Chap. 17

Bound state Perturbation Theory;

17-1- The Perturbation method;

The Rayleigh and Schrödinger Perturbation theory aplies to the discrete energy levels of a physical system whose Hamiltonian OP. H, can be broken up into two hermitian parts:

$$H = H_0 + gV$$

H_0: unperturbed part.

gV: Perturbed "

g: real parameter (strength of perturbation)

$g = 0$ to 1

Simple perturbation Theory: applies when these eigenvalues and eigenfunctions. can be expanded in Powers of g, in the hope that for practical calculations only the first few terms need be considered

I) Non-degenerate Case

We wish to solve;

$$H|n\rangle = E_n|n\rangle$$

we suppose that <u>unperturbed</u> eigenvalue problem

$$H_0|n^0\rangle = E_n^0|n^0\rangle$$

has already been solved.

Under perturbation;

$$E_n^0 \xrightarrow{g} E_n^0 + \Delta E_n$$

$$|n^0\rangle \longrightarrow |n^0\rangle + |\Delta n\rangle$$

$$(H_0 + gV)(|n^0\rangle + |\Delta n\rangle) = (E_n^0 + \Delta E_n)(|n^0\rangle + |\Delta n\rangle)$$

$$H_0|n^0\rangle + H_0|\Delta n\rangle + gV|n^0\rangle + \underbrace{gV|\Delta n^0\rangle}_{\sim 0} =$$

$$E_n^0|n^0\rangle + E_n^0|\Delta n\rangle + \Delta E_n|n^0\rangle + \underbrace{\Delta E_n|\Delta n\rangle}_{\sim 0}$$

$$(H_0 - E_n^0)|\Delta n\rangle = (\Delta E_n - gV)|n^0\rangle$$

The projection of this eqn on the direction $|n^0\rangle$;

$$\langle n^0|(H^0 - E_n^0)|\Delta n\rangle = \langle n^0|(\Delta E_n - gV)|n^0\rangle$$

Using the property: $(H_0|n^0\rangle)^* = \langle n^0|H_0^+ = \langle n^0|H_0$

$$(E_n - E_n)\langle n^\circ|\Delta n\rangle = \Delta E_n \langle n^\circ|n^\circ\rangle - \langle n^\circ|gV|n^\circ\rangle$$

$$0 = \Delta E_n - \langle n^\circ|gV|n^\circ\rangle$$

$$\Delta E_n = \langle n^\circ|gV|n^\circ\rangle$$

The state $(\Delta E_n - gV)|n^\circ\rangle$ has no component along $|n^\circ\rangle$ because $\langle n^\circ|(\Delta E_n - gV)|n^\circ\rangle = 0$. Then $\frac{1}{H_0 - E_n^\circ}$ can act on this state

Now consider;

$$(H_0 - E_n^\circ)|\Delta n\rangle = (\Delta E_n - gV)|n^\circ\rangle$$

the sol.;

$$|\Delta n\rangle = C_n^\circ|n^\circ\rangle + \frac{1}{H_0 - E_n^\circ}(\Delta E_n - gV)|n^\circ\rangle$$

where $C_n^\circ|n^\circ\rangle$ is the sol. of homogenious eqn;

$$(H_0 - E_n^\circ)|n^\circ\rangle = 0$$

Since $|n\rangle = |n^\circ\rangle + |\Delta n\rangle$

$$\Rightarrow \quad |n\rangle = (1 + C_n^\circ)|n^\circ\rangle + \frac{1}{H_0 - E_n^\circ}(\Delta E_n - gV)|n^\circ\rangle$$

The last term must be computed. { as $V \to 0$, $\Delta E_n \to 0$

Systematic treatment;

$$H|n\rangle = E_n|n\rangle$$

$$H = H_0 + gV$$

Assumption; $H_0|n^\circ\rangle = E_n^\circ|n^\circ\rangle$ are already known.

But let us first consider;

17-2 Inhomogeneous Linear Eqns.

Consider: $Au = v$ inhomogeneous eqn.

A: hermitian op with complete set of eigenvectors

v: a known vector

u: unknown vector

A: Square matrix or differential op. or ...

→ u, v: one column vectors or ordinary fncs

There are two situations:

Remark:
$Au' = \lambda u'$
$\rightarrow (\underbrace{A - \lambda}_{A}) u' = 0$
$Au' = 0$

i) (if) $Au' = 0$ has non-trivial sols.

→ A has zero-eigenvalue ($Au' = a'u'$, $u' \neq 0$, $a' = 0$)

ii) (if) There is no nontrivial sols. for $Au' = 0$

→ $\det A \neq 0$

in this case → A has a unique inverse A^{-1}

→ $u = A^{-1} v$

For any given v this sol. is unique.

Remark:
$a_{11}x_1 + \cdots + a_{1n}x_n = 0$
$a_{21}x_1 + \cdots + a_{2n}x_n = 0$
$\vdots$
$a_{n1}x_1 + \cdots + a_{nn}x_n = 0$
The system has always trivial sol. $x_1 = x_2 = \cdots = x_n = 0$
$\begin{pmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & & \\ a_{n1} & \cdots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix} = 0$
For nontrivial sol.
$\det A = 0$

In Case (i) on the other hand $Au = v$ may have infinitely many sols.

for if f is a particular sol.

$$Af = v$$

Then any vector $u = u' + f$ $\quad (u' \neq 0)$

will automatically also be a sol.

u' the sols. of $Au' = 0$

$u = \quad \cdot \quad = Au = v$

In this case the existance of a sol. depends on a further necessary (and sufficient) cond.: (we are interested in Case i)

v must have no component in the subspace spanned by the eigenvectors u' of A which corresponds to zero eigenvalue. { Remark: If $u' = 0$ (Case ii), no Problem arise.

$u' = \{u_1', u_2' - - - u_n'\}$ subspace (eigenvectors of A)

$u' \cap v = 0$

Proof. - Let P_0 be the projection Op. which projects every vector into subspace spanned by eigenvectors u' of A.

Since $A u' = 0$ and $A = \sum_i A_i |u_i><u_i|$ A: Hermitian

then $P_0 A = P_0 \sum_i P_i A_i = 0$, Since $A_i = 0 \ \forall i$

$\rightarrow P_0 V = P_0 A u = 0$

Proves $\longrightarrow$ V is orthogonal to the space of the sols. of u' ($V \perp u'$)

We will use the cond. $P_0 V = 0$

Instead of guessing a particular sol. f, it is possible to construct one by the following procedure.

$$\begin{cases} Af = v \\ P_0 V = 0 \end{cases} \longrightarrow Af = (1 - P_0) V$$

Yet although A which has zero-eigenvalues, has no-inverse, there exist an op. K such that;

$$AK = 1 - P_0 \qquad \left(A = \sum_i A_i |i><i| \quad K = \sum_j K_j |j><j| \right.$$

we may chose j's in such a way $AK = 1 - P_0$ satisfies

There are infinitely many operators K, which satisfy this eqn.

The reason;

If K satisfy this equ., $K + P_0 B$ (B: arbitrary OP) also satisfies the equ.

$$A(K + P_0 B) = AK + 0 = 1 - P_0$$

We remove this ambiguity and select a unique sol. by imposing the cond.

$$P_0 K = 0$$

$$\begin{cases} AK = 1 - P_0 \\ P_0 K = 0 \end{cases} \longrightarrow K \equiv \frac{1 - P_0}{A} + C \quad \left(\text{a check: } P_0 K = \frac{P_0 - P_0^2}{A} = 0 \right)$$

$C = 0$ due to $P_0 K = 0$

This expression is not intended to imply $\longrightarrow$ A has an inverse. It is not permissible to apply the destributive law to it and write it as $A^{-1} - A^{-1} P_0$ or the like.

Now;

$$\begin{cases} Af = (1 - P_0) V \\ AK = 1 - P_0 \end{cases} \longrightarrow Af = AKV$$

$$\longrightarrow f = KV = \frac{1 - P_0}{A} V$$

This is a particular sol. of,

$$Af = V$$

Because of $P_0 k = 0$:

this particular sol. is <u>orthogonal</u> to the subspace $\mathcal{U}'$, i.e.

$$P_0 f = 0 \qquad \left(P_0 \frac{1-P_0}{A} V = 0 \right)$$

$\xrightarrow{\text{therefore}}$ If $Au' = 0$ possesses nontrivial sols., then $Au = V$ has the general sol.

$$u = u' + \frac{1-P_0}{A} V$$

Provided $P_0 V = 0$

Remark: Despite $P_0 V = 0$, we do not exclude it, because without this the op. $\frac{1}{A}$ is ill-defined (i.e. in some cases $\frac{1}{A} \to \frac{1}{0}$) (see also P214)

Fundamental idea:

$$E_n = E_n^0 + g E_n^1 + g^2 E_n^2 + \dots$$

$$|n\rangle = |n^0\rangle + g|n^1\rangle + g^2|n^2\rangle + \dots$$

substituting:

$$(H_0 + gV)(|n^0\rangle + g|n^1\rangle + g^2|n^2\rangle + \dots) =$$

$$= (E_n^0 + g E_n^1 + g^2 E_n^2 + \dots)(|n^0\rangle + g|n^1\rangle + g^2|n^2\rangle + \dots)$$

coeff.:

g^0: $H_0|n^0\rangle = E_n^0|n^0\rangle$

g^1: $H_0|n^1\rangle + V|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle$

g^2: $H_0|n^2\rangle + V|n^1\rangle = E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle$

⋮ - - -

The first equ. is known, and gives no information.

The second equ:

$$(H_0 - E_n^0)|n^1\rangle = (E_n^1 - V)|n^0\rangle$$ inhomogenious equ.

$|n^1\rangle$ and E_n^1 are unknowns.

Remark $\begin{cases} Au = v \\ Au = 0 \text{ homogenous} \end{cases}$

17-3 Sol. of the Perturbation Equations:

$$(H_0 - E_n^0)|n'\rangle = (E_n' - V)|n^0\rangle$$

The projection in the direction $|m^0\rangle$: $P_m^{(0)} = |m_0\rangle\langle m_0|$ hermitian

$$\langle m^0|(H_0 - E_n^0)|n'\rangle = \langle m_0|(E_n' - V)|n^0\rangle$$

$$(E_n^0 - E_n^0)\langle m^0|n'\rangle = E_n'\langle m^0|n^0\rangle - \langle n^0|V|n^0\rangle$$

i) if $m = n$

$$0 = E_n' - \langle n^0|V|n^0\rangle$$

$$E_n' = \langle n^0|V|n^0\rangle$$

Hence the first order correction of energy is:

$$E_n = E_n^0 + \langle n^0|gV|n^0\rangle$$

Substituting:

$$(H_0 - E_n^0)|n'\rangle = [\underbrace{\langle n^0|gV|n^0\rangle}_{(E_n')} I - V]\,|n^0\rangle$$

This eqn. must be solved.

ii) if $m \neq n$

$$(E_m^0 - E_n^0)\langle m^0|n'\rangle = 0 - \langle m^0|V|n^0\rangle$$

$$\langle m^0|n'\rangle = \frac{\langle m^0|V|n^0\rangle}{E_n^0 - E_n^0}$$

This is the Sol. for the following reason:

Now compare:

$$\begin{cases} (H_0 - E_n^0)\,|n'\rangle = (E_n' - V)\,|n^0\rangle \\ A\,u = v \end{cases}$$

$$\rightarrow \begin{cases} A = (H_0 - E_n^0) \\ u = |n'\rangle \\ v = (E_n' - V)\,|n^0\rangle \end{cases}$$

$$\text{Also} \begin{cases} Au' = 0 \\ (H_0 - E_n^0)\,|n^0\rangle = 0 \end{cases} \longrightarrow u' = |n^0\rangle$$

$$\text{The sol.} \longrightarrow u = u' + \frac{1 - P_0}{A} v$$

$$|n'\rangle = C_n'\,|n^0\rangle + \frac{1 - P_n^0}{H_0 - E_n^0}\,(E_n' - V)\,|n^0\rangle$$

But Since $P_0 k = 0$, hence by definition:

$$K\,|n^0\rangle \equiv \frac{1 - P_n^0}{H_0 - E_n^0}\,|n^0\rangle = 0$$

$$\rightarrow |n'\rangle = C_n'\,|n^0\rangle + \frac{1 - P_n^0}{E_n^0 - H_0}\,V\,|n^0\rangle \quad (1)$$

The choice of arbitrary consts. C_n' and the others can have no physical consequence.

Remark:
Note that:
$H_0\,|n^0\rangle = E_n^0\,|n^0\rangle$
$(H_0 - E_n^0)\,|n^0\rangle = 0$
$= 0\,|n^0\rangle$
Since $P_n^0 = |n^0\rangle\langle n^0|$
and $|n^0\rangle \in \{u'\}$
eigenvectors of
$A = H_0 - E_n^0$
P^0 projects any vector onto this subspace
$P_n^0\,|n_0\rangle = |n_0\rangle\langle n_0|n_0\rangle$
$= |n_0\rangle$

Sometimes one may choose the consts. such that at the K^{th} stage of approx. the vector,

$$|n\rangle = |n^0\rangle + g|n^1\rangle + \cdots + g^K |n^K\rangle + O(g^{K+1})$$

is normalized to unity in the sense that:

$$\langle n|n\rangle = 1 + O(g^{K+1})$$

The cond. reduces but does not entirely remove the arbitrariness of the consts..

For instance, if we require for $K=1$ that

$$\langle n|n\rangle = 1 + O(g^2) \qquad (2)$$

where $|n\rangle = |n^0\rangle + g|n^1\rangle$

it follows that c_n^1 must be purely imaginary but otherwise it is still undetermined.

(substituting (1) in (21).

However it can be shown the remaining arbitrariness corresponds merely to the option we have of multiplying $|n\rangle$ by a phase factor without destroying the normalization ($e^{i\delta}$).

The phase factor may be a fnc. of g.

