Time Dependent Two State Problem

Coupled Pendulums

Weak spring

Two normal modes.

No friction. No air resistance. Perfect Spring
Start A Swinging

Some time later -

B swings with full amplitude.
A stationary
**Electron Transfer**
Electron moves between metal centers.

**Vibrational Transfer**
Vibration moves between two modes of a molecule.

**Electronic Excitation Transfer**
Electronic excited state moves between two molecules.
Consider two molecules and their lowest two energy levels

\[
\begin{array}{c}
\text{A} \\
E_A \\
\text{B} \\
E_B \\
\end{array}
\]

Take molecules to be identical, so later will set

\[
E_A = E_B = E_0
\]

States of System

\[
|A\rangle \equiv \text{Molecule A excited} \\
\text{B unexcited} \\
|B\rangle \equiv \text{Molecule B excited} \\
\text{A unexcited}
\]

\[
|A\rangle \text{ and } |B\rangle \text{ Normalized & Orthogonal}
\]
Initially, take there to be **NO** interaction between them

No “spring”

\[
\begin{align*}
H |A\rangle &= E_A |A\rangle \\
H |B\rangle &= E_B |B\rangle
\end{align*}
\]

**\(H\) is time independent.**
Therefore

\[
|A\rangle = e^{-iE_At/\hbar} |\alpha\rangle
\]

\[
|B\rangle = e^{-iE_Bt/\hbar} |\beta\rangle
\]

Time independent kets \(\rightarrow\) Spatial wavefunction

Time dependent
Part of wavefunction
If molecules reasonably close together →

Intermolecular Interactions

Couples states $|A\rangle$ & $|B\rangle$

(Like spring in pendulum problem)

Then energy of molecule A is influenced by B.

Energy of $|A\rangle$ determined by both $|A\rangle$ & $|B\rangle$

$|A\rangle$ Will no longer be eigenket of $H$

Then:

$$H|A\rangle = He^{-iE_A t/\hbar}|\alpha\rangle = e^{-iE_A t/\hbar} H|\alpha\rangle$$

But $|\alpha\rangle$ & $|\beta\rangle$ are coupled

$$H|\alpha\rangle = E_A |\alpha\rangle + \gamma |\beta\rangle$$

Coupling strength

Energy of interaction
Thus:

$$H|A\rangle = (E_A |\alpha\rangle + \gamma |\beta\rangle) \ e^{-iE_A t / \hbar}$$

$$H|B\rangle = (E_B |\beta\rangle + \gamma |\alpha\rangle) \ e^{-iE_B t / \hbar}$$

**Coupling strength**

**Time dependent phase factors**

**Very Important**

For molecules that are identical

$$E_A = E_B = E_0$$

Pick energy scale so:

$$E_0 = 0$$

Therefore

$$H|\alpha\rangle = \gamma |\beta\rangle$$

$$H|\beta\rangle = \gamma |\alpha\rangle$$
Have two kets $|A\rangle$ & $|B\rangle$ describing states of the system.

Most general state is a superposition

$$|t\rangle = C_1 |A \rangle + C_2 |B \rangle$$

Normalized  May be time dependent

Kets $|A\rangle$ & $|B\rangle$ have time dependent parts $e^{-iEt/\hbar}$

For case of identical molecules being considered:

$$E_A = E_B = E_0 = 0$$

Then: $|A\rangle = |\alpha\rangle$ & $|B\rangle = |\beta\rangle$

Any time dependence must be in $C_1$ & $C_2$. 
Substitute \( |t\rangle = C_1 |\alpha\rangle + C_2 |\beta\rangle \) into time dependent Schrödinger Equation:

\[
i \hbar \frac{\partial}{\partial t} |t\rangle = H |t\rangle = H \left[ C_1 |\alpha\rangle + C_2 |\beta\rangle \right]
\]

Take derivative.

