

5 Approximation Methods

5.1 Time-independent perturbation theory: Non-degenerate case

Want to find E_n and $|n\rangle$ of Hamiltonian \hat{H} .

This can be challenging...

$$\text{Sometimes : } \hat{H} = \hat{H}_0 + \hat{V}$$

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"Small"

(adding \hat{V} leads to relatively small change)

We call \hat{V} perturbation

\hat{H}_0 is Hamiltonian w/ known solutions:

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

Idea: Use known $E_n^{(0)}$ and $|n^{(0)}\rangle$ to find approximations to E_n and $|n\rangle$.

For convenience of keeping track of orders, we use $\lambda \hat{V}$ for the perturbation instead of \hat{V} .

We can think of turning the potential on gradually by letting λ go from 0 to 1. We assume

analyticity of the energy eigen states and energy eigenvalues in λ -plane.

Formal development of perturbation expansion

Assumption: Energy levels are not degenerate

1-fold degenerate

$$\text{Recall: } \hat{H}_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

$$\hat{1} = \sum_n |n^{(0)}\rangle \langle n^{(0)}|$$

$$(\hat{H}_0 + \lambda \hat{V}) |n\rangle = E_n |n\rangle$$

$$\text{Define: } \Delta_n = E_n - E_n^{(0)}$$

We want to solve

$$(\hat{H}_0 + \lambda \hat{V}) |n\rangle = E_n |n\rangle$$

$\underbrace{\qquad}_{\Delta_n + E_n^{(0)}}$

rearrange $(E_n^{(0)} - \hat{H}_0) |n\rangle = (\lambda \hat{V} - \Delta_n) |n\rangle$

wanted wanted wanted

$$\text{let's write: } E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

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

Plug into SE:

$$(\hat{H}_0 + \lambda \hat{V}) (|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots)$$

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

Collect orders:

$$\lambda^0 : \boxed{\hat{H}_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle}$$

this is what we expected: we get the unperturbed eigen equation

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

To make progress, it is convenient to

define the projector $\hat{\phi}_n$:

$$\text{We have } \sum_n |n^{(0)}\rangle \langle n^{(0)}| = \hat{1}$$

$$\Rightarrow |n^{(0)}\rangle \langle n^{(0)}| + \sum_{k \neq n} |\bar{k}^{(0)}\rangle \langle \bar{k}^{(0)}| = \hat{1}$$

$$\Rightarrow \underbrace{|\bar{n}^{(0)}\rangle \langle \bar{n}^{(0)}|}_{\hat{\phi}_n} = \sum_{k \neq n} |\bar{k}^{(0)}\rangle \langle \bar{k}^{(0)}|$$

What happens when we act with $\hat{\phi}_n$ on $|n^{(0)}\rangle$?

$$\begin{aligned}\hat{\phi}_n |n^{(0)}\rangle &= (\hat{1} - |n^{(0)}\rangle \langle n^{(0)}|) |n^{(0)}\rangle \\ &= |n^{(0)}\rangle - |n^{(0)}\rangle = 0\end{aligned}$$

So: $\hat{\phi}_n$ really acts as a projector.

The strategy in the following is: introduce identity and rewrite the identity in terms of $\hat{\phi}_n + |n^{(0)}\rangle \langle n^{(0)}|$.

Work with ④ from previous page:

① Get $E_n^{(1)}$: multiply ④ from left with $\langle n^{(0)}|$

$$\begin{aligned}\langle n^{(0)} | \hat{V} | n^{(0)}\rangle + \underbrace{\langle n^{(0)} | \hat{H}_0 | n^{(0)}\rangle}_{\text{act to left}} \\ = \underbrace{\langle n^{(0)} | E_n^{(1)} | n^{(0)}\rangle}_{\text{cancel}} + \underbrace{\langle n^{(0)} | E_n^{(0)} | n^{(0)}\rangle}_{\text{cancel}}\end{aligned}$$

$$\Rightarrow \boxed{E_n^{(1)} = \langle n^{(0)} | \hat{V} | n^{(0)}\rangle}$$

underlined terms
cancel

② Get $|n^{(1)}\rangle$: Rearrange ④

$$(\hat{H}_0 - E_n^{(0)}) |n^{(1)}\rangle = (E_n^{(1)} - \hat{V}) |n^{(0)}\rangle$$

$$\Rightarrow |n^{(1)}\rangle = (\hat{H}_0 - E_n^{(0)})^{-1} (E_n^{(1)} - \hat{V}) |n^{(0)}\rangle$$

want to insert complete set here

"separate" $\hat{E}_n^{(1)} - \hat{V}$ into two pieces 5-5

$$\Rightarrow |n^{(1)}\rangle = (\hat{H}_0 - \hat{E}_n^{(0)})^{-1} |E_n^{(1)}|_{n^{(0)}}\rangle$$

$$= (\hat{H}_0 - \hat{E}_n^{(0)})^{-1} \left(\underbrace{\hat{\phi}_n + |n^{(0)}\rangle \langle n^{(0)}|}_{= \hat{1}} \right) \hat{V} |n^{(0)}\rangle$$

Separate the second line into two pieces

$$= \underline{\underline{E_n^{(1)} (\hat{H}_0 - \hat{E}_n^{(0)})^{-1} |n^{(0)}\rangle}}$$

$$\underline{\underline{-(\hat{H}_0 - \hat{E}_n^{(0)})^{-1} |n^{(0)}\rangle \underbrace{\hat{V} |n^{(0)}\rangle}_{\hat{E}_n^{(1)}}}}$$

$$- (\hat{H}_0 - \hat{E}_n^{(0)})^{-1} \hat{\phi}_n |V|_{n^{(0)}}\rangle$$

underlined terms cancel

inserting expression for $\hat{\phi}_n$

$$= - (\hat{H}_0 - \hat{E}_n^{(0)})^{-1} \sum_{k \neq n} |g_k^{(0)}\rangle \langle k^{(0)}| \hat{V} |n^{(0)}\rangle$$

$$= - \sum_{k \neq n} \frac{\langle k^{(0)}| \hat{V} |n^{(0)}\rangle}{\hat{E}_k^{(0)} - \hat{E}_n^{(0)}} |g_k^{(0)}\rangle$$

$$\Rightarrow |n^{(1)}\rangle = \boxed{\sum_{k \neq n} \frac{\langle k^{(0)}| \hat{V} |n^{(0)}\rangle}{\hat{E}_k^{(0)} - \hat{E}_n^{(0)}} |g_k^{(0)}\rangle}$$

Working with λ^2 expression, one can find

$$\boxed{\hat{E}_n^{(2)} = \sum_{k \neq n} \frac{|k^{(0)}| \langle V | g_k^{(0)} \rangle|^2}{\hat{E}_k^{(0)} - \hat{E}_n^{(0)}}}$$

Let's look at the second-order energy shift in more detail.

④ Let $n=0$: $E_0^{(2)} = \sum_{\ell \neq 0} \frac{|\langle \ell^{(0)} | \hat{V} | \ell^{(0)} \rangle|^2}{E_0^{(0)} - E_\ell^{(0)}}$

$$\downarrow \\ E_0^{(0)} < E_\ell^{(0)}$$

recall : non-degenerate case

$\Rightarrow E_0^{(2)}$ is negative

⑤ Let's look at energy levels $E_i^{(0)}$ and $E_j^{(0)}$ with

$$E_i^{(0)} < E_j^{(0)} :$$

$$— E_j^{(0)}, |j^{(0)}\rangle$$

$$— E_i^{(0)}, |i^{(0)}\rangle$$

In 2nd-order non-degenerate PT, we have

$$E_\ell^{(2)} = \sum_{\ell \neq i} \frac{|\langle i^{(0)} | \hat{V} | \ell^{(0)} \rangle|^2}{E_i^{(0)} - E_\ell^{(0)}} = \boxed{\frac{|\langle i^{(0)} | \hat{V} | j^{(0)} \rangle|^2}{E_i^{(0)} - E_j^{(0)}}} + \sum_{\ell \neq i,j}$$

$$E_\ell^{(2)} = \sum_{\ell \neq j} \frac{|\langle j^{(0)} | \hat{V} | \ell^{(0)} \rangle|^2}{E_j^{(0)} - E_\ell^{(0)}} = \boxed{\frac{|\langle j^{(0)} | \hat{V} | i^{(0)} \rangle|^2}{E_j^{(0)} - E_i^{(0)}}} + \sum_{\ell \neq i,j}$$

the red terms have the same magnitude but opposite signs

→ the i^{th} level gets pushed down due to the presence of the j^{th} level

→ the j^{th} level gets pushed up due to the presence of the i^{th} level

Imagine that there is only one non-zero matrix element, namely $\langle i^{(0)} | \hat{V} | j^{(0)} \rangle$.

Then

$$\begin{array}{ccc} E_i^{(0)} & \xrightarrow{\delta} & E_i^{(0)} + \delta E_i^{(2)} \\ E_j^{(0)} & \xrightarrow{\delta} & E_j^{(0)} + \delta E_j^{(2)} \end{array}$$

$$(\text{with } |E_i^{(2)}| = |E_j^{(2)}|)$$

This is referred to as no-level-crossing theorem.

The convergence of the perturbation series needs to be investigated carefully. The series will not always converge. As a rule of thumb, we want

$$\left| \frac{\langle n^{(0)} | \hat{V} | k^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \right|$$

to be small.