$|n'\rangle$ can be broken into the terms

$$|n'\rangle = |n'_{\parallel}\rangle + |n'_{\perp}\rangle$$

where: $|n'_{\parallel}\rangle \parallel |n^0\rangle$ and $|n'_{\perp}\rangle \perp |n^0\rangle$

For the first correction:

$$|n\rangle = |n^0\rangle + g|n^1\rangle = |n^0\rangle + g|n'_{\parallel}\rangle + g|n'_{\perp}\rangle$$

If we require, $\langle n|n\rangle = 1 + O(g^2)$

$$\longrightarrow \langle n|n\rangle = \langle n^0|n^0\rangle + g\langle n^0|n'_{\parallel}\rangle + g\langle n^0|n'_{\perp}\rangle +$$
$$+ g\langle n'_{\parallel}|n_0\rangle + g^2\langle n'_{\parallel}|n'_{\parallel}\rangle + g^2\langle n'_{\parallel}|n'_{\perp}\rangle +$$
$$+ g\langle n'_{\perp}|n_0\rangle + g^2\langle n_{\perp}|n_{\parallel}\rangle + g^2\langle n_{\perp}|n_{\perp}\rangle$$

$$\langle n|n\rangle = 1 + g\langle n^0|n'_{\parallel}\rangle + g\langle n'_{\parallel}|n_0\rangle + O(g^2)$$

$$\longrightarrow 1 = 1 + g\langle n^0|n'_{\parallel}\rangle + g\langle n'_{\parallel}|n_0\rangle$$

$$\hookrightarrow \langle n^0|n'_{\parallel}\rangle = -\langle n'_{\parallel}|n_0\rangle$$

$$\langle n^0|n'_{\parallel}\rangle = -\langle n_0|n'_{\parallel}\rangle^*$$

If $a = -a^* \longrightarrow a = i\alpha$

$$\longrightarrow \langle n_0|n'_{\parallel}\rangle = i\alpha$$

Remark:
$\langle n_0|n'_{\parallel}\rangle = \langle n_0|n'\rangle = i\alpha = C'_n$
See equation (P2091) and (P2164)

Now;

$$\langle n^0|n\rangle = \langle n^0|n^0\rangle + g\langle n^0|n'_{\parallel}\rangle + g\langle n^0|n'_{\perp}\rangle$$

$$\langle n^0|n\rangle = 1 + igq \simeq e^{igq} \quad \text{for small } g$$

Also. Since, $\{|n^0\rangle\}$ is a complete set with the Hamiltonian op. H, we can expad $|n'\rangle$ in terms of $|n^0\rangle$;

$$|n'\rangle = \sum_m \langle m^0|n'\rangle |m^0\rangle$$

For the component $|n'_\perp\rangle$;

$$|n'_\perp\rangle = \sum_{m\neq n} \langle m^0|n'\rangle |m^0\rangle$$

$$\rightarrow |n'_\perp\rangle = \sum_{m\neq n} \frac{\langle m^0|V|n^0\rangle}{E^0_n - E^0_m} |m^0\rangle$$

$$\rightarrow \langle n'_\perp| = \sum_{m\neq n} \frac{\langle n^0|V|m^0\rangle}{E^0_n - E^0_m} \langle m^0|$$

A check:

$$\langle n'_\perp|n^0\rangle = \sum_{m\neq n} \langle m_0|n^0\rangle \frac{\langle n^0|V|m^0\rangle}{E^0_n - E^0_m} = \sum_{m\neq n} \delta_{nm} \frac{\langle n^0|V|m^0\rangle}{E^0_n - E^0_m}$$

Since $\langle n_\perp'|n^0\rangle = 0$ and $\delta_{nm} = 0$

$$\rightarrow E^0_n - E^0_m \neq 0 \quad \text{(no degeneracy)}$$

Now;

$$|n\rangle = \underbrace{|n^0\rangle + g|n'_{\parallel}\rangle} + g|n'_{\perp}\rangle$$

$$|n\rangle = C_{\parallel}|n^0\rangle + g|n'_{\perp}\rangle$$

Since $C_i = \int \psi_i^* \psi \, d\tau \rightarrow C_{\parallel} = \langle n^0|n\rangle$

$$|n\rangle = \langle n^0|n\rangle |n^0\rangle + g|n'_{\perp}\rangle$$

$$|n\rangle = e^{i\alpha g}|n^0\rangle + g|n'_{\perp}\rangle$$

$$|n\rangle = e^{i\alpha g}|n^0\rangle + g\sum_{m\neq n} \frac{\langle m^0|V|n^0\rangle}{E_n^0 - E_m^0}|m^0\rangle$$

$$|n\rangle = |n^0\rangle + g\sum_{m\neq n} \frac{\langle m^0|V|n^0\rangle}{E_n^0 - E_m^0}|m^0\rangle$$

(New $|n^0\rangle$)

Equivalently, we could to set all arbitrary const. C_n^k equal to zero, and if desired to normalize th approximate eigenvectors at the end of the calculation.

with $C_n^1 = 0$ (i.e. $P_n^\circ |n'\rangle = 0$) in

$$|n'\rangle = C_n^1 |n^\circ\rangle + \frac{1 - P_n^\circ}{E_n^\circ - H_\circ} V |n^\circ\rangle$$

we have; $(|n'\rangle \longrightarrow |n'_\perp\rangle)$

$$|n'\rangle = \frac{1 - P_n^\circ}{E_n^\circ - H_\circ} V |n^\circ\rangle$$

or since $I = \sum_k P_k^\circ = \sum_k |k^\circ\rangle\langle k^\circ|$

$$|n'\rangle = \frac{\sum_k P_k^\circ - P_n^\circ}{E_n - H_\circ} V |n^\circ\rangle = \frac{\sum_{k \neq n} P_k^\circ}{E_n^\circ - H_\circ} V |n^\circ\rangle$$

$$|n'\rangle = \sum_{k \neq n} \frac{1}{E_n^\circ - H_\circ} \langle k^\circ | V | n^\circ \rangle |k^\circ\rangle$$

$$= \sum_{k \neq n} \frac{\langle k^\circ | V | n^\circ \rangle}{E_n^\circ - E_k^\circ} |k^\circ\rangle$$

Consideration of second order:

$$(H_0 - E_n^0)\,|n^2\rangle = E_n^2|n^0\rangle + (E_n^1 - V)\,|n^1\rangle \qquad (Au = V)$$

We have before calculated E_n^1 and $|n^1\rangle$.

Then we have two unknowns E_n^2 and $|n^2\rangle$

Projection in direction $|m^0\rangle$; (i.e. $P_n^0 V = P_n^0 Au = 0$)

$$\langle m^0|(H_0 - E_n^0)\,|n^2\rangle = E_n^2\langle m^0|n^0\rangle + \langle m^0|(E_n^1 - V)\,|n^1\rangle$$

$$(E_m^0 - E_n^0)\langle m^0|n^2\rangle = E_n^2\,\delta_{mn} + E_n^1\langle m^0|n^1\rangle - \langle m^0|V|n^1\rangle$$

i) $m = n$

$$0 = E_n^2 + E_n^1\langle n^0|n^1\rangle - \langle n^0|V|n^1\rangle$$

↓ See (P 214)

$$E_n^2 = \langle n^0|V|n^1\rangle$$

But we obtained: $|n^1\rangle = \sum_{m\neq n} |m^0\rangle \dfrac{\langle m^0|V|n^0\rangle}{E_n^0 - E_m^0}$

$$E_n^2 = \sum_{m\neq n} \langle n^0|V|m^0\rangle \dfrac{\langle m^0|V|n^0\rangle}{E_n^0 - E_m^0}$$

$$E_n^2 = \sum_{m\neq n} \dfrac{|\langle n^0|V|m^0\rangle|^2}{E_n^0 - E_m^0}$$

For Rayleigh-Schrödinger perturbation expansion converge rapidly, it is necessary the quantities $\left|\dfrac{\langle m^0|V|n^0\rangle}{E_n^0 - E_m^0}\right|$ be small

$$E_n \simeq E_n^0 + gE_n^1 + g^2 E_n^2 + \cdots$$

$$E_n \simeq E_n^0 + \langle n^0|gV|n^0\rangle + \sum_{m\neq n} \frac{|\langle n^0|gV|m^0\rangle|^2}{E_n^0 - E_m^0}$$

Here nondegeneracy is main assumption.

ii) $m \neq n$

$$(E_m^0 - E_n^0)\langle m^0|n^2\rangle = E_n^1\langle m^0|n^1\rangle - \langle m^0|V|n^1\rangle$$

$$\langle m^0|n^2\rangle = \frac{E_n^1}{E_m^0 - E_n^0}\langle m^0|n^1\rangle - \frac{\langle m^0|V|n^1\rangle}{E_m^0 - E_n^0}$$

The sol. of

$$(H_0 - E_n^0)|n^2\rangle = E_n^2|n^0\rangle + (E_n^1 - V)|n^1\rangle$$

is;

$$|n^2\rangle = C_n^2|n^0\rangle - \frac{1-P_n^0}{E_n^0 - H_0}(E_n^1 - V)|n^1\rangle$$

where $K \equiv \dfrac{1-P_n^0}{E_n^0 - H_0}$

Again we may set $C_n^2 = 0$ (i.e. $P_n^0|n^2\rangle = 0$)

and substituting $|n^1\rangle$;

$$|n^2\rangle = -\frac{1-P_n^0}{E_n^0 - H_0}(E_n^1 - V)\frac{1-P_n^0}{E_n^0 - H_0}V|n^0\rangle$$

$$|n^2\rangle = -\frac{1-P_n^0}{E_n^0-H_0} E_n' \frac{1-P_n^0}{E_n^0-H_0} V|n^0\rangle + \frac{1-P_n^0}{E_n^0-H_0} V \frac{1-P_n^0}{E_n^0-H_0} V|n^0\rangle$$

$$|n^2\rangle = -\frac{\sum_{k\neq n} P_k^0}{E_n^0-H_0} E_n' \frac{\sum_{m\neq n} P_m^0}{E_n^0-H_0} V|n^0\rangle + \frac{\sum_{k\neq n} P_k^0}{E_n^0-H_0} V \frac{\sum_{m\neq n} P_m^0}{E_n^0-H_0} V|n^0\rangle$$

But: $\sum_{k\neq n} P_k^0 = \sum_{k\neq n} |k^0\rangle\langle k^0|$

and $E_n' = \langle n^0|V|n^0\rangle$

$$|n^2\rangle = -\sum_{k\neq n}\sum_{m\neq n} \frac{|k^0\rangle\langle k^0|n^0\rangle\langle n^0|V|n^0\rangle}{(E_n^0-E_k^0)(E_n^0-E_m^0)} \langle n^0|V|n^0\rangle +$$

$$+ \sum_{k\neq n}\sum_{m\neq n} \frac{|k^0\rangle\langle k^0|V|m^0\rangle\langle m^0|V|n^0\rangle}{(E_n^0-E_k^0)(E_n^0-E_m^0)}$$

$$|n^2\rangle = -\sum_{k\neq n} \frac{\langle k^0|V|n^0\rangle\langle n^0|V|n^0\rangle}{(E_n^0-E_k^0)^2}|k^0\rangle +$$

$$+ \sum_{k\neq n}\sum_{m\neq n} \frac{\langle k^0|V|m^0\rangle\langle m^0|V|n^0\rangle}{(E_n^0-E_k^0)(E_n^0-E_m^0)}|k^0\rangle$$

$$E_n = E_n^0 + gE_n' + g^2E_n^2 + \ldots$$

$$|n\rangle = |n^0\rangle + g|n'\rangle + g^2|n^2\rangle + \ldots$$

$$|n^2\rangle = \sum_m \langle n^0|n^2\rangle |n^0\rangle$$

$|n^2\rangle$ can be broken into $|n^2_{\parallel}\rangle$ and $|n^2_{\perp}\rangle$

$$|n^2\rangle = |n^2_{\parallel}\rangle + |n^2_{\perp}\rangle$$

where $|n^2_{\parallel}\rangle \parallel |n^0\rangle$

and $|n^2_{\perp}\rangle \perp |n^0\rangle$

$$|n^2_{\perp}\rangle = \sum_{m\neq n} |m^0\rangle \frac{E^1_n}{E^0_n - E^0_n} \langle m^0|n^1\rangle - \sum_{m\neq n} |m^0\rangle \frac{\langle n^0|V|n^1\rangle}{E^0_m - E^0_n}$$

$$|n^2_{\perp}\rangle = \sum_{m\neq n} |m^0\rangle \frac{E^1_n}{E^0_n - E^0_n} \frac{\langle n_0|V|n^0\rangle}{E^0_n - E^0_m} - \sum_{m\neq n} |n_0\rangle \frac{\langle n_0|V|n^1\rangle}{E^0_m - E^0_n}$$

$$\langle n^0|n^2_{\perp}\rangle = \sum_{m\neq n} \langle n^0|n^0\rangle \quad " \quad " \quad -\sum_{m\neq n} \langle n_0|n_0\rangle \quad "$$

$$\langle n^0|n^2_{\perp}\rangle = \sum_{m\neq n} \delta_{nm} \quad " \quad " \quad -\sum_{m\neq n} \delta_{nm} \quad "$$

$\delta_{nm} = 0 \quad (\text{since } n \neq m)$

$$\rightarrow \langle n^0|n^2_{\perp}\rangle = 0$$

17-5 Degenerate Perturbation Theory:

When the unperturbed states are degenerate we face some difficulties:

i) In the expansion of the perturbed state we <u>don't know</u> into which unperturbed state, the perturbed state collapses as $g \to 0$. (i.e. $|n\rangle \longrightarrow a|n_1^0\rangle + b|n_2^0\rangle + \cdots$ as $g \to 0$)

ii) Furthermore in the expansion of the state kets and energies, some of the denominators <u>vanish</u>. When this happen, the perturbation expansions become meaningless (except $V_{nk}=0$). These difficulties arrise not only if the unperturbed are strictly degenerate, but also if they are close in energy. (i.e. $\frac{V_{nk}}{E_n^0 - E_k^0}$ is large if $E_n^0 \approx E_k^0$ and cause large scale mixing in the expansion)

Now, suppose we have double degeneracy:

$$H_0 |n_0^1\rangle = E_n^0 |n_0^1\rangle$$
$$H_0 |n_0^2\rangle = E_n^0 |n_0^2\rangle$$

where $|n_1^0\rangle$ and $|n_2^0\rangle$ are linearly-indep. (orthogonal)

Now $H = H_0 + gV$

$$H|n_1\rangle = E_{n1}|n_1\rangle$$
$$H|n_2\rangle = E_{n2}|n_2\rangle$$

where

$$E_{n_1} = E_n^0 + g E_{n_1}^1 + g^2 E_{n_1}^2 + \cdots$$

$$E_{n_2} = E_n^0 + g E_{n_2}^1 + g^2 E_{n_2}^2 + \cdots$$

with the eigenvectors:

$$|n_1\rangle = \left[c_{11}|n_1^0\rangle + c_{21}|n_2^0\rangle\right] + g|n_1^1\rangle + g^2|n_1^2\rangle + \cdots$$

$$|n_2\rangle = \left[c_{12}|n_1^0\rangle + c_{22}|n_2^0\rangle\right] + g|n_2^1\rangle + g^2|n_2^2\rangle + \cdots$$

$$(H_0 + gV)\left(c_{11}|n_1^0\rangle + c_{21}|n_2^0\rangle + g|n_1^1\rangle + \cdots\right) =$$

$$= \left(E_n^0 + gE_{n_1}^1 + \cdots\right)\left(c_{11}|n_1^0\rangle + c_{21}|n_2^0\rangle + g|n_1^1\rangle + \cdots\right) \quad (1)$$

$$(H_0 + gV)\left(c_{12}|n_1^0\rangle + c_{22}|n_2^0\rangle + g|n_2^1\rangle + \cdots\right) =$$

$$= \left(E_n^0 + gE_{n_2}^1 + \cdots\right)\left(c_{12}|n_1^0\rangle + c_{22}|n_2^0\rangle + g|n_2^1\rangle + \cdots\right) \quad (2)$$

The coeff. of eqn. (1):

g^0: $$(H_0 - E_n^0)\left(c_{11}|n_1^0\rangle + c_{21}|n_2^0\rangle\right) = 0 \quad (3)$$

g: $$(H_0 - E_n^0)|n_1^1\rangle = \left(E_{n_1}^1 - V\right)\left(c_{11}|n_1^0\rangle + c_{21}|n_2^0\rangle\right) \quad (4)$$

The coeff. of eqn (2):

g^0: $$(H_0 - E_n^0)\left(c_{12}|n_1^0\rangle + c_{22}|n_2^0\rangle\right) = 0 \quad (5)$$

g: $$(H_0 - E_n^0)|n_2^1\rangle = \left(E_{n_2}^1 - V\right)\left(c_{12}|n_1^0\rangle + c_{22}|n_2^0\rangle\right) \quad (6)$$

(4) and (6) are inhomogeneous eqns. - The criterion for solubility of these eqns. is that the inhomogeneous terms must have no-component in the subspace spanned by the sols. $|n_1^\circ\rangle$ and $|n_2^\circ\rangle$ of the homogeneous eqns. (3) and (5).