\[
i \hbar \left( \dot{C}_1 |\alpha\rangle + \dot{C}_2 |\beta\rangle \right) = C_1 \gamma |\beta\rangle + C_2 \gamma |\alpha\rangle \quad |\alpha\rangle \ & \ |\beta\rangle \ t \text{ independent}
\]

\[
\dot{C}_1 = \frac{\partial C_1}{\partial t} \quad \dot{C}_2 = \frac{\partial C_2}{\partial t}
\]

Left multiply by \( \langle \alpha | \) normalized

\[
i \hbar \dot{C}_1 = \gamma C_2
\]

\( |\alpha\rangle \ & \ |\beta\rangle \ \text{orthogonal}

Left multiply by \( \langle \beta | \)

\[
i \hbar \dot{C}_2 = \gamma C_1
\]

Then:

\[
i \hbar \dot{C}_1 = \gamma C_2 \quad \text{Eq. of motion of coefficients}
\]

\[
i \hbar \dot{C}_2 = \gamma C_1
\]

\( |\alpha\rangle \ & \ |\beta\rangle \ \text{time independent. All time dependence in } C_1 \ & \ C_2 \)
Solving Equations of Motion:

have:

\[ i\hbar \dot{C}_1 = \gamma C_2 \]

Take \( \frac{d}{dt} \)

\[ i\hbar \ddot{C}_1 = \gamma \dot{C}_2 \]

\[ \ddot{C}_1 = -\frac{i\gamma}{\hbar} \dot{C}_2 \]

but:

\[ \dot{C}_2 = -\frac{i\gamma}{\hbar} C_1 \]

then:

\[ \ddot{C}_1 = -\frac{\gamma^2}{\hbar^2} C_1 \]

Second derivative of function equals negative constant times function – solutions, sin and cos.

\[ C_1 = Q \sin(\gamma t/\hbar) + R \cos(\gamma t/\hbar) \]
\[ C_1 = Q \sin(\gamma t/\hbar) + R \cos(\gamma t/\hbar) \]

And:

\[ C_2 = \frac{i \hbar}{\gamma} \dot{C}_1 \]

\[ C_2 = i [Q \cos(\gamma t/\hbar) - R \sin(\gamma t/\hbar)] \]
$|t\rangle$ normalized

$$\langle t|t\rangle = 1 = (C_1^* \langle \alpha | + C_2^* \langle \beta |)(C_1 |\alpha \rangle + C_2 |\beta \rangle)$$

$$= C_1^* C_1 + C_2^* C_2$$

$$C_1^* C_1 + C_2^* C_2 = 1 \quad \text{Sum of probabilities equals 1.}$$

This yields

$$R^2 + Q^2 = 1$$

To go further, need initial condition

Take for $t = 0$

$$\begin{align*}
C_1 &= 1 \\
C_2 &= 0
\end{align*}$$

Means: Molecule A excited at $t = 0$, B not excited.
\[ C_1 = Q \sin(\gamma t/\hbar) + R \cos(\gamma t/\hbar) \quad C_2 = i \left[ Q \cos(\gamma t/\hbar) - R \sin(\gamma t/\hbar) \right] \]

For \( t = 0 \)

\[
\left\{ \begin{array}{c}
C_1 = 1 \\
C_2 = 0
\end{array} \right. \quad \text{Means: Molecule A excited at } t = 0, \text{ B not excited.}
\]

\[ R = 1 \quad \& \quad Q = 0 \]

For these initial conditions:

\[
C_1 = \cos(\gamma t/\hbar) \quad \text{probability amplitudes} \\
C_2 = -i \sin(\gamma t/\hbar)
\]
Projection Operator:

\[ |t\rangle = C_1 |A\rangle + C_2 |B\rangle = \cos(\gamma t/\hbar) |A\rangle - i \sin(\gamma t/\hbar) |B\rangle \]

Time dependent coefficients

Consider \( |A\rangle \langle A| \)

