

# 1. INTRODUCTION

## 1.1. Time Evolution with a Time-Independent Hamiltonian

The time evolution of the state of a quantum system is described by the time-dependent Schrödinger equation (TDSE):

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \hat{H}(\vec{r}, t) \psi(\vec{r}, t) \quad (1.1)$$

$\hat{H}$  is the Hamiltonian operator which describes all interactions between particles and fields, and determines the state of the system in time and space.  $\hat{H}$  is the sum of the kinetic and potential energy. For one particle under the influence of a potential

$$\hat{H} = -\frac{\hbar^2}{2m} \hat{\nabla}^2 + \hat{V}(\vec{r}, t) \quad (1.2)$$

The state of the system is expressed through the wavefunction  $\psi(\vec{r}, t)$ . The wavefunction is complex and cannot be observed itself, but through it we obtain the probability density  $P = |\psi(\vec{r}, t)|^2$  which characterizes the spatial probability distribution for the particles described by  $\hat{H}$  at time  $t$ . Also, it is used to calculate the expectation value of an operator  $\hat{A}$

$$\langle \hat{A}(t) \rangle = \int \psi^*(\vec{r}, t) \hat{A} \psi(\vec{r}, t) d\vec{r} = \langle \psi(t) | \hat{A} | \psi(t) \rangle \quad (1.3)$$

Physical observables must be real, and therefore will correspond to the expectation values of Hermitian operators ( $\hat{A} = \hat{A}^\dagger$ ).

Our first exposure to time-dependence in quantum mechanics is often for the specific case in which the Hamiltonian  $\hat{H}$  is assumed to be independent of time:  $\hat{H} = \hat{H}(\vec{r})$ . We then assume a solution with a form in which the spatial and temporal variables in the wavefunction are separable:

$$\psi(\vec{r}, t) = \varphi(\vec{r}) T(t) \quad (1.4)$$

$$i\hbar \frac{1}{T(t)} \frac{\partial}{\partial t} T(t) = \frac{\hat{H}(\vec{r}) \varphi(\vec{r})}{\varphi(\vec{r})} \quad (1.5)$$

Here the left-hand side is a function only of time, and the right-hand side is a function of space only ( $\vec{r}$ , or rather position and momentum). Equation (1.5) can only be satisfied if both sides are equal to the same constant,  $E$ . Taking the right-hand side we have

$$\frac{\hat{H}(\vec{r}) \varphi(\vec{r})}{\varphi(\vec{r})} = E \quad \Rightarrow \quad \hat{H}(\vec{r}) \varphi(\vec{r}) = E \varphi(\vec{r}) \quad (1.6)$$

This is the Time-Independent Schrödinger Equation (TISE), an eigenvalue equation, for which  $\varphi(\vec{r})$  are the eigenstates and  $E$  are the eigenvalues. Here we note that  $\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle = E$ , so  $\hat{H}$  is the operator corresponding to  $E$  and drawing on classical mechanics we associate  $\langle \hat{H} \rangle$  with the expectation value of the energy of the system.

Now taking the left-hand side of (1.5) and integrating:

$$i\hbar \frac{1}{T(t)} \frac{\partial T}{\partial t} = E \quad \Rightarrow \quad \left( \frac{\partial}{\partial t} + \frac{iE}{\hbar} \right) T(t) = 0 \quad (1.7)$$

$$T(t) = \exp(-iEt / \hbar) \quad (1.8)$$

So, in the case of a bound potential we will have a discrete set of eigenfunctions  $\varphi_n(\vec{r})$  with corresponding energy eigenvalues  $E_n$  from the TISE, and there are a set of corresponding solutions to the TDSE.

$$\psi_n(\vec{r}, t) = \varphi_n(\vec{r}) \exp(-iE_n t / \hbar) \quad (1.9)$$

Since the only time-dependence is a phase factor, the probability density for an eigenstate is independent of time:  $P = |\psi_n(t)|^2 = \text{constant}$ . Therefore, the eigenstates  $\varphi(\vec{r})$  do not change with time and are called *stationary states*.