Projection of (4) in $|n_1^\circ\rangle$ direction:

$$\langle n_1^\circ | (H_0 - E_n^\circ) |n_1'\rangle = \langle n_1^\circ | (E_{n1}' - V)\left(c_{11}|n_1^\circ\rangle + c_{21}|n_2^\circ\rangle\right)$$

$$(E_n^\circ - E_n^\circ)\langle n_1^\circ | n_1'\rangle = c_{11}\langle n_1^\circ | (E_{n1}' - V)|n_1^\circ\rangle + c_{21}\langle n_1^\circ | (E_{n1}' - V)|n_2^\circ\rangle$$

$$0 = c_{11}E_{n1}'\langle n_1^\circ | n_1^\circ\rangle - c_{11}\langle n_1^\circ | V | n_1^\circ\rangle + c_{21}E_{n1}'\langle n_1^\circ | n_2^\circ\rangle - c_{21}\langle n_1^\circ | V | n_2^\circ\rangle$$

Projection of (4) in $|n_2^\circ\rangle$ direction:

$$\langle n_2^\circ | (H_0 - E_n^\circ) |n_1'\rangle = \langle n_2^\circ | (E_{n1}' - V)\left(c_{11}|n_1^\circ\rangle + c_{21}|n_2^\circ\rangle\right)$$

$$\rightarrow \quad 0 = c_{11}E_{n1}'\langle n_2^\circ | n_1^\circ\rangle - c_{11}\langle n_2^\circ | V | n_1^\circ\rangle + c_{21}E_{n1}'\langle n_2^\circ | n_2^\circ\rangle - c_{21}\langle n_2^\circ | V | n_2^\circ\rangle$$

$$\rightarrow \begin{cases} c_{11}\left(\langle n_1^\circ | V | n_1^\circ\rangle - E_{n1}'\right) + c_{21}\langle n_1^\circ | V | n_2^\circ\rangle = 0 \\ c_{11}\langle n_2^\circ | V | n_1^\circ\rangle + c_{21}\left(\langle n_2^\circ | V | n_2^\circ\rangle - E_{n1}'\right) = 0 \end{cases}$$

Take $\langle n_i^\circ | V | n_j^\circ\rangle = V_{ij}$

$$\begin{pmatrix} V_{11}-E'_{n1} & V_{12} \\ V_{21} & V_{22}-E'_{n1} \end{pmatrix} \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} = 0$$

with $V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$

$$V \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} = E'_{n1} \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix}$$

Sol. $VX = \lambda X$

$(V - \lambda I) X = 0$

$\det(V - \lambda I) = 0$

$$\begin{vmatrix} V_{11}-E'_{n1} & V_{12} \\ V_{21} & V_{22}-E'_{n1} \end{vmatrix} = 0 \quad \text{for non trivial sols.} \quad (7)$$

The projection of eqn (6) in $|n_1^\circ\rangle$ and $|n_2^\circ\rangle$ directions leads to:

$$\begin{pmatrix} V_{11}-E'_{n2} & V_{12} \\ V_{21} & V_{22}-E'_{n2} \end{pmatrix} \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix} = 0$$

$$V \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix} = E'_{n2} \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix}$$

This leads to the same secular eqn. (7).

E_{n1}' and E_{n2}' are eige-values of V.

$$\begin{vmatrix} V_{11}-\lambda & V_{12} \\ V_{21} & V_{22}-\lambda \end{vmatrix} = 0$$

$$\lambda^2 - (V_{11}+V_{22})\lambda + (V_{11}V_{22} - V_{12}V_{21}) = 0$$

$$\lambda = \frac{V_{11}+V_{22}}{2} \pm \sqrt{\left(\frac{V_{11}-V_{22}}{2}\right)^2 + V_{12}V_{21}}$$

If $\sqrt{\quad} \neq 0$, the degeneracy is lifted by the perturbation.

But: if $V_{11}=V_{22}$ and $V_{12}=V_{21}=0$ the degeneracy still persists. (for Hermitian op. $V_{12}=V_{21}^*$)

In this case, the degeneracy may still be removable in a higher approx.

$\lambda_1 \longrightarrow E_{n1}'$

$\lambda_2 \longrightarrow E_{n2}'$

Summarizing:

If E_n° is d-fold degenerate, we construct:

$$V = \begin{pmatrix} \langle n_0^1|V|n_0^1\rangle & \cdots & \langle n_0^1|V|n_0^d\rangle \\ \vdots & & \\ \langle n_0^d|V|n_0^1\rangle & \cdots & \langle n_0^d|V|n_0^d\rangle \end{pmatrix} \quad ; \quad \begin{vmatrix} V_{11}-\lambda & V_{12} & \cdots & V_{1d} \\ V_{21} & V_{22}-\lambda & \cdots & V_{2d} \\ \vdots & & & \\ V_{d1} & \cdots & & V_{dd}-\lambda \end{vmatrix} = 0$$

The λ-roots give, $E_1^1, E_2^1, \cdots E_d^1$

In first order perturbation theory requires the calculation of a d-dim. Hamiltonian submatrix in the subspace of degenerate eigenkets corresponding to the eigenvalue E_n°

$$\{|n_1^\circ\rangle, |n_2^\circ\rangle, \cdots |n_d^\circ\rangle\} \in E_n^\circ$$

At this level of approx., all other unperturbed eigenstates are simply ignored and the eigenvalue prob. for the truncated H is solved exactly (Partial exact diagonalization).

Complex systems:

We take the subspace of the calculations as;

$$\{\underbrace{|n_1^\circ\rangle, |n_2^\circ\rangle \cdots |n_d^\circ\rangle}_{\in E_n^\circ}, \underbrace{|n_{d+1}^\circ\rangle \cdots |n_{d+k}^\circ\rangle}_{\text{not strictly degenerate with } E \simeq E_n^\circ}\}$$

and exclude the other states, such that;

i) $\{|n_\ell^\circ\rangle, \ell > d+k\}$ with $E_\ell \neq E_n^\circ$ very different

ii) $\langle n_p^\circ | V | n_q^\circ \rangle \approx 0$ $\quad p \in (0 - d+k)$
$\quad q \in (> d+k)$

Then we say the interaction between included and excluded states is negligible.

Although we can solve dxd or $(d+k)\times(d+k)$ matrix and find the first order energy shifts, nevertheless time and incidentally physical insight, can be gained if we take full advantage of the symmetry properties of the system.

If certain symmetries of the unperturbed system survive in the presence of the perturbation $\longrightarrow \exists A$ such that;

$$[H_0, A] = [H, A] = [V, A] = 0$$

Example: An electron in a central field is now placed in a uniform external mag. field in z-dir.

$\longrightarrow$ Now we have cylindrical symmetry,

$$[H_0, L_z] = [H, L_z] = [V, L_z] = 0$$

(Despite the full spherical symmetry of H is destroyed by the external field.)

If such an op. A exists; the eigenvectors of H may be selected to be also eigenvectors of A and this can be required for all values of g-

Consequently; in constructing the correct linear combinations of unperturbed eigenvectors we need to include only those eigenvectors which belong to the same eigenvalue A' of A-

Finally; the simplification comes about, because if $[A,V]=0 \longrightarrow \langle A'|V|A''\rangle \delta_{A'A''}$

See examples of (P224), (P229, 230)

Ex.- Hydrogen Atom in a weak Magnetic field:

(Spin is not included)

$$H = H_0 + qV$$

$$H_0 = \frac{p^2}{2m} + V(r) \qquad qV = V_{Mag} = -\mu \cdot B$$

$$H = H_0 - \mu \cdot B$$

$$H_0 |n,l,m\rangle_0 = E_n^0 |n,l,m\rangle_0$$

$$\begin{cases} n \longrightarrow H_0 \\ l \longrightarrow L^2 \\ m \longrightarrow L_z \end{cases}$$

For unperturbed energy we have: $E_n^0 = -\left(\frac{me^4}{2\hbar^2}\right)\frac{1}{n^2}$

$$\text{Degeneracy} = \sum_{l=0}^{n-1} (2l+1) = n^2$$

Ex. $n=3$

$l=2, l=1, l=0$

$5 + 3 + 1$

We choose $B \parallel \hat{z}$

$$\rightarrow \quad H = H_0 - \mu_z B$$

where $\mu_z = \frac{e}{2mc} L_z \equiv \gamma L_z$

$$\rightarrow \quad H = H_0 - \gamma B L_z$$

$$H |n,l,m\rangle = E_n |n,l,m\rangle$$

P223/3 $\rightarrow$

|unperturbed state⟩ = linear combination of the eigenvectors of L_z with the same m. (Since $[H, L_z] = 0$) That is just $|n,l,m\rangle$.

$$E_n = \langle n,l,m|H|n,l,m\rangle = \langle n,l,m|(H_0 - \gamma B L_z)|n,l,m\rangle$$

$$E_n = E_n^0 - \gamma B \langle n,l,m|L_z|n,l,m\rangle$$

$$E_n = E_n^0 - \gamma B \hbar m$$

$$E_n = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} - \gamma B \hbar m$$

Degeneracy $= n^2$ for $n=2$ $\quad n^2 = 4$

$n=2 \longrightarrow \ell = 0, 1$

$\ell = 0 \longrightarrow m = 0$

$\ell = 1 \longrightarrow m = \begin{cases} 1 \\ 0 \\ -1 \end{cases}$

$E_2 = E_2^\circ - \gamma B \hbar m$

For $m=0$ $\quad E_2 = E_2^\circ$

" $m=-1$ $\quad E_2 = E_2^\circ + \gamma B \hbar$

" $m=+1$ $\quad E_2 = E_2^\circ - \gamma B \hbar$

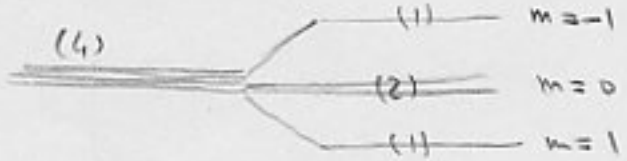
m \ ℓ	0	1
1	/	$E_n^\circ - \gamma B \hbar$
0	E_n°	E_n°
−1	/	$E_n^\circ + \gamma B \hbar$

Remark:

This prob. is degenerate but since the unperturbed states are eigenstates of the operators that commute with perturbation pot. V i.e. $[V, L^2] = [V, L_z] = 0$

$\rightarrow \begin{cases} \langle n^\circ, \underbrace{(\ell, m)}_{\alpha} | V | n^\circ, \underbrace{(\ell', m')}_{\alpha'} \rangle = 0 \\ \text{for } \ell \neq \ell', \; m = m' \end{cases}$

i.e. the degenerate states $|n_1^\circ\rangle \equiv |n^\circ \ell, m\rangle, |n_2^\circ\rangle \equiv |n^\circ, \ell', m'\rangle$ ... belonging to E_n° are not connected to first order



In this prob. the perturbed states are the same as unperturbed states (This can be seen by solving the prob. using the degenerate formalism) -

Stark Effect - Non degeneracy:

Consider an electron bound in an atom which is placed in a weak uniform electric field $\bar{E}$.

$$\varphi(r) = -\int \bar{E}\cdot d\bar{r} = -\bar{E}\cdot\bar{r}$$

$$H = H_0 + qV$$

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$$

$$qV = -e\varphi(r) = e\bar{E}\cdot\bar{r} \qquad (e>0)$$

$$E_n = E_n^0 + \langle n^0|qV|n^0\rangle + \sum_{m\neq n} \frac{|\langle n^0|qV|m^0\rangle|^2}{E_n^0 - E_m^0}$$

$$E_n = E_n^0 + e\bar{E}\cdot\langle n^0|\bar{r}|n^0\rangle + \sum_{m\neq n} \frac{|e\bar{E}\cdot\langle n^0|\bar{r}|m^0\rangle|^2}{E_n^0 - E_m^0}$$

linear — quadratic

$$r = \frac{Z}{\zeta_\theta}$$

We choose $\bar{E} \parallel \hat{z}$

$$E_n = E_n^0 + eE\langle n^0|z|n^0\rangle + \sum_{m\neq n} \frac{|eE\langle n^0|z|m^0\rangle|^2}{E_n^0 - E_m^0}$$

The shift of energy levels in an electric filed is known as Stark effect.

Parity conservation results → The absence of first order terms in almost all atomic states (with important exception of the excited states in Hydrogenic atoms.)

If $[H_0, \Pi] = 0$ ⟶ energy eigenstates may be taken to have definite parity.

$$\langle n^0 | r | n^0 \rangle = \int r |\psi_n^0|^2 d\tau = 0$$ First order term

⟶ The external electric field can in general produce no first order or linear Stark effect.

$$E_n = E_n^0 + eE\langle n^0 | z | n^0 \rangle$$

$n=1$ $$E_1 = E_1^0 + eE\langle 100 | z | 100 \rangle = E_1^0 + 0 = E_1^0$$

$$\int \psi_{100}^* z \psi_{100} d\tau = 0$$

Exception: If the central field is pure coulomb field (Hydrogenic atoms), the excited states of such atoms exhibit degeneracy of states with opposite parity. Superposition of such states yields energy eigenstates which have no definite parity and expectation values of r need no longer vanish.