Projection Operator

\[ |A\rangle \langle A | t\rangle = C_1 |A\rangle \]

Gives piece of \(|t\rangle\) that is \(|A\rangle\)

In general:

\[ |S\rangle = \sum_i C_i |i\rangle \]

\[ |k\rangle \langle k | S\rangle = C_k |k\rangle \]

Coefficient – Amplitude (for normalized kets)
Consider: \[
\langle S | k \rangle \langle k | S \rangle = C_k^* C_k = |C_k|^2
\]

Absolute value squared of amplitude of particular ket \( |k \rangle \) in superposition \( |S \rangle \).

\(|C_k|^2 \Rightarrow \text{Probability of finding system in state } |k \rangle \ \text{given that it is in superposition of states} \ |S \rangle \)
Projection Ops. ➔ Probability of finding system in $|A\rangle$ or $|B\rangle$
given it is in $|t\rangle$

$$|t\rangle = C_1|A\rangle + C_2|B\rangle = \cos(\gamma t/\hbar)|A\rangle - i \sin(\gamma t/\hbar)|B\rangle$$

$$P_A = \langle t|A\rangle\langle A|t\rangle = C_1^*C_1 = \cos^2 \gamma t/\hbar$$

$$P_B = \langle t|B\rangle\langle B|t\rangle = C_2^*C_2 = \sin^2 \gamma t/\hbar$$

Total probability is always 1 since $\cos^2 + \sin^2 = 1$

$\gamma \Rightarrow$ energy

$\hbar \Rightarrow$ energy-sec

$$\frac{\gamma}{\hbar} = \omega \Rightarrow \text{rad/sec}$$
\[ P_A = \langle t | A \rangle \langle A | t \rangle = C_1^* C_1 = \cos^2 \gamma \frac{t}{\hbar} \]

\[ P_B = \langle t | B \rangle \langle B | t \rangle = C_2^* C_2 = \sin^2 \gamma \frac{t}{\hbar} \]

At \( t = 0 \)

\[ P_A = 1 \quad \text{(A excited)} \]
\[ P_B = 0 \quad \text{(B not excited)} \]

When \( \gamma \frac{t}{\hbar} = \pi / 2 \)

\[ t = \hbar / 4\gamma \]

\[ P_A = 0 \quad \text{(A not excited)} \]
\[ P_B = 1 \quad \text{(B excited)} \]

Excitation has transferred from A to B in time \( t = \hbar / 4\gamma \)

At \( t = 2\hbar / 4\gamma \) (A excited again)
(B not excited)

In between times → Probability intermediate
Stationary States

Consider two superpositions of $|A\rangle$ & $|B\rangle$

$|+\rangle = \frac{1}{\sqrt{2}}(|A\rangle + |B\rangle)$

$|-\rangle = \frac{1}{\sqrt{2}}(|A\rangle - |B\rangle)$

Then

$H|+\rangle = \frac{1}{\sqrt{2}}(H|A\rangle + H|B\rangle)$

$\quad = \frac{1}{\sqrt{2}}(\gamma|B\rangle + \gamma|A\rangle)$

$H|+\rangle = \gamma|+\rangle \quad $ Eigenstate, $\gamma$ Eigenvalue

Similarly

$H|-\rangle = -\gamma|-\rangle \quad $ Eigenstate, $-\gamma$ Eigenvalue

Observables of Energy Operator

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Recall $E_0 = 0$
If $E_0$ not 0, splitting still symmetric about $E_0$ with splitting $2\gamma$.