However, more generally, a system may exist as a linear combination of eigenstates:

$$\psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}, t) = \sum_n c_n e^{-iE_n t / \hbar} \varphi_n(\vec{r}) \quad (1.10)$$

where  $c_n$  are complex amplitudes, with  $\sum_n |c_n|^2 = 1$ . For such a case, the probability density will oscillate with time. As an example, consider two eigenstates

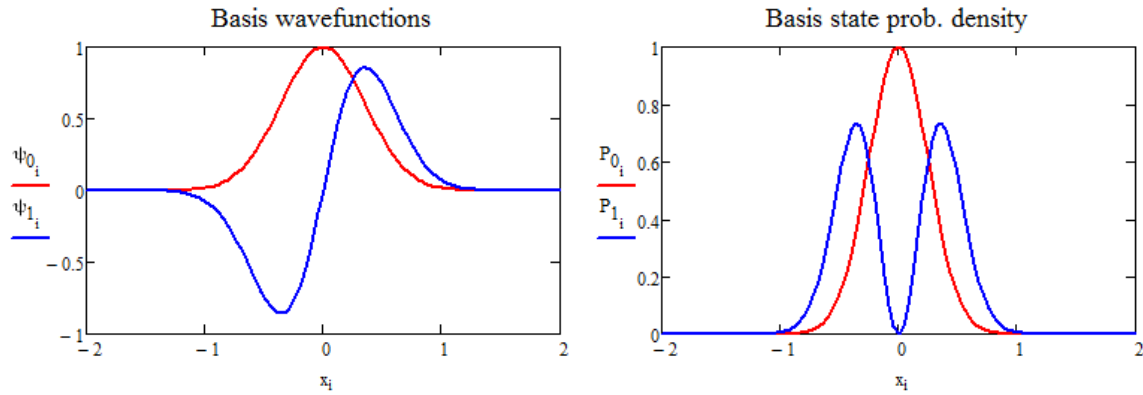
$$\psi(\vec{r}, t) = \psi_1 + \psi_2 = c_1 \varphi_1 e^{-iE_1 t / \hbar} + c_2 \varphi_2 e^{-iE_2 t / \hbar} \quad (1.11)$$

For this state the probability density oscillates in time as

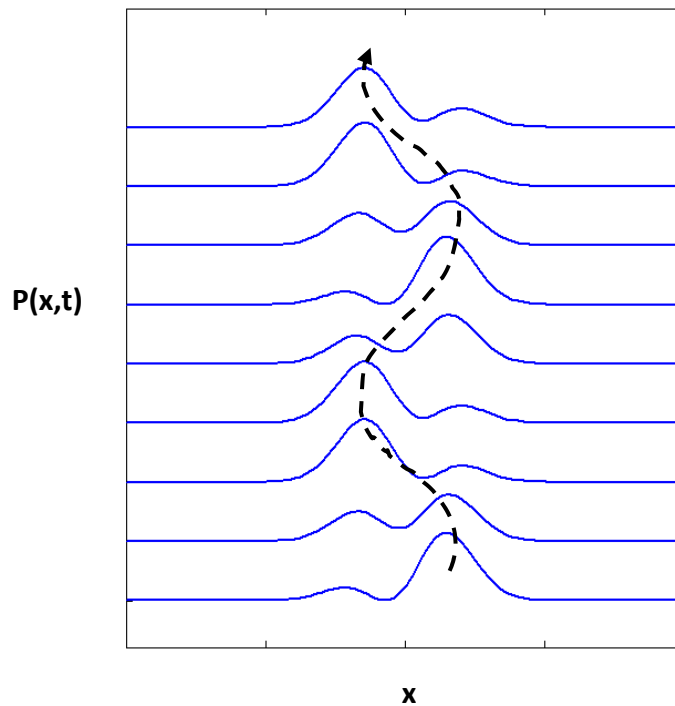
$$\begin{aligned} P(t) &= |\psi|^2 = |\psi_1 + \psi_2|^2 \\ &= |c_1 \varphi_1|^2 + |c_2 \varphi_2|^2 + c_1^* c_2 \varphi_1^* \varphi_2 e^{-i(\omega_2 - \omega_1)t} + c_2^* c_1 \varphi_2^* \varphi_1 e^{+i(\omega_2 - \omega_1)t} \\ &= |\psi_1|^2 + |\psi_2|^2 + 2|\psi_1 \psi_2| \cos((\omega_2 - \omega_1)t) \end{aligned} \quad (1.12)$$

where  $\omega_n = E_n / \hbar$ . We refer to this state of the system that gives rise to this time-dependent oscillation in probability density as a coherent superposition state, or *coherence*. More generally, the oscillation term in eq. (1.12) may also include a time-independent phase factor  $\phi$  that arises from the complex expansion coefficients.

As an example, consider the superposition of the ground and first excited states of the quantum harmonic oscillator. The basis wavefunctions,  $\psi_0(x)$  and  $\psi_1(x)$ , and their stationary probability densities  $P_i = \langle \psi_i(x) | \psi_i(x) \rangle$  are



If we create a superposition of these states with eqn. (1.11), the time-dependent probability density oscillates, with  $\langle x(t) \rangle$  bearing similarity to the classical motion. (Here  $c_0 = 0.5$  and  $c_1 = 0.87$ .)



