Chapter 8

Time Dependent Two State Problem
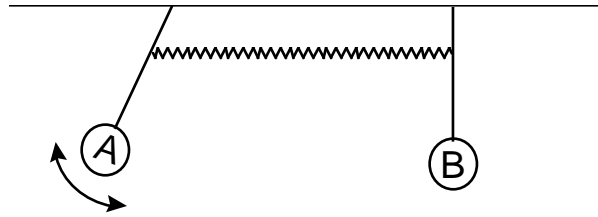
Coupled Pendulums
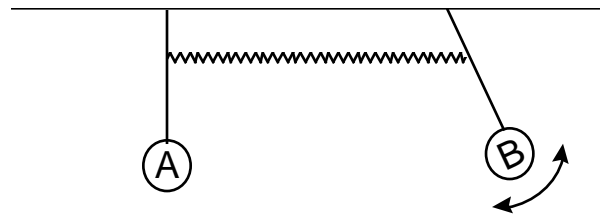

Weak spring
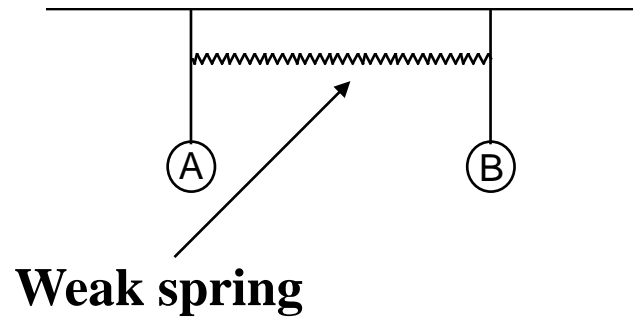
Two normal modes.

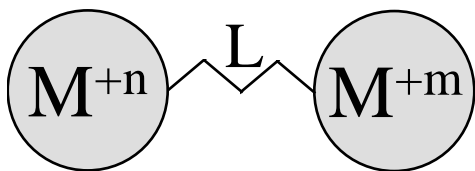## No friction. No air resistance. Perfect Spring
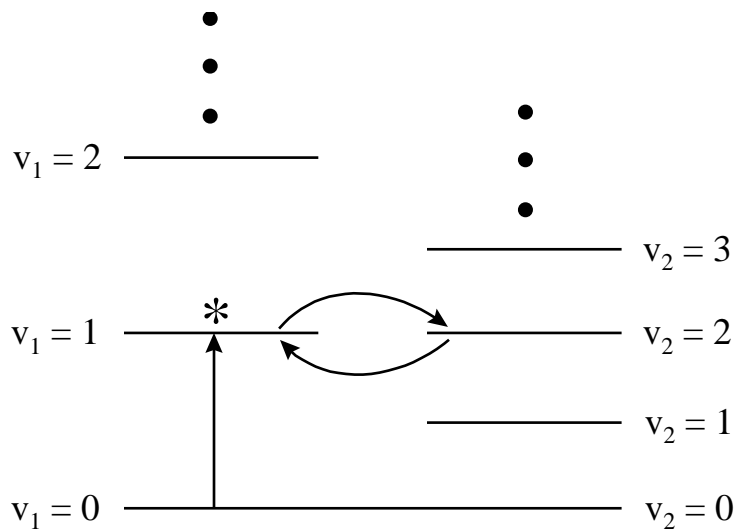
Start A Swinging

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.
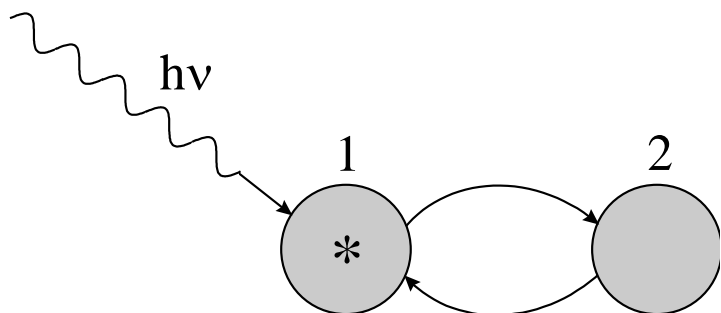
Electronic Excitation Transfer
Electronic excited state moves between two molecules.