The parity selection rule insures that the trivial degeneracy of magnetic substates (i.e. the states $|n,\ell,m\rangle, |n,\ell,m'\rangle \cdots$) does not interfere with the applicability of the second order correction (in non-deg. case).

The state $|n,\ell,m\rangle$ and $|n,\ell,m'\rangle$ have the same energy, but these two states have also the same parity, then we have $\frac{0}{0}$ terms instead of $\frac{c}{0} \to \infty$ and can be omitted in summation of the second order term.

Stark effect - Degenerate Case: (linear effect)

$$H = H_0 + qV \qquad H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$$

$$\varphi(r) = -\int E \cdot dr = -\vec{E} \cdot r \qquad qV = -e\varphi(r) = e\vec{E} \cdot r$$

Weak

Choose $\vec{E} \parallel \hat{z}$

$$r = \frac{z}{\cos\theta} \qquad qV \longrightarrow eEz$$

1S-state of Hydrogen atom is nondegenerate with even parity $\xrightarrow{\text{hence}}$ no linear Stark effect occurs.

And there is no permanent dipole moment for the ground-state 1S.

The situation is different for the excited states.

The lowest excited states are 2S-state and three 2P states.

2S : even parity $(n=2,\ l=0\quad m=0)$

2P : odd parity $(n=2\quad l=1\quad m=-1,0,1)$

H shares cylindrical symmetry with H_0

and $[H, L_z]=0 \longrightarrow$ they have common eigenstates.

degeneracy $n^2=4$-fold

Possible states : $|200\rangle, |21-1\rangle, |210\rangle, |211\rangle$

All the states have the same energy $E_2=-\frac{mc^4}{2\hbar^2}\frac{1}{2^2}$

$$V_{ij} = \langle n_i | z | n_j \rangle = \int \psi^*_{nlm} z \psi_{n'l'm'} d\tau$$

Parity of $\psi_i = (-1)^{l_i}$

Parity of $\psi_j = (-1)^{l_j}$ $\longrightarrow$ Parity of $\psi_i^* z \psi_j = (-1)^{l_i+l_j+1}$

$$\int \psi_i^* z \psi_j \, d\tau = \begin{cases} 0 \\ \neq 0 \text{ (in general)} \end{cases}$$

for l_i+l_j+1 odd

" " even

(1)

Also $\int \psi^*_{n\ell m} z \psi_{n'\ell'm'} d\tau = 0$ for $m \neq m'$ (2)

(due to $[L_z, z] = 0$)

($r'_\theta = z$)

Therefor we can only connect the states with the same m and different ℓ:

i.e. $|200\rangle$ and $|210\rangle$

Remark: $[z, L^2] \neq 0$

$|n_1^0\rangle = |200\rangle$ $\quad$ $|n_2^0\rangle = |210\rangle$

See ($P_{223/2}$, $P_{223/3}$)

$$V = \begin{pmatrix} \langle 200|z|200\rangle & \langle 200|z|210\rangle & \langle 200|z|211\rangle & \langle 200|z|21-1\rangle \\ \langle 210|z|200\rangle & - & - & - \\ \langle 211|z|200\rangle & - & - & - \\ \langle 21-1|z|200\rangle & - & - & - \end{pmatrix}$$

$$V = \begin{pmatrix} 0 & \langle 200|z|210\rangle & 0 & 0 \\ \langle 210|z|200\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\rightarrow V = \begin{pmatrix} 0 & \langle n_1^0|z|n_2^0\rangle \\ \langle n_2^0|z|n_1^0\rangle & 0 \end{pmatrix} = \begin{pmatrix} 0 & \langle 200|z|210\rangle \\ \langle 210|z|200\rangle & 0 \end{pmatrix}$$

$$\psi_{200} = \left(\frac{1}{2a}\right)^{3/2}\left(2-\frac{r}{a}\right)e^{-\frac{r}{2a}}\,Y_{00}$$

$$\psi_{210} = \left(\frac{1}{2a}\right)^{3/2}\left(\frac{r}{a}\right)e^{-\frac{r}{2a}}\,Y_{10}$$

where $Y_{00} = \frac{1}{\sqrt{4\pi}}$

$$Y_{10} = \frac{1}{\sqrt{4\pi}}\cos\theta$$

$$V_{12} = \langle 200|z|210\rangle = \langle 200|r\cos\theta|210\rangle =$$

$$= \frac{1}{4\pi}\left(\frac{1}{2a}\right)^3\frac{1}{a}\int_0^\infty\int_0^\pi\int_0^{2\pi} r^4\left(2-\frac{r}{a}\right)e^{-\frac{r}{a}}\cos^2\theta\,\sin\theta\,dr\,d\theta\,d\varphi$$

change of variables: $\begin{cases} \frac{r}{a_0} = u & du = \frac{dr}{a_0} \\ \cos\theta = x \end{cases}$

$$\rightarrow V_{12} = -3a$$

$$V_{21} = V_{12}^* = -3a$$

$$V = \begin{pmatrix} 0 & -3a \\ -3a & 0 \end{pmatrix} \qquad \left(a = \frac{\hbar^2}{me^4}\right)$$

$$\begin{pmatrix} 0 & -3a \\ -3a & 0 \end{pmatrix} \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} = E^1_{n1} \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} \qquad (1)$$

$$\begin{pmatrix} 0 & -3a \\ -3a & 0 \end{pmatrix} \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix} = E^1_{n2} \begin{pmatrix} c_{12} \\ c_{22} \end{pmatrix} \qquad (2)$$

$$\det(V - \lambda I) = 0 \qquad \begin{vmatrix} -\lambda & -3a \\ -3a & -\lambda \end{vmatrix} = 0$$

$$\lambda^2 - 9a^2 = 0 \qquad \lambda = \pm 3a \longrightarrow \begin{cases} E^1_{n1} = 3a \\ E^1_{n2} = -3a \end{cases}$$

$$(1) \rightarrow \begin{cases} -3a\, c_{21} = 3a\, c_{11} \\ -3a\, c_{11} = 3a\, c_{21} \end{cases} \quad \text{there are the same} \longrightarrow c_{11} = -c_{21}$$

$$(2) \rightarrow \begin{cases} -3a\, c_{22} = -3a\, c_{12} \\ -3a\, c_{12} = -3a\, c_{22} \end{cases} \quad \text{" " "} \longrightarrow c_{22} = c_{12}$$

$$|n_1\rangle = \left[c_{11} |n_1^\circ\rangle + c_{21} |n_2^\circ\rangle \right] + g\,|n_1'\rangle + g^2 |n_1^2\rangle + \cdots$$

$$|n_2\rangle = \left[c_{12} |n_1^\circ\rangle + c_{22} |n_2^\circ\rangle \right] + g\,|n_2'\rangle + g^2 |n_2^2\rangle + \cdots$$

Normalization:

$$\begin{cases} c_{11}^2 + c_{21}^2 = 1 \\ c_{11} = -c_{21} \end{cases} \longrightarrow \begin{array}{l} c_{11} = \frac{1}{\sqrt{2}} \\ c_{21} = -\frac{1}{\sqrt{2}} \end{array} \longrightarrow C = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

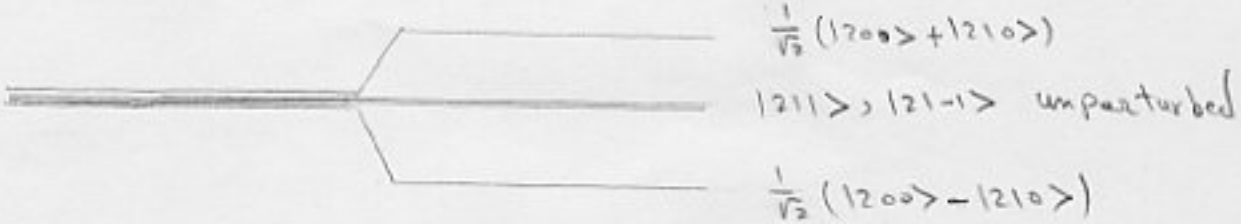
$$|n_1\rangle = \frac{1}{\sqrt{2}}\left(|n_1^\circ\rangle - |n_2^\circ\rangle\right) = \frac{1}{\sqrt{2}}\left(|200\rangle - |210\rangle\right)$$

Zero order correction

Also:

$$\begin{cases} c_{12}^2 + c_{22}^2 = 1 \\ c_{22} = c_{12} \end{cases} \longrightarrow \begin{matrix} c_{12} = \frac{1}{\sqrt{2}} \\ c_{22} = \frac{1}{\sqrt{2}} \end{matrix} \longrightarrow C' = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$|n_2\rangle = \frac{1}{\sqrt{2}}\left(|n_1^\circ\rangle + |n_2^\circ\rangle\right) = \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right)$$



Note that $R = \left(\left(C\right)\left(C'\right)\right) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$ diagonalizes V

$$RVR^T = \begin{pmatrix} -3a & 0 \\ 0 & 3a \end{pmatrix}$$ (See p 233/4)

$E_e^1 = \langle e^\circ | V | e^\circ \rangle \rightarrow E_{n_1}^1 = \langle C|V|C\rangle = -3a \quad E_{n_2}^1 = \langle C'|V|C'\rangle = +3a$

In the degenerate case, specifying the states with energy eigenvalues is not enough and the additional quantum numbers are needed. Suppose there is another observable such that;

$[H_0, A] = 0 \longrightarrow |n, a^\circ\rangle \equiv |K^\circ\rangle$ simultaneous eigenket of H_0 and A

K: collective index

When $[A, V] \neq 0 \rightarrow [H, A] \neq 0$

$\longrightarrow$ The zero-order eigenkets for H are in fact not A eigenkets.

Example: $A \equiv L^2$, $B = L_z$ $\quad H_0 = \frac{p^2}{2m} - \frac{e}{r}$

$|K^\circ\rangle = |n, l, m\rangle \qquad H_0 |n, l, m\rangle = E_n |n, l, m\rangle$

$V = -\mu \cdot B \qquad H = H_0 + gV$

$|\ \rangle = a|n, l, m\rangle + b|n, l, m'\rangle + \cdots$

$L^2 |\ \rangle \neq c |\ \rangle \quad ; \quad L_z |\ \rangle \neq c' |\ \rangle$

Vanishing denominators may be avoided by choosing our base Kets in such a way that V has no off-diagonal matrix elements:

i.e. $V_{nm} = 0$ for $n \neq m$ $\left(\text{So } \frac{V_{nm}}{E_m^\circ - E_n^\circ} = \frac{0}{0} \text{ finite}\right)$

In other words: We should use the linear combinations of the degenerate unperturbed Kets that diagonalize H in the subspace spanned by the degenerate unperturbed kets. (This in fact diagonalizes H).

Suppose there is q-fold degeneracy before introducing V. i.e. q-states have energy E_D°

Now let $\{|m^\circ\rangle\}$ unperturbed base kets (degenerate)

and $\{|\ell\rangle\}$ degeneracy removed states (by V)

As $g \to 0 \Rightarrow |\ell\rangle \to |\ell^\circ\rangle$

Even though $H_0 |\ell^\circ\rangle = E_m^\circ |\ell^\circ\rangle$

however $|\ell^\circ\rangle \neq |m^\circ\rangle$

or $\{|\ell^\circ\rangle\} \neq \{|m^\circ\rangle\}$

Indeed

$$|\ell^0\rangle = \sum_{m \in D} \langle m^0|\ell^0\rangle |m^0\rangle$$

D: degenerate subspace spaned either by $\{|m^0\rangle\}$ or $\{|\ell^0\rangle\}$

Now; $(H_0 + gV)|\ell\rangle = E_\ell |\ell\rangle$

We suppose; $|\ell\rangle = |\ell^0\rangle + g|\ell^1\rangle + g^2|\ell^2\rangle + \cdots$

$$E_\ell = E_0^0 + gE_\ell^1 + g^2 E_\ell^2 + \cdots$$

$$(H_0+gV)(|\ell^0\rangle + g|\ell^1\rangle + g^2|\ell^2\rangle + \cdots) = (E_0^0 + gE_\ell^1 + g^2E_\ell^2 + \cdots)(|\ell^0\rangle + g|\ell^1\rangle + g^2|\ell^2\rangle + \cdots)$$

g^0: $H_0|\ell^0\rangle = E_0^0|\ell^0\rangle$

g^1: $H_0|\ell^1\rangle + V|\ell^0\rangle = E_0^0|\ell^1\rangle + E_\ell^1|\ell^0\rangle$

$$\rightarrow (H_0 - E_0^0)|\ell^1\rangle = (E_\ell^1 - V)|\ell^0\rangle \qquad (1)$$

$$= (E_\ell^1 - V)\left[\sum_{m \in D} |m^0\rangle\langle m^0|\ell^0\rangle\right]$$

$$\langle n^0|(H_0 - E_0^0)|\ell^1\rangle = \langle n^0|(E_\ell^1 - V)\left[\sum_{m \in D} |m^0\rangle\langle m^0|\ell^0\rangle\right]$$

$$(E_0^0 - E_0^0)\langle n^0|\ell^1\rangle = E_\ell^1\langle n^0|\ell^0\rangle - \sum_{m \in D} \underbrace{\langle n^0|V|m^0\rangle}_{V_{nm}}\langle m^0|\ell^0\rangle$$

where $|n^0\rangle \in \{|m^0\rangle\}$

$$\sum_{m\in D} V_{nm} \langle n^\circ|\ell^\circ\rangle = E_\ell' \langle n^\circ|\ell^\circ\rangle$$

$$\rightarrow \begin{pmatrix} V_{11} & V_{12} & \cdots \\ V_{21} & V_{22} & \cdots \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} \langle 1^\circ|\ell^\circ\rangle \\ \langle 2^\circ|\ell^\circ\rangle \\ \vdots \end{pmatrix} = E_\ell' \begin{pmatrix} \langle 1^\circ|\ell^\circ\rangle \\ \langle 2^\circ|\ell^\circ\rangle \\ \vdots \end{pmatrix} \qquad (2)$$

$$\det(V - E_\ell' I) = 0 \quad \text{or} \quad \det(V - \lambda I) = 0$$

The roots of $\lambda \xrightarrow{\text{determine}} E_\ell'$ (q-in number)

Substituting E_ℓ''s in (2), we can solve for $\langle m^\circ|\ell^\circ\rangle$ for each ℓ up to an overall normalization const., which determine zero-order eigenkets. (i.e. $|\ell^\circ\rangle_1 \cdots |\ell^\circ\rangle_q$ all with the same energy E_D°)

Note that:

(1) $\langle \ell^\circ|(H_1 - E_D^\circ)|\ell'\rangle = \langle \ell^\circ|(E_\ell' - V)|\ell^\circ\rangle$

$0 = E_\ell' - \langle \ell^\circ|V|\ell^\circ\rangle$

$E_\ell' = \langle \ell^\circ|V|\ell^\circ\rangle$

Remark: As $g \to 0$

$|\ell'\rangle_1$ with $E_{\ell 1}' \longrightarrow |\ell_1^\circ\rangle$ with E_D°

$\vdots$

$|\ell'\rangle_q$ with $E_{\ell q}' \longrightarrow |\ell_q^\circ\rangle$ with E_D°

Notice that the zero-order kets $\{|\ell^\circ\rangle\}$ we obtain as $g \to 0$, diagonalize the Perturbation V, the diagonal elements give the first-order shift. i.e. the matrix

$$\begin{pmatrix} \langle 1^\circ|\ell_1^\circ\rangle & \langle 1^\circ|\ell_2^\circ\rangle & \cdots & \langle 1^\circ|\ell_q^\circ\rangle \\ \langle 2^\circ|\ell_1^\circ\rangle & \langle 2^\circ|\ell_2^\circ\rangle & & \langle 2^\circ|\ell_q^\circ\rangle \\ \vdots & & & \vdots \end{pmatrix}$$

diagonalizes V.