**Readings**

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 405.
2. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Ch. 1.
3. Schatz, G. C.; Ratner, M. A., *Quantum Mechanics in Chemistry*. Dover Publications: Mineola, NY, 2002; Ch. 2.

## 1.2. Exponential Operators

Throughout our work, we will make use of exponential operators of the form

$$\hat{T} = e^{-i\hat{A}}$$

We will see that these exponential operators act on a wavefunction to move it in time and space. Of particular interest to us is the time-propagator or time-evolution operator,  $\hat{U} = e^{-i\hat{H}t/\hbar}$ , which propagates the wavefunction in time. Note the operator  $\hat{T}$  is a *function of an operator*,  $f(\hat{A})$ . A function of an operator is defined through its expansion in a Taylor series, for instance

$$\hat{T} = e^{-i\hat{A}} = \sum_{n=0}^{\infty} \frac{(-i\hat{A})^n}{n!} = 1 - i\hat{A} - \frac{\hat{A}\hat{A}}{2} - \dots \quad (1.13)$$

Since we use them so frequently, let's review the properties of exponential operators that can be established with eq. (1.13). If the operator  $\hat{A}$  is Hermitian, then  $\hat{T} = e^{-i\hat{A}}$  is unitary, i.e.,  $\hat{T}^\dagger = \hat{T}^{-1}$ . Thus the Hermitian conjugate of  $\hat{T}$  reverses the action of  $\hat{T}$ . For the time-propagator  $\hat{U}$ ,  $\hat{U}^\dagger$  is often referred to as the time-reversal operator.

The eigenstates of the operator  $\hat{A}$  also are also eigenstates of  $f(\hat{A})$ , and eigenvalues are functions of the eigenvalues of  $\hat{A}$ . Namely, if you know the eigenvalues and eigenvectors of  $\hat{A}$ , i.e.,  $\hat{A}\varphi_n = a_n\varphi_n$ , you can show by expanding the function that

$$f(\hat{A})\varphi_n = f(a_n)\varphi_n \quad (1.14)$$

Our most common application of this property will be to exponential operators involving the Hamiltonian. Given the eigenstates  $\varphi_n$ , then  $\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$  implies

$$e^{-i\hat{H}t/\hbar}|\varphi_n\rangle = e^{-iE_n t/\hbar}|\varphi_n\rangle \quad (1.15)$$

Just as  $\hat{U} = e^{-i\hat{H}t/\hbar}$  is the time-evolution operator, which displaces the wavefunction in time,  $\hat{D}_x = e^{-i\hat{p}_x x/\hbar}$  is the spatial displacement operator that moves  $\psi$  along the  $x$  coordinate. If we define  $\hat{D}_x(\lambda) = e^{-i\hat{p}_x \lambda/\hbar}$ , then the action of is to displace the wavefunction by an amount  $\lambda$ .

$$|\psi(x - \lambda)\rangle = \hat{D}_x(\lambda)|\psi(x)\rangle \quad (1.16)$$

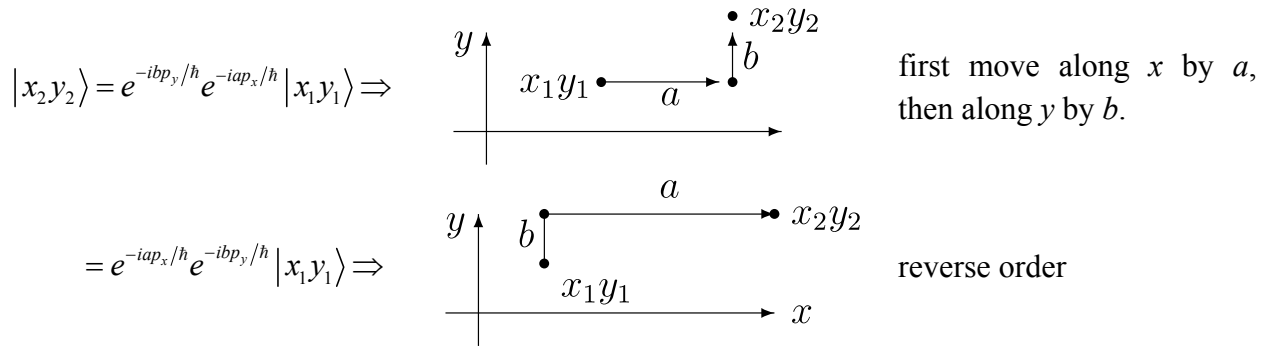
Also, applying  $\hat{D}_x(\lambda)$  to a position operator shifts the operator by  $\lambda$