Consider two molecules and their lowest two energy levels

A   B
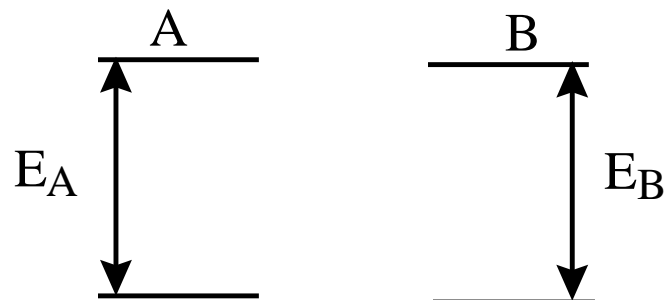
E_A E_B

Take molecules to be identical, so later will set

$$E_A = E_B = E_0$$

States of System

$|A\rangle \equiv$ **Molecule A excited**

B unexcited

$|B\rangle \equiv$ **Molecule B excited**

A unexcited

$|A\rangle$ **and** $|B\rangle$ **Normalized & Orthogonal**

Initially, take there to be NO interaction between them

No "spring"

$$\underline{H}\,|A\rangle = E_A\,|A\rangle$$

$$\underline{H}\,|B\rangle = E_B\,|B\rangle$$

$\underline{H}$ is time independent.
Therefore

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

$$|B\rangle = e^{-iE_B t/\hbar}\,|\beta\rangle$$

Time independent kets →
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 $\underline{H}$

Then:

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

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

$$\underline{H}|\alpha\rangle = E_A|\alpha\rangle + \gamma|\beta\rangle$$

Coupling strength
Energy of interaction

Thus:

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

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

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

$$\underline{H}\,|\alpha\rangle = \gamma\,|\beta\rangle$$

$$\underline{H}\,|\beta\rangle = \gamma\,|\alpha\rangle$$

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:**

$$i\hbar\frac{\partial}{\partial t}|t\rangle = \underline{H}|t\rangle = \underline{H}\left[C_1|\alpha\rangle + C_2|\beta\rangle\right] \qquad \text{Take derivative.}$$

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

$$\dot{C}_1 = \frac{\partial C_1}{\partial t} \qquad \dot{C}_2 = \frac{\partial C_2}{\partial t}$$

Left multiply by $\langle\alpha|$ **normalized**

$$i\hbar\dot{C}_1 = \gamma C_2 \qquad |\alpha\rangle \,\&\, |\beta\rangle \text{ orthogonal}$$

Left multiply by $\langle\beta|$

$$i\hbar\dot{C}_2 = \gamma C_1$$

Then: $\qquad\qquad\quad i\hbar\dot{C}_1 = \gamma C_2$

$\qquad\qquad\qquad\qquad\qquad i\hbar\dot{C}_2 = \gamma C_1$ **Eq. of motion of coefficients**

$|\alpha\rangle \,\&\, |\beta\rangle$ **time independent. All time dependence in** C_1 **&** C_2

Solving Equations of Motion:

have:

$$i\hbar \dot{C}_1 = \gamma C_2$$

Take $\dfrac{d}{dt}$

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

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

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:

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

$$C_2 = i\left[Q\cos\gamma t/\hbar - R\sin\gamma t/\hbar\right]$$

$|t\rangle$ normalized

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

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

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

This yields

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

To go further, need initial condition

Take for $t = 0$

$$\left.\begin{array}{l} C_1 = 1 \\ C_2 = 0 \end{array}\right\}$$

Means: Molecule A excited at $t = 0$, B not excited.

$$C_1 = Q\sin(\gamma t/\hbar) + R\cos(\gamma t/\hbar) \qquad C_2 = i\left[Q\cos\gamma t/\hbar - R\sin\gamma t/\hbar\right]$$

For $t = 0$

$$\left.\begin{array}{l} C_1 = 1 \\ \\ C_2 = 0 \end{array}\right\}$$

Means: Molecule A excited at $t = 0$,
B not excited.

➔ $R = 1$ & $Q = 0$

For these initial conditions:

$$C_1 = \cos(\gamma\, t/\hbar)$$

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

$$|A\rangle\langle A|t\rangle = C_1|A\rangle \qquad \text{Gives piece of } |t\rangle \text{ that is } |A\rangle$$

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:

Closed Brackets ➔ Number

$$\langle S \mid k \rangle \langle k \mid S \rangle = C_k^* C_k = \left| C_k \right|^2$$

Absolute value squared of amplitude of particular ket $\left| k \right\rangle$ in superposition $\left| S \right\rangle$.

