

5.74 TIME-DEPENDENT QUANTUM MECHANICS

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

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

Most of what you have previously covered is time-independent quantum mechanics, where we mean that \hat{H} is assumed to be independent of time: $\hat{H} = \hat{H}(\vec{r})$.

We then assume a solution of the form:

$$\begin{aligned} \psi(\vec{r}, t) &= \varphi(\vec{r})T(t) \\ i\hbar \frac{1}{T(t)} \frac{\partial}{\partial t} T(t) &= \frac{\hat{H}(\vec{r})\varphi(\vec{r})}{\varphi(\vec{r})} \end{aligned}$$

Here the left-hand side is a function of t only, and the right-hand side is a function of \vec{r} only.

This can only be satisfied if both sides are equal to the same constant, E

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

Time-Independent
Schrödinger Eqn.

H is operator corresponding to E

Second eqn.:

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

Solution:

$$T(t) = A \exp(-iEt / \hbar) = A \exp(-i\omega t)$$

So, for a set of eigenvectors $\varphi_n(\vec{r})$ with corresponding eigenvalues E_n , there are a set of corresponding eigensolutions to the TDSE.

$$\psi_n(\vec{r}, t) = a_n \varphi_n(\vec{r}) \exp(-i\omega_n t) \quad \omega_n = E_n / \hbar$$

While the complete wavefunction includes time-dependent terms, the probability density

$$P = \int \psi^*(\vec{r}, t) \psi(\vec{r}, t) d\vec{r} = \langle \psi(\vec{r}, t) | \psi(\vec{r}, t) \rangle$$

is independent of time. Therefore, $\varphi(\vec{r})$ are called **stationary states**.

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

$$\psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}, t) = \sum_n c_n e^{-i\omega_n t} \varphi_n(\vec{r})$$

For such a case, the probability density will oscillate with time: **coherence**.

e.g., two eigenstates

$$\psi(r, t) = c_1 \varphi_1 e^{-i\omega_1 t} + c_2 \varphi_2 e^{-i\omega_2 t}$$

$$p(t) = \psi^* \psi = |c_1 \varphi_1|^2 + |c_2 \varphi_2|^2 + c_1^* c_2 \varphi_1^* \varphi_2 e^{-i(\omega_2 - \omega_1)t} + c_2^* c_1 \varphi_2^* \varphi_1 e^{+i(\omega_2 - \omega_1)t}$$

probability density oscillates as $\cos(\omega_2 - \omega_1)t$

This is a simple example of coherence. Including momentum (a wavevector) of particle leads to a wavepacket.

TIME EVOLUTION OPERATOR

More generally, we want to understand how the wavefunction evolves with time. The TDSE is linear in time. Since the TDSE is deterministic, we will define an operator that describes the dynamics of the system:

$$\psi(t) = U(t, t_0)\psi(t_0)$$

For the time-independent Hamiltonian:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) + \frac{iH}{\hbar} \psi(\vec{r}, t) = 0 \quad (1)$$

To solve this, we will define an operator $T = \exp(-iHt / \hbar)$, which is a **function of an operator**.

A function of an operator is defined through its expansion in a Taylor series:

$$\begin{aligned} T = \exp[-iHt/\hbar] &= 1 - \frac{iHt}{\hbar} + \frac{1}{2!} \left(\frac{iHt}{\hbar}\right)^2 - \dots \\ &= f(H) \end{aligned}$$

Multiplying eq. 1 from the left by $T^{-1} = \exp(iHt / \hbar)$ we have:

$$\frac{\partial}{\partial t} \left[\exp\left(\frac{iHt}{\hbar}\right) \psi(\vec{r}, t) \right] = 0$$

integrating $t_0 \rightarrow t$:

$$\begin{aligned} \exp\left(\frac{iHt}{\hbar}\right) \psi(\vec{r}, t) - \exp\left(\frac{iHt_0}{\hbar}\right) \psi(\vec{r}, t_0) &= 0 \\ \psi(r, t) = \exp\left(\frac{-H(t-t_0)}{\hbar}\right) \psi(r, t_0) &= U(t, t_0)\psi(r, t_0) \end{aligned}$$