$$\hat{D}_x^\dagger \hat{x} \hat{D}_x = \hat{x} + \lambda \quad (1.17)$$

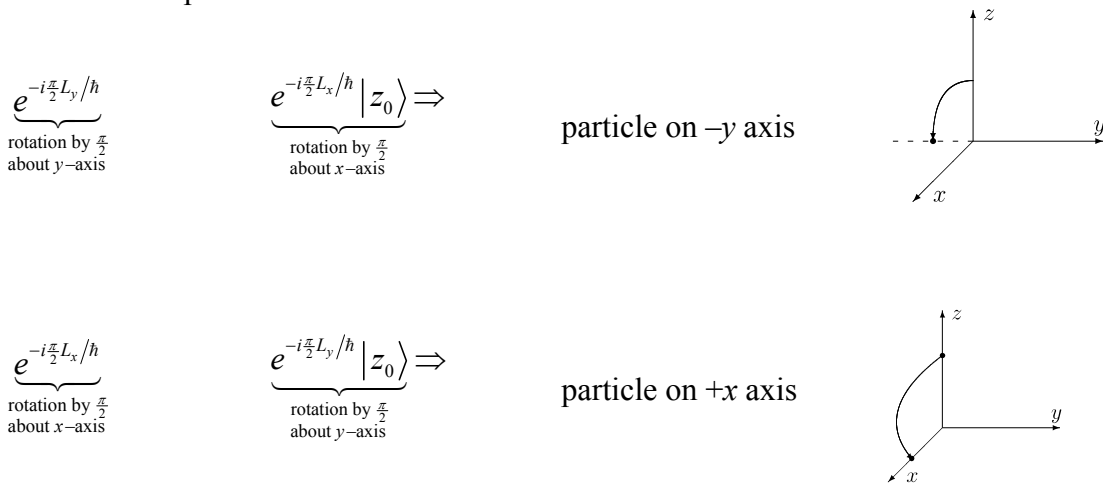
Thus  $e^{-i\hat{p}_x \lambda/\hbar}|x\rangle$  is an eigenvector of  $\hat{x}$  with eigenvalue  $x + \lambda$  instead of  $x$ . The operator  $\hat{D}_x = e^{-i\hat{p}_x \lambda/\hbar}$  is a displacement operator for  $x$  position coordinates. Similarly,  $\hat{D}_y = e^{-i\hat{p}_y \lambda/\hbar}$  generates displacements in  $y$  and  $\hat{D}_z$  in  $z$ . Similar to the time-propagator  $\hat{U}$ , the displacement

operator  $\hat{D}$  must be unitary, since the action of  $\hat{D}^\dagger \hat{D}$  must leave the system unchanged. That is if  $\hat{D}$  shifts the system to  $x$  from  $x_0$ , then  $\hat{D}^\dagger$  shifts the system from  $x$  back to  $x_0$ .

We know intuitively that linear displacements commute. For example, if we wish to shift a particle in two dimensions,  $x$  and  $y$ , the order of displacement does not matter. We end up at the same position. These displacement operators commute, as expected from  $[p_x, p_y] = 0$ .



Similar to the displacement operator, we can define rotation operators that depend on the angular momentum operators,  $L_x$ ,  $L_y$ , and  $L_z$ . For instance,  $\hat{R}_x(\phi) = e^{-i\phi L_x/\hbar}$  gives a rotation by angle  $\phi$  about the  $x$ -axis. Unlike linear displacement, rotations about different axes do not commute. For example, consider a state representing a particle displaced along the  $z$ -axis,  $|z_0\rangle$ . Now the action of two rotations  $\hat{R}_x$  and  $\hat{R}_y$  by an angle of  $\pi/2$  on this particle differs depending on the order of operation.



The results of these two rotations taken in opposite order differ by a rotation about the  $z$ -axis. Thus, because the rotations about different axes do not commute, we must expect the angular momentum operators, which generate these rotations, not to commute. Indeed, we know that  $[L_x, L_y] = i\hbar L_z$ , where the commutator of rotations about the  $x$  and  $y$  axes is related by a  $z$ -axis

rotation. As with rotation operators, we will need to be careful with time-propagators to determine whether the order of time-propagation matters. This, in turn, will depend on whether the Hamiltonians at two points in time commute.

