Lecture #19 Supplement: Perturbation Theory: Matrix Notation, Applications to Dynamics

Derivation of formulas of NDPT

key is that $\left|\dfrac{\mathbf{H}^{(1)}_{nm}}{E^{(0)}_n - E^{(0)}_m}\right| \ll 1$ no limit on $\mathbf{H}^{(1)}_{nn}$ because it becomes part of $\mathbf{H}^{(0)}$

Otherwise we need to diagonalize a piece of an ∞ dimension $\mathbf{H}$. Not treated in 5.61.

Everything comes from

$$\mathbf{H}^{(0)}\psi^{(0)}_n = E^{(0)}_n\psi^{(0)}_n \qquad \left\{E^{(0)}_n\right\}\left\{\psi^{(0)}_n\right\}$$

for exactly solved problem.

usually all $\mathbf{H}^{(1)}_{nm}$ are easily derived: "scaling" by quantum numbers.

language:

- basis set, basis–function, zero–order
- level repulsion
- energy denominator
- interaction term
- mixing coefficient or mixing angle
- dominant or "nominal" character

Nondegenerate Perturbation Theory

$$E_n = E^{(0)}_n + \mathbf{H}^{(1)}_{nn} + \sum_m{}' \underbrace{\frac{|H_{nm}|^2}{E^{(0)}_n - E^{(0)}_m}}_{\Delta_{nm}} \qquad \text{often } \sum_m{}' \frac{|V_{nm}|^2}{\Delta_{nm}}$$

$$\psi_n = \psi^{(0)}_n + \sum_m{}' \underbrace{\frac{H_{nm}}{E^{(0)}_n - E^{(0)}_m}}_{\Delta_{nm}}\psi^{(0)}_m$$

Now in Matrix Notation: $\mathbf{Hc} = E\mathbf{c}$

$$\underbrace{\mathbf{T}^\dagger\mathbf{H}\mathbf{T}}_{\widetilde{\mathbf{H}}}\underbrace{\mathbf{T}^\dagger\mathbf{c}}_{\tilde{\mathbf{c}}} = E\underbrace{\mathbf{T}^\dagger\mathbf{c}}_{\tilde{\mathbf{c}}} \quad \text{an eigenvector equation}$$

$$\widetilde{\mathbf{H}} = \mathbf{T}^\dagger\mathbf{H}\mathbf{T} = \begin{pmatrix} E_1 & 0 & 0 & 0 \\ 0 & E_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & E_N \end{pmatrix}$$

$$\tilde{\mathbf{c}} = \mathbf{T}^\dagger\mathbf{c} \qquad \text{or} \qquad c^i = (\mathbf{T}^\dagger\mathbf{c})^i = \begin{pmatrix} T^\dagger_{i1} \\ \vdots \\ T^\dagger_{ii} \\ \vdots \\ T_{iN} \end{pmatrix} \leftarrow \text{i}^{\text{th}} \text{ position}$$

$$\tilde{\mathbf{c}}^i = \underbrace{\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}}_{\text{better to normalize } \mathbf{T}^\dagger_{ii}} + {\sum_{\substack{j=1 \\ j\neq i}}^{N}}' \mathbf{T}^\dagger_{ji} \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} \leftarrow \text{j}^{\text{th}} \text{ position}$$

$$\mathbf{T}_{ii} = \left[1 - \left({\sum_{j=1}^{N}}' \mathbf{T}^{\dagger 2}_{ji}\right)\right]^{1/2} \qquad \boxed{\text{why is } T_{ii} < 1?}$$

Suppose we want to know about some property other than E: $\mathbf{A}$ is any other operator.

$$A^{(0)}_{jk} = \int \psi^{(0)}_j \hat{A} \psi^{(0)}_k d\tau$$

usually automatic to get the matrix elements, e.g. Q^n for Harmonic Oscillator.

