Perturbation Theory I

(See CTDL 1095-1107, 1110-1119)

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

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

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

dimensionless quantities

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

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

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

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

a little more:

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

$$\mathbf{a} = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} & 0 \\ 0 & 0 & 0 & 0 & \ddots \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

(one step to right of main diagonal)

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

(n steps to right)

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

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

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

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

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

The actual value of the matrix element depends on the order in which 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 $\mathbf{a}^{\dagger}\mathbf{a}$

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

We already have:
1. WKB: local solution, local k(x), stationary phase
2. Numerov–Cooley: exact solution - no restrictions
3. Discrete Variable Representation: exact solution, ψ as linear combination of H-O.

Why perturbation theory?

- replace exact **H** which is usually of ∞ dimension by $\mathbf{H}^{\text{eff}}$ 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 the n-dependent observable and n
  e.g. $\frac{E_n}{hc} = \omega_e(n+1/2) - \omega_e x_e(n+1/2)^2 + \omega_e y_e(n+1/2)^3$
- establish relationship between a molecular constant (ω_e, $\omega_e x_e$, …) and the parameters that define V(x) e.g. $\omega_e x_e \leftrightarrow ax^3$

There are 2 kinds of garden variety perturbation theory:

1. Nondegenerate (Rayleigh-Schrödinger) P.T. → simple formulas

2. Quasi-Degenerate P.T. → matrix $\mathbf{H}^{\text{eff}}$
   finite $\mathbf{H}^{\text{eff}}$ 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 "neglected" terms in exact **H**
* correct all other observables indirectly through corrected ψ

Formal treatment

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

$$\psi_n = \lambda^0 \psi_n^{(0)} + \lambda^1 \psi_n^{(1)}$$ usually stop at λ^1
(because all observables involve $\psi \times \psi'$)

$$\mathbf{H} = \lambda^0 \mathbf{H}^{(0)} + \lambda^1 \mathbf{H}^{(1)}$$ 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 $0 \le \lambda \le 1$.

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

<u>λ^0 terms</u>

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

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 $\psi_n^{(0)}$

$\downarrow$ $\downarrow$

eigenvalues $\left\{E_n^{(0)}\right\}$ and eigenfunctions $\left\{\psi_n^{(0)}\right\}$ of $\mathbf{H}^{(0)}$ CALLED BASIS FUNCTIONS

$\rightarrow$ CALLED ZERO ORDER MODEL

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

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

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

Now return to the Schr. Eq. and examine the λ^1 and λ^2 terms.

<u>λ^1 terms</u>

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

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

from **H** operating to left

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

same

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

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

return to λ^1 equation and this time multiply by $\left\langle \psi^{(0)}_{m} \right|$

$$H^{(1)}_{mn} + E^{(0)}_{m} \left\langle \psi^{(0)}_{m} \middle| \psi^{(1)}_{n} \right\rangle = 0 + E^{(0)}_{n} \left\langle \psi^{(0)}_{m} \middle| \psi^{(1)}_{n} \right\rangle$$

$$H^{(1)}_{mn} = \left\langle \psi^{(0)}_{m} \middle| \psi^{(1)}_{n} \right\rangle \left(E^{(0)}_{n} - E^{(0)}_{m} \right)$$

$$\left\langle \psi^{(0)}_{m} \middle| \psi^{(1)}_{n} \right\rangle = \frac{H^{(1)}_{mn}}{E^{(0)}_{n} - E^{(0)}_{m}}$$

completeness of $\left\{ \psi^{(0)} \right\}$: $\sum_k \left| \psi^{(0)}_{k} \right\rangle \left\langle \psi^{(0)}_{k} \right|$

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

$$\boxed{\psi^{(1)}_{n} = \sum_k \left| \psi^{(0)}_{k} \right\rangle \frac{H^{(1)}_{kn}}{E^{(0)}_{n} - E^{(0)}_{k}}}$$

* index of $\psi^{(1)}_{n}$ matches 1st index in denominator
* $n = k$ is problematic. Insist Σ'_k exclude $k = n$.
* we could have demanded $\left\langle \psi^{(0)}_{n} \middle| \psi^{(1)}_{n} \right\rangle = 0$

λ^2 terms

most important in real problems although excluded from many text books.

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

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

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

$\uparrow$

completeness

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

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

matrix element squared
over
energy difference in "energy denominator"

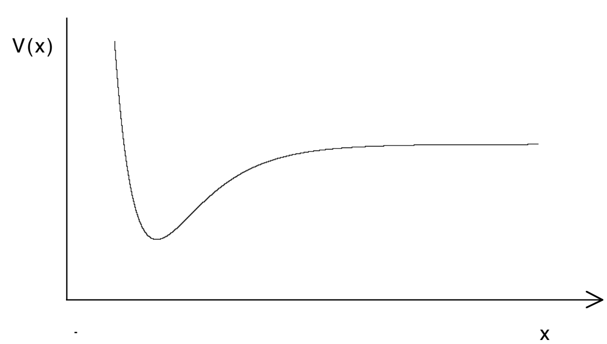
$\uparrow$

always first

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

Examples

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



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

$$H^{(1)} = ax^3$$

(actually 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?)

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

two ways to do this

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

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

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

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

each group in ( ) has their own Δv selection rule (see pages 13-8 and 9):
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" appears at the far right and exploit $\mathbf{a}^\dagger\mathbf{a}|n\rangle = n|n\rangle$

Only nonzero elements:

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

square root
of larger q.n.

$$\left(\mathbf{a}^\dagger\mathbf{aa} + \mathbf{aa}^\dagger\mathbf{a} + \mathbf{aaa}^\dagger\right) = 3\mathbf{aa}^\dagger\mathbf{a}$$

because $\mathbf{a}^\dagger\mathbf{aa} = \mathbf{aa}^\dagger\mathbf{a} + [\mathbf{a}^\dagger,\mathbf{a}]\mathbf{a} = \mathbf{aa}^\dagger\mathbf{a} - \mathbf{a}$

$$\mathbf{aaa}^\dagger = \mathbf{aa}^\dagger\mathbf{a} + \mathbf{a}[\mathbf{a},\mathbf{a}^\dagger] = \mathbf{aa}^\dagger\mathbf{a} + \mathbf{a}$$

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

$$\left(\mathbf{a}\mathbf{a}^{\dagger}\mathbf{a}^{\dagger} + \mathbf{a}^{\dagger}\mathbf{a}\mathbf{a}^{\dagger} + \mathbf{a}^{\dagger}\mathbf{a}^{\dagger}\mathbf{a}\right) = 3\mathbf{a}^{\dagger}\mathbf{a}^{\dagger}\mathbf{a} + 3\mathbf{a}^{\dagger}$$

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

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

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

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

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

for H - O

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

(only $\Delta n = \pm 1$ transitions)

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

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

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

$$\begin{array}{ccc} \text{1st index} & & \begin{array}{c}\text{Allowed}\\ \text{2nd Indices}\end{array} \\ \begin{pmatrix} n+3 \\ n+1 \\ n \\ n-1 \\ n-3 \end{pmatrix} & \mathbf{X} & \begin{pmatrix} n+4, n+2 \\ n+2, n \\ n+1, n-1 \\ n, n-2 \\ n-2, n-4 \end{pmatrix} \end{array}$$

For matrix elements of **X**.

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

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

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

other less extreme Δn transitions go as lower powers of $\frac{1}{\omega}$ and n