Finally, it is worth noting some relationships that are important in evaluating the action of exponential operators:

(1) The Baker–Hausdorff relationship:

$$\begin{aligned} \exp(i\hat{G}\lambda)\hat{A}\exp(-i\hat{G}\lambda) &= \hat{A} + i\lambda[\hat{G},\hat{A}] + \left(\frac{i^2\lambda^2}{2!}\right)[\hat{G},[\hat{G},\hat{A}]] + \dots \\ &+ \left(\frac{i^n\lambda^n}{n!}\right)[\hat{G},[\hat{G},[\hat{G},\dots[\hat{G},\hat{A}]]]] + \dots \end{aligned} \quad (1.18)$$

(2) If  $\hat{A}$  and  $\hat{B}$  do not commute, but  $[\hat{A},\hat{B}]$  commutes with  $\hat{A}$  and  $\hat{B}$ , then

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\frac{1}{2}[\hat{A},\hat{B}]} \quad (1.19)$$

$$(3) \quad e^{\hat{A}}e^{\hat{B}} = e^{\hat{B}}e^{\hat{A}}e^{-[\hat{B},\hat{A}]} \quad (1.19)$$

## Time-Evolution Operator

Since the TDSE is deterministic and linear in time, we can define an operator that describes the dynamics of the wavefunction:

$$\psi(t) = \hat{U}(t, t_0)\psi(t_0) \quad (1.20)$$

$U$  is the time-propagator or time-evolution operator that evolves the quantum system as a function of time. It represents the solution to the time-dependent Schrödinger equation. To investigate its form we consider the TDSE for a *time-independent Hamiltonian*:

$$\frac{\partial}{\partial t}\psi(\bar{r}, t) + \frac{i\hat{H}}{\hbar}\psi(\bar{r}, t) = 0 \quad (1.21)$$

To solve this, we will define an exponential operator  $\hat{T} = \exp(-i\hat{H}t/\hbar)$ , which is defined through its expansion in a Taylor series:

$$\hat{T} = \exp(-i\hat{H}t/\hbar) = 1 - \frac{i\hat{H}t}{\hbar} + \frac{1}{2!}\left(\frac{i\hat{H}t}{\hbar}\right)^2 - \dots \quad (1.22)$$

You can also confirm from the expansion that  $\hat{T}^{-1} = \exp(i\hat{H}t/\hbar)$ , noting that  $\hat{H}$  is Hermitian and  $\hat{H}$  commutes with  $\hat{T}$ . Multiplying eq. (1.21) from the left by  $\hat{T}^{-1}$ , we can write

$$\frac{\partial}{\partial t}\left[\exp\left(\frac{i\hat{H}t}{\hbar}\right)\psi(\bar{r}, t)\right] = 0, \quad (1.23)$$

and integrating  $t_0 \rightarrow t$ , we get

$$\exp\left(\frac{i\hat{H}t}{\hbar}\right)\psi(\bar{r}, t) - \exp\left(\frac{i\hat{H}t_0}{\hbar}\right)\psi(\bar{r}, t_0) = 0 \quad (1.24)$$

$$\psi(\bar{r}, t) = \exp\left(\frac{-i\hat{H}(t-t_0)}{\hbar}\right)\psi(\bar{r}, t_0) \quad (1.25)$$

So, comparing to (1.20), we see that the time-propagator is

$$\hat{U}(t, t_0) = \exp\left(\frac{-i\hat{H}(t-t_0)}{\hbar}\right). \quad (1.26)$$

For the time-independent Hamiltonian for which we know the eigenstates  $\varphi_n$  and eigenvalues  $E_n$ , we can express this in a practical form using eq. (1.14)

$$\psi_n(\bar{r}, t) = e^{-iE_n(t-t_0)/\hbar}\psi_n(\bar{r}, t_0) \quad (1.27)$$



Alternatively, if we substitute the projection operator (or identity relationship)

$$\sum_n |\varphi_n\rangle\langle\varphi_n| = 1 \quad (1.28)$$

into eq. (1.26), we see

$$\begin{aligned} \hat{U}(t, t_0) &= e^{-i\hat{H}(t-t_0)/\hbar} \sum_n |\varphi_n\rangle\langle\varphi_n| \\ &= \sum_n e^{-i\omega_n(t-t_0)} |\varphi_n\rangle\langle\varphi_n| \end{aligned} \quad \omega_n = \frac{E_n}{\hbar} \quad (1.29)$$

So now we can write our time-developing wave-function as

$$\begin{aligned} |\psi_n(\bar{r}, t)\rangle &= |\varphi_n\rangle \sum_n e^{-i\omega_n(t-t_0)} \langle\varphi_n|\psi_n(\bar{r}, t_0)\rangle \\ &= \sum_n e^{-i\omega_n(t-t_0)} c_n \\ &= \sum_n c_n(t) |\varphi_n\rangle \end{aligned} \quad (1.30)$$