NOW:

using perturbation theory, we **approximately** diagonalize $\mathbf{H}$:

$$\widetilde{\mathbf{H}} \approx \mathbf{T}^\dagger\mathbf{H}\mathbf{T} \qquad \text{where } \mathbf{T}^\dagger, \mathbf{T} \text{ are from perturbation theory}$$

$$\left(\mathbf{H}^{(0)} + \mathbf{H}^{(1)}\right)$$

$$\tilde{\mathbf{c}}^i = \mathbf{T}^\dagger c^i = \begin{pmatrix} T^\dagger_{i1} \\ \vdots \\ T^\dagger_{iN} \end{pmatrix} \quad \text{i}^{\text{th}} \text{ column of } \mathbf{T}^\dagger$$

from Perturbation Theory

$$T^\dagger_{ij} = \frac{H^{(1)}_{ij}}{E^{(0)}_i - E^{(0)}_j} = \frac{V_{ij}}{\Delta_{ij}} \qquad \boxed{\text{I am being careless about } \mathbf{H}^{(1)*}_{ij}}$$

so

$$\widetilde{\mathbf{A}} \approx \mathbf{T}^\dagger \mathbf{A}^{(0)} \mathbf{T}.$$

$$\widetilde{\mathbf{A}}_{ij} = \sum_{k\ell} T^\dagger_{ik} A^{(0)}_{k\ell} T_{\ell j}$$

$$\Downarrow$$

$$\frac{V_{ik}}{\Delta_{ik}}$$

What is $T_{\ell j}$? How do we get it from $T^\dagger_{j\ell}$?

$$T^\dagger_{j\ell} = (T_{\ell j})^*$$

$$\left(T^\dagger_{j\ell}\right)^* = T_{\ell j}$$

$$\Downarrow$$

$$\left(\frac{V^*_{j\ell}}{\Delta_{j\ell}}\right)$$

$$T_{ii} = \left[1 - \sum_{j=1}^{N} \left(T^\dagger_{ij}\right)^2\right]^{1/2}$$

So we have the whole thing!

This could be useful for $\widehat{Q}$ or $\widehat{P}$ time–dependent expectation values (0 for HO, $\neq 0$ for anharmonic) or transition moments, $e\widehat{Q}$.

This is "mechanical anharmonicity".

There is also "electronic anharmonicity" where

$$M(Q) = M_0 + \left.\frac{dM}{dQ}\right|_{\mathbf{Q}=0} + \frac{1}{2}\frac{d^2M}{dQ^2}\mathbf{Q}^2 + \ldots$$

For the next part of today's lecture, we have a Supplement to Typed Notes: Worked examples for diatomic and polyatomic molecules.

Overview

1. Diatomic Molecule

   has only one vibrational mode

   "diagonal anharmonicity"

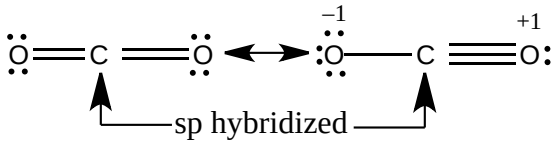
   What do $a\widehat{Q}^3$ and $b\widehat{Q}^4$ do to the energy levels?

   Qualitative Franck–Condon factors for $e'v' \leftrightarrow e''v''$ vibrational transitions

2. Polyatomic Molecules

   $3N - 6$ normal modes

   CO_2 valence bond theory from Organic Chemistry



   both linear. What will bending vibration do to stretching modes? Increase or decrease the frequency?

   Off–diagonal (inter–mode) and diagonal (intra-mode)

   anharmonicity – this is how valence bond ideas are verified and quantified.