Dimer splitting $\Rightarrow 2\gamma$

$|+\rangle = \frac{1}{\sqrt{2}} (|A\rangle + |B\rangle)$
$|-\rangle = \frac{1}{\sqrt{2}} (|A\rangle - |B\rangle)$

Delocalized States

Probability of finding either molecule excited is equal

$\langle + | A \rangle \langle A | + \rangle = \frac{1}{2}$
Use projection operators to find probability of being in eigenstate, given that the system is in $|t\rangle$

$$\langle t|+\rangle\langle +|t\rangle = \left[ (C_1^* \langle A| + C_2^* \langle B|) \frac{1}{\sqrt{2}} (|A\rangle + |B\rangle) \right] \cdot [C,C.]$$

$$= \frac{1}{\sqrt{2}} \left( C_1^* + C_2^* \right) \frac{1}{\sqrt{2}} (C_1 + C_2)$$

complex conjugate of previous expression

$$= \frac{1}{2} [C_1^* C_1 + C_2^* C_2 + C_1^* C_2 + C_2^* C_1]$$

$$= \frac{1}{2} [\cos^2(\gamma t/\hbar) + \sin^2(\gamma t/\hbar) - i \cos(\gamma t/\hbar) \sin(\gamma t/\hbar) + i \sin(\gamma t/\hbar) \cos(\gamma t/\hbar)]$$

$$\langle t|+\rangle\langle +|t\rangle = \frac{1}{2}$$

Make energy measurement ➔

Equal probability of finding $\gamma$ or $-\gamma$

Also

$$\langle t|-\rangle\langle -|t\rangle = \frac{1}{2}$$

$|t\rangle$ is not an eigenstate

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Expectation Value

Half of measurements yield $+\gamma$, half $-\gamma$

One measurement on many systems $\Rightarrow$ Expectation Value – should be 0.

$$
\langle t|H|t\rangle = \left(C_1^{*} \langle A| + C_2^{*} \langle B| \right) H \left(C_1 \langle A| + C_2 \langle B| \right)
$$

$$
= C_1^{*} C_1 \langle \alpha|H|\alpha\rangle + C_2^{*} C_1 \langle \beta|H|\alpha\rangle + C_1^{*} C_2 \langle \alpha|H|\beta\rangle + C_2^{*} C_2 \langle \beta|H|\beta\rangle
$$

Using $H|\alpha\rangle = \gamma|\beta\rangle$

$$
H|\beta\rangle = \gamma|\alpha\rangle
$$

$$
= \gamma C_2^{*} C_1 + \gamma C_1^{*} C_2
$$

$$
= \gamma \left(i \sin(\gamma t/\hbar) \cos(\gamma t/\hbar) - i \sin(\gamma t/\hbar) \cos(\gamma t/\hbar)\right)
$$

$$
\langle t|H|t\rangle = 0 \quad \text{Expectation Value - Time independent}
$$

If $E_0 \neq 0$, get $E_0$
Non-Degenerate Case

\[ P_A = C_1^* C_1 = \frac{\Delta E^2 + 2\gamma^2}{\Delta E^2 + 4\gamma^2} + \frac{2\gamma^2}{\Delta E^2 + 4\gamma^2} \cos \frac{\sqrt{\Delta E^2 + 4\gamma^2}}{\hbar} t \]

\[ P_B = C_2^* C_2 = \frac{2\gamma^2}{\Delta E^2 + 4\gamma^2} \left( 1 - \cos \frac{\sqrt{\Delta E^2 + 4\gamma^2}}{\hbar} t \right) \]

As \( \Delta E \) increases \( \Rightarrow \) Oscillations Faster

Less Probability Transferred

Thermal Fluctuations change \( \Delta E \) & \( \gamma \)
Using Bloch Theorem of Solid State Physics ➔ can solve problem of $n$ molecules or atoms where $n$ is very large, e.g., $10^{20}$, a crystal lattice.
Excitation of a One Dimensional Lattice

\[ |\phi_j\rangle \text{ ground state of the } j^{th} \text{ molecule in lattice (normalized, orthogonal)} \]

\[ |\phi_j^e\rangle \text{ excited state of } j^{th} \text{ molecule} \]