As written in eq. (1.20), we see that the time-propagator  $\hat{U}(t, t_0)$  acts to the right (on *kets*) to evolve the system in time. The evolution of the conjugate wavefunctions (*bras*) is under the Hermitian conjugate of  $\hat{U}(t, t_0)$  acting to the left:

$$\langle\psi(t)| = \langle\psi(t_0)| \hat{U}^\dagger(t, t_0) \quad (1.31)$$

From its definition as an expansion and recognizing  $\hat{H}$  as Hermitian, you can see that

$$\hat{U}^\dagger(t, t_0) = \exp\left[\frac{i\hat{H}(t-t_0)}{\hbar}\right] \quad (1.32)$$

Noting that  $\hat{U}$  is unitary,  $\hat{U}^\dagger = \hat{U}^{-1}$ , we often refer to  $\hat{U}^\dagger$  as the time reversal operator.

### 1.3. Two-Level System

Let's use the time-propagator in a model calculation that we will refer to often. It is common to reduce or map quantum problems onto a two level system (2LS). We will pick the most important states for our problem and find strategies for discarding or simplifying the influence of the remaining degrees of freedom. Consider a 2LS with two unperturbed or “zerth order” states  $|\varphi_a\rangle$  and  $|\varphi_b\rangle$  with energies  $\varepsilon_a$  and  $\varepsilon_b$ , which are described by a zero-order Hamiltonian  $H_0$ :

$$\begin{aligned}\hat{H}_0 &= |\varphi_a\rangle \varepsilon_a \langle \varphi_a| + |\varphi_b\rangle \varepsilon_b \langle \varphi_b| \\ &= \begin{pmatrix} \varepsilon_a & 0 \\ 0 & \varepsilon_b \end{pmatrix}\end{aligned}\quad (1.33)$$

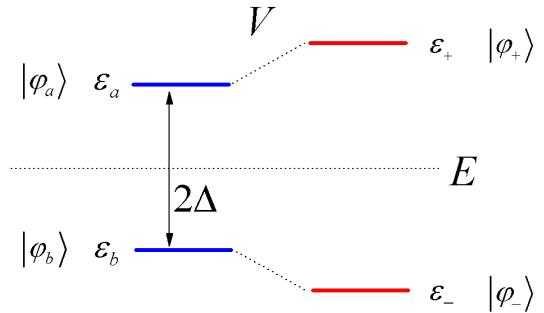
These states interact through a coupling  $V$  of the form

$$\begin{aligned}\hat{V} &= |\varphi_a\rangle V_{ab} \langle \varphi_b| + |\varphi_b\rangle V_{ba} \langle \varphi_a| \\ &= \begin{pmatrix} 0 & V_{ab} \\ V_{ba} & 0 \end{pmatrix}\end{aligned}\quad (1.34)$$

The full Hamiltonian for the two coupled states is  $V_{ab}$ .

The zero-order states are

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{V} \\ &= \begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ba} & \varepsilon_b \end{pmatrix}\end{aligned}\quad (1.35)$$



We will ask: If we prepare the system in state  $|\varphi_a\rangle$ , what is the time-dependent probability of observing it in  $|\varphi_b\rangle$ ? The coupling mixes these states, leading to two eigenstates of  $\hat{H}$ ,  $|\varphi_+\rangle$  and  $|\varphi_-\rangle$ , with corresponding energy eigenvalues  $\varepsilon_+$  and  $\varepsilon_-$ . Since  $|\varphi_a\rangle$  and  $|\varphi_b\rangle$  are not eigenstates of  $H$ , and since our time-propagation will be performed in the eigenbasis using eq. (1.29), we will need to find the transformation between these bases.