   "bright" and "dark" states

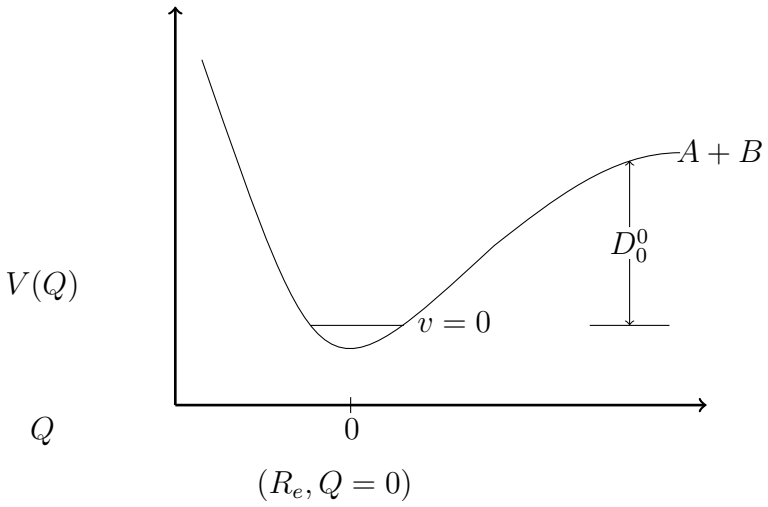
   Intramolecular Vibrational Redistribution (IVR) [Bond Specific activation cannot work.]

   Isomerization

   Dynamics: Eigenstates Encode Dynamics

1. Diatomic Molecules

potential curve



$$V(Q) = \frac{1}{2}k\widehat{Q}^2 + \frac{1}{6}a\widehat{Q}^3 + \frac{1}{24}b\widehat{Q}^4$$

power series constants a, b are derivatives of $V(Q)$ evaluated at $Q = 0$

Vibrational Energy Levels

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3$$

molecular constants (ω_e, $\omega_e x_e$, $\omega_e y_e$) are what we measure in spectra

What are contributors of a, b to $\omega_e x_e$ and $\omega_e y_e$ etc.

What do we know from perturbation theory about integrals

$$\int \psi_v(Q)^\star \widehat{Q}^n \psi_{v+n}(Q) dQ?$$

Selection Rules for $\widehat{Q}^3$ + $\widehat{Q}^4$ and prediction of the leading power of $(v + 1/2)$ in $G(v)$.

(i) $\widehat{Q}^3$ selection rule

$(v + 1/2)^m$ leading term?
what power of m?

(ii) sensitivity to sign of a or b?

For $\widehat{Q}^3$ $\Delta v = \pm 3, \pm 1$,

$$E_v^{(2)} = \frac{+(\text{const})[(v)(v-1)(v-2)]}{+3\omega} + \frac{+(\text{const})[(v+1)(v+2)(v+3)]}{-3\omega}$$

(lose sign information about a because we square the $\Delta v = \pm 3$ matrix element)

The v^3 terms cancel.

$$\text{Get} \qquad E_v^{(2)} = \underset{\uparrow}{\text{const.}}(v+1/2)^2 + \ldots$$

a^2 (no information about sign of a)

For $\widehat{Q}^4$ $\Delta v = \pm 4, \pm 2, 0$,

$$E_v^{(2)} = \frac{+(\text{const}')[(v)(v-1)(v-2)(v-3)]}{+4\omega} + \frac{+(\text{const}')[(v+1)(v+2)(v+3)(v+4)]}{-4\omega}$$

$$\text{Get} \qquad E_v^{(2)} = \underset{\uparrow}{\text{const.}}'(v+1/2)^2 + \ldots$$

b^2

General Rule

$\widehat{Q}^n$ in $\mathbf{H}^{(1)}$ gives

Matrix Element squared

$E(v)$ leading term $(v+1/2)^{2(\frac{n}{2})-1}$ ← cancellation of highest order term

$Q^n \to v^{n/2}$

Something else that is special. For $\widehat{Q}^4$ we also get

$$E_v^{(1)} = \underset{\uparrow}{b}(v+1/2)^{4/2} \quad \text{first-order contribution}$$

sign is explicitly present

$$E(v) = \underset{\uparrow}{\omega_e}(v+1/2) - \underset{\uparrow}{\omega_e x_e}(v+1/2)^2 + \underset{\uparrow}{\omega_e y_e}(v+1/2)^3$$

contributions from (mostly k (a^2, b^2) a^2, b (b^2) b^2)

Lots of examples in typed notes.