Ground state of crystal with \( n \) molecules

\[ |\Phi^g\rangle = |\phi_0\rangle |\phi_1\rangle |\phi_2\rangle \cdots |\phi_{n-1}\rangle \quad \text{Take ground state to be zero of energy.} \]

Excited state of lattice, \( j^{th} \) molecule excited, all other molecules in ground states

\[ |\Phi_j^e\rangle = |\phi_0\rangle |\phi_1\rangle |\phi_2\rangle \cdots |\phi_{j-1}\rangle |\phi_j^e\rangle \cdots |\phi_{n-1}\rangle \quad \text{energy of single molecule} \]

\[ |\Phi_j^e\rangle \text{ set of } n\text{-fold degenerate eigenstates} \]

\[ \text{in the absence of intermolecular interactions} \]

\[ \text{because any of the } n \text{ molecules can be excited.} \]
Bloch Theorem of Solid State Physics – Periodic Lattice Eigenstates

Lattice spacing - \( \alpha \)

Translating a lattice by any number of lattice spacings, \( \alpha \), lattice looks identical.

Because lattice is identical, following translation

- Potential is unchanged by translation
- Hamiltonian unchanged by translation
- Eigenvectors unchanged by translation

Bloch Theorem – from group theory and symmetry properties of lattices

\[
|\psi_p(x + \alpha)\rangle = e^{2\pi ip\alpha/L} |\psi_p(x)\rangle
\]

The exponential is the translation operator. It moves function one lattice spacing.

\( p \) is integer ranging from 0 to \( n-1 \).

\( L = \alpha n \), size of lattice

\( k = 2\pi p/L \)
Any number of lattice translations produces an equivalent function, result is a superposition of the kets with each of the $n$ possible translations.

$$|\psi(k)\rangle = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} e^{ik\alpha j} |\Phi^e_j\rangle$$

**Bloch Theorem – eigenstates of lattice**

Ket with excited state on $j^{th}$ molecule (single site function)

Sum over all $j$ possible positions (translations) of excited state.

Normalization so there is only a total of one excited state on entire lattice.

$k$ is a wave vector. Different values of $k$ give different wavelengths.

**Different number of half wavelengths on lattice.**

In two state problem, there were two molecules and two eigenstates.
For a lattice, there are $n$ molecules, and $n$ eigenstates.

There are $n$ different orthonormal

$$|\psi(k)\rangle$$

arising from the $n$ different values of the integer $p$, which give $n$ different values of $k$. $k = 2\pi p/L$
One dimensional lattice problem with nearest neighbor interactions only

\[ H = H_M + H_{j,j\pm 1} \]

Intermolecular coupling between adjacent molecules. Couples a molecule to molecules on either side. Like coupling in two state (two molecule) problem.

Molecular Hamiltonian in absence of intermolecular interactions.

\[ H_M = H_{M_1} + H_{M_2} + \cdots + H_{M_j} + \cdots + H_{M_{n-1}} \]

Sum of single molecule Hamiltonians

\[ H_M \left| \Phi^e_j \right\rangle = E^e \left| \Phi^e_j \right\rangle \]

The \( j \)th term gives \( E^e \), the other terms give zero because the ground state energy is zero.

\[ H_M \left| \psi(k) \right\rangle = H_M \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} e^{ik\alpha j} \left| \Phi^e_j \right\rangle = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} e^{ik\alpha j} H_M \left| \Phi^e_j \right\rangle = E^e \left| \psi(k) \right\rangle \]

In the absence of intermolecular interactions, the energy of an excitation in the lattice is just the energy of the molecular excited state.
Inclusion of intermolecular interactions breaks the excited state degeneracy.

\[ \mathcal{H}_{j,j\pm 1} \Phi_j^e = \gamma \Phi_{j+1}^e + \gamma \Phi_{j-1}^e \]

state with \( j\)th molecule excited

coupling strength

Operate \( \mathcal{H}_{j,j\pm 1} \) on Bloch states – eigenstates.