We start by searching for the eigenvalues of the Hamiltonian. Since the Hamiltonian is Hermitian, ( $H_{ij} = H_{ji}^*$ ), we write

$$V_{ab} = V_{ba}^* = V e^{-i\phi} \quad (1.36)$$

$$\hat{H} = \begin{pmatrix} \varepsilon_a & V e^{-i\phi} \\ V e^{+i\phi} & \varepsilon_b \end{pmatrix} \quad (1.37)$$

Often the couplings we describe are real, and we can neglect the phase factor  $\phi$ . Now we define variables for the mean energy and energy splitting between the uncoupled states

$$E = \frac{\varepsilon_a + \varepsilon_b}{2} \quad (1.38)$$

$$\Delta = \frac{\varepsilon_a - \varepsilon_b}{2} \quad (1.39)$$

We can then obtain the eigenvalues of the coupled system by solving the secular equation

$$\det(H - \lambda I) = 0 \quad (1.40)$$

giving

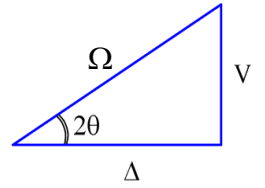
$$\varepsilon_{\pm} = E \pm \Omega \quad (1.41)$$

Here I defined another variable

$$\Omega = \sqrt{\Delta^2 + V^2} \quad (1.42)$$

To determine the eigenvectors of the coupled system  $|\varphi_{\pm}\rangle$ , it proves to be a great simplification to define a mixing angle  $\theta$  that describes the relative magnitude of the coupling relative to the zero-order energy splitting through

$$\tan 2\theta = \frac{V}{\Delta} \quad (1.43)$$



We see that the mixing angle adopts values such that  $0 \leq \theta \leq \pi/4$ . Also, we note that

$$\sin 2\theta = V/\Omega \quad (1.44)$$

$$\cos 2\theta = \Delta/\Omega \quad (1.45)$$

In this representation the Hamiltonian eq. (1.37) becomes

$$\hat{H} = E\bar{I} + \Delta \begin{pmatrix} 1 & \tan 2\theta e^{-i\phi} \\ \tan 2\theta e^{+i\phi} & -1 \end{pmatrix} \quad (1.46)$$

and we can express the eigenvalues as

$$\varepsilon_{\pm} = E \pm \Delta \sec 2\theta \quad (1.47)$$

Next we want to find  $S$ , the transformation that diagonalizes the Hamiltonian and which transforms the coefficients of the wavefunction from the zero-order basis to the eigenbasis. The eigenstates can be expanded in the zero-order basis in the form

$$|\varphi_{\pm}\rangle = c_a |\varphi_a\rangle + c_b |\varphi_b\rangle \quad (1.48)$$

So that the transformation can be expressed in matrix form as

$$\begin{pmatrix} \varphi_+ \\ \varphi_- \end{pmatrix} = S \begin{pmatrix} \varphi_a \\ \varphi_b \end{pmatrix} \quad (1.49)$$

To find  $S$ , we use the Schrödinger equation  $\hat{H}|\varphi_{\pm}\rangle = \varepsilon_{\pm}|\varphi_{\pm}\rangle$  substituting eq. (1.48). This gives

$$S = \begin{pmatrix} \cos \theta e^{-i\phi/2} & \sin \theta e^{i\phi/2} \\ -\sin \theta e^{-i\phi/2} & \cos \theta e^{i\phi/2} \end{pmatrix} \quad (1.50)$$

Note that  $S$  is unitary since  $S^{\dagger} = S^{-1}$  and  $(S^T)^* = S^{-1}$ . Also, the eigenbasis is orthonormal:  $\langle \varphi_+ | \varphi_+ \rangle + \langle \varphi_- | \varphi_- \rangle = 1$ .

Now, let's examine the eigenstates in two limits:

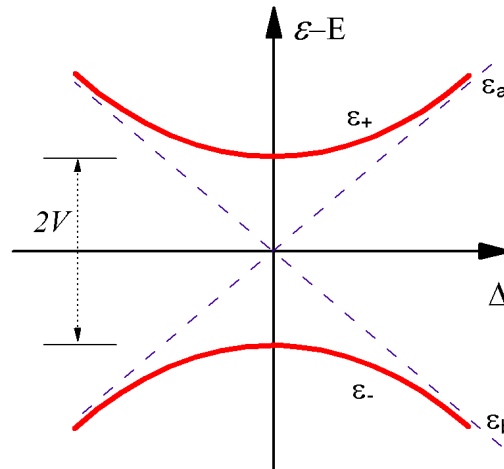
**(1) Weak coupling ( $|V/\Delta| \ll 1$ ).** Here  $\theta \approx 0$ , and  $|\varphi_+\rangle$  corresponds to  $|\varphi_a\rangle$  weakly perturbed by the  $V_{ab}$  interaction.  $|\varphi_-\rangle$  corresponds to  $|\varphi_b\rangle$ . In another way, as  $\theta \rightarrow 0$ , we find  $|\varphi_+\rangle \rightarrow |\varphi_a\rangle$  and  $|\varphi_-\rangle \rightarrow |\varphi_b\rangle$ .

