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” \( x^n_{ij} \quad |i-j| \leq n \) in steps of 2 \( \text{e.g.} \ x^3: \Delta n = \pm 3, \pm 1 \)

“scaling” \( x^n_{ii} \propto i^{n/2} \)

dimensionless quantities

\[
\begin{align*}
\bar{x} &= \left( \frac{m\omega}{\hbar} \right)^{1/2} x \\
\bar{p} &= (\hbar m\omega)^{-1/2} p \\
\bar{H} &= \frac{1}{\hbar\omega} H
\end{align*}
\]

“annihilation” \( a = 2^{-1/2}(x + ip) \) \( a|n\rangle = n^{1/2}|n-1\rangle \)

“creation” \( a^\dagger = 2^{-1/2}(x - ip) \) \( a^\dagger|n\rangle = (n+1)^{1/2}|n+1\rangle \)

“number” \( a^\dagger a \) (not \( aa^\dagger \)) \( a^\dagger a|n\rangle = n|n\rangle \)

“commutator” \([a, a^\dagger] = +1\)
a little more:

\[ a_{01} = 1^{1/2} \]

\[ a = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} & 0 \\ 0 & 0 & 0 & 0 & \ddots \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{(one step to right of main diagonal)} \]

\[ a^n = \begin{pmatrix} 0 & \cdots & (n)^{1/2} & 0 & 0 \\ 0 & 0 & \cdots & \left(\frac{(n+1)!}{1!}\right)^{1/2} & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & \cdots & \cdots & \left(\frac{(n+q)!}{q!}\right)^{1/2} \end{pmatrix} \quad \text{(n steps to right)} \]

selection rule for \( a^n_{ij} \) \( j - i = n \)
selction rule for \( a^\dagger_{ij} \) \( j - i = -n \)

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

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

Selection rules are obtained simply by counting the numbers of \( a^\dagger \) and \( a \) and taking the difference.

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

Lots of nice tricks and shortcuts using \( a, a^\dagger \) and \( a^\dagger a \)
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, \( \psi \) as linear combination of H-O.

Why perturbation theory?

* replace exact \( H \) which is usually of \( \infty \) dimension by \( H_{\text{eff}} \) 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. \( \frac{E_n}{\hbar c} = \omega_e(n + 1/2) - \omega_e x_e(n + 1/2)^2 + \omega_e y_e(n + 1/2)^3 \)

* establish relationship between a molecular constant (\( \omega_e, \omega_e x_e, \dots \)) 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. \( \rightarrow \) simple formulas

2. Quasi-Degenerate P.T. \( \rightarrow \) matrix \( H_{\text{eff}} \)
  
finite \( H_{\text{eff}} \) is corrected for “out-of-block” perturbers by “van Vleck” or “contact” transformation

~4 Lectures

**Derive Perturbation Theory Formulas**

* correct \( E_n \) and \( \psi_n \) directly for
  “neglected” terms in exact \( H \)
* correct all other observables indirectly through corrected \( \psi \)
Formal treatment

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

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

\[ H = \lambda^0 H^{(0)} + \lambda^1 H^{(1)} \]
order-sorting is MURKY

\( \lambda \) 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 \( H^{(1)} \). Equations must be valid for
\( 0 \leq \lambda \leq 1 \).

Plug 3 equations into Schr. Equation \( H \psi_n = E_n \psi_n \) and collect terms according to
order of \( \lambda \).

\( \lambda^0 \) terms

\[ H^{(0)} |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \]
left multiply by \( \langle \psi_m^{(0)} | \)

\[ H_{mn}^{(0)} = E_n^{(0)} \delta_{mn} \]
requires that \( H^{(0)} \) be diagonal in \( \psi_n^{(0)} \)

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

\[ \Rightarrow \text{CALLED ZERO ORDER MODEL} \]
So we choose $H^{(0)}$ to be the part of $H$ 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 Oscillator: $V(x) = bx^4$
- n-fold hindered rotor: $V_n(\phi) = \left(\frac{v_n^0}{2}\right)(1 - \cos n\phi)$

Now return to the Schrödinger Eq. and examine the $\lambda^1$ and $\lambda^2$ terms.

\[ \lambda^1 \] terms

\[ H^{(1)} \left| \psi_n^{(0)} \right\rangle + H^{(0)} \left| \psi_n^{(1)} \right\rangle = E^{(1)} \left| \psi_n^{(0)} \right\rangle + E^{(0)} \left| \psi_n^{(1)} \right\rangle \]

multiply by $\left\langle \psi_n^{(0)} \right|$ from $H$ operating to left

\[ H^{(1)}_{nn} \left\langle \psi_n^{(0)} \right| \psi_n^{(0)} \right\rangle = E^{(1)} \left\langle \psi_n^{(0)} \right| \psi_n^{(1)} \right\rangle + E^{(0)} \left\langle \psi_n^{(0)} \right| \psi_n^{(1)} \right\rangle \]

