5.73 Lecture #14

Perturbation Theory I

(See CTDL 1095-1107, 1110-1119)

Last time: derivation of all matrix elements for Harmonic-Oscillator: **x, p, H**

"selection rules" $x_{ij}^n \quad |i-j| \le n$ in steps of 2 $\left(\text{e.g. } x^3 : \Delta n = \pm 3, \pm 1\right)$

"quantum number scaling" $x_{ii}^n \propto i^{n/2}$

dimensionless quantities

$$\underset{\sim}{\mathbf{x}} = \left(\frac{m\omega}{\hbar}\right)^{1/2} \mathbf{x}$$

$$\underset{\sim}{\mathbf{p}} = (\hbar m\omega)^{-1/2} \mathbf{p}$$

$$\underset{\sim}{\mathbf{H}} = \frac{1}{\hbar\omega}\mathbf{H}$$

$$\underset{\sim}{\mathbf{x}} = 2^{-1/2}(\mathbf{a} + \mathbf{a}^\dagger)$$

$$\underset{\sim}{\mathbf{p}} = 2^{-1/2} i(\mathbf{a}^\dagger - \mathbf{a})$$

"annihilation"	$\mathbf{a} = 2^{-1.2}\left(\underset{\sim}{\mathbf{x}} + i\mathbf{p}\right)$	$\mathbf{a}\left\|n\right\rangle = n^{1/2}\left\|n-1\right\rangle$
"creation"	$\mathbf{a}^\dagger = 2^{-1/2}(\mathbf{x} - i\mathbf{p})$	$\mathbf{a}^\dagger\left\|n\right\rangle = (n+1)^{1/2}\left\|n+1\right\rangle$
"number"	$\mathbf{a}^\dagger\mathbf{a}$ (not $\mathbf{a}\mathbf{a}^\dagger$)	$\mathbf{a}^\dagger\mathbf{a}\left\|n\right\rangle = n\left\|n\right\rangle$
"commutator"	$[\mathbf{a},\mathbf{a}^\dagger] = +\mathbf{1}$	

a little more:

$$a_{01} = 1^{1/2}$$

$$\mathbf{a} = \begin{array}{c} \begin{array}{cccc} 0 & 1 & 2 & 3 \end{array} \\ \left(\begin{array}{ccccc} 0 & \sqrt{1} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} & 0 \\ 0 & 0 & 0 & 0 & \ddots \\ 0 & 0 & 0 & 0 & 0 \end{array}\right) \end{array} \begin{array}{l} 0 \\ 1 \\ 2 \\ 3 \end{array} \text{ row}$$

column

(one step to right of main diagonal)

convenience of having only one and not two diagonals filled

$$\mathbf{a}^n = \begin{pmatrix} 0 & \cdots & (n!)^{1/2} & 0 & 0 \\ 0 & 0 & \cdots & \left(\frac{(n+1)!}{1!}\right)^{1/2} & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & \cdots & \cdots & \left(\frac{(n+q)!}{q!}\right)^{1/2} \end{pmatrix} \begin{array}{l} 0 \\ 1 \\ \\ q \end{array}$$

(n steps to right)

selection rule for a_{ij}^{n} $\quad j - i = n$

selection rule for $a_{ij}^{\dagger n}$ $\quad j - i = -n$

operate on right with $\mathbf{a}^n$ first

operate on left with $(\mathbf{a}^\dagger)^m$ second

$$|n\rangle = [n!]^{-1/2} \left(\mathbf{a}^\dagger\right)^n |0\rangle$$

$$\left[\left(\mathbf{a}^\dagger\right)^m (\mathbf{a})^n\right]_{jk} = \underbrace{\delta_{j,k-n+m}}_{\text{selection rule}} \left[\frac{(k!)}{(k-n)!} \frac{(j!)}{(j-m)!}\right]^{1/2}$$

Selection rules are obtained simply by counting the numbers of $\mathbf{a}^\dagger$ and $\mathbf{a}$ operators and taking the difference.

The actual value of the matrix element depends on the order in which the individual $\mathbf{a}^\dagger$ and $\mathbf{a}$ factors are arranged, but the selection rule does not.