**(2) Strong coupling ( $|V/\Delta| \gg 1$ ).** In this limit  $\theta = \pi/4$ , and the  $a/b$  basis states are indistinguishable. The eigenstates are symmetric and antisymmetric combinations:

$$|\varphi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\varphi_b\rangle \pm |\varphi_a\rangle) \quad (1.51)$$

Note from eq. (1.50) that the sign of  $V$  dictates whether  $|\varphi_+\rangle$  or  $|\varphi_-\rangle$  corresponds to the symmetric or antisymmetric eigenstate. For negative  $V \gg \Delta$ ,  $\theta = -\pi/4$ , and the correspondence in eq (1.51) changes to  $\mp$ .

We can schematically represent the energies of these states with the following diagram. Here we explore the range of  $\varepsilon_{\pm}$  available given a fixed coupling  $V$  and varying the splitting  $\Delta$ .



This diagram illustrates an avoided crossing effect. The strong coupling limit is equivalent to a degeneracy point ( $\Delta \sim 0$ ) between the states  $|\varphi_a\rangle$  and  $|\varphi_b\rangle$ . The eigenstates completely mix the unperturbed states, yet remain split by the strength of interaction  $2V$ . We will return to the

discussion of avoided crossings when we describe potential energy surfaces and the adiabatic approximation, where the dependence of  $V$  and  $\Delta$  on position  $R$  must be considered.

Now we can turn to describing dynamics. The time evolution of this system is given by the time-propagator

$$U(t) = |\varphi_+\rangle e^{-i\omega_+ t} \langle\varphi_+| + |\varphi_-\rangle e^{-i\omega_- t} \langle\varphi_-| \quad (1.52)$$

where  $\omega_{\pm} = \varepsilon_{\pm}/\hbar$ . Since  $\varphi_a$  and  $\varphi_b$  are not the eigenstates, preparing the system in state  $\varphi_a$  will lead to time evolution! Let's prepare the system so that it is initially in  $|\varphi_a\rangle$ .

$$|\psi(0)\rangle = |\varphi_a\rangle \quad (1.53)$$

Evaluating the time-dependent amplitudes of initial and final states with the help of  $S$ , we find

$$\begin{aligned} c_a(t) &= \langle\varphi_a|U(t)|\varphi_a\rangle \\ &= e^{-iEt} \left[ \cos^2 \theta e^{i\Omega_R t} + \sin^2 \theta e^{-i\Omega_R t} \right] \end{aligned} \quad (1.54)$$

$$\begin{aligned} c_b(t) &= \langle\varphi_b|U(t)|\varphi_a\rangle \\ &= 2 \sin \theta \cos \theta e^{-iEt} \sin \Omega_R t \end{aligned} \quad (1.55)$$

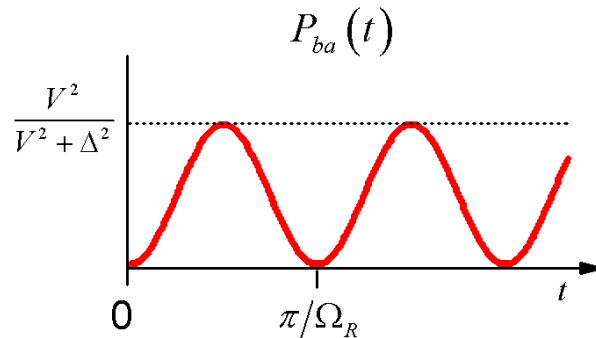
So, what is the probability that it is found in state  $|\varphi_b\rangle$  at time  $t$ ?

$$\begin{aligned} P_{ba}(t) &= |c_b(t)|^2 \\ &= \frac{V^2}{V^2 + \Delta^2} \sin^2 \Omega_R t \end{aligned} \quad (1.56)$$

where

$$\Omega_R = \frac{1}{\hbar} \sqrt{\Delta^2 + V^2} \quad (1.57)$$

$\Omega_R$ , the Rabi Frequency, represents the frequency at which probability amplitude oscillates between  $\varphi_a$  and  $\varphi_b$  states.



Notice for the weak coupling limit ( $V \rightarrow 0$ ),  $\varphi_{\pm} \rightarrow \varphi_{a,b}$  (the eigenstates resemble the stationary states), and the time-dependence disappears. In the strong coupling limit ( $V \gg \Delta$ ), amplitude is

exchanged completely between the zero-order states at a rate given by the coupling:  $\Omega_R \rightarrow V/\hbar$ . Even in this limit it takes a finite amount of time for amplitude to move between states. To get  $P=1$  requires a time  $\tau = \pi/2\Omega_R = \hbar\pi/2V$ .

### Readings

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