Remark: When a matrix is diagonalized the diagonal elements give the eigenvalues.

Here since $E_\ell' = \langle \ell^\circ | V | \ell^\circ \rangle \quad \forall \ell$ (q in number)

$\longrightarrow$ the off diagonal elements vanish.

Also this is obvious from;

$$\langle \ell^{\circ\prime} | (H_0 - E_D^\circ) | \ell' \rangle = \langle \ell^{\circ\prime} | (E_\ell' - V) | \ell^\circ \rangle$$

$$0 = \langle \ell^{\circ\prime} | \ell^\circ \rangle E_\ell' - \langle \ell^{\circ\prime} | V | \ell^\circ \rangle$$

$$\longrightarrow \langle \ell^{\circ\prime} | V | \ell^\circ \rangle = 0 \qquad \forall\ |\ell^{\circ\prime}\rangle \neq |\ell^\circ\rangle \quad \left(|\ell^{\circ\prime}\rangle \in \{|\ell^\circ\rangle \text{ degenerate subspace}\}\right)$$

Remark: $\langle \alpha | V | \ell^\circ \rangle \neq 0$ in general when $|\alpha\rangle \notin \{|\ell^\circ\rangle\}$

Note that: $E_\ell' = \langle \ell^\circ | V | \ell^\circ \rangle$ looks just first-order energy shift in the non-degenerate case, except that here we have to make sure that the base kets used, are such that $\langle \ell^{\circ\prime} | V | \ell^\circ \rangle = 0 \quad \forall\ |\ell^{\circ\prime}\rangle \neq |\ell^\circ\rangle \left(|\ell^{\circ\prime}\rangle \in \{|\ell^\circ\rangle\}\right)$ ↑ degenerate subspace

If V op. is already diagonal in the base ket representation we are using, we can immediately write down the first order shift by taking the expectation value of V, just as in the nondegenerate case.

Remark: If the degenerate subspace were the whole space, we would have solved the prob. exactly in this manner.

(See the example of P233).

Now let $P_0 = \sum_{m \in D}^{q} |m^0\rangle\langle m^0|$

(or equivalently: $P_0 = \sum_{\ell \in D}^{q} |\ell^0\rangle\langle \ell^0|$ because the two subspaces are equivalent)

Also we have

$$(H_0 - E_D^0)|\ell'\rangle = (E_\ell' - V)|\ell^0\rangle$$

Where $\begin{cases} A = (H_0 - E_D^0) \\ U = |\ell'\rangle \\ V = (E_\ell' - V)|\ell^0\rangle \end{cases}$

Also $\begin{cases} AU' = 0 \\ (H_0 - E_D^0)|\ell^0\rangle = 0 \end{cases} \rightarrow U' = |\ell^0\rangle$

The sol. $\rightarrow$ $U = U' + \frac{1 - P_0}{A} V$

$$|\ell'\rangle = C_\ell' |\ell^0\rangle + \frac{1 - P_0}{H_0 - E_D^0} (E_\ell' - V)|\ell^0\rangle$$

But $\frac{1 - P_0}{H_0 - E_D^0}|\ell^0\rangle = \frac{1}{H_0 - E_D^0}(|\ell^0\rangle - |\ell^0\rangle) = 0$

$$|\ell'\rangle = C_\ell' |\ell^0\rangle - \frac{1 - P_0}{H_0 - E_D^0} V|\ell^0\rangle$$

We may choose $C_\ell' = 0$ (as before)

$$|\ell'\rangle = -\frac{1 - P_0}{H_0 - E_D^0} V|\ell^0\rangle$$

But $1 - P_0 = \sum_{k \notin D} |k^0\rangle\langle k^0|$

$$|\ell'\rangle = \sum_{k \notin D} \frac{\langle k^0|V|\ell^0\rangle}{E_D^0 - E_k^0} |k^0\rangle = \sum_{k \notin D} \frac{V_{k\ell}}{E_D^0 - E_k^0} |k^0\rangle$$

We exclude all $k \in D$.

But in nondegenerate case we just excluded $m = n$.

Now, we equate the g^2-coeffs. from the both sides;

g^2: $\quad H_0|\ell^2\rangle + V|\ell'\rangle = E_D^0 |\ell^2\rangle + E_\ell^1 |\ell'\rangle + E_\ell^2 |\ell^0\rangle$

$$\langle \ell^0|H_0|\ell^2\rangle + \langle \ell^0|V|\ell'\rangle = E_D^0 \langle \ell^0|\ell^2\rangle + E_\ell^1 \langle \ell^0|\ell'\rangle + E_\ell^2 \langle \ell^0|\ell^0\rangle$$

($\langle \ell^0|\ell^2\rangle$: $C_\ell^2 = 0$; $\langle \ell^0|\ell'\rangle$: $C_\ell' = 0$)

$$\rightarrow E_\ell^2 = \langle \ell^0|V|\ell'\rangle$$

$$E_\ell^2 = \langle \ell^0| V \left[\sum_{k \notin D} \frac{V_{k\ell}}{E_D^0 - E_k^0} |k^0\rangle \right]$$

$$E_\ell^2 = \sum_{k \notin D} \frac{|V_{k\ell}|^2}{E_D^0 - E_k^0}$$

Our procedure works provided there is no degeneracy in the roots of secular equ. $\det(V - E_k^{(1)} I) = 0$

Otherwise we still have an ambiguity as to which linear combination of the degenerate unperturbed kets, the perturbed kets are reduced in the limit $g \to 0$.

Hydrogen atom with spin-orbit interaction:

(fine structure)

A moving charge (an electron) in the electric field of nucleus (Coulomb field), feels a magnetic field of

$$B_{eff} = -\frac{v}{c} \times E$$

$$V(r) = e\varphi \qquad e<0$$

$$eE = -e\nabla\varphi = -\frac{r}{r}\frac{dV}{dr} \qquad E = -\frac{1}{e}\frac{r}{r}\frac{dV}{dr}$$

$$B_{eff} = \frac{v}{c} \times \left(\frac{1}{e}\frac{r}{r}\frac{dV}{dr}\right)$$

$$H_{LS} = -\mu \cdot B \qquad \mu = \frac{eS}{mc}$$

$$H_{LS} = \frac{-e}{mc} S \cdot \left[\frac{v}{c} \times \left(\frac{1}{e}\frac{r}{r}\frac{dV}{dr}\right)\right]$$

$$H_{LS} = \frac{1}{mc^2} S \cdot \left[-v \times r \frac{1}{r}\frac{dV}{dr}\right] = \frac{1}{m^2c^2}\frac{1}{r}\frac{dV}{dr} L \cdot S$$

There is a correction to this due to spin precession which is called Thomas term.

$$H_{Thomas} = -\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr} L \cdot S$$

Then the total spin-orbit interaction is the sum of two terms:

$$H'_{LS} = H_{LS} + H_{Thomas} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr} L\cdot S$$

$$H = H_0 + L'_{LS} = H_0 + gV \qquad (L'_{LS}: \text{Perturbation})$$

where $H_0 = \frac{p^2}{2m} + V(r)$

The problem is to find a <u>new</u> basis in which V is diagonal (diagonal elements of eigenvalues).

$$J = L + S \longrightarrow L\cdot S = \tfrac{1}{2}(J^2 - L^2 - S^2)$$

$L\cdot S$ is diagonal in $|j\ m\rangle$ basis

$$E_{n(j,\ell,s)} = \langle n,j,m \mid H \mid n,j,m\rangle$$

$$= \langle n,j,m \mid H_0 + f(r)(J^2 - L^2 - S^2) \mid n,j,m\rangle$$

Remark: $S\cdot L$ is scalar op. & off-diagonal elements vanish

where $f(r) = \frac{1}{2}\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}$

$$E_{n(j,\ell,s)} = E_r^0 + C\hbar^2\left[j(j+1) - \ell(\ell+1) - \tfrac{1}{2}\tfrac{3}{2}\right]$$ Lande interval rule

C : const from radial component integration

degeneracy $= 2(2\ell+1)$ for a particular ℓ

$$|\ell - \tfrac{1}{2}| \le j \le \ell + \tfrac{1}{2}$$

i) $j = |\ell - \tfrac{1}{2}|$

$$E_{n\ell j=\ell-\frac{1}{2}} = E_n^\circ + Ch^2\left[\ell^2 - \tfrac{1}{4} - \ell^2 - \ell - \tfrac{3}{4}\right]$$

$$= E_n^\circ - Ch^2(\ell+1) \qquad \ell > 0 \qquad \text{degeneracy} = 2(\ell - \tfrac{1}{2}) + 1 = 2\ell$$

ii) $j = \ell + \tfrac{1}{2}$

$$E_{n\ell j=\ell+\frac{1}{2}} = E_n^\circ + Ch^2\left[\ell^2 + 2\ell + \tfrac{3}{4} - \ell^2 - \ell - \tfrac{3}{4}\right]$$

$$= E_n^\circ + Ch^2\ell \qquad \text{degeneracy} = 2(\ell + \tfrac{1}{2}) + 1 = 2(\ell+1)$$

degeneracy $= 2j+1$

for $n=2$

i) $E_{2,\ell,\ell-\frac{1}{2}} = E_2^\circ - \begin{cases} 2Ch^2 & \leftarrow \ell = 1 \quad (2P_{1/2}) \text{ degen.} = 2 \end{cases}$

degeneracy $= 2|(\ell - \tfrac{1}{2})| + 1$

ii) $E_{2,\ell,\ell+\frac{1}{2}} = E_2^\circ + \begin{cases} 0 & \text{for } \ell = 0 \quad (2S_{1/2}) \text{ degen.} = 2 \\ Ch^2 & \leftarrow \ell = 1 \quad (2P_{3/2}) \text{ degen.} = 4 \end{cases}$

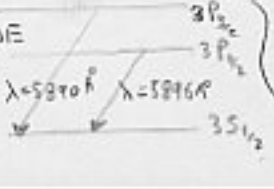
degeneracy $= 2(\ell + \tfrac{1}{2}) + 1 = 2\ell + 2$

i.e.
$\ell = 0 \rightarrow j = \tfrac{1}{2} \rightarrow m_j = \pm\tfrac{1}{2}$
$\ell = 1 \rightarrow j = \tfrac{3}{2} \rightarrow m_j = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}$

Ex: Sodium D-lines;

$(1s)^2(2s)^2(2p)^6(3s)$
spherically sym. electron cloud

Fine structure $\{\Delta E$ due to S.L int
(in the absence of S.L int, $\Delta E = 0$)



Zeeman Effect: (Anomalous Zeeman effect, the electron spin is taken into account.)

Now we discuss Hydrogen or Hydrogenlike (one-electron) atoms in a uniform magnetic field:

The magnetic field B is derivable from a vector potential A:

$$A = \frac{1}{2}(B \times r)$$

choose $\bar{B} \parallel \hat{z}$

$$A = -\frac{1}{2}(B_y \hat{x} - B_x \hat{y})$$

$$p \longrightarrow (p - \frac{e}{c} A)$$

$$H = \frac{p^2}{2m} + V(r) \longrightarrow H = \frac{p^2}{2m} - \frac{e}{2mc}(p \cdot A + A \cdot p) + \frac{e^2 A^2}{2mc^2} + V(r)$$

$$p \cdot A = \frac{\hbar}{i} \nabla \cdot A$$

$$p \cdot A \psi = \frac{\hbar}{i} \nabla \cdot (A\psi) = \psi \left(\frac{\hbar}{i} \nabla \cdot A\right) + \frac{\hbar}{i} A \cdot \nabla \psi$$

If $\nabla \cdot A = 0$

$$p \cdot A \psi = \frac{\hbar}{i} A \cdot \nabla \psi = A \cdot \left(\frac{\hbar}{i} \nabla \psi\right) = A \cdot p \psi$$

$$\longrightarrow p \cdot A = A \cdot p$$

$$A \cdot P = B\left(-\tfrac{1}{2} y P_x + \tfrac{1}{2} x P_y\right) = \tfrac{1}{2} B L_z$$

and $A^2 = \frac{1}{4} B^2 (x^2 + y^2)$

$$H = \frac{p^2}{2m} + V(r) - \frac{e}{2mc} B L_z + \frac{e^2}{8mc^2} B^2 (x^2 + y^2)$$

To this we add the spin magnetic moment interaction;

$$-\mu \cdot B = \frac{-e}{mc} \bar{S} \cdot \bar{B} = -\frac{e}{mc} B S_z$$

$$H = \frac{p^2}{2m} + V(r) - \frac{e}{2mc} B (L_z + 2 S_z) + \cancel{O(B^2)}$$

Now we add also spin-orbit interaction:

$$H = \underbrace{\frac{p^2}{2m} + V(r)}_{H_0} + \underbrace{\lambda L \cdot S}_{\text{(or) } H_0 \text{ (in } J^2, J_z, L^2, S^2 \text{ basis)}} - \frac{e}{2mc} B (g_L L_z + g_s S_z)$$

When we have changed the coeffs. of L_z and S_z to cover the general case (more than one electron)

or

$$H = H_0 + \lambda L \cdot S + \mu L_z + \nu S_z \quad (1)$$

$$H = H_0 + \lambda L \cdot S + \mu J_z + (\nu - \mu) S_z$$

$$H = \underbrace{H_0 + \frac{\lambda}{2}(J^2 - L^2 - S^2) + \mu J_z}_{H_0'} + \underbrace{(\nu - \mu) S_z}_{gV} \quad (2)$$

Remarks: we can study the effect of gV using of H_0' - the J^2, J_z eigenkets as our base kets.