Transition Selection Rules

Vibrational Transition (Mei)

$\frac{d\mu}{dQ}\mathbf{Q}$ $\Delta v = \pm 1$ fundamentals

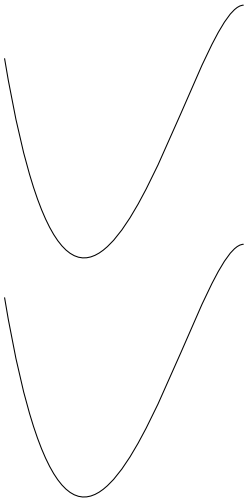
(increase with v because $\langle v|Q|v+1\rangle \propto (v+1)^{1/2}$)

$\frac{d^2\mu}{dQ^2}\mathbf{Q}^2$ $\Delta v = \pm 2$ overtones

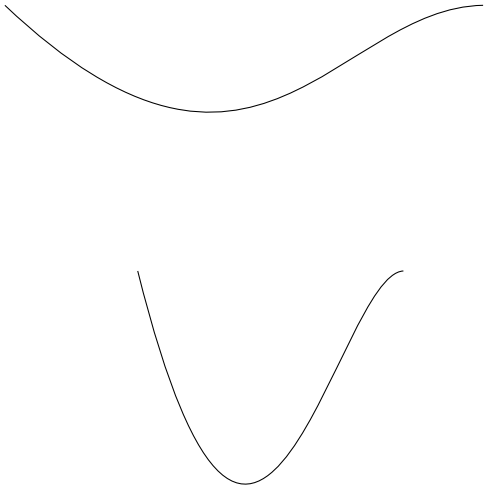
(increase with v because anharmonic contributions to ψ_v)

etc.

Electronic Transitions for Diatomic Molecules



identical ($\Delta v = 0$ transitions)
PE Curves



long vibrational progressions

For Polyatomic Molecules

We look at spectrum and measure:

$$\begin{aligned}\frac{E(v_1,v_2,v_3)}{hc} = \quad & \omega_1(v+1/2)+\omega_2(v_2+1/2)+\omega_3(v_3+1/2)+ \\ & x_{11},x_{22},x_{33} \qquad (v_i+1/2)^2 \\ & x_{12},x_{13},x_{23} \qquad (v_i+1/2)^2(v_j+1/2)\end{aligned}$$

These x_{ij} tell us how binding changes: VB Theory informed and tested by $\{\omega_i\}+\{x_{ij}\}$. We can also build a time–dependent picture to show how excitation in one normal mode leaks into other modes. The cause of this leakage is cross-anharmonicity terms in $\mathbf{H}^{(1)}$ like $k_{122}\widehat{Q}_1\widehat{Q}_2^2$.

"Bright/Dark" States

Quantum Beats, Non–radiative Decay, IVR

Simplest case first. Makes use of Perturbation Theory to describe both energy and wavefunction (favorite for exams).

Language:

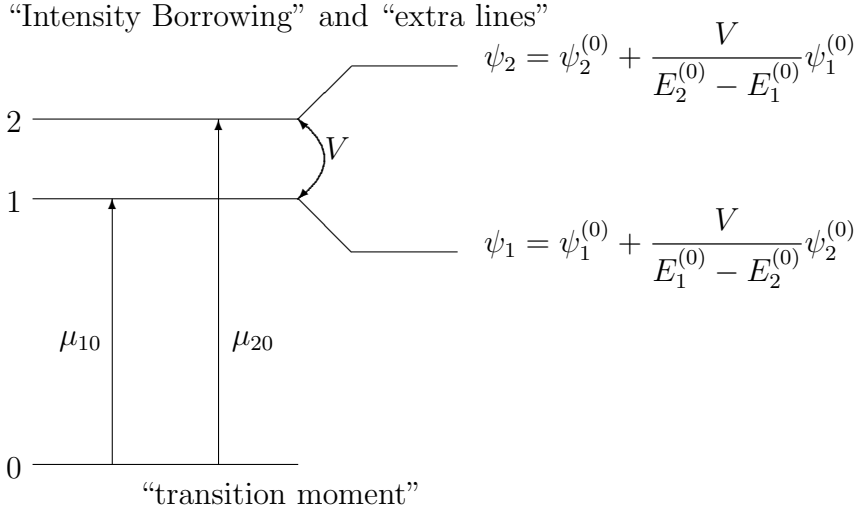
Bright, Dark

Intensity Borrowing

Extra Lines

Quantum Beats

"Intensity Borrowing" and "extra lines"



"transition moment"

If "transition moment" $\mu_{20} = 0$ and $\mu_{10} \neq 0$ we can get "extra line" by "intensity borrowing".

