Perturbation theory

Only a few physical systems can be solved precisely, even those only in some simplified cases.

Assume $\hat{H}_0$, describes an unperturbed exactly solvable system

$\hat{H}_0 |n^{(0)}\rangle = E^{(0)}_n |n^{(0)}\rangle$

$\{ |n^{(0)}\rangle \}$ - known eigenvectors of the unperturbed system

$E^{(0)}_n$ - known eigenenergies of the unperturbed system

Now, this known system is slightly modified

$\hat{H} = \hat{H}_0 + \lambda \hat{V}$

where sometimes $\lambda << 1$ or $\hat{V}$ is weak, and $\lambda$ is just a marker to keep track of the perturbation terms.

For now, consider stationary (i.e. non-time varying) perturbation $\lambda \neq \text{V(t)}$ and non-degenerate set of $\{ |n^{(0)}\rangle \}$

(i.e. $E^{(0)}_n = E^{(0)}_m$ only for $n = m$)

Since the perturbation is weak, it changes the energy spectrum and the eigenstates only slightly, can use a power series for the modified states

$\hat{H} |n\rangle = E_n |n\rangle$  \hspace{1cm} (1)

We are looking in the solution in the form

$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + ...$

$E_n^{(1)} = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...$

Plan: substitute into (1) and collect terms of the same order in $\lambda$. 
\[ \hat{H} |n> = E_n |n> \]

\[ (\hat{H}_0 + \hat{V}) [ |n^{(0)}> + \lambda |n^{(1)}> + \lambda^2 |n^{(2)}> + ... ] = \]

\[ (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...) (|n^{(0)}> + \lambda |n^{(1)}> + \lambda^2 |n^{(2)}> + ...) \]

\(\lambda^0: \quad \hat{H}_0 |n^{(0)}> = E_n^{(0)} |n^{(0)}> \quad \text{no surprises} \)

\(\lambda: \quad \hat{H}_0 |n^{(1)}> + \hat{V} |n^{(0)}> = E_n^{(0)} |n^{(1)}> + E_n^{(1)} |n^{(0)}> \)

\(\lambda^{(k)}: \quad \hat{H}_0 |n^{(k)}> + \hat{V} |n^{(k-1)}> = E_n^{(0)} |n^{(k)}> + E_n^{(k)} |n^{(k-1)}> + E_n^{(k)} |n^{(0)}> \)

Starting from the bottom, \(k = 1\)

\[ \langle n^{(0)} | \hat{H}_0 | n^{(1)} > + \langle n^{(0)} | \hat{V} | n^{(0)} > = E_n^{(0)} \langle n^{(0)} | n^{(1)} > + E_n^{(1)} \]

Since \( \langle n^{(0)} | \hat{H}_0 | n^{(0)} > = \langle n^{(0)} | E_n^{(0)} | n^{(0)} > \)

Thus, the first order energy correction is

\[ E_n^{(1)} = \langle n^{(0)} | \hat{V} | n^{(0)} > \]

Energy correction = average value of the perturbation in that state

\[ (\hat{H}_0 - E_n^{(0)}) |n^{(1)}> = (E_n^{(0)} - \hat{V}) |n^{(1)}> \]

\[ |n^{(1)}> = \sum_{m \neq n} C_{m} |m^{(0)}> \]

\[ \sum_{m \neq n} C_{m} (E_m^{(0)} - E_n^{(0)}) |m^{(0)}> = (E_n^{(0)} - \hat{V}) |n^{(1)}> \]