[\text{same}]

get rid of them

\[ \left\langle \psi_n^{(0)} \right| \psi_n^{(1)} \right\rangle = 0 \]

we do require this later
1st-order correction to $E$ is just expectation value of perturbation term in $H$: $H^{(1)}$.

return to $\lambda^1$ equation and this time multiply by $\langle \psi_m^{(0)} \rangle$

$$H_{mn}^{(1)} + E_m^{(0)} \langle \psi_m^{(0)} \vert \psi_n^{(1)} \rangle = 0 + E_n^{(0)} \langle \psi_m^{(0)} \vert \psi_n^{(1)} \rangle$$

$$H_{mn}^{(1)} = \langle \psi_m^{(0)} \vert \psi_n^{(1)} \rangle (E_n^{(0)} - E_m^{(0)})$$

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

completeness of $\{\psi^{(0)}\}$: $\sum_k \langle \psi_k^{(0)} \vert \psi_k^{(0)} \rangle$

$$\psi_n^{(1)} = \sum_k \langle \psi_k^{(0)} \vert \psi_k^{(0)} \rangle \langle \psi_k^{(0)} \vert \psi_n^{(1)} \rangle$$

but we know this

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

* index of $\psi_n^{(1)}$ matches 1st index in denominator
* $n = k$ is problematic. Insist $\sum_k$ exclude $k = n$.
* we could have demanded $\langle \psi_n^{(0)} \vert \psi_n^{(1)} \rangle = 0$
most important in real problems although excluded from many text books.

\[ H^{(1)} \left| \psi^{(1)}_n \right\rangle = E^{(1)}_n \left| \psi^{(1)}_n \right\rangle + E^{(2)}_n \left| \psi^{(0)}_n \right\rangle \]

multiply by \( \left\langle \psi^{(0)}_n \right| \quad \left\langle \psi^{(0)}_n \right| \psi^{(1)}_n \rangle = 0 \)

\[ \left\langle \psi^{(0)}_n \right| H^{(1)} \left| \psi^{(1)}_n \right\rangle = 0 + E^{(2)}_n \]

completeness

\[ \sum_k \left\langle \psi^{(0)}_n \right| H^{(1)} \left| \psi^{(0)}_k \right\rangle \left\langle \psi^{(0)}_k \right| \psi^{(1)}_n \rangle = E^{(2)}_n \]

\[ H^{(1)}_{n,k} \quad \sum_k \frac{H^{(1)}_{k,n}}{E^{(0)}_n - E^{(0)}_k} \]

\[ E^{(2)}_n = \sum_k \frac{|H^{(1)}_{k,n}|^2}{E^{(0)}_n - E^{(0)}_k} \]

\[ \uparrow \quad \text{matrix element squared over energy difference in “energy denominator”} \]

we have derived all needed formulas

\[ E^{(0)}_n, E^{(1)}_n, E^{(2)}_n, \psi^{(0)}_n, \psi^{(1)}_n \]

Examples

\[ V(x) = \frac{1}{2} k x^2 + ax^3 \quad (a < 0) \]

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

\[ H^{(1)} = ax^3 \]

(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 $x^3$

two ways to do this

* matrix multiplication

$$x^{3\ell} = \sum_{j,k} x_{ij} x_{jk} x_{k\ell}$$

* $a_\dagger a$ tricks

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

each group in ( ) has their own $\Delta v$ selection rule (see pages 13-8 and 9):
simplify using $[a, a^\dagger] = 1$

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

Only nonzero elements:

\[
\begin{align*}
a_{n-3n}^3 &= \left[n(n-1)(n-2)\right]^{1/2} \\
a_{n+3n}^\dagger^3 &= \left[(n+3)(n+2)(n+1)\right]^{1/2}
\end{align*}
\]

square root of larger q.n.

\[
\left(a^\dagger a + a + a a^\dagger + a a a^\dagger\right) = 3a^\dagger a
\]

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

\[
a a a^\dagger = a a^\dagger a + a[a, a^\dagger] = a a^\dagger a + a
\]

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

\[ 3a^n a^{n+1} = 3(n+1)^{1/2} + 3(n+1)^{1/2} = 3(n+1)^{3/2} \]

So we have worked out all \(x^n\) 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 \(H - O\)

\[ |x_{nn'}|^2 = \left( \frac{\hbar}{2(km)^{1/2}} \right)_{n>0} \delta_{n_n, n_{n+1}} \]

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

for a perturbed \(H-O\), e.g. \(H^{(1)} = ax^3\)

\[
|\psi_n\rangle = |\psi_n^{(0)}\rangle + \sum_k H_{nk}^{(1)} E_n^{(0)} - E_k^{(0)} |\psi_k^{(0)}\rangle
\]

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

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

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

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