For functions of an operator A : Given a set of eigenvalues and eigenvectors of A , i.e., $A\varphi_n = a_n\varphi_n$, you can show by expanding the function as a polynomial that $f(\hat{A})\varphi_n = f(a_n)\varphi_n$

$$\therefore \psi_n(\vec{r}, t) = e^{-E_n(t-t_0)/\hbar} \psi_n(\vec{r}, t_0)$$

or

$$U(t, t_0) = \sum_n e^{-i\omega_n(t-t_0)} |\varphi_n\rangle\langle\varphi_n| \quad \omega_n = \frac{E_n}{\hbar}$$

This form is useful when φ_n are characterized; we'll develop $U(t, t_0)$ more later.

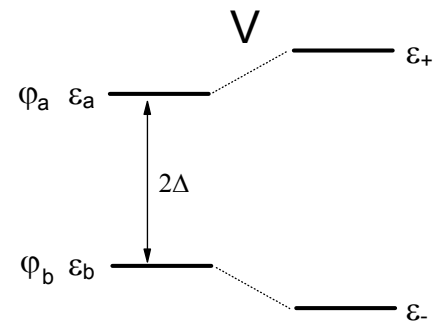
Time-evolution of a coupled two-level system (2LS)

It is common to reduce or map problem onto a 2LS. We then discard remaining degrees of freedom, or incorporate them as a heat bath, $H = H_0 + H_{\text{bath}}$.

Let's discuss the time-evolution of a 2LS with a time-independent Hamiltonian.

Consider a 2LS with two (unperturbed) eigenstates φ_a and φ_b with eigenenergies ε_a and ε_b , which are then coupled through an interaction V_{ab} .

$$\begin{aligned} H &= |a\rangle\varepsilon_a\langle a| + |b\rangle\varepsilon_b\langle b| + |a\rangle V_{ab}\langle b| + |b\rangle V_{ba}\langle a| \\ &= \begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ba} & \varepsilon_b \end{pmatrix} \end{aligned}$$



Since the Hamiltonian is Hermetian, ($H_{ij} = H_{ji}^*$), we suggest

$$\begin{aligned} V_{ab} &= V_{ba}^* = V e^{-i\phi} \\ H &= \begin{pmatrix} \varepsilon_a & V e^{-i\phi} \\ V e^{+i\phi} & \varepsilon_b \end{pmatrix} \end{aligned}$$

If we define the variables

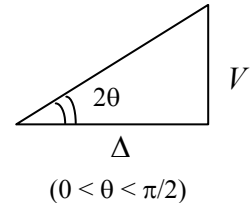
$$\begin{aligned} E &= \frac{\varepsilon_a + \varepsilon_b}{2} \\ \Delta &= \frac{\varepsilon_a - \varepsilon_b}{2} \end{aligned}$$

Then we can solve for the eigenvalues of the coupled systems:

$$\varepsilon_{\pm} = E \pm \sqrt{\Delta^2 + V^2}$$

Because the expressions get messy, we don't choose to find the eigenvectors for the coupled system using this expression. Rather, we use a substitution where we define:

$$\tan 2\theta = \frac{V}{\Delta}$$



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

We now find that we can express the eigenvalues as

$$\varepsilon_{\pm} = E \pm \Delta \sec 2\theta$$

We now want to find the eigenstates of the Hamiltonian, $|\varphi_{\pm}\rangle$, $H|\varphi_{\pm}\rangle = \varepsilon_{\pm}|\varphi_{\pm}\rangle$

where e.g. $|\varphi_{+}\rangle = c_a|\varphi_a\rangle + c_b|\varphi_b\rangle$:

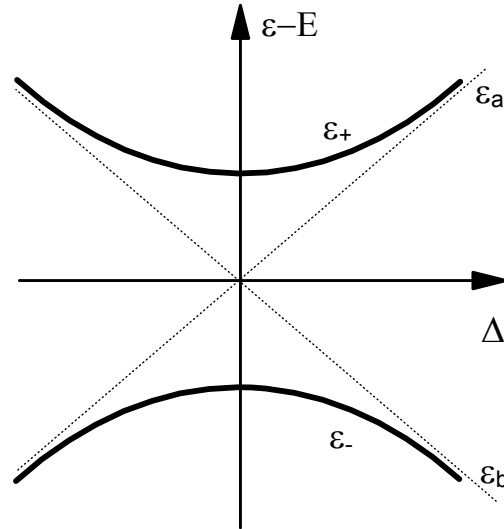
$$\begin{aligned} |\varphi_{+}\rangle &= \cos \theta e^{-i\phi/2} |\varphi_a\rangle + \sin \theta e^{i\phi/2} |\varphi_b\rangle \\ |\varphi_{-}\rangle &= -\sin \theta e^{-i\phi/2} |\varphi_a\rangle + \cos \theta e^{i\phi/2} |\varphi_b\rangle \end{aligned}$$

Orthonormal complete + orthogonal: $\langle \varphi_a | \varphi_a \rangle + \langle \varphi_b | \varphi_b \rangle = 1$

Notice that $|\varphi_{+}\rangle$ corresponds to $|\varphi_a\rangle$ perturbed by the V_{ab} interaction.

$$\begin{aligned} &|\varphi_{-}\rangle \text{ corresponds to } |\varphi_b\rangle \\ &(\text{for } \theta \rightarrow 0 \quad |\varphi_{+}\rangle \rightarrow |\varphi_a\rangle; |\varphi_{-}\rangle \rightarrow |\varphi_b\rangle) \end{aligned}$$

We can schematically represent the energies of these states:



These eigenstates exhibit avoided crossing.

The time-evolution of this system is given by our time-evolution operator.

$$U(t, t_0) = |\varphi_+\rangle e^{-i\omega_+(t-t_0)} \langle\varphi_+| + |\varphi_-\rangle e^{-i\omega_-(t-t_0)} \langle\varphi_-|$$

$$\omega_{\pm} = \frac{\varepsilon_{\pm}}{\hbar}$$

Now φ_a and φ_b are not the eigenstates—preparing φ_a will lead to time-evolution!

Let's prepare the system so that it is initially in state $|\varphi_a\rangle$.

$$(t_0 = 0) \quad |\psi(0)\rangle = |\varphi_a\rangle$$

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

$$P_{ba}(t) = \left| \langle\varphi_b|\psi(t)\rangle \right|^2 = \left| \langle\varphi_b|U(t, t_0)|\varphi_a\rangle \right|^2$$

To evaluate this, you need to know the transformation from the $|\varphi_{a,b}\rangle$ to the $|\varphi_{\pm}\rangle$ basis,

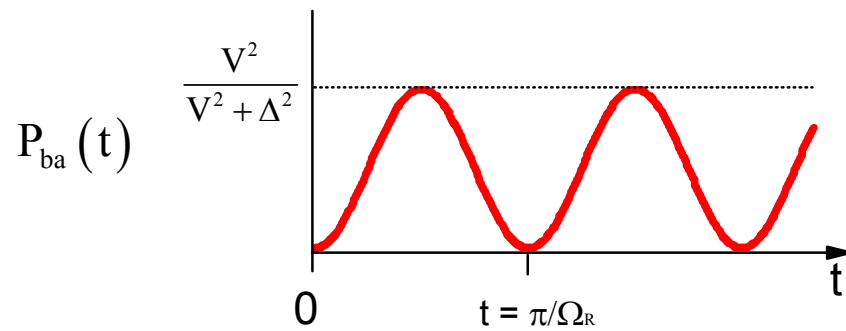
$$S_{a+} = \langle\varphi_a|\varphi_+\rangle$$

This gives:

$$P_{ba}(t) = \frac{V^2}{V^2 + \Delta^2} \sin^2 \Omega_R t$$

where the Rabi Frequency $\Omega_R = \frac{1}{\hbar} \sqrt{\Delta^2 + V^2}$

Ω_R represents the frequency at which probability amplitude oscillates between φ_a and φ_b states.