Now let:

$$H_0 = \frac{p^2}{2m} + V(r)$$

$$H_{L\cdot S} = \frac{1}{2mc^2}\,\frac{1}{r}\,\frac{dV(r)}{dr}\,L\cdot S$$

$$H_B = \frac{-e|\bar{B}|}{2mc}\,(L_z + 2S_z)$$

If $\bar{B}$ is weak, then H_B can be treated as a <u>small</u> perturbation.

We can study the effect of H_B using the eigenkets of $H_0 + H_{L\cdot S}$ – the J^2, J_z eigenkets – as our base kets.

First order shift; $H = H_0 + H_{L\cdot S} + H_B$

$$H = \underbrace{H_0 + H_{L\cdot S} - \frac{e|\bar{B}|}{2mc} J_z}_{\text{no degeneracy?}} - \underbrace{\frac{e|\bar{B}|}{2mc} S_z}_{H''} \qquad E^1 = \langle n^0|V|n^0\rangle$$

$$E^1 = \langle jm|H''|jm\rangle = \frac{-e|\bar{B}|}{2mc}\langle jm|S_z|jm\rangle$$

when $j = l \pm \frac{1}{2}$

$$|j = l\pm\tfrac{1}{2}, m\rangle = \pm\sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}}\;|m_l = m - \tfrac{1}{2}\;\; m_s = \tfrac{1}{2}\rangle +$$

$$\sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}}\;|m_l = m + \tfrac{1}{2}\;\; m_s = -\tfrac{1}{2}\rangle$$

$$\langle j = l \pm \tfrac{1}{2}\; m|S_z|j = l \pm \tfrac{1}{2}\; m\rangle = \pm\frac{m\hbar}{(2l+1)}$$

Remark: $\langle j'm'|S_z|jm\rangle \neq 0$ in general

$$E_1 = \frac{-e\hbar B}{2m_e c}\,\frac{m\hbar}{2l+1} \qquad \text{due to } H''$$

$$E_1' = \frac{-e\hbar B}{2m_e c}\, m\left[1 \pm \frac{1}{2l+1}\right] \qquad \text{due to } H_B$$

$\langle S_z \rangle$ can also be obtained by using the projection theorem:

$$\langle \alpha', j m' | V_q | \alpha, j m \rangle = \frac{\langle \alpha', j m | \mathbf{J}\cdot\mathbf{V} | \alpha j m \rangle}{\hbar^2 j(j+1)} \langle j m' | J_q | j m \rangle$$

$V_q \longrightarrow S_z$, $\mathbf{J}\cdot\mathbf{V} \longrightarrow \mathbf{J}\cdot\mathbf{S} = J^2 + S^2 - L^2$

If $\bar{B}$ is strong (Paschen-Back limit); H_B will be more important than $H_{L\cdot S}$, so $H_{L\cdot S}$ can be regarded as a small perturbation; In this case

$$H = \underbrace{H_0 + H_B}_{} + \underbrace{H_{L\cdot S}}_{\text{perturbation}}$$

with $H_0 + H_B$ the good quantum numbers are L_z and S_z (J^2 is not good quantum number, because strong B destroys the spherical symmetry, we are left with cylindrical symmetry only).

So $\longrightarrow$ L_z and S_z eigenkets $|l, m_l, s=\frac{1}{2}, m_s\rangle$ are to be used as our base kets.

$$\langle l, m_l, s=\tfrac{1}{2}, m_s | H_B | l, m_l\ s=\tfrac{1}{2}, m_s\rangle = -\frac{e|B|\hbar}{2mc}(m_l + 2m_s)$$

Note that for H_1 we had $2(2l+1)$-degeneracy in m_l and m_s

Now since $m_s = \pm\frac{1}{2} \longrightarrow m_l + 2m_s = m_l \pm 1$

For example for $l=1$: $m_l + 2m_s = -2, -1, 0, 0, 1, 2$

$$E' = \langle n^0 | V | n^0 \rangle$$

$$\langle l, m_l, s=\tfrac{1}{2}, m_s | L\cdot S | l, m_l, s=\tfrac{1}{2}, m_s\rangle =$$

$$= \langle L_z S_z + \tfrac{1}{2}(L_+ S_- + L_- S_+)\rangle = \hbar^2 m_l m_s$$

where we have used $\langle L_\pm \rangle_{m_l} = 0$ $\quad$ $\langle S_\pm \rangle_{m_s} = 0$

$$E' = \langle H_{L\cdot S}\rangle_{m_l m_s} = \frac{\hbar^2 m_l m_s}{2m^2c^2}\left\langle \frac{1}{r}\frac{dV(r)}{dr}\right\rangle$$

Remark: $\langle l', m_l', s=\frac{1}{2}, m_s' | L\cdot S | l, m_l, s=\frac{1}{2}, m_s\rangle \neq 0$ (in general)

	Dominant interaction	Almost good*	No good	Always good
Weak $\vec{B}$	$H_{L\cdot S}$	J^2 or $(L\cdot S)$	L_z, S_z	L^2, S^2, J_z
Strong $\vec{B}$	H_B	L_z, S_z	J^2 or $(L\cdot S)$	

* almost good simply means good to the extent that the less dominant interaction could be ignored.

Remark: Note that with the perturbation term the wave funcs. which we are using in each of the basis is an approximate wave func.

Evidently, in order to minimize the work of computing matrix elements, it is desirable to use as many consts. of the motion as possible for the specification of the complete set of ops. whose eigenvectors are to serve as basis.

The aim is to solve the eigenvalue prob.:

$$H\Psi = E\Psi$$

With $H = H_0 + H' = H_0' + H^{\circ}$

This can be solved in any representation, but a judicious choice of basis may save a considerable amount of labor.

If we choose the eigenvectors of $\{L^2, S^2, J^2, J_z\}$ as our basis, we see that, since

$$[H', J^2] \neq 0 \longrightarrow [S_z, J^2] = 0$$

Thus the only nonvanishing off-diagonal matrix elements are of the form:

$$\langle l s, j' m | H' | l, s\, j\, m \rangle \neq 0 \longrightarrow \langle l s, j' m | S_z | l s\, j\, m \rangle \neq 0$$

(H°)

Note that since $S_z = T_{k=1}^{q=0}$ $\longrightarrow m = m'$

In other words; $|l,s,j\,m\rangle$ are not eigenvectors of H'' (They are eigenvectors of H_0 and H')

Now since $|j\,m\rangle = \sum_{m_s} \langle l, m-m_s; s, m_s | j\,m\rangle \, |l, m-m_s; s, m_s\rangle$

$$\rightarrow \langle j'm'|S_z|jm\rangle = \hbar \sum_{m_s} m_s \langle \underbrace{m-m_s}_{m_l}, m_s | j'm'\rangle \langle m-m_s, m_s | jm\rangle$$

For special case $s=\frac{1}{2}$ (which includes one-electron atoms);

$$\langle l, \tfrac{1}{2}, l\pm\tfrac{1}{2}, m | S_z | l, \tfrac{1}{2}, l\pm\tfrac{1}{2}, m\rangle = \pm \frac{m\hbar}{2l+1}$$

$$\langle \quad " \quad | S_z | \quad " \quad , \quad " \mp " \rangle = -\frac{\hbar}{2l+1}\sqrt{(l+\tfrac{1}{2})^2 - m^2}$$

Note that the degeneracy must be considered with respect to

$H_0' = H_0 + \frac{\lambda}{2}(J^2 - L^2 - S^2) + \mu J_z$.

The eigenvalues of H_0' depend on j, l, s, m_z .

$$E_0' = E_n^0 + \frac{\lambda}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]\hbar^2 - \mu m \hbar$$

As an important example; Consider a ^2P-state ($l=1$)

i.e. a system in unperturbed state with $n=2$, $l=1$

with total angular mom. $j=\frac{1}{2}$, $j=\frac{3}{2}$

$$E_0' = E_n^0 + \frac{\lambda}{2}\left[j(j+1) - 1(1+1) - \frac{1}{2}\frac{3}{2}\right]\hbar^2 + \mu m \hbar$$

The non-vanishing off-diagonal matrix elements of S_z are; (See p 239/1)

$$\langle \tfrac{1}{2}\ \tfrac{1}{2} | S_z | \tfrac{3}{2}\ \tfrac{1}{2}\rangle = \langle \tfrac{3}{2}\ \tfrac{1}{2} | S_z | \tfrac{1}{2}\ \tfrac{1}{2}\rangle \neq 0$$

$$\langle \tfrac{1}{2}\ -\tfrac{1}{2} | S_z | \tfrac{3}{2}\ -\tfrac{1}{2}\rangle = \langle \tfrac{3}{2}\ -\tfrac{1}{2} | S_z | \tfrac{1}{2}\ -\tfrac{1}{2}\rangle \neq 0$$

Alternative approach:

$$H = \underbrace{\frac{p^2}{2m} - \frac{e^2}{r} + \lambda L\cdot S}_{H_c} + \frac{eB}{2mc}(L_z + 2S_z)$$

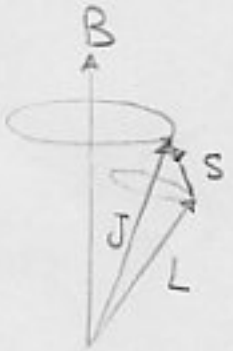
$$H = H_c + \frac{eB}{2mc}(L_z + 2S_z) = H_c + \frac{eB}{2mc}(J_z + S_z)$$

$$E_n = \langle n\ell, j, m|\left(H_c + \frac{eB}{2mc}(J_z + S_z)\right)|n, \ell, j, m\rangle$$

$$= E_n^\circ + \frac{eB}{2mc}\, m\hbar + \frac{eB}{2mc}\langle n\ell j m|S_z|n\ell j m\rangle$$

Consider:

Projection of $\bar{S}$ on $\bar{J}$



$$\bar{S}_J = \frac{S\cdot J}{|J|}\cdot\frac{|J|}{|J|} = \frac{(S\cdot J)J}{J^2}$$

$$J = L + S \qquad J - S = L$$

$$J^2 + S^2 - 2S\cdot J = L^2 \qquad S\cdot J = \frac{1}{2}(J^2 + S^2 - L^2)$$

$$\bar{S}_J = \frac{(J^2 + S^2 - L^2)}{2J^2}\bar{J}$$

$$S_z = \frac{(J^2 + S^2 - L^2)}{2J^2} J_z$$

$$E_n = E_n^\circ + \frac{eB}{2mc} m\hbar + \frac{eB}{2mc}\,\frac{j(j+1) + S(S+1) - \ell(\ell+1)}{2j(j+1)}\, m\hbar$$

where $j = |\ell - \frac{1}{2}|$ and $S = \frac{1}{2}$

$J = (\ell + \frac{1}{2})$

Ex.— Consider a Harmonic oscillator potential:

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \qquad (\omega = \frac{k}{m})$$

we introduce an extra potential term as below:

$$gV = \frac{1}{2} \epsilon m\omega^2 x^2 \qquad \epsilon \ll 1$$

Exact sol. is immediately obtained by replacing:

$$\omega \longrightarrow \sqrt{1+\epsilon}\,\omega$$

But we are interested to solve the problem by using the method of perturbation:

Under the perturbation:

$$|n\rangle = |n^0\rangle + \sum_{m \neq n} |m^0\rangle \frac{\langle m^0|gV|n^0\rangle}{E_n^0 - E_m^0}$$

$$E_n = E_n^0 + \langle n^0|gV|n^0\rangle + \sum_{m \neq n} \frac{|\langle n^0|gV|m^0\rangle|^2}{E_n^0 - E_m^0}$$

$$\langle 0^0|gV|0^0\rangle = \langle 0^0| \frac{\epsilon m\omega^2}{2} x^2 |0^0\rangle = \frac{\epsilon\hbar\omega}{4}$$

$$\langle 1^0|gV|0^0\rangle = 0$$

$$\langle 2^0|gV|0^0\rangle = \frac{\epsilon\hbar\omega}{2\sqrt{2}} \qquad \text{(Prob. 5)}$$

All other $\langle k^0|gV|0^0\rangle = 0$

$$|0\rangle = |0^\circ\rangle + |2^\circ\rangle \frac{\frac{\epsilon\hbar\omega}{2\sqrt{2}}}{\frac{1}{2}\hbar\omega - \frac{5}{2}\hbar\omega} + O(\epsilon^2)$$

$$|0\rangle = |0^\circ\rangle - \frac{\epsilon}{4\sqrt{2}}|2^\circ\rangle$$

$$E_0 = E_0^\circ + gE_0^1 + g^2E_0^2 + \cdots \qquad \left(E_0^2 = \frac{|\langle 0^\circ|V|2^\circ\rangle|^2}{E_0^\circ - E_2^\circ}\right)$$

$$E_0 - E_0^\circ \equiv \Delta_0 = gE_0^1 + g^2E_0^2 + \cdots$$

$$\Delta_0 = \frac{\epsilon\hbar\omega}{4} + \frac{\left(\frac{\epsilon\hbar\omega}{2\sqrt{2}}\right)^2}{\frac{1}{2}\hbar\omega - \frac{5}{2}\hbar\omega} + O(\epsilon^3)$$

$$\Delta_0 = \hbar\omega\left(\frac{\epsilon}{4} - \frac{\epsilon^2}{16}\right)$$

Compare with the exact sol.:

$$\frac{\hbar\omega}{2} \longrightarrow \left(\frac{\hbar\omega}{2}\right)\sqrt{1+\epsilon} = \frac{\hbar\omega}{2}\left(1 + \frac{\epsilon}{2} - \frac{\epsilon^2}{8} + \cdots\right)$$

Remark: Notice the ground state ket $|0\rangle$ (perturbed state) does not contain a component along first excited state (i.e. $|1^\circ\rangle$ with odd parity).

This is obvious also from $[H, \Pi] = 0$

Then → the energy eigenstate is expected to be a parity eigenstate.