Example 1: 1D Harmonic oscillator with perturbation $\propto x$

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2$$

$$\hat{V} = \varepsilon \frac{\hat{x}}{b}$$

Want: 1st order energy shift

$$E_n^{(1)} = \langle n^{(0)} | \varepsilon \frac{\hat{x}}{b} | n^{(0)} \rangle$$

$$= \frac{\varepsilon}{b} \langle n^{(0)} | \hat{x} | n^{(0)} \rangle$$

$$\xrightarrow{\quad} = 0$$

by symmetry

(eigenstates have definite parity)

→ integral over odd function will be zero)

Need to go to the next order to get non-vanishing energy shift.

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle n^{(0)} | \hat{x} | k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \left| \frac{\varepsilon}{b} \right|^2$$

$$\text{Denominator: } E_n^{(0)} - E_k^{(0)} = \left(n + \frac{1}{2} - k - \frac{1}{2} \right) \hbar \omega$$

$$= (n - k) \hbar \omega$$

Numerator: Need to evaluate

$$\langle h^{(0)} | \hat{x} | k^{(0)} \rangle \text{ for any}$$

n, k combination.

n is fixed $\Rightarrow k$ needs to

be equal to $n+1$ or $n-1$

to get non-zero matrix element

(we can see this by thinking

about \hat{x} in terms of lowering

and raising operators.

$$\Rightarrow E_n^{(2)} = \sum_{\ell=n-1, n+1} \frac{\#}{\hbar \omega} \left| \frac{\varepsilon}{\hbar} \right|^2 \frac{\hbar}{m \omega}$$

dimensionless number that depends on k

$$|\langle h^{(0)} | \hat{x} | k^{(0)} \rangle|^2$$

has units of

length square

Even though the 2nd-order energy shift contains, in general, infinitely many terms, in this specific case the infinite sum reduces to two terms due to the selection rules.

Example 2: Quadratic Stark effect

Consider hydrogenic atom subjected to a uniform electric field in the positive z-direction:

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{r} - e |\vec{E}| z$$

$$\underbrace{\hat{H}_0}_{\uparrow} + \underbrace{e |\vec{E}| z}_{\text{perturbation } V}$$

the eigenenergies $E_n^{(0)}$
and eigenstates $\psi_{nlm}^{(0)}(\vec{r})$
are known

the electric field strength should be such that the energy shift is smaller than the energy difference $|E_1^{(0)} - E_2^{(0)}|$

$\uparrow \quad \uparrow$
gr. st. first exc.
 $(n=1)$ state ($n=2$)

Since the perturbation does not depend on spin, we can ignore the spin degrees of freedom \rightarrow we can apply non-degenerate PT to get the energy shift of ground state.

First-order energy shift (general expression):

$$E_0^{(1)} = \langle 0^{(0)} | \hat{V} | 0^{(0)} \rangle$$

↑ ↓ ↗

this zero stands
for "unperturbed"
this zero stands for "gr. st."

→ in the case of the H-atom (hydrogenic atom), the unperturbed gr. st. energy is "labeled" by $n=1$ and the unperturbed gr. st. wave function by $(n, l, m) = (1, 0, 0)$.

It makes sense to write:

$$E_{\text{gr}}^{(1)} = \langle 1, 0, 0 | \hat{V} | 1, 0, 0 \rangle$$

Here, it is understood that

$\langle \vec{x} | 1, 0, 0 \rangle = R_{10}(r) Y_0^0(\hat{\tau})$ denotes the unperturbed hydrogenic gr. st. wave function (we dropped the superscript "(0)" for notational convenience).

Since $V \propto Y_1^0(\hat{\tau})$, we can use the orthogonality of spherical harmonics to conclude that $E_{\text{gr}}^{(1)} = 0$.

go to second order:

$$E_{\text{gr}}^{(2)} = \sum_{\text{exc}} \frac{|\langle 1,0,0 | \hat{V} | n,l,m \rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

this sum runs over all $(n,l,m) \neq (1,0,0)$

It is important to note that the sum runs over bound states and scattering states. Since the scattering states form a continuum, the sum is really a "sum + integral":

$$\sum_{\text{exc}} \rightarrow \int_{\text{exc}}$$

$$E_{\text{gr}}^{(2)} = \int_{\text{exc}} \frac{|\langle 1,0,0 | \hat{V} | n,l,m \rangle|^2}{E_i^{(0)} - E_{\text{exc}}^{(0)}} e^{\pm i \vec{E} \cdot \vec{r}}$$

$E_n^{(0)}$ for b.st.

$\frac{\hbar^2 k^2}{2m}$ for sc. st.

Look at matrix element:

$$\langle l, 0, 0 | z | n, l, m \rangle = \begin{cases} \neq 0 \text{ for } m=0, \\ l=1 \\ 0 \text{ otherwise} \end{cases}$$

$\propto Y_l^0(\hat{r})$

$$\Rightarrow \bar{E}_{gr}^{(2)} = \sum_{\substack{\text{exc.} \\ l=12 \\ m=0}} \frac{|\langle l, 0, 0 | z | n, l, 0 \rangle|^2}{E_l^{(0)} - E_{\text{exc}}^{(0)}} e^{z|E|^2}$$

This sum can be evaluated exactly;
 Dalgarno and Lewis proposed a neat
 method that interprets the PT expression
 in terms of a reduced Green's function.

See : Proceedings of the Royal Society A (London)
233, 70 (1955).

The result is :

$$\bar{E}_{gr}^{(2)} = -\frac{1}{2} \propto |E|^2 ; \alpha = 4.5 a_0^3$$

$$\alpha = -2e^z \sum_{\text{exc}} \frac{|\langle gr^{(0)} | z | \text{exc}^{(0)} \rangle|^2}{E_{gr}^{(0)} - E_{\text{exc}}^{(0)}}$$

this eq. defines polarizability

Even though the sum / integral can be evaluated exactly, here we pursue an approximate approach.

$$\text{Note: } E_1^{(0)} - E_{\text{exc}}^{(0)} \leq E_1^{(0)} - E_2^{(0)} + \text{exc. energies}$$

$$\Rightarrow -E_1^{(0)} + E_{\text{exc}}^{(0)} \geq \underbrace{E_2^{(0)} - E_1^{(0)}}_{\frac{3e^2}{8a_0}}$$

$$\Rightarrow \alpha < Ze^2 \frac{8a_0}{3e^2} \nmid \underbrace{|\langle gr^{(0)} | z | \text{exc}^{(0)} \rangle|^2}_{\text{exc}}$$

$$\nmid \underbrace{\langle gr^{(0)} | z | \text{exc}^{(0)} \rangle \langle \text{exc}^{(0)} | z | gr^{(0)} \rangle}_{\text{exc}}$$

$$= \langle gr^{(0)} | z | \sum_{\text{exc}} |\text{exc}^{(0)} \rangle \langle \text{exc}^{(0)} | z | gr^{(0)} \rangle$$

Since $\langle gr^{(0)} | z | gr^{(0)} \rangle = 0$, we can ~~not~~ extend the sum and include the ground state

$$= \langle gr^{(0)} | z | \sum_{\substack{\text{all} \\ k}} |k^{(0)} \rangle \langle k^{(0)} | z | gr^{(0)} \rangle$$

$\boxed{\text{II}} \text{ (closure)}$

$$= \langle gr^{(0)} | z^2 | gr^{(0)} \rangle$$

$$= \frac{1}{3} \langle gr^{(0)} | r^2 | gr^{(0)} \rangle$$

$$= a_0^2$$

$$\Rightarrow \alpha < \frac{16}{3} a_0^3 \approx 5.3 a_0^3$$

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not so bad if compared
with $\frac{9}{2} a_0^3 = 4.5 a_0^3$ (exact)

5.2 Time-independent perturbation theory:

The degenerate case

Recall: So far, we have assumed that the energy levels are not degenerate.

Now: Allow for degeneracies.

It is clear that we will encounter "trouble" if we try to apply the formalism we currently have:

$$E_n^{(1)} = \langle n^{(0)} | \hat{V} | n^{(0)} \rangle$$

X

which of the degenerate states should be used?

higher-order expressions:
$$\frac{\langle n^{(0)} | \hat{V} | k^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}}$$

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how do we avoid dividing by zero if we have degeneracies?

What can we do?

The key thing to notice is that any linear combination of degenerate basis sets is again an eigenbasis with the same eigenenergy.

Recall: this is what we used when we switched from $|L\rangle, |R\rangle$ basis to $|S\rangle, |A\rangle$ basis.

Let's say we have g degenerate states with energy $E_D^{(0)}$. Let's call the eigen basis $|m^{(0)}\rangle$.

Then: We can form a new set of eigen basis

$$|l^{(0)}\rangle,$$

$$|l^{(0)}\rangle = \sum_{m \in D} \langle m^{(0)} | l^{(0)} \rangle |m^{(0)}\rangle,$$



States that live
in the degenerate
subspace

such that the perturbation V_1 , expressed using $|l^{(0)}\rangle$ is diagonal.

Note: this assumes that the degeneracy of the energy levels is broken in first-order PT.

In practice, this means that we need to solve a determinantal equation.