$\left| C_k \right|^2$ ➔**Probability of finding system in state $\left| k \right\rangle$ given that it is in superposition of states $\left| S \right\rangle$**

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**

$$\frac{\gamma}{\hbar} = \omega \Rightarrow \quad \mathbf{rad/sec}$$

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

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

At $t = 0$ $\qquad\qquad$ $P_A = 1$ $\qquad$ **(A excited)**

$\qquad\qquad\qquad\qquad\qquad$ $P_B = 0$ $\qquad$ **(B not excited)**

When

$$\gamma t/\hbar = \pi/2$$

$$t = h/4\gamma$$

$\qquad\qquad\qquad$ $P_A = 0$ $\qquad$ **(A not excited)**

$\qquad\qquad\qquad$ $P_B = 1$ $\qquad$ **(B excited)**

Excitation has transferred from A to B in time $t = h/4\gamma$

At $t = 2h/4\gamma$ $\quad$ **(A excited again)**

$\qquad\qquad\qquad\qquad\quad$ **(B not excited)**

In between times ➜ Probability intermediate

Stationary States

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

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

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

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

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

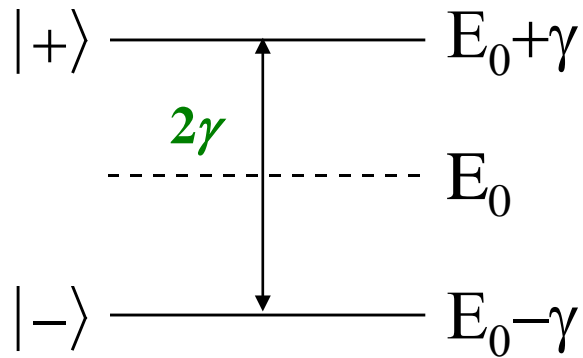$$\underline{H}|\alpha\rangle = \gamma|\beta\rangle$$

$$\underline{H}|\beta\rangle = \gamma|\alpha\rangle$$

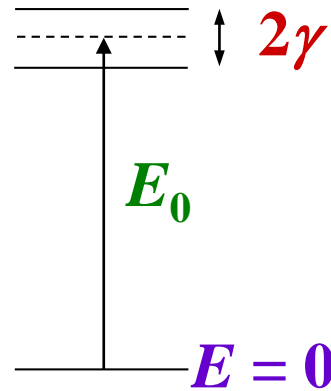$$\underline{H}|+\rangle = \gamma|+\rangle \qquad \text{**Eigenstate,**} \ \gamma \ \text{**Eigenvalue**}$$

Similarly

$$\underline{H}|-\rangle = -\gamma|-\rangle \qquad \text{**Eigenstate,**} \ -\gamma \ \text{**Eigenvalue**}$$

Observables of Energy Operator

$|+\rangle$ ———————— $E_0 + \gamma$

2γ --------- E_0

$|-\rangle$ ———————— $E_0 - \gamma$

Dimer splitting ➔ 2γ

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

2γ

E_0

$E = 0$

$|+\rangle = \dfrac{1}{\sqrt{2}}\left(|A\rangle + |B\rangle\right)$

$|-\rangle = \dfrac{1}{\sqrt{2}}\left(|A\rangle - |B\rangle\right)$

Delocalized States

Probability of finding either molecule excited is equal

$$\langle +|A\rangle\langle A|+\rangle = \dfrac{1}{2}$$

Use projection operators to find probability of being in eigenstate, given that the system is in $|t\rangle$

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

complex conjugate of previous expression

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

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

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

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

Also

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

Make energy measurement ➜

equal probability of finding γ or -γ

$|t\rangle$ **is not an eigenstate**

Expectation Value

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

Average of one measurement on many systems ➔

Expectation Value – should be 0.

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

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

Using $\quad \underline{H}|\alpha\rangle = \gamma|\beta\rangle$

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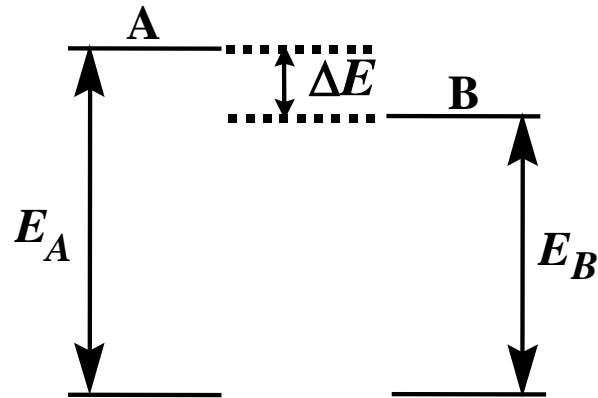
$$= \gamma C_2^*C_1 + \gamma C_1^*C_2$$