Let us check the change in the wave-func.

when $\omega \to \sqrt{1+\epsilon}\,\omega$

$$\langle x|0^\circ\rangle = \frac{1}{\pi^{1/4}} \frac{1}{\sqrt{x_0}} e^{-\frac{x^2}{2x_0^2}}$$

where $x_0 = \sqrt{\frac{\hbar}{m\omega}}$

$$\omega \to \sqrt{1+\epsilon}\,\omega \implies x_0 \to \frac{x_0}{(1+\epsilon)^{1/4}}$$

Since: $\langle x|2^\circ\rangle = \frac{1}{2\sqrt{2}} \langle x|0^\circ\rangle H_2\left(\frac{x}{x_0}\right)$

$$= \frac{1}{2\sqrt{2}} \frac{1}{\pi^{1/4}} \frac{1}{\sqrt{x_0}} e^{-\frac{x^2}{2x_0^2}} \left[-2 + 4\left(\frac{x}{x_0}\right)^2\right]$$

where H_2 is Hermite polynomial of order 2.

$$\to \langle x|0^\circ\rangle \to \frac{1}{\pi^{1/4}\sqrt{x_0}} (1+\epsilon)^{1/8} \exp\left(-\left(\frac{x^2}{2x_0^2}\right)(1+\epsilon)^{1/2}\right)$$

$$\simeq \frac{1}{\pi^{1/4}} \frac{1}{\sqrt{x_0}} e^{-\frac{x^2}{2x_0^2}} + \frac{\epsilon}{\pi^{1/4}\sqrt{x_0}} e^{-\frac{x^2}{2x_0^2}} \left[\frac{1}{8} - \frac{1}{4}\frac{x^2}{x_0^2}\right]$$

$$= \langle x|0^\circ\rangle - \frac{\epsilon}{4\sqrt{2}} \langle x|2^\circ\rangle$$

Variational Method:

In many actual applications of quantum mechanics the Schrödinger equ. cannot be solved rigorously, nor can a neighboring unperturbed Hamiltonian be found which affords a good approx. and a suitable starting point for a perturbation treatment.

⟶ Variational method may be used.

The variational method has its roots in the following mathematical prob.

Consider a functional of the form:

$$\mathcal{L} = \langle \varphi | H | \psi \rangle - \lambda \langle \varphi | \psi \rangle$$

H: linear op

$$\begin{cases} \dfrac{\delta \mathcal{L}}{\delta \varphi} = 0 \rightarrow (H - \lambda)|\psi\rangle = 0 \\ \dfrac{\delta \mathcal{L}}{\delta \psi} = 0 \rightarrow \langle \varphi | (H - \lambda) = 0 \rightarrow (H^{\dagger} - \lambda^{*})|\varphi\rangle = 0 \end{cases}$$

$\mathcal{L}$ is stationary under these conds.

i.e. $\mathcal{L}$ is stationary if φ and ψ are respectively, left and right eigenvector of H and that λ is an eigenvalue.

If $H = H^+ \longrightarrow$ At the cond. of stationary $\begin{cases} \lambda = \lambda^+ \\ |\varphi\rangle = |\psi\rangle \end{cases}$

But it is useful to treat φ and ψ as independent fcns.

We choose trial fcns. for φ and ψ

$$\varphi = \varphi(\alpha_1, \alpha_2 \cdots \alpha_n)$$

$$\psi = \psi(\beta_1, \beta_2 \cdots \beta_n)$$

$\longrightarrow$ We vary these parameters to find the stationary points of $\mathcal{L}$ $\longrightarrow$ we can find approxs. to the eigenvalues of H.

In general, these stationary points are neither maxima nor minima.

They are inflection points (saddle points) in very high dimensional space.

Variational Theorem:

If $H = H^+$ and E_0 is the lowest eigenvalue of H, $\xrightarrow{\text{then}}$

$\forall \psi$ we have $E_0 \leq \dfrac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$

Proof: $|\psi\rangle = \sum_n |\psi_n\rangle\langle\psi_n|\psi\rangle$

where $H|\psi_n\rangle = E_n|\psi_n\rangle$

$$\langle\psi|H|\psi\rangle = \sum_n E_n |\langle\psi|\psi_n\rangle|^2 \geq E_0 \sum_n |\langle\psi|\psi_n\rangle|^2 = E_0 \langle\psi|\psi\rangle$$

The equality sign holds when $|\psi\rangle = |\psi_k\rangle$, and $\langle\psi|\psi_n\rangle = 0$ except for $n=k$

Procedure:

1- Choose a trial func. $\psi(\alpha_1, \alpha_2 \cdots \alpha_n)$

2- Find the Min. of $\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ by varying the parameters

A common type of variational trial func.:

$$|\psi^{Var}\rangle = \sum_{n=1}^{N} a_n |n\rangle$$

$$\mathcal{L} = \langle\psi^{Var}|(H-E)|\psi^{Var}\rangle = \sum_n \sum_m a_n^* a_m \langle n|H|m\rangle - E\sum a_n^* a_n$$

$$\frac{\partial \mathcal{L}}{\partial a_j^*} = 0 \quad j=1,\cdots N \longrightarrow \sum_m \langle j|H|m\rangle a_m = E a_j \qquad (1)$$

$$\frac{\partial \mathcal{L}}{\partial a_j} = 0 \quad j=1,\cdots N$$

This cods. due to ($H=H^\dagger$) lead to the complex conjugate of (1) $\longrightarrow$ give no extra information.

Note: a_j and a_j^* may be considered as indep. parameters

Since $a_j = (\alpha + i\beta)_j$:

$$(1) \rightarrow \sum_m H_{jm} a_m = E a_j \longrightarrow \begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & & & \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$$

Indeed this is nothing but the original eigenvalue eqn. $H|\psi\rangle = E|\psi\rangle$ truncated to the N-dim. subspace in which the variational func. $|\psi^{var}\rangle$ has been confined.

The lowest eigenvalue of the N×N matrix will be an upper bound for the true E_0. (But the sign of the error in the other approximate eigenvalues is unknown)

The accuracy:

$$E_n^{var} = \frac{\langle \psi^{var}|H|\psi^{var}\rangle}{\langle \psi^{var}|\psi^{var}\rangle}$$

Assume $|\psi^{var}\rangle = |\psi_n\rangle + |\epsilon\rangle$

$|\psi_n\rangle$: true eigenvector

$|\epsilon\rangle$: error vector

and assume $\langle \psi^{var}|\psi^{var}\rangle = \langle \psi_n|\psi_n\rangle = 1$

$$E_n^{var} = \langle \psi^{var}|H|\psi^{var}\rangle = \langle \psi_n|H|\psi_n\rangle + \langle \epsilon|H|\psi_n\rangle + \langle \psi_n|H|\epsilon\rangle + \langle \epsilon|H|\epsilon\rangle$$

$$= E_n + E_n\{\langle \epsilon|\psi_n\rangle + \langle \psi_n|\epsilon\rangle + O(\epsilon^2)\}$$

The appearance that there are both first and second order terms in ϵ is deceptive.

From normalization;

$$\langle \psi^{var}|\psi^{var}\rangle = \langle \psi_n|\psi_n\rangle + \langle \epsilon|\psi_n\rangle + \langle \psi_n|\epsilon\rangle + \langle \epsilon|\epsilon\rangle$$

$$1 = 1 + \langle \epsilon|\psi_n\rangle + \langle \psi_n|\epsilon\rangle + \langle \epsilon|\epsilon\rangle$$

$$\underbrace{\langle \epsilon|\psi_n\rangle + \langle \psi_n|\epsilon\rangle}_{\text{sum is of order 2 in } \epsilon} = -\langle \epsilon|\epsilon\rangle$$

$\longrightarrow$ Relatively <u>poor</u> trial wave func. can give a <u>fairly</u> good energy estimate for the <u>ground</u> state.

<u>Ex.</u> The Hydrogen Atom Ground state (exactly solvable):

$$H = -\frac{p^2}{2\mu} - \frac{e^2}{r}$$

$\psi(r) = e^{-r/a}$ trial func.

$$\langle H\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{K+P}{N}$$

$K = \langle\psi|p^2|\psi\rangle/2\mu$ $\qquad P = -\langle\psi|\frac{e^2}{r}|\psi\rangle$, $N = \langle\psi|\psi\rangle$

$$N = \int |\psi(r)|^2 d^3r = 4\pi \int_0^\infty e^{-2r/a} r^2 dr = \pi a^3$$

$$K = \frac{1}{2\mu}\left(\langle\psi|\bar{p}\right)\cdot\left(\bar{p}|\psi\rangle\right) = \frac{1}{2\mu}\left(\langle\psi|-i\hbar\nabla\right)\cdot\left(-i\hbar\nabla|\psi\rangle\right)$$

$$= \frac{\hbar^2}{2\mu}\int \left|\frac{\partial\psi}{\partial r}\right|^2 d^3r = \frac{\hbar^2 4\pi}{2\mu a^2}\int_0^\infty e^{-2r/a} r^2 dr = \frac{\hbar^2 \pi a}{2\mu}$$

$$P = -\int |\psi|^2 \frac{e^2}{r} d^3r = -e^2 4\pi \int_0^\infty e^{-2r/a} r\, dr = -\pi e^2 a^2$$

$$\rightarrow \langle H\rangle = \frac{\hbar^2}{2\mu a^2} - \frac{e^2}{a}$$

$$\frac{\partial \langle H \rangle}{\partial a} = 0 \rightarrow a = \frac{\hbar^2}{\mu e^2} \rightarrow \langle H \rangle_{min} = -\frac{\mu e^4}{2\hbar^2}$$

This is the exact value of the grand state energy of the Hydrogen atom.

The reason: $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \sim \psi(r) = e^{-r/a}$

exact trial

a_0 : Bohr radius

a : Variational parameter

Variational calculations of the Hydrogen Atom Ground state

$\psi(r)$	$Ce^{-r/a}$	$C(r^2+a^2)^{-1}$	$Cre^{-r/a}$
$\langle H \rangle_{min}/\lvert E_{100} \rvert$	-1	-0.81	-0.75
$1 - \lvert\langle \psi \lvert \psi_{100} \rangle\rvert^2$	0	0.21	0.05

The table shows, in order to get a good approximate energy, it is more important for the state func. to be accurate at small distances than large distances

$Cre^{-r/a}$: not accurate near $r = 0$

Although the variational theorem applies to the lowest eigenvalue, it is possible to generalize it to calculate low-lying excited states.

Suppose we wish to calculate the excited state eigenvalue $E_{m'}$

If we can constrain the trial func. $|\psi\rangle$ to satisfy;

$$\langle\psi|\psi_{n'}\rangle = 0 \qquad \forall n' \text{ such that } E_{n'} < E_m$$

$$\longrightarrow \langle\psi|H|\psi\rangle \leq E_m \sum_n |\langle\psi|\psi_n\rangle|^2 = E_m\langle\psi|\psi\rangle$$

$\longrightarrow$ We can calculate E_m by minimizing;

$$\langle H\rangle \equiv \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

Subject to the constraint that $|\psi\rangle$ be orthogonal to all state funcs. at energies lower than E_m.

This is easy to do if the constraint can be ensured by symmetry.

Ex. Central Pot.

$$\psi \sim Y_\ell^m(\theta,\varphi)$$

For a certain n (Principle number) we can calculate the lowest energy level for each ℓ with no more difficulty.
But if the upper and lower states have the same symmetry (same Y_ℓ^m) as do the 1s and 2s states, the orthogonality constraint is not so trivial to impose.

Ex: $V = \begin{cases} 0 & |x| < a \\ \infty & |x| > a \end{cases}$

$\rightarrow \begin{cases} \langle x|\psi\rangle = \psi(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{\pi x}{2a}\right) \\ E_0 = \left(\frac{\hbar^2}{2m}\right)\left(\frac{\pi^2}{4a^2}\right) \end{cases}$ exact Sol.

Solving by variational method;

$\psi(x) = a^2 - x^2$ trial $\longrightarrow \begin{cases} \psi(x) = 0 \text{ at } x = \pm a \\ \psi(x) \sim \text{Cte} \times \end{cases}$

$$\langle H\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\left(-\frac{\hbar^2}{2m}\right)\int_{-a}^{a}(a^2-x^2)\frac{d^2}{dx^2}(a^2-x^2)\,dx}{\int_{-a}^{a}(a^2-x^2)\,dx}$$

$$= \left(\frac{10}{\pi^2}\right)\left(\frac{\pi^2\hbar^2}{8a^2m^2}\right) \simeq 1.01132\,E_0 \qquad (1.3\% \text{ deviation})$$

A more sophisticated trial wave fun.;

$$\langle x|\psi\rangle = \psi(x) = |a|^\lambda - |x|^\lambda$$

$$\rightarrow \langle H\rangle = \left[\frac{(\lambda+1)(2\lambda+1)}{(2\lambda-1)}\right]\left(\frac{\hbar^2}{4m^2a^2}\right)$$

$$\frac{\partial\langle H\rangle}{\partial\lambda} = 0 \rightarrow \lambda = \frac{(1+\sqrt{6})}{2} \simeq 1.72$$

$$\langle H\rangle_{min} = \left(\frac{5+2\sqrt{6}}{\pi^2}\right)E_0 = 1.002981\,E_0 \qquad (0.3\% \text{ deviation})$$

An estimate;

A sum $\psi(x)$ is normalized. Ground state — due to parity cons.

$$\langle H\rangle_{min} = \sum_{k=0} |\langle k|\psi\rangle|^2 E_k = |\langle 0|\psi\rangle|^2 E_0 + \overset{0}{|\langle 1|\psi\rangle|^2 E_1} + |\langle 2|\psi\rangle|^2 E_2 + \ldots$$

↑ second excited state

where we have used $|\psi\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\psi\rangle$ → neglecting the other terms

$$\langle H\rangle_{min} \geq |\langle 0|\psi\rangle|^2 E_0 + 9E_0\left(1 - |\langle 0|\psi\rangle|^2\right) \quad |\langle 0|\psi\rangle|^2 \geq \frac{9E_0 - \langle H\rangle_{min}}{8E_0} = 0.99963$$

$\langle 0|\psi\rangle = \cos\theta \rightarrow \theta \leq 1.1° \rightarrow |0\rangle$ and $|\psi\rangle$ nearly parallel — (Departure from unity → $|\psi\rangle$ has a component in a dir orthogonal to $|\psi\rangle$)

Time Dependent Potentials – The Interaction Picture;

i) In Time-indep. perturbation Theory: $\frac{\partial H}{\partial t} = 0$

ii) " " -dep " " $\frac{\partial H}{\partial t} \neq 0$

In the later case H can be split into two parts:

$$H = H_0 + V(t)$$

where $\frac{\partial H_0}{\partial t} = 0$

The prob. for $V(t) = 0$ is assumed to be solved:

$$H_0 |n\rangle = E_n |n\rangle$$

Suppose, in the <u>absence</u> of $V(t)$, the state is populated in <u>only one</u> of the energy eigenstates of H_0, for example $|i\rangle$.

As t increases ⟶ States other than $|i\rangle$ are populated because of $V(t) \neq 0$

⟶ We are <u>no longer</u> dealing with <u>stationary</u> problems.

⟶ The Time-evolution Op. is <u>no longer</u> as simple as $e^{-i\frac{Ht}{\hbar}}$ when H itself involves time.

$V(t)$ $\xrightarrow{\text{Can Cause}}$ transitions to states other than $|i\rangle$

Question; ?

What is the probability as a func. of time for the syste to be found in $|n\rangle$ with $n \neq i$?