Let's say that we have g eigenkets $|m^{(0)}\rangle$ that all have the energy $E_m^{(0)}$. To distinguish the g different eigenkets $|m^{(0)}\rangle$, I introduce a subscript k :

$$|m_1^{(0)}\rangle, |m_2^{(0)}\rangle, \dots, |m_g^{(0)}\rangle$$

We need to solve:

$$\det \begin{pmatrix} \langle m_1^{(0)} | V | m_1^{(0)} \rangle - E_m^{(1)} & \langle m_1^{(0)} | V | m_2^{(0)} \rangle & \dots \\ \langle m_2^{(0)} | V | m_1^{(0)} \rangle & \langle m_2^{(0)} | V | m_2^{(0)} \rangle - E_m^{(1)} & \dots \\ \vdots & \ddots & \end{pmatrix} = 0$$

This gives us g solutions: $E_{m,k}^{(1)}$ with $k=1, \dots, g$.

For each of these solutions / roots, we can find the eigenvector \rightarrow the eigenvector tells us the linear combinations of the kets $|m_k^{(0)}\rangle$ that diagonalize the 1st-order PT matrix.

Example: Linear Stark effect

$$V = -e z |\vec{E}|$$

$\hat{H}_0 \hat{\equiv}$ hydrogenic atom (kinetic energy + Coulomb pot.)

We saw earlier that $E_{\text{gr}}^{(1)} = 0$

The unperturbed gr. st. is non-degenerate (we ignore spin degrees of freedom)

Is $E_n^{(1)}$ equal to zero for $n=2$? The answer is, as we will show, no.

$n=2$ manifold is 4-fold degenerate:

$$(n,l,m) = (2,0,0), (2,0,-1), (2,1,0), (2,1,1).$$

We already worked out that

$$\langle n', l', m' | \hat{V} | n, l, m \rangle$$

is non-zero only if

$$-m' = m$$

$$\& l' = l \pm 1$$

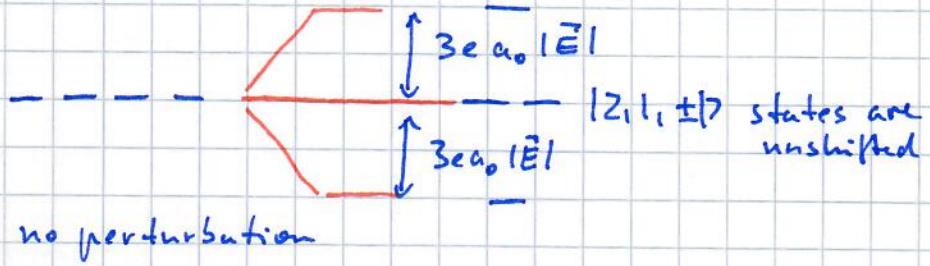
This means that the perturbation can only couple the states $(2,0,0)$ and $(2,1,0)$.

This is good news: instead of diagonalizing a 4×4 matrix, we ^{only} need to diagonalize a 2×2 matrix. the matrix element $\langle 2, 0, 0 | z | 2, 1, 0 \rangle = 0$

$$\det \begin{pmatrix} 0 - E_2^{(1)} & \langle 2, 0, 0 | -e/\vec{E} | z | 2, 1, 0 \rangle \\ \langle 2, 1, 0 | -e/\vec{E} | z | 2, 0, 0 \rangle & 0 - E_2^{(1)} \end{pmatrix} = 0$$

this matrix element evaluates to $-3ea_0|\vec{E}|$

$$\Rightarrow E_{2,\pm}^{(1)} = \pm 3ea_0|\vec{E}|$$



What are the shifted states?

Plug $E_{2,\pm}^{(1)}$ into

$$\begin{pmatrix} 0 & -3ea_0|\vec{E}| \\ -3ea_0|\vec{E}| & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_{2,\pm}^{(1)} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

For $E_{2,+}^{(1)}$, we find $\vec{c}_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} +1 \\ -1 \end{pmatrix}$

For $E_{2,-}^{(1)}$, we find $\vec{c}_- = \frac{1}{\sqrt{2}} \begin{pmatrix} +1 \\ +1 \end{pmatrix}$

This means that the "new" states are

$$\frac{1}{\sqrt{2}}(|2,0,0\rangle - |2,1,0\rangle) \text{ for } E_{2,+}^{(1)}$$

$$\frac{1}{\sqrt{2}}(|2,0,0\rangle + |2,1,0\rangle) \text{ for } E_{2,-}^{(1)}$$

The discussion here assumed that the $n=2$ energy levels of hydrogenic atoms are, indeed, degenerate. This is not the case (see the next section (Sec. 5.3)). Importantly, if the electric field is such that ^{the} energy shift $3ea_0|\vec{E}|$ is notably larger than the splitting / shifts to be determined in the next section, then the energy shifts should be - to a good approximation - linear in $|\vec{E}|$, i.e., the fine structure splitting (next section) can be neglected compared to the linear Stark effect.

5.3 Hydrogen-like atoms : Fine structure and the Zeeman effect

Basically, this section looks at applications of the perturbation theory framework.

We want to look at corrections of the non-relativistic energy of hydrogen-like atoms.

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_e} - \frac{Ze^2}{r}$$

The electron has spin- $\frac{1}{2}$ and the relativistic treatment of hydrogenic atoms is based on the Dirac equation. We will consider the Dirac equation in Chapter 8.

Taylor expanding of the Dirac Hamiltonian gives rise to three different corrections to the non-relativistic Hamiltonian. We will denote these corrections (perturbations) by V_1 , V_2 , and V_3 . We will motivate the forms of V_1 , V_2 , and V_3 but their rigorous derivation will be postponed till Chapter 8.

$$\hat{V}_1 = -\frac{\hat{\mathbf{p}}^4}{8m_e^3 c^2}$$

relativistic correction to the kinetic energy

$$\hat{V}_2 = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

spin-orbit coupling

$$\hat{V}_3 = \frac{\pi \hbar^2}{2m_e^2 c^2} Z e^2 \delta(r)$$

Darwin term (relativistic correction to the potential energy)

We will now treat \hat{V}_1 , \hat{V}_2 , \hat{V}_3 separately.

We will find energy shifts ΔE^1 , ΔE^2 , ΔE^3 .

the notation here is confusing: the superscript stands for perturbation \hat{V}^i . (ΔE^i is the energy shift due to perturbation \hat{V}^i)

Once we have ΔE^1 , ΔE^2 , and ΔE^3 , we will add them up.

Something to note already: ΔE^1 depends on n and l

ΔE^2 depends on n, l , and j

ΔE^3 depends on n and l

$$\underbrace{\Delta E^1 + \Delta E^2 + \Delta E^3}_{\text{each of these shifts is determined in 1st order PT}} = \Delta E^{(1)}$$

depends on n and j

$\Delta E'$: Relativistic correction to the kinetic energy

Where does the expression for \hat{V}_i come from?

Classical expression for kinetic energy: $\sqrt{m_e^2 c^4 + p^2 c^2}$

$$\text{Taylor expand: } \sqrt{m_e^2 c^4 + p^2 c^2} \approx m_e c^2 + \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3 c^2}$$

$$\text{Correspondence principle: } -\frac{p^4}{8m_e^3 c^2} \rightarrow -\frac{\hat{p}^4}{8m_e^3 c^2} = -\frac{(\hat{p}^2)^2}{8m_e^3 c^2}$$

Now that we know where the expression comes from.

we want to treat \hat{V}_i in 1st-order PT.

Unperturbed states are $|n, l, m, m_s\rangle$ with $E_n^{(0)}$.

We have degeneracies! Can we choose basis states / unperturbed kets such that \hat{V}' is diagonal?

Note: \hat{V}' commutes with \hat{S}_z , \hat{L}_z , and \hat{L}^2 .

If we use $|n, l, m, m_s\rangle$ kets, then \hat{V}' will be diagonal in l, m, m_s .

This is excellent since this implies that we can use non-degenerate PT.

We need to evaluate:

$$\langle n, l, m, m_s | \hat{V} | n, l, m, m_s \rangle$$

1

$$-\frac{1}{2m_e c^2} \left(\frac{\vec{p}}{2m_e} \right)^2 = -\frac{1}{2m_e c^2} \left(\vec{H}_0 + \frac{2e\vec{c}^2}{r} \right)^2$$

$$\frac{\hat{p}^2}{2m} = \hat{H}_0 + \frac{ze^2}{T}$$

$$= -\frac{1}{2m_e c^2} \left(\hat{H}_0^2 + \hat{H}_0 \frac{\hat{z} e^2}{r} + \frac{\hat{z} e^2}{r} \hat{H}_0 + \frac{\hat{z}^2 e^4}{r^2} \right)$$

using that the over integration gives one: $\langle \hat{W}_B/mg \rangle = 1$

$$= -\frac{1}{2m_e c^2} \langle n, l, m | \hat{H}_0 + \hat{H}_0 \frac{\hat{z} e^2}{r} + \frac{\hat{z} e^2}{r} \hat{H}_0 + \frac{\hat{z}^2 e^4}{r^2} | n, l, m \rangle$$


 yields $(E_m^{(0)})^2$ when
 acting on ψ_0 .

$$= -\frac{1}{2m_ec^2} \left\{ (E_n^{(0)})^2 + 2E_n^{(0)} \langle n,l,m | \frac{e^2}{r} | n,l,m \rangle \right.$$

$$= Ze^2 \frac{Zme^2}{t^2 h}$$

$$+ \left\langle n, l, m \mid \frac{z^2 e^4}{r^2} \mid n, l, m \right\rangle \right\}$$

$$= 2^z e^4 \frac{2^z (m_0 e^z)^2}{h^4 n^3 (l + \frac{1}{2})}$$

Collecting terms

$$\Delta E' = -E_n^{(0)} \left(\frac{2\alpha}{n}\right)^2 \left(\frac{3}{4} - \frac{n}{l+\frac{1}{2}}\right)$$

ΔE^2 : Spin-orbit coupling term

Where does the expression $\hat{V}^2 = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r} \vec{L} \cdot \vec{S}$ come from?