Lots of nice tricks and shortcuts using $\mathbf{a}$, $\mathbf{a}^\dagger$, and $\mathbf{a}^\dagger\mathbf{a}$

This makes writing computer programs trivially easy and transparent.

One of the places where these tricks come in handy is perturbation theory.

We already have:

1. WKB: local solution, local k(x), locate and exploit stationary phase (Lecture #3)
2. Numerov–Cooley: exact solution - no restrictions (Lecture #9)
3. Discrete Variable Representation: exact solution, ψ as linear combination of H-O eigenstates (Lecture #11)

Why perturbation theory?

- replace exact **H**, which is usually of ∞ dimension, by $\mathbf{H}^{eff}$, which is of finite dimension. Truncate infinite matrix so that any eigenvalue and eigenfunction can be computed with error < some preset tolerance.
  "Fit model" that is physical (because it makes localization and coupling mechanisms explicit) yet parametrically parsimonious

- derive explicit ***functional*** relationship between an n-dependent observable (e.g. E_n) and n
  e.g. $$\frac{E_n}{hc} = \omega_e\left(n+1/2\right) - \omega_e x_e\left(n+1/2\right)^2 + \omega_e y_e\left(n+1/2\right)^3$$

- establish relationship between a molecular constant (ω_e, $\omega_e x_e$, …) and the parameters that define V(x) e.g. $\omega_e x_e \leftrightarrow a x^3$

There are 2 kinds of garden variety perturbation theory:

1. Nondegenerate (Rayleigh-Schrödinger) P.T. → simple formulas.
   This breaks down when the interacting basis states are "near degenerate."

2. Quasi-Degenerate P.T. → matrix $\mathbf{H}^{eff}$
   Finite $\mathbf{H}^{eff}$ is corrected for "out-of-block" perturbers by "van Vleck" or "contact" transformation

~4 Lectures

Derive Perturbation Theory Formulas

* correct E_n and ψ_n directly for effects of "neglected" terms in exact **H**
* correct all other observables indirectly through corrected ψ

Perturbation Theory I. Begin Cubic Anharmonic Perturbation

Formal treatment

$E_n = \lambda^0 E_n^{(0)} + \lambda E_n^{(1)} + \lambda E_n^{(2)}$ usually stops at λ^2

$\psi_n = \lambda^0 \psi_n^{(0)} + \lambda^1 \psi_n^{(1)}$ usually stops at λ^1 (because all observables involve $\psi \times \psi'$, hence orders go up to λ^2).

$\mathbf{H} = \lambda^0 \mathbf{H}^{(0)} + \lambda^1 \mathbf{H}^{(1)}$ order sorting is MURKY

λ is an order-sorting parameter with no physical significance. Set $\lambda = 1$ after all is done. $\lambda = 0 \rightarrow 1$ is like turning on the effect of $\mathbf{H}^{(1)}$. Equations must be valid for the entire range of λ. $0 \leq \lambda \leq 1$.

Plug 3 equations into Schrödinger Equation, $\mathbf{H}\psi_n = E_n\psi_n$, and collect terms into separate equations according to the order of λ.

λ^0 terms:

$\mathbf{H}^{(0)} \left| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(0)} \right\rangle$

left multiply by $\left\langle \psi_m^{(0)} \right|$

$$\boxed{H_{mn}^{(0)} = E_n^{(0)} \delta_{mn}}$$

requires that $\mathbf{H}^{(0)}$ be diagonal in $\left\{ \psi_n^{(0)} \right\}$

know the eigenvalues $\left\{ E_n^{(0)} \right\}$ and eigenfunctions $\left\{ \psi_n^{(0)} \right\}$ of $\mathbf{H}^{(0)}$

CALLED BASIS FUNCTIONS

CALLED "ZERO–ORDER" MODEL

So we choose $\mathbf{H}^{(0)}$ to be the part of $\mathbf{H}$ for which:

* it is easy to write and exploit a *complete* set of eigenfunctions and eigenvalues
* it is easy to evaluate matrix elements of commonly occurring "perturbation" terms in this basis set
* sometimes the choice of basis set is based on convenience rather than "goodness" — doesn't matter as long as the basis set is complete.