Taking inner product \( \langle s^{(0)} | \)

\[ C_s (E_s^{(0)} - E_n^{(0)}) = - \langle s^{(0)} | \hat{V} | n^{(0)} > \]

\[ C_s = \frac{V_{ns}}{E_n^{(0)} - E_s^{(0)}} \]

\[ |n^{(1)}> = \sum_{m \neq n} \frac{V_{mn}}{E_m^{(0)} - E_n^{(0)}} |m^{(0)}> \]

\[ |n> = |n^{(0)}> + \lambda \sum_{m \neq n} \frac{V_{mn}}{E_m^{(0)} - E_n^{(0)}} |m^{(0)}> + O(\lambda^2) \]
\[ H |n\rangle = E_n |n\rangle \]

\[ (\hat{H}_0 + \hat{V}) |n^{(0)}\rangle + \hat{V} |n^{(0)}\rangle = (E_n^{(0)} + \hat{V} |n^{(0)}\rangle + E_n^{(0)} |n^{(0)}\rangle + \hat{V} |n^{(0)}\rangle + E_n^{(0)} |n^{(0)}\rangle + \ldots) = \]

\[ = (E_n^{(0)} + \hat{V} E_n^{(0)} + E_n^{(0)} + \hat{V}) |n^{(0)}\rangle + \hat{V} |n^{(0)}\rangle + E_n^{(0)} |n^{(0)}\rangle + \hat{V} |n^{(0)}\rangle + E_n^{(0)} |n^{(0)}\rangle + \ldots) = \]

\[ \lambda_0 : \overrightarrow{H} |h^{(0)}\rangle = E_n^{(0)} \text{ no surprises} \]

\[ \lambda_1 : \overrightarrow{H} |h^{(1)}\rangle + \hat{V} |h^{(1)}\rangle = E_n^{(0)} |h^{(1)}\rangle + E_n^{(1)} |h^{(1)}\rangle \]

\[ \ldots \lambda_k : \overrightarrow{H} |h^{(k)}\rangle + \hat{V} |h^{(k)}\rangle = E_n^{(0)} |h^{(k)}\rangle + E_n^{(1)} |h^{(k)}\rangle + \ldots + E_n^{(k)} |h^{(k)}\rangle \]

At that point we need to agree on the normalization of the wave function.

Choose

\[ \langle h^{(0)} | h^{(0)} \rangle = 1 \quad \Rightarrow \quad |h^{(0)}\rangle = |h^{(0)}\rangle + \lambda |n^{(1)}\rangle + \ldots \]

\[ \lambda \langle h^{(0)} | h^{(1)} \rangle + \lambda^2 \langle h^{(0)} | h^{(2)} \rangle + \ldots = 0 \quad \text{for all} \lambda \]

\[ \Rightarrow \quad \langle h^{(0)} | h^{(k)} \rangle = 0 \quad \text{for all} \ k \neq 0 \]

Let's check back to the general expression

\[ \overrightarrow{H} |h^{(k)}\rangle + \hat{V} |h^{(k)}\rangle = E_n^{(0)} |h^{(k)}\rangle + E_n^{(1)} |h^{(k)}\rangle + \ldots + E_n^{(k)} |h^{(k)}\rangle \]

Let's take the inner product with \( \langle h^{(0)} | \)

\[ \langle h^{(0)} | \overrightarrow{H} |h^{(k)}\rangle + \langle h^{(0)} | \hat{V} |h^{(k)}\rangle = E_n^{(k)} \]

\[ E_n^{(0)} \downarrow \quad \text{for} \ k = 1 \quad E_n^{(1)} = \langle h^{(0)} | \hat{V} |h^{(1)}\rangle \]

Let's now figure out the corrections to the wave function.

\[ (\overrightarrow{H} - E_n^{(0)}) |h^{(k)}\rangle = (\hat{V} + E_n^{(0)}) |h^{(k)}\rangle + E_n^{(1)} |h^{(k)}\rangle + \ldots + E_n^{(k)} |h^{(k)}\rangle \]

\[ \sum_{m \neq n} E_m^{(0)} |h^{(k)}\rangle = \sum_{m \neq n} \langle m^{(0)} | (\hat{V} + E_n^{(0)}) |h^{(k)}\rangle + \ldots + E_n^{(1)} |m^{(0)} |h^{(k)}\rangle \]