As in correction to kinetic energy case, start with classical formulation (it get's the functional form correctly but not the pre-factor):

$$\begin{aligned}
 -\vec{\mu} \cdot \vec{B}_{\text{eff}} &= -\frac{e}{m_e c} \vec{S} \cdot \left(-\frac{\vec{p}}{m_e c} \times \vec{x} \left(-\frac{1}{e} \right) \frac{\partial V}{\partial r} \right) \\
 &\quad \xrightarrow{\substack{\text{magnetic moment} \\ \text{of electron:}}} \quad \uparrow \\
 &\quad \xrightarrow{\substack{\text{moving charge} \\ \text{subjected to electric} \\ \text{field feels an effective} \\ \text{magnetic field } \vec{B}_{\text{eff}}:}} \\
 \vec{\mu} &= \frac{e}{m_e c} \vec{S} \\
 \vec{B}_{\text{eff}} &= -\frac{B}{c} \times \vec{E} \\
 \vec{E} &= -\frac{1}{e} \underbrace{\nabla V(r)}_{\substack{\text{Coulomb potential}}} \\
 &= \frac{1}{m_e^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r} \underbrace{\vec{S} \cdot (\vec{x} \times \vec{p})}_{\vec{L}}
 \end{aligned}$$

$$= \frac{1}{m_e^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r} \vec{S} \cdot \vec{L} \quad \left(\text{off by a factor of } \frac{1}{2} \right)$$

Quantizing and adding the factor of 2 gives the correct expression.

$$\text{Evaluate } \frac{\partial V}{\partial r} : \quad \frac{\partial V}{\partial r} = \frac{\partial}{\partial r} \left(-\frac{2e^2}{r} \right) = \frac{2e^2}{r^2}$$

$$\text{So: } V^2 = \varepsilon(r) \hat{L} \cdot \hat{S} \quad \text{with } \varepsilon(r) = \frac{2e^2}{2m_e^2 c^2} \frac{1}{r^3}$$

We notice: $\hat{L} \cdot \hat{S}$ does not commute with \hat{L}_z and \hat{S}_z

I should stick in S_z
but I dropped it for brevity

$\Rightarrow |n, l, m_s\rangle$ are not "good" unperturbed eigenkets for treating \hat{V}^2 . It will be much better to use $|n, l, s, j, m_j\rangle$

$$\hat{j} = \hat{L} + \hat{S} \Rightarrow \hat{L} \cdot \hat{S} = \frac{1}{2} \left(\hat{j}^2 - \hat{L}^2 - \hat{S}^2 \right)$$

↑ ↑ →

We know how these operators act on $|n, l, s, j, m_j\rangle$

$\hat{L} \cdot \hat{S}$ commutes w/ \hat{H}_0 and $|n, l, s, j, m_j\rangle$ are simultaneous eigenkets of $\hat{H}_0, \hat{L}^2, \hat{S}^2, \hat{j}^2$ and \hat{j}_z .

Using $|n, l, s, j, m_j\rangle$, we can use non-degenerate PT.

$$\Delta E^2 = \langle n, l, s, j, m_j | \Sigma(r) \hat{L} \cdot \hat{\vec{S}} | n, l, s, j, m_j \rangle$$

$$= \frac{1}{2} \langle n, l, s, j, m_j | \Sigma(r) [j(j+1) - l(l+1) - s(s+1)] | n, l, s, j, m_j \rangle$$

$$= \frac{1}{2} \left[j(j+1) - l(l+1) - s(s+1) \right] \frac{2e^2}{2m_e c^2} \left(\frac{me^2}{h^2} \right)^3 \frac{Z^3}{l(l+\frac{1}{2})(l+1)}$$

Collecting terms and using $s = \frac{1}{2}$

$$= -E_n^{(0)} \frac{(2\alpha)^2}{2nl(l+\frac{1}{2})(l+1)} \left[j(j+1) - l(l+1) - \frac{3}{4} \right]$$

Since we have $j = l \pm \frac{1}{2}$, we can try to simplify further.

Consider $j = l + \frac{1}{2}$:

$$j(j+1) - l(l+1) - \frac{3}{4} = l$$

Consider $j = l - \frac{1}{2}$:

$$j(j+1) - l(l+1) - \frac{3}{4} = -l-1$$

$$\Rightarrow \boxed{\Delta E^2 = -E_n^{(0)} \frac{(2\alpha)^2}{2nl(l+\frac{1}{2})(l+1)} \times \begin{cases} l & \text{for } j = l + \frac{1}{2} \\ -l-1 & \text{for } j = l - \frac{1}{2} \end{cases}}$$

ΔE^3 : Darwin term

The derivation of the Darwin term is a bit involved and requires knowledge of the Dirac equation. We will not go through this here — we just note that this term is a correction to the potential energy.

$$\hat{V}^3 = \frac{\pi \hbar^2}{2m_e^2 c^2} (2e^2) \delta(\vec{r}) \quad \rightarrow \text{independent of } \hat{S}_z^2, \hat{S}_x, \hat{I}_z$$

diagonal in $|l, m_l, s, m_s\rangle$
lets

Non-degenerate PT:

$$\Delta E^3 = \langle n, l, m_l, s, m_s | \hat{V}^3 | n, l, m_l, s, m_s \rangle$$

$$= \frac{\pi \hbar^2}{2m_e^2 c^2} (2e^2) \left| \langle \vec{x} | n, l, m_l, s, m_s \rangle \right|^2 \Big|_{\vec{x}=0}$$

$$= \begin{cases} 0 & \text{for } l \neq 0 \\ \frac{2^3}{\pi n^3} \left(\frac{m_e e^2}{\hbar^2} \right)^3 & \text{for } l=0 \end{cases}$$

$$\Rightarrow \Delta E^3 = \begin{cases} 0 & \text{for } l > 0 \\ -E_n^{(0)} \frac{(2\alpha)^2}{n} & \text{for } l=0 \end{cases}$$

Putting it all together: $\Delta E^1 + \Delta E^2 + \Delta E^3$

$$\Delta E^1 + \Delta E^2 + \Delta E^3 = E_n^{(0)} \left(\frac{2\alpha}{n}\right)^2 \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} - \frac{n}{2j(j+\frac{1}{2})(j+1)} \times \begin{cases} j \\ -j-1 \end{cases} \right] + \begin{cases} 0 \\ n \end{cases}$$

↑ ↑
for $j = l + \frac{1}{2}$ for $l > 0$
for $j = l - \frac{1}{2}$ for $l = 0$

Let $j = l + \frac{1}{2}$ and $l > 0$:

$$[] = \frac{n}{j} - \frac{3}{4} - \frac{n}{2j(j+\frac{1}{2})} = \frac{n}{j+\frac{1}{2}} - \frac{3}{4}$$

Let $j = l - \frac{1}{2}$ and $l > 0$:

$$[] = \frac{n}{j+\frac{1}{2}} - \frac{3}{4} + \frac{n(l+1)}{2(j+\frac{1}{2})(j+1)(l+1)} = \frac{n}{j+\frac{1}{2}} - \frac{3}{4}$$

Let $l=0$ ($l=0$ implies $j=\frac{1}{2}$):

$$[] = 2n - \frac{3}{4} + n = \frac{n}{\frac{1}{2} + \frac{1}{2}} - \frac{3}{4} = \frac{n}{j+\frac{1}{2}} - \frac{3}{4}$$

Thus :

$$\Delta E_{nj}^{(1)} = E_n^{(0)} \left(\frac{2\alpha}{n}\right)^2 \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right]$$

kin. energy corr. + Spin-orbit + Darwin term

$\alpha \approx \frac{1}{137}$
 $\alpha^2 \sim 10^{-4}$

dependence
on n and j
(rotational invariance)

$$\Rightarrow \boxed{E_{nj} \approx E_n^{(0)} \left[1 + \left(\frac{2\alpha}{n}\right)^2 \left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right) + \dots \right]}$$

We will see later that this agrees with the Taylor expansion of the full energy expression for hydrogenic atoms obtained by solving the Dirac equation.

5.4 Variational methods

If we do not know how to find the exact eigenkets $|E\rangle$ of \hat{H} , we can make a guess.

Let's call the guess $|\tilde{\psi}\rangle$.