} easier to think "nature" intended a simpler reality

examples:

Harmonic Oscillator	$V(x) = \frac{1}{2}kx^2$
Morse Oscillator	$V(x) = D\left[1 - e^{-ax}\right]^2$ $\quad$ [D, a, and R_e]
Quartic Oscillator	$V(x) = bx^4$
n-fold hindered rotor	$V_n(\phi) = \left(V_n^0/2\right)\left(1 - \cos n\phi\right)$

Now return to the Schrödinger Equation and examine the λ^1 and λ^2 terms.

λ^1 terms

$$\mathbf{H}^{(1)}\left|\psi_n^{(0)}\right\rangle + \mathbf{H}^{(0)}\left|\psi_n^{(1)}\right\rangle = E_n^{(1)}\left|\psi_n^{(0)}\right\rangle + E_n^{(0)}\left|\psi_n^{(1)}\right\rangle$$

multiply by $\left\langle\psi_n^{(0)}\right|$

from $\mathbf{H}^{(0)}$ operating to left

$$\underbrace{H_{nn}^{(1)} + E_n^{(0)}\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle}_{\text{same}} = \underbrace{E_n^{(1)} + E_n^{(0)}\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle}_{\text{get rid of them}}$$

$\left(\text{could also require } \left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle = 0\right)$

we do require this later

$H_{nn}^{(1)} = E_n^{(1)}$ 1st-order correction to E is just the expectation value of the perturbation term in **H**: $\mathbf{H}^{(1)}$.

Return to λ^1 equation and this time multiply by $\left\langle \psi_m^{(0)} \right|$

$$H_{mn}^{(1)} + E_m^{(0)} \left\langle \psi_m^{(0)} \middle| \psi_n^{(1)} \right\rangle = 0 + E_n^{(0)} \left\langle \psi_m^{(0)} \middle| \psi_n^{(1)} \right\rangle$$

$$H_{mn}^{(1)} = \left\langle \psi_m^{(0)} \middle| \psi_n^{(1)} \right\rangle \left(E_n^{(0)} - E_m^{(0)} \right)$$

$$\left\langle \psi_m^{(0)} \middle| \psi_n^{(1)} \right\rangle = \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}}$$

Now, to get $\left| \psi_{\mathrm{n}}^{(1)} \right\rangle$, we use the completeness of $\left\{ \psi^{(0)} \right\}$: $\sum_k \left| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \right|$

$$\psi_n^{(1)} = \sum_k \left| \psi_k^{(0)} \right\rangle \underbrace{\left\langle \psi_k^{(0)} \middle| \psi_n^{(1)} \right\rangle}_{\text{but we already know this}}$$

$$\psi_n^{(1)} = \sum_k \left| \psi_k^{(0)} \right\rangle \frac{H_{kn}^{(1)}}{E_n^{(0)} - E_k^{(0)}}$$

indices in opposite order from naïve expectation

* index of $\psi_n^{(1)}$ matches 1st index of $E_n^{(0)}$ in denominator
* $n = k$ is problematic. Insist on Σ_k' which means exclude the $k = n$ term
* we cold have demanded $\left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle = 0$
* counter - intuitive order of indices $\mathrm{H}_{kn}^{(1)}$

λ^2 terms

most important in real problems although mindlessly excluded from most textbooks.

$$\mathbf{H}^{(1)}\left|\psi_n^{(1)}\right\rangle = E_n^{(1)}\left|\psi_n^{(1)}\right\rangle + E_n^{(2)}\left|\psi_n^{(0)}\right\rangle$$

multiply by $\left\langle\psi_n^{(0)}\right|$ $\qquad \left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle = 0$

$$\left\langle\psi_n^{(0)}\middle|\mathbf{H}^{(1)}\middle|\psi_n^{(1)}\right\rangle = 0 + E_n^{(2)}$$