Notice for $V \rightarrow 0$ $\varphi_{\pm} \rightarrow \varphi_{a,b}$ (the stationary states), and there is no time-dependence.

For $V \gg \Delta$, then $\Omega_R = \frac{V}{\hbar}$ and $P=1$ after $t = \frac{\pi}{2\Omega_R} = \frac{\hbar\pi}{2V}$.

TIME-INDEPENDENT HAMILTONIAN

There are two types of values that we often calculate:

Correlation amplitude: $C(t) = \langle \beta | \varphi(t) \rangle$

measures the resemblance between the state of your system at time t and a target state $|\beta\rangle$. The probability amplitude $P(t) = |C(t)|^2$

for a set of eigenstates $|\varphi_n\rangle$

$$\begin{aligned} C(t) &= \langle \beta | \psi(t) \rangle = \langle \beta | U(t, t_0) | \psi(0) \rangle \\ &= \sum_{m,n,j} c_m^* \langle m | j \rangle e^{-i\omega_j t} \langle j | n \rangle c_n \\ &= \sum_n c_m^* c_n e^{-i\omega_n t} \end{aligned}$$

Expectation values: $\langle A(t) \rangle = \langle \psi(t) | A | \psi(t) \rangle$

$$|\psi(t)\rangle = \sum_n e^{-i\omega_n t} c_n |\varphi_n\rangle = \sum_n c_n |\varphi_n\rangle$$

$$\langle \psi(t) | = \sum_m e^{-i\omega_m t} c_m^* \langle \varphi_m |$$

$$\begin{aligned} \langle A(t) \rangle &= \sum_{m,n} c_m^* c_n e^{-i\omega_{nm} t} \langle \varphi_m | A | \varphi_n \rangle \\ &= \sum_{m,n} c_m^*(t) c_n(t) A_{mn} \end{aligned} \quad \omega_{nm} = \frac{E_n - E_m}{\hbar} = \omega_n - \omega_m$$

DENSITY MATRIX

For a system described by a wavefunction $|\psi(t)\rangle = \sum_n c_n(t)|n\rangle$ we showed

$$\begin{aligned}\langle A(t) \rangle &= \langle \psi(t) | A | \psi(t) \rangle \\ &= \sum_{n,m} c_m^*(t) c_n(t) \langle m | A | n \rangle\end{aligned}$$

We will often find it useful to define a density operator

$$\begin{aligned}\rho(t) &\equiv |\psi(t)\rangle \langle \psi(t)| \\ &= \sum_{n,m} c_n(t) c_m^*(t) |n\rangle \langle m| \\ &= \sum_{n,m} \rho_{nm}(t) |n\rangle \langle m| \quad (\text{by definition})\end{aligned}$$

ρ_{nm} are the density matrix elements. Substituting, we see that

$$\begin{aligned}\langle A(t) \rangle &= \sum_{n,m} A_{mn} \rho_{nm}(t) \\ &= \text{Tr}[A \rho(t)]\end{aligned}$$

Trace Properties: 1) cyclic invariance $\text{Tr}(ABC) = \text{Tr}(CAB) = \text{Tr}(BCA)$

2) invariant to unitary transformation $\text{Tr}(S^\dagger A S) = \text{Tr}(A)$

Pure vs. Mixed States

Why would we need the density matrix? It helps for mixed states.

- 1) pure states: a system characterized by a wavefunction (previous page)
- 2) mixed states: not characterized by single wavefunction
 - > statistical mixtures—ensemble at thermal equilibrium
 - > independently prepared states
 - > no phase relationship between elements of mixture

For an **ensemble** of systems with a probability p_k of occupying quantum state $|\varphi_k\rangle$, with

$$\sum_k p_k = 1$$

$$\langle A(t) \rangle = \sum_k p_k \langle \psi_k(t) | A | \psi_k(t) \rangle$$

$$\rho(t) \equiv \sum_k p_k |\psi_k(t)\rangle \langle \psi_k(t)|$$

$$\langle A(t) \rangle = \text{Tr}[A\rho(t)]$$

Properties:

- 1) ρ is Hermetian $\rho_{nm}^* = \rho_{mn}$
- 2) $\text{Tr}(\rho) = 1$ Normalization
- 3) $\text{Tr}(\rho^2) = 1$ for pure state
 < 1 for mixed state

Let's look at the density matrix elements for a mixture:

$$\rho_{nm} = \langle n | \rho | m \rangle = \sum_k p_k \langle n | \psi_k \rangle \langle \psi_k | m \rangle$$

$$\text{where } |\varphi_k\rangle = \sum_n c_n^k |n\rangle$$

c_n^k : expansion coefficient for
eigenstate n of wavefunction k

$$= \sum_k p_k c_n^k (c_m^k)^*$$

$$= \overline{c_n c_m^*} \quad \text{coefficients for eigenstate averaged over mixture}$$

Diagonal elements ($n = m$)

$$\rho_{nn} = \sum_k p_k |c_n^k|^2 = \overline{c_n c_n^*} = p_n$$

probability of finding a system in mixture in state $|n\rangle$

POPULATION (≥ 0)

Off-Diagonal Elements ($n \neq m$) —complex—have phase factor

describe the evolution of coherent superpositions.

COHERENCES

For an arbitrary state $|\chi\rangle$, the expectation value of the density matrix:

$$\langle \chi | \rho | \chi \rangle$$

gives the total probability of finding a particle in the pure state $|\chi\rangle$ within the mixture.

We will sometimes refer to the density matrix at thermal equilibrium ρ_0 (or ρ_{eq}), which is characterized by thermally distributed populations in the quantum states

$$\rho_{nn} = p_n = \frac{e^{-\beta E_n}}{Z}$$

where Z is the partition function. More generally, the density matrix can be defined as

$$\rho = \frac{e^{-\beta H}}{Z}$$

where $Z = \text{Tr}(e^{-\beta H})$. For $H|n\rangle = E_n |n\rangle$,

$$\begin{aligned} \rho_{nm} &= \langle n | e^{-\beta H} | m \rangle \\ &= e^{-\beta E_n} \delta_{nm} \end{aligned}$$

TIME-EVOLUTION OF DENSITY MATRIX

Follows naturally from definition of ρ and T.D.S.E.

$$\frac{\partial}{\partial t}|\psi\rangle = \frac{-i}{\hbar}H|\psi\rangle \quad \frac{\partial}{\partial t}\langle\psi| = \frac{i}{\hbar}\langle\psi|H \quad (H^\dagger = H)$$

$$\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial t}[|\psi\rangle\langle\psi|] = \left[\frac{\partial}{\partial t}|\psi\rangle\right]\langle\psi| + |\psi\rangle\frac{\partial}{\partial t}\langle\psi|$$

$$= \frac{-i}{\hbar}H|\psi\rangle\langle\psi| + \frac{i}{\hbar}|\psi\rangle\langle\psi|H$$

$$\frac{\partial\rho}{\partial t} = \frac{-i}{\hbar}[H, \rho]$$

Liouville-Von Neumann Eqn.

For a time-independent Hamiltonian:

$$\rho_{nm}(t) = \langle n|\rho(t)|m\rangle = \langle n|\psi(t)\rangle\langle\psi(t)|m\rangle$$

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle = \sum_{ni} |n\rangle e^{-i\omega_n(t-t_0)} \langle n|\psi(t_0)\rangle$$

$$\rho_{nm}(t) = e^{-i\omega_n(t-t_0)} \langle n|\psi(t_0)\rangle \langle\psi(t_0)|m\rangle e^{+i\omega_m(t-t_0)}$$

$$= e^{-i\omega_{nm}(t-t_0)} \rho_{nm}(t_0)$$

$$\omega_{nm} = \frac{E_n - E_m}{\hbar}$$

Populations: $\rho_{nn}(t) = \rho_{nn}(t_0)$ time-invariant

Coherences: oscillate at energy splitting ω_{nm}