\[ \mathcal{H}_{j,j\pm 1} \psi(k) = \mathcal{H}_{j,j\pm 1} \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} e^{i\alpha j} \Phi_j^e \]

\[ = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} e^{i\alpha j} \mathcal{H}_{j,j\pm 1} \Phi_j^e \]

\[ = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} \left[ e^{i\alpha j} \gamma \Phi_{j+1}^e + e^{i\alpha j} \gamma \Phi_{j-1}^e \right] \]
\[ H_{j,j \pm 1} |\psi(k)\rangle = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} \left[ e^{ik\alpha_j} \gamma |\Phi^e_{j+1}\rangle + e^{ik\alpha_j} \gamma |\Phi^e_{j-1}\rangle \right] \]

Each of the terms in the square brackets can be multiplied by

\[ e^{ik\alpha} e^{-ik\alpha} = 1 \]

\[ H_{j,j \pm 1} |\psi(k)\rangle = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} \left[ e^{ik\alpha_j} e^{ik\alpha} e^{-ik\alpha} \gamma |\Phi^e_{j+1}\rangle + e^{ik\alpha_j} e^{-ik\alpha} e^{ik\alpha} \gamma |\Phi^e_{j-1}\rangle \right] \]

combining

combining

\[ = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} \left[ e^{-ik\alpha} \gamma e^{ik\alpha(j+1)} |\Phi^e_{j+1}\rangle + e^{ik\alpha} \gamma e^{ik\alpha(j-1)} |\Phi^e_{j-1}\rangle \right] \]

\[ j + 1 \]

\[ j - 1 \]

In spite of difference in indices, the sum over \( j \) is sum over all lattice sites because of cyclic boundary condition.

Therefore, the exp. times ket, summed over all sites \((j)\) → \( |\psi(k)\rangle \)
Replacing exp. times ket, summed over all sites \((j)\) with \(\mid \psi(k) \rangle\)

\[
H_{j,j\pm1} \mid \psi(k) \rangle = e^{-ik\alpha} \gamma \mid \psi(k) \rangle + e^{ik\alpha} \gamma \mid \psi(k) \rangle
\]

\[
= \gamma \left(e^{ik\alpha} + e^{-ik\alpha}\right) \mid \psi(k) \rangle \quad \text{factor out} \quad \gamma \mid \psi(k) \rangle
\]

\[
= 2\gamma \cos(k\alpha) \mid \psi(k) \rangle
\]

Adding this result to

\[
H_M \mid \psi(k) \rangle = E^e \mid \psi(k) \rangle
\]

Gives the energy for the full Hamiltonian.

\[
E(k) = E^e + 2\gamma \cos(k\alpha)
\]

The nearest neighbor interaction with strength \(\gamma\) breaks the degeneracy.
Result (one dimension, nearest neighbor interaction only, $\gamma$)

\[ E(k) = E^e + 2\gamma \cos(k\alpha) \]

$k \implies$ wave vector – labels levels $\alpha \implies$ lattice spacing

**Exciton Band** \[ E(k) = E^e + 2\gamma \cos(k\alpha) \]

Each state delocalized over entire crystal.

**Brillouin zone**

Quasi-continuous Range of energies from $2\gamma$ to $-2\gamma$
Exciton Transport

Exciton wave packet ➔ more or less localized like free particle wave packet

Dispersion Relation:

\[ \omega(k) = \frac{1}{\hbar} E(k) = \frac{1}{\hbar} \left[ E^e + 2\gamma \cos(k\alpha) \right] \]

Group Velocity:

\[ V_g = \frac{d\omega(k)}{dk} = -\frac{2\gamma\alpha}{\hbar} \sin(k\alpha) \]

Exciton packet moves with well defined velocity. Coherent Transport.

Thermal fluctuations (phonon scattering)

➔ localization, incoherent transport, hopping