\[ \sum_{m \neq n} E_m^{(0)} |h^{(k)}\rangle = \sum_{m \neq n} \langle m^{(0)} |h^{(k)}\rangle \]

\[ \sum_{m \neq n} |h^{(k)}\rangle = \sum_{m \neq n} \frac{1}{E_n^{(0)} - E_m^{(0)}} \]

\[ |h^{(k)}\rangle = \frac{1}{E_n^{(0)} - E_m^{(0)}} \sum_{m \neq n} \langle m^{(0)} |h^{(k)}\rangle \]

\[ \text{or} \quad |h^{(0)}\rangle = \frac{1}{E_n^{(0)} - E_m^{(0)}} \sum_{m \neq n} \langle m^{(0)} |h^{(k)}\rangle \]

\[ \frac{1}{E_n^{(0)} - E_m^{(0)}} \sum_{m \neq n} \langle m^{(0)} |h^{(k)}\rangle \]

\[ \text{orthogonality} \quad \frac{\langle m^{(0)} |h^{(k)}\rangle}{E_n^{(0)} - E_m^{(0)}} \]
Two-level system

\[ E_{n}^{(2)} = \frac{\langle n^{(0)} | \hat{V} | n^{(0)} \rangle}{E_{n}^{(0)} - E_{m}^{(0)}} \]

\[ E_{n}^{(2)} = \frac{\sum_{m \neq n} |V_{mn}|^2}{E_{n}^{(0)} - E_{m}^{(0)}} \]

\[ V_{mn} = V_{nm} \]

Fun fact! the ground level always shifts down!

1. In order to affect the energy states in the first order, the perturbation matrix must have diagonal terms.

\[ \hat{V}_{1} = \begin{pmatrix} V_{11} & 0 \\ 0 & V_{22} \end{pmatrix} \]

Trivial case, \[ V_{1n} = V_{n1} \] no change in eigenstates

\[ E_{n} = E_{n}^{(0)} + \lambda V_{n} \]

2. Suppose that \( \hat{V} \) has off-diagonal terms.

\[ \hat{V} = V_{12} \langle 2^{(0)} | 1^{(0)} \rangle + V_{21} \langle 1^{(0)} | 2^{(0)} \rangle \]

\[ \hat{H} = \begin{pmatrix} E_{1}^{(0)} & \lambda V_{12} \\ \lambda V_{21} & E_{2}^{(0)} \end{pmatrix} \]

\[ E_{1,2} = \frac{E_{1}^{(0)} + E_{2}^{(0)}}{2} \pm \sqrt{\frac{(E_{1}^{(0)} - E_{2}^{(0)})^2}{4} + \lambda^2 V_{12}^2} \]

\[ \lambda V_{12} \ll |E_{1}^{(0)} - E_{2}^{(0)}| \]

Small compared to the energy splitting

Second-order

\[ \Delta V_{12} \ll |E_{1}^{(0)} - E_{2}^{(0)}| \]

Exactly as expected from perturbation theory
In fact, this is a very general behavior: levels repel when coupled. Special term — avoided crossing!

If two levels $E_n^{(0)}$ and $E_n^{(0)}$ are closed, $E_n - E_n <<$ all other energy splittings.

If they are coupled:

$$E_n^{(2)} = \frac{\hbar \omega n}{2} \left( \frac{1}{E_n^{(0)} - E_n^{(0)}} \right) \approx \frac{\hbar \omega n}{2} \left( \frac{1}{E_n^{(0)} - E_m^{(0)}} \right)$$

and analogously:

$$E_m^{(2)} = \frac{\hbar \omega m}{2} \left( \frac{1}{E_m^{(0)} - E_m^{(0)}} \right)$$

avoided crossings in the presence of coupling.