And let's imagine that we calculate the expectation value of \hat{H} with respect to $|\tilde{\psi}\rangle$:

$$E_{\text{var}} = \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle}$$

Theorem 5.1: $E_{\text{var}} \geq E_0$

↑
exact gr. st. energy

Proof: Expand $|\tilde{\psi}\rangle$ in terms of exact eigenkets $|E\rangle$:

$$|\tilde{\psi}\rangle = \sum_k \langle E_k | \tilde{\psi} \rangle |E_k\rangle \quad \text{we can always expand in terms of complete set}$$

$$\hat{H} |E_k\rangle = E_k |E_k\rangle$$

↑
this is how the $|E\rangle$ are defined

Stick \oplus into E_{var} : $= E_k \underbrace{\langle E_k | \hat{H} | E_k \rangle}_{= E_k \delta_{kk}} = E_k \delta_{kk}$

$$E_{\text{var}} = \frac{\sum_{k_1} \sum_{k_2} \langle E_{k_1} | \hat{H} | E_{k_2} \rangle \langle E_{k_1} | \tilde{\psi} \rangle^* \langle E_{k_2} | \tilde{\psi} \rangle}{\sum_{k_1} \sum_{k_2} \langle E_{k_1} | E_{k_2} \rangle \langle E_{k_1} | \tilde{\psi} \rangle^* \langle E_{k_2} | \tilde{\psi} \rangle}$$

$$= \frac{\sum_k E_k |\langle E_k | \tilde{\psi} \rangle|^2}{\sum_k |\langle E_k | \tilde{\psi} \rangle|^2}$$

$$= E_0 - E_0 \frac{\sum_k |\langle \varphi_k | \tilde{O} \rangle|^2}{\sum_k |\langle \varphi_k | \tilde{O} \rangle|^2} + \frac{\sum_k |\langle \varphi_k | \tilde{O} \rangle|^2 E_k}{\sum_k |\langle \varphi_k | \tilde{O} \rangle|^2}$$

we added zero

combine in next line

$$= E_0 + \frac{\sum_k |\langle \varphi_k | \tilde{O} \rangle|^2 (\bar{E}_k - E_0)}{\sum_k |\langle \varphi_k | \tilde{O} \rangle|^2} \geq 0 \text{ for } k \neq 0$$

and = 0 for $k = 0$

$$\Rightarrow E_{\text{var}} \geq E_0$$

this is what was to be shown.



note: $E_{\text{var}} = E_0$ if and only if $|\tilde{O}\rangle = |O\rangle$.

Any trial set gives an upper bound for the exact ground state energy.



If we don't know how to exact gr. st. energy, we can get upper bound.

Note: we still need to evaluate E_{var} .

And we need to come up with a trial set \rightarrow we typically use physical intuition

If we introduce a variational parameter λ into our ket $(|\tilde{\phi}(\lambda)\rangle)$, then E_{var} depends on λ :

$$E_{\text{var}}(\lambda) = \frac{\langle \tilde{\phi}(\lambda) | \hat{H} | \tilde{\phi}(\lambda) \rangle}{\langle \tilde{\phi}(\lambda) | \tilde{\phi}(\lambda) \rangle}$$

The best trial ket is then given by looking for

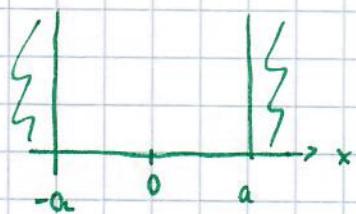
$$\frac{d E_{\text{var}}(\lambda)}{d \lambda} = 0$$

best within the family of kets spanned by λ

this condition determines the optimal λ : λ_{optimal}

$E_{\text{var}}(\lambda_{\text{optimal}}) \hat{=} \text{best that can be done within the family of kets considered.}$

Example:



$$V(x) = \begin{cases} 0 & \text{for } |x| < a \\ \infty & \text{for } |x| > a \end{cases}$$

$$\text{We know: } E_0 = \frac{\hbar^2 \pi^2}{2m(2a)^2}$$

$$\langle \Psi | \Psi \rangle = \frac{1}{2a} \cos\left(\frac{\pi x}{2a}\right)$$

let's pretend that we didn't know
how to obtain $\langle x | \hat{0} \rangle$.

guess: $\langle x | \hat{0} \rangle = |a|^\lambda - |x|^\lambda$ for $|x| < a$
(and zero otherwise)

This guess has some reasonable properties:

- $|x| = a \Rightarrow \langle x | \hat{0} \rangle = 0$
- symmetric with respect to
 $x = 0$

Evaluate:

$$\begin{aligned} E_{\text{var}}(\lambda) &= \frac{-\frac{\hbar^2}{2m} \int_a^a (|a|^\lambda - |x|^\lambda) \frac{\partial^2}{\partial x^2} (|a|^\lambda - |x|^\lambda) dx}{\int_{-\infty}^{\infty} (|a|^\lambda - |x|^\lambda)^2 dx} \\ &= \frac{(\lambda+1)(2\lambda+1)}{2\lambda-1} \frac{\hbar^2}{m(2a)^2} \end{aligned}$$

Calculate $\frac{dE_{\text{var}}(\lambda)}{d\lambda}$

and set equal to zero. $\Rightarrow \lambda_{\text{opt}} \approx 1.72$

Plug λ_{opt} into $E_{\text{var}}(\lambda)$ to get

$$E_{\text{var}}(\lambda_{\text{opt}}) \approx 1.003 E_0$$

quite good!

5.5 Time-dependent potentials: The interaction picture

Let us consider time-independent Hamiltonian \hat{H} .

$$\hat{H} |n\rangle = E_n |n\rangle \rightarrow |n\rangle \text{ energy eigen ket}$$

E_n eigen value
energy

$|n\rangle$: complete set

Assume: at $t=0$, the state ket of physical system is given by $|\alpha\rangle$:

$$|\alpha\rangle = \sum_n c_n(0) |n\rangle$$

$|c_n(0)|^2$ gives the probability to be in eigenket $|n\rangle$ at time $t=0$ [the expansion coefficients $c_n(0)$ are complex (in general), i.e., there exists a phase relationship between the different kets that contribute to $|\alpha\rangle$)

$$\Rightarrow |\alpha, t_0=0; t\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$$

we include this factor for convenience...

$|\alpha, t_0=0; t\rangle$: State ket in Schrödinger picture at time t of a physical system whose state ket at time $t=0$ was found to be $|\alpha\rangle$

Recall :

$$|\alpha, t_0=0; t\rangle = e^{-i\hat{H}t/\hbar} |\alpha\rangle \quad (*)$$

If $\hat{H}|n\rangle = E_n|n\rangle$, then :

$$|\alpha, t_0=0; t\rangle = e^{-i\hat{H}t/\hbar} \left(\sum_n c_n(0) |n\rangle \right)$$

$$= \sum_n c_n(0) e^{-iE_n t/\hbar} |n\rangle$$

no time dependence

the only time-dependence comes from this piece
 \rightarrow the reason is that we assumed that \hat{H} is time-independent

From (*) :

$$e^{i\hat{H}t/\hbar} |\alpha, t_0=0; t\rangle = |\alpha\rangle$$

Rewrite using "Heisenberg" and "Schrödinger" labels:

$$|\alpha\rangle_H = e^{i\hat{H}t/\hbar} |\alpha, t_0; t\rangle_S$$

In Heisenberg picture:

State ket: no change

Observable: Evolution determined by \hat{A}
(operator)

$$\hat{A}_H = e^{i\hat{H}t/\hbar} \hat{A}_S e^{-i\hat{H}t/\hbar}$$

$$\frac{d\hat{A}_H}{dt} = \frac{1}{i\hbar} [\hat{A}_H, \hat{H}]$$

↑

this assumes $\frac{\partial}{\partial t} \hat{A}_S = 0$



In Schrödinger picture:

Observable: no change
(operator)

State ket: Evolution determined
by \hat{H} (see Eq.(*)

Of course: $\langle \hat{A}_H \rangle = \langle \hat{A}_S \rangle$. Can be seen from

$$\langle \hat{A}_H \rangle = \underbrace{\langle \alpha |}_{H} \underbrace{e^{i\hat{H}t/\hbar}}_{\hat{A}_S} \underbrace{e^{-i\hat{H}t/\hbar}}_{\hat{A}_S} \underbrace{|\alpha\rangle_H}_{H}$$

$$= \underbrace{\langle \alpha, t_0; t |}_{H} \underbrace{e^{-i\hat{H}t/\hbar}}_{\hat{A}_S} \underbrace{e^{i\hat{H}t/\hbar}}_{\hat{A}_S} \underbrace{e^{-i\hat{H}t/\hbar}}_{\hat{A}_S} \underbrace{e^{i\hat{H}t/\hbar}}_{\hat{A}_S} \underbrace{|\alpha, t_0; t\rangle}_{H}$$

plugging in $|\alpha\rangle_H$
from above

$$= \langle \alpha, t_0; t | \hat{A}_s | \alpha, t; t \rangle$$

$$= \langle \hat{A}_s \rangle$$

All of this was review, assuming \hat{H} is time-independent.

Now: $\hat{H} = \hat{H}_0 + \underbrace{\hat{V}(t)}_{\text{time-dependent potential}}$

Goal: Want to determine $c_n(t)$:

$$|\alpha, t_0; t\rangle_s = \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$$

the change of the $c_n(t)$ are introduced by t-dep. of $V(t)$

where $|n\rangle$ are now energy eigenkets of \hat{H}_0 with energy eigenvalue E_n

We use $|n\rangle$ as our base kets.

Define:
$$|\alpha, t_0; t\rangle_g = e^{i\hat{H}_0 t/\hbar} |\alpha, t_0; t\rangle_s$$

$$\Rightarrow |\alpha, t_0; t\rangle_g = e^{i\hat{H}_0 t/\hbar} \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$$

↑
replacing $|\alpha, t_0; t\rangle_s$

So : The definition implies $|\alpha, t_0; t\rangle_j = \sum_n c_n(t) |n\rangle$

↑
the subscript j
stands for interaction -
as we will see, this is
kind of a hybrid between
Schrödinger picture and
Heisenberg picture

Also define:

$$\hat{A}_j = e^{i\hat{H}_0 t/t_0} \hat{A}_s e^{-i\hat{H}_0 t/t_0}$$

\hat{H}_0 in exponent -
not \hat{H} !