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

$$\langle t|\underline{H}|t\rangle = 0 \qquad \textbf{Expectation Value - Time independent}$$

If $E_0 \neq 0$, get E_0

Non-Degenerate Case

$$P_A = C_1^* C_1 = \frac{\Delta E^2 + 2\gamma^2}{\Delta E^2 + 4\gamma^2} + \frac{2\gamma^2}{\Delta E^2 + 4\gamma^2} \cos \frac{\sqrt{\Delta E^2 + 4\gamma^2}}{\hbar} t$$
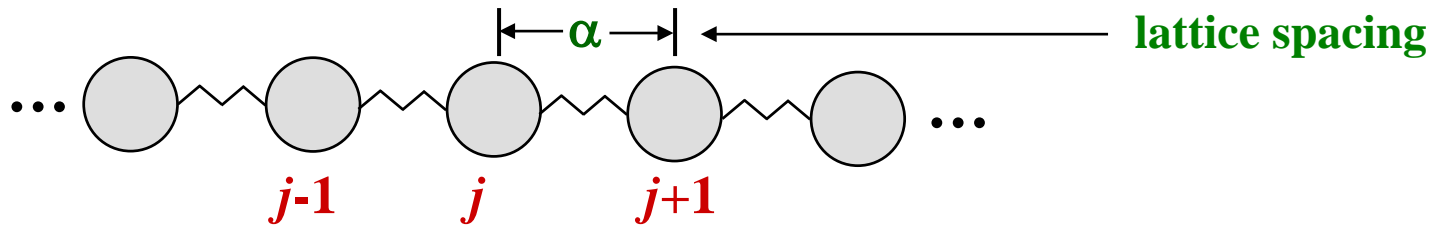
$$\frac{1}{2} + \frac{1}{2} \cos 2x = \cos^2 x$$

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

As ΔE increases ➜ Oscillations Faster
Less Probability Transferred

Thermal Fluctuations change ΔE & γ

Excitation of a One Dimensional Lattice

$|\varphi_j\rangle$ **ground state of the jth molecule in lattice (normalized, orthogonal)**

$|\varphi_j^e\rangle$ **excited state of jth molecule**

Ground state of crystal with n molecules

$$|\Phi^g\rangle = |\varphi_0\rangle|\varphi_1\rangle|\varphi_2\rangle\cdots|\varphi_{n-1}\rangle$$ **Take ground state to be zero of energy.**

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

$$|\Phi_j^e\rangle = |\varphi_0\rangle|\varphi_1\rangle|\varphi_2\rangle\cdots|\varphi_j^e\rangle\cdots|\varphi_{n-1}\rangle$$ **energy of single molecule in excited state, E^e**

$|\Phi_j^e\rangle$ **set of n-fold degenerate eigenstates in the absence of intermolecular interactions**

because any of the n molecules can be excited.

Bloch Theorem of Solid State Physics – Periodic Lattice Eigenstates

Lattice spacing - α

Translating a lattice by any number of lattice spacings, α, ➡️
        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

$$\left| \psi_p(x+\alpha) \right\rangle = e^{2\pi i p \alpha / L} \left| \psi_p(x) \right\rangle$$

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

$$= e^{ik\alpha} \left| \psi_p(x) \right\rangle$$

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.

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

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

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

arising from the n different values of the integer p, which give n different values of k. $\quad k = 2\pi p / L$

One dimensional lattice problem with nearest neighbor interactions only

$$\underline{H} = \underline{H}_M + \underline{H}_{j,j\pm1}$$ ← **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.

$$\underline{H}_M = \underline{H}_{M_1} + \underline{H}_{M_2} + \cdots + \underline{H}_{M_j} + \cdots + \underline{H}_{M_{n-1}}$$ **Sum of single molecule Hamiltonians**

$$\underline{H}_M \left| \Phi_j^e \right\rangle = E^e \left| \Phi_j^e \right\rangle$$ **The jth term gives E^e, the other terms give zero because the ground state energy is zero.**

$$\underline{H}_M \left| \psi(k) \right\rangle = \underline{H}_M \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} e^{ik\alpha j} \left| \Phi_j^e \right\rangle$$

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

$$= \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} e^{ik\alpha j} \underline{H}_M \left| \Phi_j^e \right\rangle$$

$$= E^e \left| \psi(k) \right\rangle$$

Inclusion of intermolecular interactions breaks the excited state degeneracy.

$$\underline{H}_{j,j\pm1}\left|\Phi^e_j\right\rangle = \gamma\left|\Phi^e_{j+1}\right\rangle + \gamma\left|\Phi^e_{j-1}\right\rangle$$

state with j^{th} molecule excited

coupling strength

Operate $\underline{H}_{j,j\pm1}$ on Bloch states – eigenstates.