Some parameter of the system

Couple examples:

**Infinite square well**

\[ H_0 = \begin{cases} 0 & 0 < x < L \\ \infty & \text{elsewhere} \end{cases} \]

\[ V = \begin{cases} V_0 & \frac{L}{2} - \frac{a}{2} < x < \frac{L}{2} + \frac{a}{2} \\ 0 & \text{elsewhere} \end{cases} \]

Physically: small bump can "slow down" a particle near the center. Expect stronger effect for odd states (linear effect).

\[ V_{nn} = V_0 \frac{L}{2} \int_{-\frac{a}{2}}^{\frac{a}{2}} \sin^2 \frac{\pi x}{2L} \, dx = V_0 \frac{L}{2} \sin^2 \frac{\pi n}{2L} \leq \frac{2V_0}{L} \text{ for } n = 2k+1 \]

Need "extra" kinetic energy to compensate for the higher potential energy.
Second order correction

\[ V_{nm} = V_0 \frac{2}{L} \int_{l-q}^{l+q} \sin \frac{\pi n x}{L} \sin \frac{\pi m x}{L} \, dx \]

\[ = 2aV_0 \frac{\sin \frac{\pi n}{2} \sin \frac{\pi m}{2}}{L} = \frac{2aV_0}{L} \text{ for odd } n, m \]

\[ E_n^{(2)} = \sum_{m=1 \text{ odd}} \frac{4aV_0^2 / L^2}{\pi^2 h^2 \left( n^2 - m^2 \right)} = \frac{8ma^2 V_0^2}{\pi^2 h^2} \sum_{n \neq m} \frac{1}{n^2 h^2 - m^2} \]

Particle giving rise to interference

More fun with the infinite potential!

If we stretch it a little?

\[ E_n^{(0)} = \frac{\pi^2 h^2}{2mL^2} \]

\[ E_n = \frac{\pi^2 h^2}{2m(L+\delta L)^2} + \frac{\pi^2 h^2}{2mL^2} \frac{\delta L}{L} \]

Can we use the perturbation theory? Yes

\[ x = x' \left( 1 + \frac{\delta L}{L} \right) \]

\[ \hat{H}_0 = \frac{p^2}{2m} \]

\[ \hat{H} = -\frac{\hbar^2}{2m} \left( 1 - \frac{2\delta L}{L} \right) \frac{d^2}{dx^2} \]

\[ = \frac{p^2}{2m} - \frac{2\delta L p^2}{L} \]

\[ E_n^{(1)} = \langle n | \hat{H} | n \rangle = \langle n | -\frac{2\delta L p^2}{L} \frac{1}{2m} | n \rangle = -\frac{2\delta L p^2}{L} \frac{n^2 \hbar^2 \delta h}{2mL^2} \]
A bit of a housekeeping...

Waveform renormalization

Remember we picked \( \langle n/n^{(0)} \rangle = 1 \)?

Let's renormalize \( \ln \) to follow more conventional norm: \( \langle n/\ln n \rangle = 1 \,

\[
\langle n/\ln n \rangle = Z_n^{1/2} \ln n \Rightarrow Z_n = \frac{\langle n/\ln n \rangle}{\ln n}
\]

\[
\frac{1}{Z_n} = \langle \ln n \rangle = (\langle n^{(0)} \rangle + \lambda^2 \langle n^{(1)} \rangle + \cdots + \lambda^{n-1} \langle n^{(n-1)} \rangle + \cdots) = \langle n^{(0)} \rangle + \lambda^2 \langle n^{(1)} \rangle + \cdots + \lambda^{n-1} \langle n^{(n-1)} \rangle + \cdots
\]

\[
= 1 + \lambda^2 \sum_{m} \frac{V_{nm}^{*}}{E_{m}-E_{n}} \sum_{n} \frac{V_{nm}^{*}}{E_{n}-E_{m}} \langle m \rangle + \cdots = 1 + \lambda^2 \sum_{m<n} \frac{V_{nm}^{2}}{(E_{n}-E_{m})^2}
\]

always positive!