Specific application of this definition:

$$\hat{V}_j = e^{i\hat{H}_0 t/t_0} \hat{A}_s e^{-i\hat{H}_0 t/t_0}$$

Want to derive Schrödinger-like equation for $|\alpha, t_0; t\rangle_j$:

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_j = i\hbar \frac{\partial}{\partial t} \left(e^{i\hat{H}_0 t/t_0} |\alpha, t_0; t\rangle_s \right)$$

↑
plug in def. of $|\alpha, t_0; t\rangle_j$

$$\begin{aligned} &= -\hat{H}_0 e^{i\hat{H}_0 t/t_0} |\alpha, t_0; t\rangle_s \\ &\quad + i\hbar e^{i\hat{H}_0 t/t_0} \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_s \end{aligned}$$

take time derivative

for second line:

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_s$$

$$= (\hat{H}_0 + \hat{V}) |\alpha, t_0; t\rangle_s$$

$$\begin{aligned}
 & e^{i\hat{H}_0 t/\hbar} \hat{V} |\alpha, t_0; t\rangle_s \\
 & \text{cancelling terms} \\
 & = \underbrace{\left(e^{i\hat{H}_0 t/\hbar} \hat{V} e^{-i\hat{H}_0 t/\hbar} \right)}_{\hat{V}_j} e^{i\hat{H}_0 t/\hbar} |\alpha, t_0; t\rangle_s \\
 & = \hat{V}_j |\alpha, t_0; t\rangle_j
 \end{aligned}$$

insert $e^{-i\hat{H}_0 t/\hbar} e^{i\hat{H}_0 t/\hbar}$

So, we have a Schrödinger-like equation:

$$\text{ith } \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_j = \hat{V}_j |\alpha, t_0; t\rangle_j \quad (**)$$

Similarly, it is easy to show that:

$$\frac{d\hat{A}_j}{dt} = \frac{1}{i\hbar} [\hat{A}_j, \hat{H}_0]$$

assuming \hat{A}_j does not explicitly depend on t

Multiply $(**)$ from left with $\langle n |$:

$$\text{ith } \frac{\partial}{\partial t} \langle n | \alpha, t_0; t\rangle_j = \langle n | \hat{V}_j |\alpha, t_0; t\rangle_j$$

insert complete set / closure:

$$\sum_m |m\rangle \langle m|$$

$$\Rightarrow i\hbar \frac{\partial}{\partial t} \langle n | \hat{V}_g | t_0; t \rangle = \sum_m \langle n | \hat{V}_g | m \rangle \langle m | \hat{d}, t_0; t \rangle$$

Replace $\langle d, t_0; t \rangle$ by $\sum_l c_l(t) |l\rangle$:

$$i\hbar \frac{\partial}{\partial t} c_n(t) = \sum_m \langle n | \hat{V}_g | m \rangle c_m(t)$$

rewrite:

$$\langle n | \hat{V}_g | m \rangle = \langle n | e^{i\hat{H}_0 t/\hbar} V e^{-i\hat{H}_0 t/\hbar} | m \rangle$$

$$\text{recall: } \rightarrow = e^{\frac{i(E_n - E_m)t}{\hbar}} \langle n | \hat{V} | m \rangle$$

$|n\rangle, |m\rangle$

are energy
eigenkets of \hat{H}_0

$$\boxed{W_{nm} = \frac{E_n - E_m}{\hbar}} \rightarrow = e^{iW_{nm}t} \langle n | \hat{V} | m \rangle$$

Coupled set of first-order differential equations:

$$i\hbar \frac{\partial}{\partial t} c_n(t) = \sum_m e^{iW_{nm}t} \underbrace{\langle n | \hat{V} | m \rangle}_{V_{nm}} c_m(t)$$

We now have a set of equations
that determines $c_m(t)$ [equivalent
to time-dep. S.E.]

In matrix form:

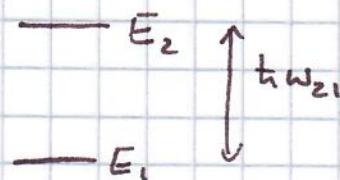
$$i\hbar \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12} e^{i\omega_2 t} & \dots \\ V_{21} e^{i\omega_1 t} & V_{22} & \ddots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

Want to stress: No approximations have been made along the way!

In general, the coupled equations are challenging to solve — possible approximate approach: time-dependent perturbation theory. We will treat that in Chapter 5.7.

Let's look at an example where an exact solution can be found: Two-level system.

$$\hat{H}_0 = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2| \quad \text{with } E_2 > E_1$$



$$\hat{V}(t) = \gamma e^{i\omega t} |1\rangle\langle 2| + \gamma e^{-i\omega t} |2\rangle\langle 1|$$

Assume: γ and ω are real

Physical system: E.g., two atomic levels coupled by electric field

In the $|1\rangle, |2\rangle$ basis:

$$\hat{H} = \begin{pmatrix} E_1 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & E_2 \end{pmatrix}$$

Equivalent of time-dependent SE:

$$i\hbar \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} 0 & \gamma e^{i(\omega + \omega_{12})t} \\ \gamma e^{-i(\omega + \omega_{12})t} & 0 \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$$

Transitions between $|1\rangle$ and $|2\rangle$ are introduced by $\hat{V}(t)$.

If $c_1(0) = 1$ and $c_2(0) = 0$, then one can show:

$$|c_2(t)|^2 = \frac{\gamma^2}{\gamma^2 + \frac{\hbar^2}{4}(\omega - \omega_{21})^2} \sin^2 \left(\sqrt{\gamma^2 + \frac{(\omega - \omega_{21})^2}{4}} \frac{t}{\hbar} \right)$$

define:
 $\Omega = \sqrt{\left(\frac{\gamma}{\hbar}\right)^2 + \left(\frac{\omega - \omega_{21}}{\hbar}\right)^2}$

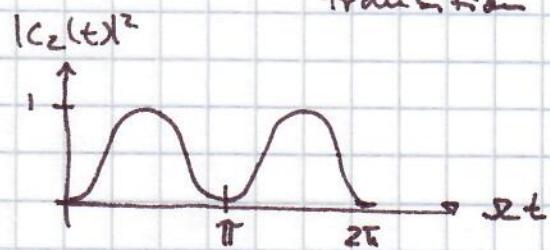
$$\Rightarrow |c_2(t)|^2 = \left(\frac{\gamma}{\hbar\omega}\right)^2 \sin^2(\omega t)$$

Rabi formula

$$|c_2(t)|^2 + |c_1(t)|^2 = 1$$

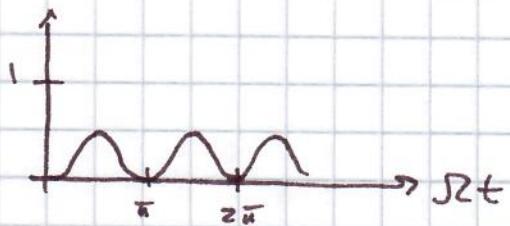
Look at $\frac{\gamma}{\hbar\omega}$: $\frac{\gamma}{\hbar\omega} \rightarrow 1$ for $\omega = \omega_{z1}$

(on resonance:
drive has same
frequency as
transition)



$$\frac{\gamma}{\hbar\omega} \rightarrow 0 \text{ for } |\hbar(\omega - \omega_{z1})| \gg \gamma$$

(off-resonance:
drive and transition
frequency differ)



We can create superposition states by applying
"pulses" on resonance: Pulse turned on for

time $T = \frac{\pi}{2\omega} = \frac{\pi t}{2\gamma}$ leads to full population transfer. Pulse turned on for $T = \frac{\pi t}{4\gamma}$ leads to 50/50 mixture.

5.6 Hamiltonian with extreme time dependence

what does "extreme" mean?

- very slow
 - very fast
 - very slow: we expect the state will be able to follow
 - very fast: we expect that the state will have no time to adjust quickly
- need to specify:
"compared to
what quantity"

Sudden Approximation:

5-46

Let's start with Schrödinger equation for time evolution operator:

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0)$$

$$\hat{U}(t_0 + dt, t_0) = \hat{1} - i \frac{\hat{H}}{\hbar} dt$$

Define $t = sT$:

$$\Rightarrow i\hbar \frac{\partial}{\partial(sT)} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0)$$

$$\Rightarrow i \frac{\partial}{\partial s} \hat{U}(t, t_0) = \frac{\hat{H}}{\hbar \Omega} \hat{U}(t, t_0)$$

$$\underbrace{\Omega}_{\Omega = T^{-1}}$$

$\hbar \Omega$: some energy scale

if $\hbar \Omega \gg$ system energy

energy scale of \hat{H} that is relevant for the physics we are interested in

If $\underbrace{\hbar \Omega}_{T \rightarrow 0 \text{ limit}}$ large, then $\hat{U}(t, t_0) \rightarrow \text{const}$

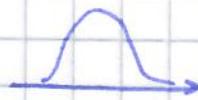
$\tilde{H}(t, t_0) \rightarrow \text{const}$ implies no dynamics

(the system doesn't have time to adjust)

→ See β -decay of tritium atom / nucleus



Some state at
time t_0 (say,
system is in energy
eigen state)



rapid
change
of Ham.

state unchanged
(but this is no
longer an eigenstate;
instead, superposition
of "new" energy
eigen states)

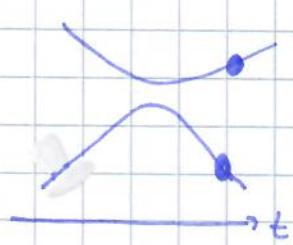
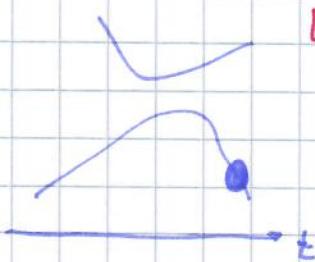
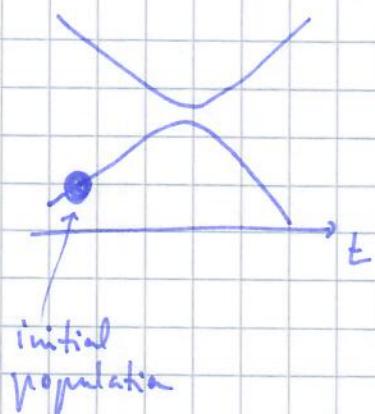
Opposite regime: Adiabatic Approximation

Say, we have a two-level system and the system is in energy eigenket at time t_0 .