↑ completeness

$$\sum_k \underbrace{\left\langle\psi_n^{(0)}\middle|\mathbf{H}^{(1)}\middle|\psi_k^{(0)}\right\rangle}_{\mathrm{H}_{n,k}^{(1)}}\underbrace{\left\langle\psi_k^{(0)}\middle|\psi_n^{(1)}\right\rangle}_{\sum_k' \frac{\mathrm{H}_{n,k}^{(1)}}{E_n^{(0)}-E_k^{(0)}}} = E_n^{(2)}$$

$$E_n^{(2)} = \sum_k{}' \frac{\left|H_{k,n}^{(1)}\right|^2}{E_n^{(0)} - E_k^{(0)}}$$

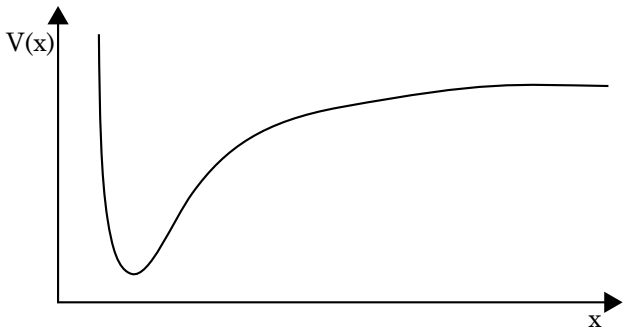
↑ always first

"matrix element squared" over energy difference in "energy denominator"

We have derived all needed formulas $E_n^{(0)}, E_n^{(1)}, E_n^{(2)}; \psi_n^{(0)}, \psi_n^{(1)}$!

Examples

$V(x) = \frac{1}{2}kx^2 + ax^3$ $\qquad$ (a < 0)



$\mathbf{H}^{(0)} = \frac{1}{2}k\mathbf{x}^2 + \frac{\mathbf{p}^2}{2m}$

$\mathbf{H}^{(1)} = a\mathbf{x}^3$

(actually the ax^3 term with a < 0 makes all potentials unbound. How can we pretend that this catastrophe does not affect the results from perturbation theory?)

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We need matrix elements of $\mathbf{x}^3$

Two ways to get them:

* matrix multiplication $x^3_{i\ell} = \sum_{j,k} x_{ij} x_{jk} x_{k\ell}$

* $\mathbf{a}, \mathbf{a}^\dagger$ tricks

$$\mathbf{x}^3 = \left(\frac{\hbar}{m\omega}\right)^{3/2} \underset{\sim}{\mathbf{x}}^3 = \left(\frac{\hbar}{m\omega}\right)^{3/2} \left[2^{-1/2}\left(\mathbf{a}+\mathbf{a}^\dagger\right)\right]^3$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{3/2} \left[\mathbf{a}^3 + \left(\mathbf{a}^\dagger\mathbf{a}\mathbf{a} + \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}\mathbf{a}\mathbf{a}^\dagger\right) + \left(\mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}\right) + \mathbf{a}^{\dagger 3}\right]$$

Each group in ( ) has its own Δv selection rule (see lecture #13 notes). Simplify using $[\mathbf{a}, \mathbf{a}^\dagger] = 1$.

Goal is to manipulate each mixed $\mathbf{a}, \mathbf{a}^\dagger$ term so that "the number operator", $\mathbf{a}^\dagger\mathbf{a}$, appears at the far right and then exploit $\mathbf{a}^\dagger\mathbf{a}|n\rangle = n|n\rangle$

All of the nonzero elements:

square root of larger q.n.

$$\Delta n = \pm 3$$

$$\mathbf{a}^3_{n-3n} = \left[n(n-1)(n-2)\right]^{1/2}$$

$$\mathbf{a}^{\dagger 3}_{n+3n} = \left[(n+3)(n+2)(n+1)\right]^{1/2}$$

$\Delta n = -1$: $\left(\mathbf{a}^\dagger\mathbf{a}\mathbf{a} + \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}\mathbf{a}\mathbf{a}^\dagger\right) = 3\mathbf{a}\mathbf{a}^\dagger\mathbf{a}$ $\boxed{-1}$

$$\text{because } \mathbf{a}^\dagger\mathbf{a}\mathbf{a} = \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \underbrace{\left[\mathbf{a}^\dagger, \mathbf{a}\right]}_{\boxed{-1}}\mathbf{a} = \mathbf{a}\mathbf{a}^\dagger\mathbf{a} - \mathbf{a}$$

