

Perturbation Theory – Time-Independent

$$H = H_0 + H'$$

• H_0 has eigen-* $\{E_n^{(0)}\}, \{|n^{(0)}\rangle\}$

Expansions for eigen-* of H : $E_n = E_n^{(0)} + E_n^{(1)} + \dots$ & $|n\rangle = |n^{(0)}\rangle + |n^{(1)}\rangle + \dots$ • $H' \ll H_0$

For a **non-degenerate** eigenvalue $E_n^{(0)}$ of H_0 : $|n^{(1)}\rangle = \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle$ with $H'_{mn} \equiv \langle m^{(0)} | H' | n^{(0)} \rangle$

$$E_n^{(j)} = \langle n^{(0)} | H' | n^{(j-1)} \rangle \rightarrow E_n^{(1)} = H'_{nn}, \quad E_n^{(2)} = \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}$$

For a **degenerate** eigenvalue $E_D^{(0)}$ of H_0 :

- Let $\{|\alpha_1^{(0)}\rangle, \dots, |\alpha_n^{(0)}\rangle\} =$ degenerate subspace D sharing eigenvalue $E_D^{(0)}$ \Rightarrow 1st-order energy correction is
- Find $\{|\beta_1^{(0)}\rangle, \dots, |\beta_n^{(0)}\rangle\} =$ eigenvectors of H' within subspace D $E_{\beta_i}^{(1)} = \langle \beta_i^{(0)} | H' | \beta_i^{(0)} \rangle$

\downarrow not on Midterm 1 \downarrow

Variational Principle

$$E_{gs} \leq \langle \psi | H | \psi \rangle \quad \forall \psi$$

Sudden / Adiabatic Approx

ψ / n unchanged by ΔH

WKB Approximation

In Allowed ($V < E$) & Blocked ($V > E$) regions, with $p(x) \equiv \sqrt{2m(E - V(x))}$,

Solution forms: $\psi_A(x) = \frac{A}{\sqrt{p(x)}} \exp\left[\pm i \int^x \frac{p(x')}{\hbar} dx'\right], \quad \psi_B(x) = \frac{B}{\sqrt{|p(x)|}} \exp\left[\pm \int^x \frac{|p(x')|}{\hbar} dx'\right]$

Connection formulae at turning points $x = a$: with $\int k \equiv \int p(x') / \hbar dx'$ & “barrier” $\equiv V > E$ region

barrier on LEFT ($x < a$): $\psi_B(x) = \frac{1}{2} \frac{C}{\sqrt{|p|}} \exp\left[-\int_x^a |k|\right]$ matches to $\psi_A(x) = \frac{C}{\sqrt{p}} \cos\left[\int_a^x k - \frac{\pi}{4}\right]$

$\psi_B(x) = \frac{1}{2} \frac{D}{\sqrt{|p|}} \exp\left[+\int_x^a |k|\right]$ matches to $\psi_A(x) = \frac{D}{\sqrt{p}} \cos\left[\int_a^x k + \frac{\pi}{4}\right]$

barrier on RIGHT ($x > a$): $\psi_B(x) = \frac{1}{2} \frac{C}{\sqrt{|p|}} \exp\left[-\int_a^x |k|\right]$ matches to $\psi_A(x) = \frac{C}{\sqrt{p}} \cos\left[\int_x^a k - \frac{\pi}{4}\right]$

$\psi_B(x) = \frac{1}{2} \frac{D}{\sqrt{|p|}} \exp\left[+\int_a^x |k|\right]$ matches to $\psi_A(x) = \frac{D}{\sqrt{p}} \cos\left[\int_x^a k + \frac{\pi}{4}\right]$

“Barrier on **right**” formulae are **IDENTICAL** to “barrier on **left**” ones except that the **order of the integral bounds is reversed**. In ALL cases, the lower bound is at smaller x than the upper bound.

Perturbation Theory – Time Dependent

• $H(t) = H^{(0)} + H'(t)$ • $\{E_n^{(0)}, |n^{(0)}\rangle\}$ = the eigen-* of $H^{(0)}$

$|\psi(t)\rangle = \sum_n c_n(t) e^{-i\omega_n t} |n^{(0)}\rangle$ where $i\hbar \dot{c}_f(t) = \sum_n H'_{fn}(t) e^{i\omega_{fn} t} c_n(t)$

- $\omega_{fn} \equiv (E_f^{(0)} - E_n^{(0)}) / \hbar$
- $H'_{fn} \equiv \langle f^{(0)} | H' | n^{(0)} \rangle$

To 1st order in $H' \ll H^{(0)}$: with $|\psi(t_0)\rangle = |i^{(0)}\rangle$, $c_f(t) \approx \delta_{fi} + \frac{1}{i\hbar} \int_{t_0}^t H'_{fi}(t') e^{i\omega_{fi} t'} dt' \rightarrow P_{i \rightarrow f} = |c_f(t)|^2$

Fermi's Golden Rule: $R_{i \rightarrow f} \equiv \frac{P_{i \rightarrow f}}{t} = \frac{2\pi}{\hbar} |V_{fi}|^2 n(E_f)$

E1 Radiation

For electron

For atom as a whole:

making transition: $\Delta S = 0$

$\Delta l = \pm 1$

$\Delta L = 0, \pm 1$ but $0 \not\rightarrow 0$ $\Delta M_L = 0, \pm 1$

$\Delta m_l = 0, \pm 1$

$\Delta J = 0, \pm 1$ but $0 \not\rightarrow 0$ $\Delta M_J = 0, \pm 1$

Spontaneous E1 emission:

rate $A = \frac{\omega_{fi}^3 |e \vec{r}_{fi}|^2}{3\pi \epsilon_0 \hbar c^3}$

• $\vec{r}_{fi} \equiv \langle f | \vec{r} | i \rangle$

lifetime $\tau = 1 / A$

• $\hbar \omega_{fi} \equiv E_f - E_i$