\[
Z_n \approx 1 - \lambda^2 \sum_{m<n} \frac{V_{nm}^{2}}{(E_{n}-E_{m})^2} = O(\lambda^4)
\]

\[
Z_n^{1/2} \approx 1 - \frac{\lambda^2}{2} \sum_{m<n} \frac{V_{nm}^{2}}{(E_{n}-E_{m})^2}
\]

correction in the second order of \( \lambda \)

thus it must be neglected when \( \langle n^{(1)} \rangle \) are calculated
Convergence of the perturbation series

In general, perturbation series do not converge for most useful problems (anharmonic oscillator, QED, etc.)

but

For weak perturbations, a series usually converges near correct answer up to some order, then diverges

Simple mathematical example

\[ f(x) = \int_{-\infty}^{\infty} dx \, e^{-\frac{1}{2} x^2} \frac{1}{x^4} \approx \int_{-\infty}^{\infty} dx \, e^{-\frac{1}{2} x^2} \left[ \sum_{k=0}^{\infty} \frac{(-1)^k x^{4k}}{4^k k!} \right] \]

\[ = \sum_{k=0}^{\infty} \frac{\lambda^k}{k!} \]

where \( \lambda_k = \sqrt{2\pi} \frac{k^{k-1/2}}{16^k k!(2k)!} \)

\[ \lambda^k \rightarrow \text{grows exponentially with} \quad k \]

\[ k! \sim \sqrt{2\pi} \quad k^k e^{-k} \quad \text{faster than exponent} \]

\[ \lambda^k f_k \rightarrow \frac{4\pi}{\lambda} (-\frac{4\pi}{\lambda})^k \quad \text{diverges badly for large} \quad k \]

but converges well for \( k \ll 1 \)

For example, \( \lambda = 0.01 \)

12 terms give accuracy of \( \approx 10^{-10} \)

25 terms give accuracy of \( \approx 10^{-12} \)

special technique to make the high orders converge are developed.
Potential energy as a small perturbation

$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{U(\vec{r})}{\text{weak}}$

$\hat{H}_0 \ket{\psi} = E \ket{\psi}$

$\ket{\psi} = \frac{1}{2\pi} e^{\pm ikx} \quad E = \frac{\hbar^2 k^2}{2m}$

$\ket{\psi} = \ket{\psi^{(0)}} + \ket{\psi^{(1)}} = \ket{\psi^{(0)}} + f(x) \ket{\psi^{(0)}}$

Small perturbation

$\frac{\hat{p}^2}{2m} (f(x) \ket{\psi^{(0)}}) + U(\vec{r}) \ket{\psi^{(0)}} = E^{(0)} + f(x) \ket{\psi^{(0)}}$

$+ \frac{\hbar^2}{2m} \frac{d^2}{dx^2} (f(x) e^{ikx}) + \frac{\hbar^2 k^2}{2m} f(x) e^{ikx} = U(x) e^{ikx}$

Let us assume that $k$ is sufficiently large such that $e^{ikx}$ oscillates much faster than charges in potential $U(x)$.

Then $\frac{df}{dx} \ll k$

$\frac{d^2}{dx^2} (f(x)e^{ikx}) = -k^2 f(x)e^{ikx} + ikf(x) \frac{df}{dx} e^{ikx}$

$\ket{\psi^{(1)}} = -\frac{i\hbar}{\hbar k} e^{ikx} (\int_0^x u(x) dx)$

For smallness,

$\frac{\hbar^2}{\hbar^2 k} U(x) \ll 1 \quad U(x) \ll \frac{\hbar^2 k}{m a}$

Such perturbation method is equivalent to the "standard" one.

$\ket{\psi} = e^{ikx} + \sum_{k' \neq k} c_{kk'} e^{ik'x}$

Indeed, we can always decompose

$f(x) = \int f(x) e^{ikx} dx$

and

$\ket{\psi^{(1)}} = \int f(x) e^{i(k+\alpha)x} dx$ for $k' = k+\alpha$