dt'\right)$$

If $H(r,t)$ is time independent, it can be taken out of the integral, and the integral evaluates to t. Hence for a time-independent Hamiltonian, the unitary evolution operator is:

$$\hat{U}(t) = \exp\left(\frac{-i}{\hbar}Ht\right)$$