$$\underline{H}_{j,j\pm1}\left|\psi(k)\right\rangle = \underline{H}_{j,j\pm1}\frac{1}{\sqrt{n}}\sum_{j=0}^{n-1}e^{ik\alpha j}\left|\Phi^e_j\right\rangle$$

$$= \frac{1}{\sqrt{n}}\sum_{j=0}^{n-1}e^{ik\alpha j}\,\underline{H}_{j,j\pm1}\left|\Phi^e_j\right\rangle$$

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

$$\underline{H}_{j,j\pm1}\left|\psi(k)\right\rangle = \frac{1}{\sqrt{n}}\sum_{j=0}^{n-1}\left[e^{ik\alpha j}\gamma\left|\Phi_{j+1}^{e}\right\rangle + e^{ik\alpha j}\gamma\left|\Phi_{j-1}^{e}\right\rangle\right]$$

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

$$e^{ik\alpha}e^{-ik\alpha} = 1$$

$$\underline{H}_{j,j\pm1}\left|\psi(k)\right\rangle = \frac{1}{\sqrt{n}}\sum_{j=0}^{n-1}\left[e^{ik\alpha j}e^{ik\alpha}e^{-ik\alpha}\gamma\left|\Phi_{j+1}^{e}\right\rangle + e^{ik\alpha j}e^{-ik\alpha}e^{ik\alpha}\gamma\left|\Phi_{j-1}^{e}\right\rangle\right]$$

combining **combining**

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

$$j+1 \qquad\qquad j-1$$

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) ➡ $\left|\psi(k)\right\rangle$

Replacing exp. times ket, summed over all sites (j) with $\left|\psi(k)\right\rangle$

$$\underline{H}_{j,j\pm1}\left|\psi(k)\right\rangle = e^{-ik\alpha}\gamma\left|\psi(k)\right\rangle + e^{ik\alpha}\gamma\left|\psi(k)\right\rangle$$

$$= \gamma\left(e^{ik\alpha} + e^{-ik\alpha}\right)\left|\psi(k)\right\rangle \qquad \textbf{factor out } \gamma\left|\psi(k)\right\rangle$$

$$= 2\gamma\cos(k\alpha)\left|\psi(k)\right\rangle$$

Adding this result to

$$\underline{H}_M\left|\psi(k)\right\rangle = E^e\left|\psi(k)\right\rangle$$

Gives the energy for the full Hamiltonian.

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

The nearest neighbor interaction with strength γ breaks the degeneracy.
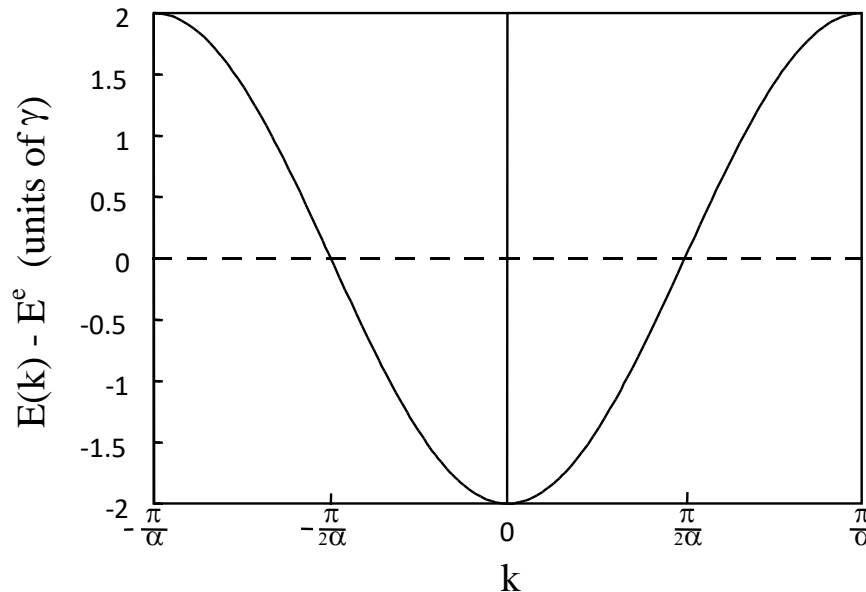
Result (one dimension, nearest neighbor interaction only, *γ*)

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

k ➜ **wave vector – labels levels**   *α* ➜ **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*γ* to -2*γ*

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