Now, at t_0 , the system Hamiltonian is starting to change and the eigen energies are changing slowly. What state will the system be in?



If the Hamiltonian changes slowly enough, we expect to remain in the lower energy level.



Formally:

Let $\hat{f}(t)$ be \hat{f} at time t . At each time t , we can write down the energy eigenkets $|n; t\rangle$ and the associated energy eigenvalues $E_n(t)$:

$$\hat{f}(t) |n; t\rangle = E_n(t) |n; t\rangle$$

For simplicity, we assume that we do not have degeneracies at any time.

Our goal is to solve the time-dependent SE:

$$i\hbar \frac{\partial}{\partial t} |\alpha; t\rangle = \hat{H}(t) |\alpha; t\rangle \quad (*)$$

for notational simplicity,
I dropped the \hbar to ...

We can write:

$$|\alpha; t\rangle = \sum_n c_n(t) e^{i\theta_n(t)} |n; t\rangle \quad (**)$$


$\theta_n(t)$ defined through

$$\theta_n(t) = -\frac{1}{\hbar} \int_0^t E_n(t') dt'$$

(we will see later why this factor is useful - for now, we can think of the inclusion of $\exp(i\theta_n(t))$ simply as a redefinition of the $c_n(t)$)

Plugging $(**)$ into $(*)$, we find:

$$i\hbar \sum_n \left(c_n(t) e^{i\theta_n(t)} |n; t\rangle + \underline{c_n(t)(i) e^{i\theta_n(t)} \frac{\partial \theta_n(t)}{\partial t} |n; t\rangle} \right)$$

$$+ \underline{c_n(t) e^{i\theta_n(t)} \frac{\partial}{\partial t} |n; t\rangle} \right) = \hat{H}(t) \sum_n \underline{c_n(t) e^{i\theta_n(t)}} |n; t\rangle$$

underlined terms cancel

$$\Rightarrow \sum_n e^{i\theta_n(t)} \left[\dot{c}_n(t) |n;t\rangle + c_n(t) \frac{\partial}{\partial t} |n;t\rangle \right] = 0$$

Multiply from left w/ $\langle m;t|$:

$$\dot{c}_m(t) = - \sum_n c_n(t) e^{i[\theta_n(t) - \theta_m(t)]} \underbrace{\langle m;t | \frac{\partial}{\partial t} |n;t\rangle}_{}$$

this arises because the Hamiltonian is time-dependent

Rewrite (treating $m=m$ and $n+m$ "separately"):

$$\dot{c}_m(t) = -c_m(t) \langle m;t | \frac{\partial}{\partial t} |m;t\rangle - \sum_{n \neq m} c_n(t) e^{-i[\theta_n(t) - \theta_m(t)]} x$$

$$\langle m;t | \frac{\partial}{\partial t} |n;t\rangle$$

From $\hat{f}(t) |n;t\rangle = E_n(t) |n;t\rangle$, we get

$$\frac{\partial}{\partial t} (\hat{f}(t) |n;t\rangle) = \frac{\partial}{\partial t} (E_n(t) |n;t\rangle)$$

$$\Rightarrow \langle m;t | \frac{\partial \hat{f}}{\partial t} |n;t\rangle + \langle m;t | \hat{f} \left(\frac{\partial}{\partial t} |n;t\rangle \right)$$

$$= \frac{\partial \bar{E}_n(t)}{\partial t} \underbrace{\langle m;t | n;t\rangle}_{=0} + \bar{E}_n(t) \langle m;t | \frac{\partial}{\partial t} |n;t\rangle$$

for $n \neq m$

$$\Rightarrow \langle m;t | \frac{\partial}{\partial t} |n;t\rangle = \frac{\langle m;t | \frac{\partial \hat{f}}{\partial t} |n;t\rangle}{E_n - E_m}$$

$$\Rightarrow \dot{c}_m(t) = -c_m(t) \langle m; t | \frac{\partial}{\partial t} | m; t \rangle \quad \text{"diagonal term"}$$

$$- \sum_{n \neq m} c_n(t) e^{i[\theta_n(t) - \theta_m(t)]} \frac{\langle m; t | \frac{\partial \hat{H}}{\partial t} | n; t \rangle}{E_n(t) - E_m(t)}$$

mixing in of other states due to time-dependence of $\hat{H}(t)$

We can neglect the second line if

$$\left| \langle m; t | \frac{\partial}{\partial t} | m; t \rangle \right| \gg \left| \frac{\langle m; t | \frac{\partial \hat{H}}{\partial t} | n; t \rangle}{E_n(t) - E_m(t)} \right|$$

$\underbrace{}$ $\underbrace{}$
 $\sim \frac{E_m}{\hbar}$ $\sim \frac{1}{\tau}$

τ : time scale for change of \hat{H}

$$\tau \gg \frac{\hbar}{E_m}$$

In the adiabatic approximation:

$$\dot{c}_m(t) = -c_m(t) \langle m; t | \frac{\partial}{\partial t} | m; t \rangle$$

$$\Rightarrow c_m(t) = e^{-i\delta_m(t)} c_m(0), \text{ where}$$

$$\delta_m(t) = i \int_0^t \langle m; t' | \frac{\partial}{\partial t} | m; t' \rangle dt'; \delta_m \text{ real}$$

So: $|c_m(t)|^2 = |c_m(0)|^2$. But, there is phase dynamics.

From a "population perspective", this is exactly what we expect: no change in the adiabatic approximation.

Non-trivial: There is phase dynamics and the phase dynamics can, maybe somewhat surprisingly (?), be measured.

Applications: Berry's phase (general)

Berry's phase for spin- $\frac{1}{2}$

Aharanov - Bohm and magnetic monopoles

5.7 Time-dependent perturbation theory

Recall :

$$|\alpha, t_0=0; t\rangle = \sum_n c_n(t) e^{-iE_n t} |n\rangle$$

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \quad \text{and} \quad \hat{H}_0 |n\rangle = E_n |n\rangle$$

$i\hbar \frac{\partial}{\partial t} |\alpha, t_0=0; t\rangle = \hat{V} |\alpha, t_0=0; t\rangle$ is equivalent to

$$i\hbar \begin{pmatrix} \dot{c}_1(t) \\ \dot{c}_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12} & \dots \\ V_{21} e^{i\omega_2 t} & V_{22} & \ddots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{pmatrix}. \quad (*)$$

Perturbation theory treatment:

$$c_n(t) = c_n^{(0)} + c_n^{(1)} + c_n^{(2)} + \dots$$

Let $c_n^{(0)} = \delta_{ni}$ where $i \equiv$ initial state, i.e., at time $t_0=0$, we assume that a single state is occupied.

Plugging the above expansion into $(*)$, we can derive expressions for $c_n^{(0)}, c_n^{(1)}, \dots$

[This is a good exercise to go through at home!] We will pursue operator approach instead.

Pyson Series

$$\text{Starting point: } |\alpha, t_0; t\rangle_j = \hat{U}_j(t, t_0) |\alpha, t_0; t_0\rangle_j$$

$$\text{We read off } \hat{U}_j(t_0; t_0) = \hat{1}$$

}

time evolution operator
in interaction picture

We had already derived:

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_j = \hat{V}_j |\alpha, t_0; t\rangle$$

where $\hat{V}_j(t) = e^{i\hat{H}_0 t/\hbar} \hat{V}(t) e^{-i\hat{H}_0 t/\hbar}$

It follows:

$$\hat{U}_j(t, t_0) = \hat{1} - \frac{i}{\hbar} \int_{t_0}^t \hat{V}_j(t') \hat{U}_j(t', t_0) dt'$$

Let us iterate this:

$$\hat{U}_j(t, t_0) = \hat{1} - \frac{i}{\hbar} \int_{t_0}^t \hat{V}_j(t') \left[\hat{1} - \frac{i}{\hbar} \int_{t_0}^{t'} \hat{V}_{j''}(t'') \hat{U}_j(t'', t_0) dt'' \right] dt'$$

do the same thing
and have integral
over t'''

+ then do the same
thing again and
again

$$\hat{U}_g(t, t_0) = \hat{1}$$

$$+ \left(-\frac{i}{\hbar}\right) \int_{t_0}^t \hat{V}_g(t') dt'$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t \hat{V}_g(t') \left(\int_{t_0}^{t'} \hat{V}_g(t'') dt'' \right) dt'$$

$$+ \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^t \hat{V}_g(t') \left(\int_{t_0}^{t'} \hat{V}_g(t'') \left(\int_{t_0}^{t''} \hat{V}_g(t''') dt''' \right) dt'' \right) dt''$$

fct. of t''
fct. of t'

+ ...