$$\mathbf{a}\mathbf{a}\mathbf{a}^\dagger = \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}\underbrace{\left[\mathbf{a}, \mathbf{a}^\dagger\right]}_{\boxed{+1}} = \mathbf{a}\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}$$

$$\left(\mathbf{a}\mathbf{a}^\dagger\mathbf{a}\right)_{n-1n} = n^{3/2}$$

$\Delta n = +1$: $\left(\mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}\mathbf{a}^\dagger + \mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}\right) = 3\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a} + 3\mathbf{a}^\dagger$

$$\Big[\underbrace{3\underbrace{\mathbf{a}^\dagger\mathbf{a}}_{n}\mathbf{a}^\dagger\mathbf{a}}_{(n+1)^{1/2}} + 3\mathbf{a}^\dagger\Big]_{n+1\,n} = 3n\left(n+1\right)^{1/2} + 3\left(n+1\right)^{1/2} = 3\left(n+1\right)^{3/2}$$

(This is neither typo nor approximation.)

So we have worked out all $\mathbf{x}^3$ matrix elements — leave the rest to P.S. #5.

Properties other than E_n? Use $\psi_n = \psi_n^{(0)} + \psi_n^{(1)}$

e.g. transition probability (electric dipole allowed vibrational transitions)

$P_{nn'} \propto \left|x_{nn'}\right|^2$

for H-O

$$\left|x_{nn'}\right|^2 = \left(\frac{\hbar}{2\cancel{(km)^{1/2}}}\right) n_> \delta_{n_>, n_<+1}$$

($n_>$ here means the larger of $n_>$ and $n_<$)

(selection rule: only $\Delta n = \pm 1$ transitions).

For a perturbed H–O, e.g. $\mathbf{H}^{(1)} = a\mathbf{x}^3$

$$\left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + \Sigma'_k \frac{H_{kn}^{(1)}}{E_n^{(0)} - E_k^{(0)}}\left|\psi_k^{(0)}\right\rangle$$

$$\left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + \underbrace{\frac{H_{nn+3}^{(1)}}{-3\hbar\omega}\left|\psi_{n+3}^{(0)}\right\rangle} + \underbrace{\frac{H_{nn+1}^{(1)}}{-\hbar\omega}\left|\psi_{n+1}^{(0)}\right\rangle} + \underbrace{\frac{H_{nn-1}^{(1)}}{+\hbar\omega}\left|\psi_{n-1}^{(0)}\right\rangle} + \underbrace{\frac{H_{nn-3}^{(1)}}{+3\hbar\omega}\left|\psi_{n-3}^{(0)}\right\rangle}$$

Note the pairwise simplicity in the denominators.
The $\mathbf{H}_{nn'}^{(1)}$ terms are matrix elements of $\mathbf{x}^3$.

1st index (initial state)		Allowed 2nd indices (final state)
$n+3$		$n+4, n+2$
$n+1$		$n+2, n$
n	**x**	$n+1, n-1$
$n-1$		$n, n-2$
$n-3$		$n-2, n-4$

1st index reflects anharmonic mixing of initial state due to a$\mathbf{x}^3$ term

2nd indices refer to final state reached via electric dipole allowed transition, controlled by matrix elements of **x**.

Cubic anharmonicity of V(x) can give rise to $\Delta n = \pm 7, \pm 5, \pm 4, \pm 3, \pm 2, \pm 1, 0$ transitions.

$$\left\langle n\left|\mathbf{x}\right|n+7\right\rangle = \left(\frac{\hbar}{2\omega m}\right)^{7/2} \frac{a^2}{\left(-3\hbar\omega\right)^2}\left[\underbrace{\frac{(n+7)!}{n!}}_{\approx n^{7/2}}\right]^{1/2}$$

$$\left|x_{nn+7}\right|^2 \approx \frac{a^4}{m^7\omega^{11}} n^7$$

Other less extreme Δn transition strengths are given by smaller powers of $\frac{1}{\omega}$ and n.

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