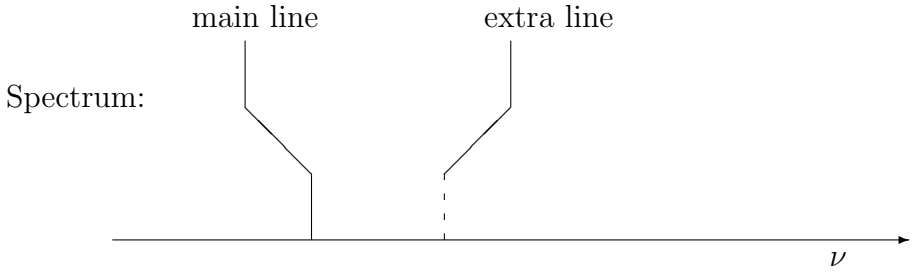
$$\mu_{10} = \int d\tau \psi_1^{(0)} \boldsymbol{\mu} \psi_0^{(0)}$$

$$I_{20} = \left| \int d\tau \psi_2 \boldsymbol{\mu} \psi_0 \right|^2$$

$$= \left| \mu_{20} + \frac{V}{E_2^{(0)} - E_1^{(0)}} \mu_{10} \right|^2$$

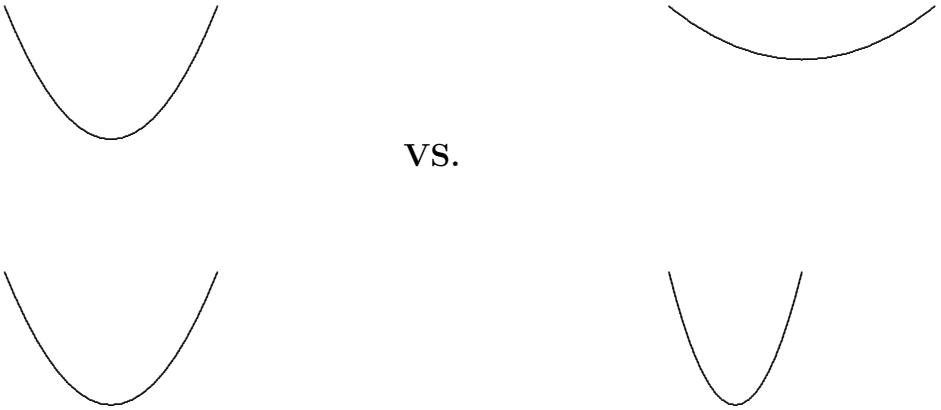
$$= |\mu_{20}|^2 + \left| \frac{V}{E_2^{(0)} - E_1^{(0)}} \right|^2 |\mu_{10}|^2$$

(μ_{20}: $\uparrow$ 0; $\frac{V}{E_2^{(0)} - E_1^{(0)}}$: $\uparrow$ borrowed intensity)



Polyatomic Molecules

Franck-Condon Principle for Diatomics



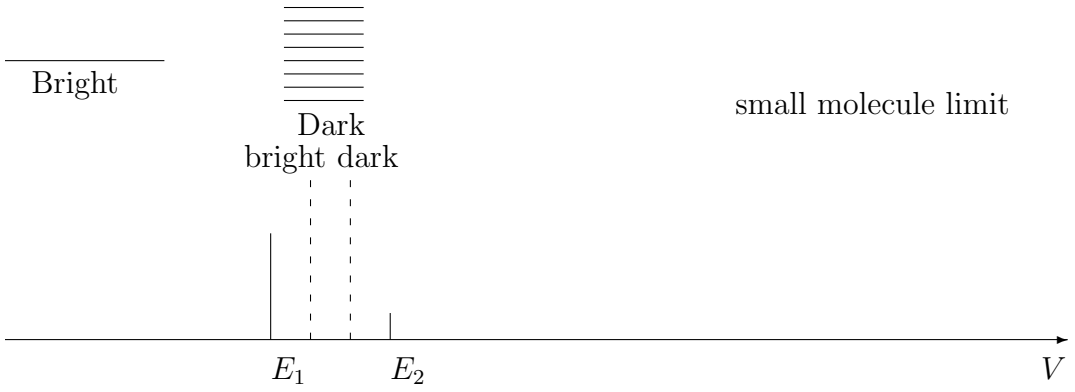
VS.