This is the Dyson series.

So: in principle, we can calculate $\hat{U}_g(t, t_0)$ using the Dyson series. We want to relate this to the expansion we looked at earlier, namely

$$|i, t_0; t\rangle = \sum_n c_n(t) |n\rangle$$

~~~~~

$|c_n(t)|^2$  gives us the

probability to make a

transition to state  $n$ , provided

our initial state is  $i$

From earlier:

$$|\alpha, t_0; t\rangle_j = \hat{U}_j(t, t_0) |\alpha, t_0; t_0\rangle_j$$

Compare (i.e., set the two r.h.s.'s equal to each other):

$$\sum_n c_n(t) |n\rangle = \hat{U}_j(t, t_0) |\alpha, t_0; t_0\rangle_j$$

Come in from left with  $|m\rangle$  and let  $|\alpha, t_0; t_0\rangle_j$  be given by  $|i\rangle$  (this stands for one of the energy eigen kets of  $\hat{t}_0$ ):

$|i\rangle$ : initial state

$$c_m(t) = \langle m | \hat{U}_j(t, t_0) | i \rangle$$

we have an expression for this (the Dyson series)

Write this as  
 $c_m^{(0)} + c_m^{(1)} + c_m^{(2)}$

$0^{\text{th}}$ -order  
in  $\hat{V}_j$

$1^{\text{st}}$ -order  
in  $\hat{V}_j$

$2^{\text{nd}}$ -order  
in  $\hat{V}_j$

Plug the Dyson series in and compare order by order:

$$c_m^{(0)}(t) = \langle m | \hat{1} | i \rangle = \delta_{mi} \quad (\text{time-independent})$$

$$c_m^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t \langle m | \hat{V}_g(t') | i \rangle dt'$$

$$= -\frac{i}{\hbar} \int_{t_0}^t e^{i\omega_m t} \langle m | \hat{V}(t') | i \rangle dt'$$

$$c_m^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^t \langle m | \hat{V}_g(t') \int_{t_0}^{t'} \hat{V}_g(t'') dt'' | i \rangle dt'$$

insert  $\sum_n |n\rangle \langle n|$

$$= \left(-\frac{i}{\hbar}\right)^2 \sum_n \int_{t_0}^t \langle m | \hat{V}(t') | n \rangle e^{i\omega_m t'} \left( \int_{t_0}^{t'} \langle n | \hat{V}(t'') | i \rangle \times \right.$$

$$\left. e^{-i\omega_n t''} dt'' \right) dt'$$

Transition probability to go from  $|i\rangle$  to  $|m\rangle$  with  $m \neq i$  is given by

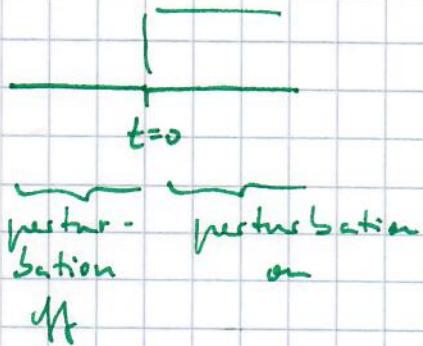
$$P(i \rightarrow m) = |c_m^{(1)}(t) + c_m^{(2)}(t) + \dots|^2$$

note:

$c_m^{(0)} = 0$  since  
the system  
starts in state  $|i\rangle$   
(by assumption)

Example 1:

$$\hat{V}(t) = \begin{cases} 0 & \text{for } t < 0 \\ V_0 \hat{x} & \text{for } t \geq 0 \end{cases}$$



$$c_n^{(0)}(t) = c_n^{(0)}(0) = \delta_{ni}$$

$$c_n^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \langle n | \hat{V}(t') | i \rangle e^{i\omega_n t'} dt'$$

$$= -\frac{i}{\hbar} \langle n | V_0 \hat{x} | i \rangle \int_0^t e^{i\omega_n t'} dt'$$

—————

$$-\frac{1 - e^{i\omega_n t}}{i\omega_n}$$

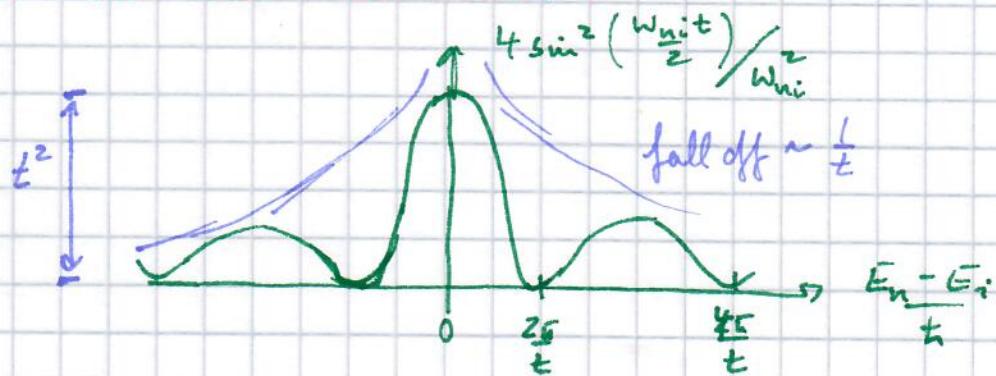
$$= \frac{\langle n | V_0 \hat{x} | i \rangle}{E_n - E_i} (1 - e^{i\omega_n t})$$

—————

independent  
of time

$$|c_n^{(1)}(t)|^2 = \frac{4 k_n |V_0 \hat{x}|^2}{|E_n - E_i|^2} \sin^2 \left( \frac{(E_n - E_i)t}{2\hbar} \right)$$

How does this look like?



roughly, the  $\sin^2(\theta)/\omega^2$   
gives something as long  
as  $\omega t \approx 2\pi$

(this is really just characterizing  
how wide the figure is)

$T$   
we are thinking  
about this  
energy difference  
as a continuous  
variable

Let  $t$  (time the perturbation has been on) be  
small  $\rightarrow$  peak is broad (fair amount  
of energy non-conservation  
 $\Delta E \text{ at } t \approx h$ )

Let  $t$  be large  $\rightarrow$  peak is narrow (approximate energy conservation is required)

For  $E_n$  very close to  $E_i$ , we find  $4\sin^2(\theta)/\omega_n^2$   
is equal to  $t^2 \Rightarrow$  the larger  $t$ , the  
larger the probability to make a transition.  
 $\Rightarrow$  quadratic rather than linear ...

Let's say we have a whole bunch of states w/ energy around  $E_i$ :

Calculate

$$\sum_{n, E_n \approx E_i} |c_n^{(1)}(t)|^2$$

$$\sum_{n, E_n \approx E_i} |c_n^{(1)}(t)|^2 \rightarrow \int |c_n^{(1)}(t)|^2 \rho(E_n) dE_n$$

number of states  
within energy  
interval  $(E_i, E_i + dE)$

$$= 4 \int \sin^2\left(\frac{(E_n - E_i)t}{2\hbar}\right) \frac{|V_{ni}|^2}{|E_n - E_i|^2} \rho(E_n) dE_n$$

$$\lim_{t \rightarrow \infty} \frac{1}{|E_n - E_i|^2} \sin^2\left(\frac{(E_n - E_i)t}{2\hbar}\right)$$

$$= \frac{\pi t}{2\hbar} \delta(E_n - E_i)$$

$$\rightarrow \frac{2\pi}{\hbar} \overline{|V_{ni}|^2} \rho(E_n) t \Big|_{E_n \approx E_i}$$

$$\text{Define: } \omega_i \rightarrow [n] = \frac{d}{dt} \left( \sum_n |c_n^{(1)}(t)|^2 \right)$$

transition  
rate

↑  
group of  
states

$$\begin{aligned} \text{"overbar" means } \overline{\dots} &= \frac{2\pi}{\hbar} \overline{|V_{ni}|^2} \rho(E_n) \Big|_{E_n = E_i} \\ &= \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i) \end{aligned} \quad \left. \right\} \text{Fermi's Golden Rule}$$

Going to second-order:

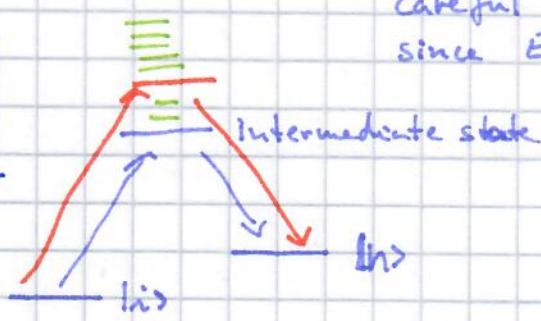
$$W_i \rightarrow [n] = \frac{2\pi}{h} \left| V_{ni} + \sum_m \frac{V_{nm} V_{mi}}{E_i - E_m} \right|^2 g(E_n) \Big|_{E_n \approx E_i}$$

used in Ch. 5.9

"direct transition"

"virtual"

intermediate states  
(virtual transitions that  
are not  
energy con-  
serving)



note: need to be very  
careful with this  
since  $E_m \approx E_i$ :