Same $V(x)$ shifted and distorted $V(x)$

Electronic Transition vibrational selection rule

$\Delta v = 0$	$\Delta v =$ many
$v'v''$	$v'v''$
$0-0$	$1-0$
$1-1$	$2-0$
$2-2$	$3-0$
	$4-0$
"sequence"	"progression"
hot bands	from $v''=0$

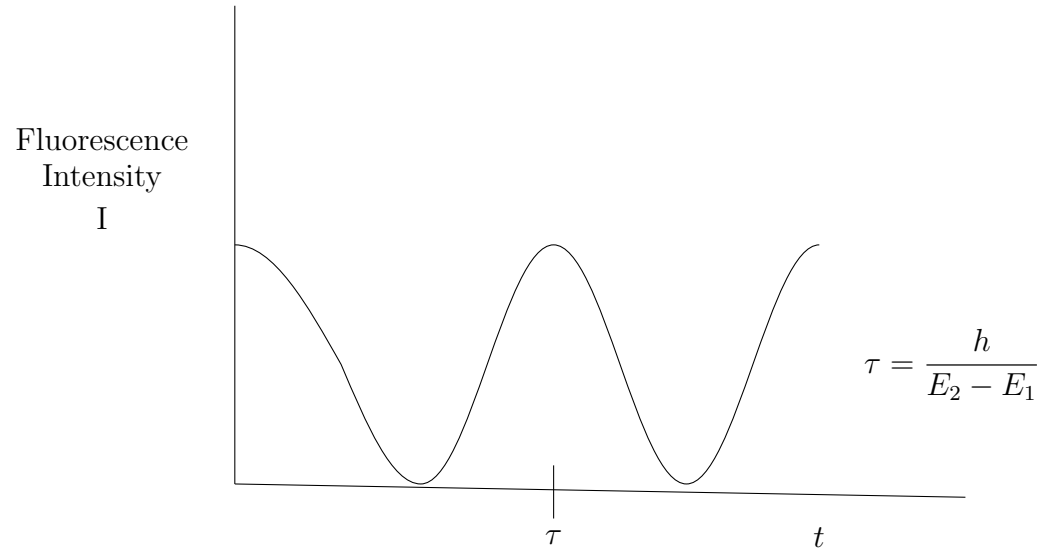
Polyatomic Molecule – vibrational density of states can get very large.



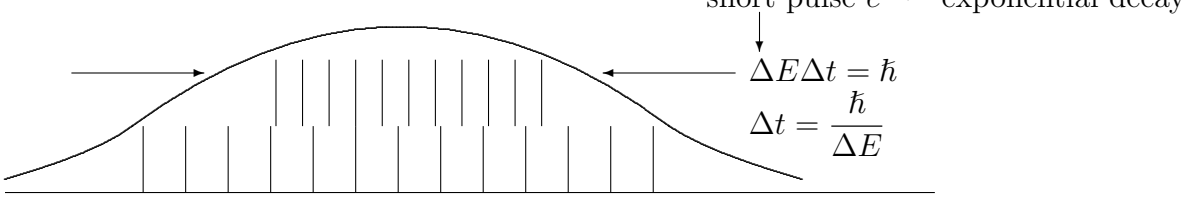
Resolved lines

Short pulse excitation – prepare bright zero-order state at $t = 0$. Superposition of several energy eigenstates.

"Quantum Beats"



Large Molecule limit



Broadened feature consisting of many unresolved transitions.

Intramolecular Vibrational Redistribution (IVR)

Mode specific chemistry

Below dissociation limit there is no true continuum.
Eigenstates encode dynamical mechanism. { Tunneling / Isomerization

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