Suppose at $t = 0$

$$|\alpha\rangle_S = \sum_n C_n(0)\,|n\rangle$$

We wish to find $C_n(t)$ for $t > 0$ such that;

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

Note that; if $V(t) = 0$, then

$$|\alpha, t_0 = 0, t\rangle_S = \sum_n C_n(0)\, e^{-E_n t/\hbar}\, |n\rangle$$

The probability of finding $|n\rangle$ is found by evaluating $|C_n(t)|^2$.

$\rightarrow$ time-dep. of $C_n(t)$ is due to $V(t)$

The Interaction Picture – Dirac Picture;

Suppose an arbitrary state ket in the Schrödinger picture;

$|\alpha\rangle_S$ at $t = t_0$ (often take $t_0 = 0$)

$|\alpha, t_0, t\rangle_S$ at $t = t$

We define interaction picture;

$$|\alpha, t_0, t\rangle_I = e^{iH_0 t/\hbar} |\alpha, t_0, t\rangle_S$$

The matrix element of an arbitrary op. A_S in the interaction picture;

$$\underset{S}{\langle}\alpha, t_0, t | A_S | \alpha, t_0, t\underset{S}{\rangle} = \underset{I}{\langle}\alpha, t_0, t | e^{iH_0 t/\hbar} A_S e^{-iH_0 t/\hbar} |\alpha, t_0, t\underset{I}{\rangle}$$

suggests that;

$$A_I = e^{iH_0 t/\hbar} A_S e^{-iH_0 t/\hbar}$$

In particular;

$$V_I = e^{iH_0 t/\hbar} V_S e^{-iH_0 t/\hbar}$$

Now;

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0, t\rangle_I = i\hbar \frac{\partial}{\partial t} \left(e^{iH_0 t/\hbar} |\alpha, t_0, t\rangle_S \right)$$

$$= -H_0 e^{iH_0 t/\hbar} |\alpha, t_0, t\rangle_S + i\hbar e^{iH_0 t/\hbar} \frac{\partial}{\partial t} |\alpha, t_0, t\rangle_S$$

$$= -H_0 e^{iH_0 t/\hbar} |\alpha, t_0, t\rangle_S + e^{iH_0 t/\hbar} (H_0 + V_S) |\alpha, t_0, t\rangle_S$$

$$= e^{iH_0 t/\hbar} V |\alpha, t_0, t\rangle_S$$

$$= e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} |\alpha, t_0, t\rangle_I$$

$$= V_I |\alpha, t_0, t\rangle_I$$

$$\longrightarrow \quad i\hbar \frac{\partial}{\partial t} |\alpha, t_0, t\rangle_I = V_I |\alpha, t_0, t\rangle_I$$

This is Schrödinger-like equ. with the total H replaced by V_I.

$\longrightarrow$ $|\alpha, t_0, t\rangle_I$ would be a ket <u>fixed</u> in time if V_I were <u>absent</u>.

Now, $$\frac{dA_I}{dt} = \frac{d}{dt} \left(e^{iH_0 t/\hbar} A_S e^{-iH_0 t/\hbar} \right)$$

$$= \frac{i}{\hbar} H_0 e^{iH_0 t/\hbar} A_S e^{-iH_0 t/\hbar} + e^{iH_0 t/\hbar} \frac{\partial A_S}{\partial t} e^{-iH_0 t/\hbar} - \frac{i}{\hbar} e^{-iH_0 t/\hbar} A_S \underbrace{H_0 e^{-iH_0 t/\hbar}}$$

If $\frac{\partial A_S}{\partial t} = 0$

$$\longrightarrow \quad \frac{dA_I}{dt} = \frac{1}{i\hbar}[A_I, H_0]$$

which is Heisenberg like eqn. with H replaced by H_0.

	Heisenberg Picture	Interaction Picture	Schrödinger Picture
State Ket $\|\rangle$ (Evolution)	$\frac{\partial \|\rangle_H}{\partial t} = 0$	$i\hbar \frac{\partial}{\partial t}\|\rangle_I = V_I \|\rangle_I$	$i\hbar \frac{\partial}{\partial t}\|\rangle_S = H\|\rangle_S$
Observable A (Evolution)	$e^{iHt/\hbar} A_S e^{-iHt/\hbar}$	$e^{iH_0t/\hbar} A_S e^{-iH_0t/\hbar}$	$\frac{\partial A_S}{\partial t} = 0$

In the interaction picture we continue using $|n\rangle$ as our base kets

$$\longrightarrow \quad |\alpha, t_0, t\rangle_I = \sum_n C_n(t)\,|n\rangle$$

With $t_0 = 0$, we see that $C_n(t)$ appearing here are the same as $C_n(t)$ introduced in

$$|\alpha, t_0 = 0, t\rangle_S = \sum_n C_n(t)\, e^{-iE_nt/\hbar}\,|n\rangle$$

because, multiplying of both sides of this eqn by $e^{iH_0t/\hbar}$ yields;

$$e^{iH_0 t/\hbar} |\alpha, t_0=0, t\rangle_S = \sum_n C_n(t)\, e^{-iE_n t/\hbar}\, e^{iH_0 t/\hbar} |n\rangle$$

$$\longrightarrow |\alpha, t_0=0, t\rangle_I = \sum_n C_n(t) |n\rangle \qquad (1)$$

Now;

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0, t\rangle_I = V_I |\alpha, t_0, t\rangle_I$$

$$i\hbar \frac{\partial}{\partial t} \langle n|\alpha, t_0, t\rangle_I = \langle n| V_I |\alpha, t_0, t\rangle$$

$$= \sum_m \langle n| V_I |m\rangle \langle m|\alpha, t_0, t\rangle_I$$

but $\langle n| V_I |m\rangle = \langle n| e^{iH_0 t/\hbar} V_S e^{-iH_0 t/\hbar} |m\rangle$

$$= \langle n| V_S |m\rangle\, e^{i(E_n - E_m)t/\hbar} = V_{nm}(t)\, e^{i(E_n - E_m)t/\hbar}$$

$$\longrightarrow \langle n| V_I |m\rangle = V_{nm}(t)\, e^{i\omega_{nm} t}$$

where $\omega_{nm} \equiv \frac{E_n - E_m}{\hbar} = -\omega_{mn}$

Since: $C_n(t) = \langle n|\alpha, t_0, t\rangle_I$ (from (1))

$$\longrightarrow i\hbar \frac{d}{dt} C_n(t) = \sum_m V_{nm}(t)\, e^{i\omega_{nm} t}\, C_m(t)$$

Explicitly:

$$i\hbar \begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \\ \vdots \\ \vdots \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & \cdots & \cdots \\ V_{21}e^{i\omega_{21}t} & V_{22} & \cdots & \cdots \\ \cdots & \cdots & V_{33} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ \vdots \\ \vdots \end{pmatrix}$$

This is the basic coupled differential eqn that must be solved to obtain the probability of finding $|n\rangle$ as a func. of t.

Time-dep. Two-state Prob.:

This Prob. has exact s.l.

$(E_2 > E_1)$

$$H_0 = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2|$$

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

where $\gamma > 0 \quad \omega > 0$

we had; $|\alpha, t_0; t\rangle_I = \sum_n C_n(t) |n\rangle$

$$\rightarrow i\hbar \frac{\partial}{\partial t} \langle n|\alpha, t_0; t\rangle_I = \sum_m \langle n|V_I|m\rangle \langle m|\alpha, t_0; t\rangle_I$$

$$\langle n| e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} |m\rangle = V_{nm}(t) e^{i(E_n - E_m)t/\hbar}$$

ad. $C_n(t) = \langle n|\alpha, t_0; t\rangle$

$$i\hbar \frac{d}{dt} C_n(t) = \sum_m V_{nm} e^{i\omega_{nm} t} C_m(t)$$

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar} = -\omega_{mn}$$

$$i\hbar \begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12} e^{i\omega_{12} t} \\ V_{21} e^{i\omega_{21} t} & V_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad \text{(in our case)}$$

$$V_{12} = V_{21}^* = \gamma e^{i\omega t}$$

$$V_{11} = V_{22} = 0$$

Because for example; $V_{12} = \langle 1| \left(\gamma e^{i\omega t} |1\rangle\langle 2| + \gamma e^{-i\omega t} |2\rangle\langle 1| \right) |2\rangle$

$$= \gamma e^{i\omega t}$$

Therefor, we can have a transition between the two-states

$|1\rangle \rightleftarrows |2\rangle$

suppose at $t=0$, $C_1(0)=1$, $C_2(0)=0$

It can be shown;

$$|C_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega-\omega_{21})^2/4} \sin^2\left\{\left[\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}\right]^{1/2} t\right\}$$

Rabi's formula

$$|C_1(t)|^2 = 1 - |C_2(t)|^2 \qquad \text{(Prob. 30)}$$

The probability of finding the upper state E_2 exhibits an oscillatory time-dependence with angular frequency,

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

The amplitude of oscillation is very large when;

$$\omega \simeq \omega_{21} = \frac{E_2 - E_1}{\hbar}$$

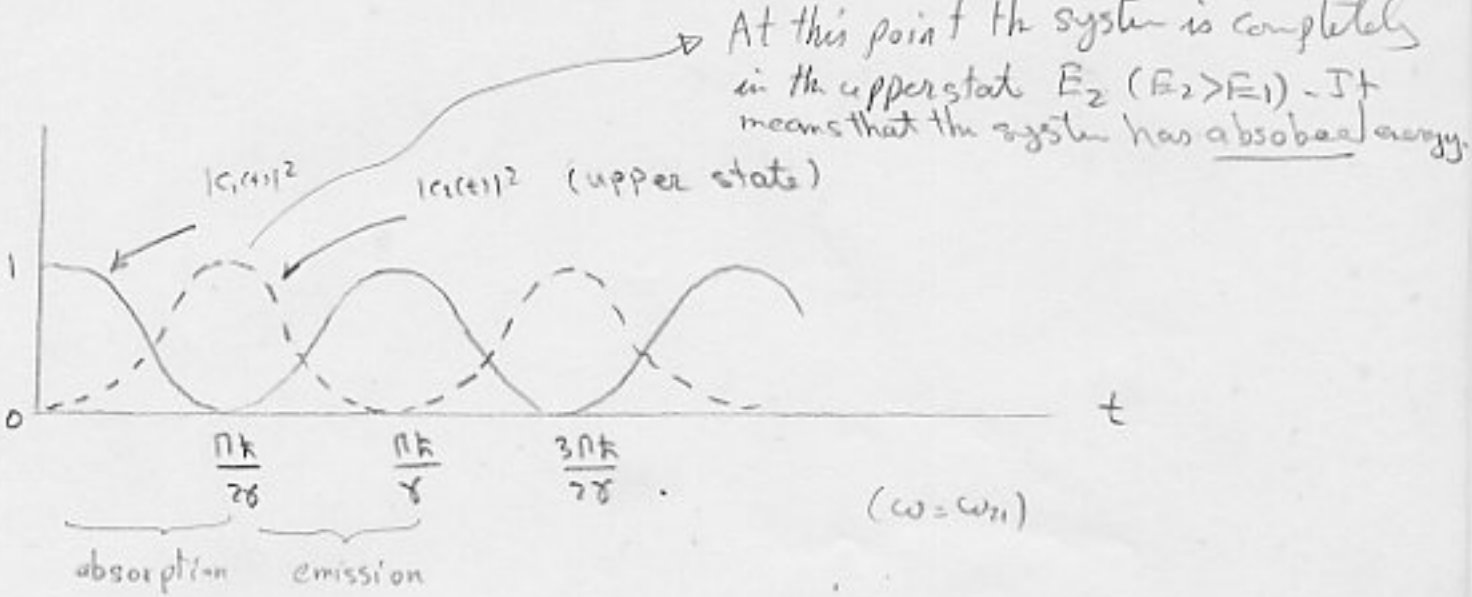
ω : angular frequency of the applied electric or magnetic field

ω_{21} : angular frequency characteristic of the two-state system

At resonance;

$$\omega = \omega_{21} \qquad \Omega = \frac{\gamma}{\hbar}$$

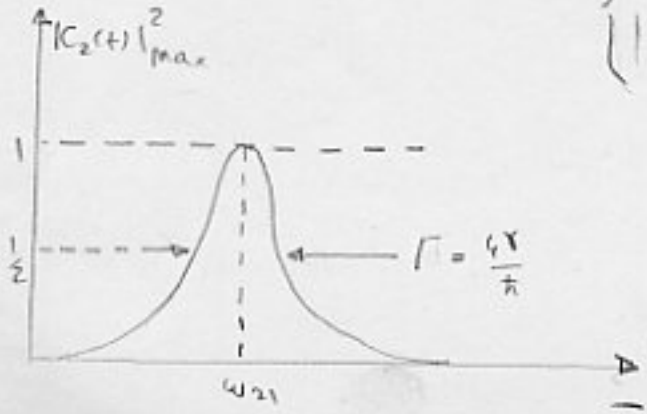
$$|C_2(t)|^2 = \Omega^2 \frac{\gamma}{\hbar} t$$



Absorption of energy by the two-level system from $V(t)$: $t_1 = 0$ to $t_2 = \frac{\pi\hbar}{2\gamma}$

Giving up the excess energy (of the excited (upper) state) to $V(t)$: $t_2 = \frac{\pi\hbar}{2\gamma}$ to $t_3 = \frac{\pi\hbar}{\gamma}$

If $\omega_{21} \neq \omega \longrightarrow \begin{cases} |C_2(t)|^2_{max} < 1 \\ |C_1(t)|^2_{min} > 0 \end{cases}$



Ex.- Spin Magnetic Resonance:

Consider a spin $\frac{1}{2}$ system, say a bound electron subjected to a t-indep. uniform magnetic field in the z-dir. and in addition, a t-dep. magnetic field rotating in the xy-plane.

$$\mathbf{B} = B_0 \hat{z} + B_1 (\hat{x} \cos\omega t + \hat{y} \sin\omega t)$$

Since $\mu = \frac{e}{m_e c} S$

and $S_z = \frac{\hbar}{2} [|+\rangle\langle +1| - |-\rangle\langle -1|]$

$$S_+ = \hbar\, |+\rangle\langle -1|$$
$$S_- = \hbar\, |-\rangle\langle +1|$$

$$S_\pm = S_x \pm i S_y$$

$$H = -\mu \cdot \mathbf{B} = H_0 + V(t)$$

$$\rightarrow H_0 = -\left(\frac{e\hbar B_0}{2 m_e c}\right)\left(|+\rangle\langle +1| - |-\rangle\langle -1|\right)$$

$$V(t) = -\left(\frac{e\hbar B_1}{2 m_e c}\right)\left[\cos\omega t \left(|+\rangle\langle -1| + |-\rangle\langle +1|\right) + \sin\omega t \left(-i|+\rangle\langle -1| + i|-\rangle\langle +1|\right)\right]$$

with $e < 0$ E_+ has a higher energy than E_-.

$\Longrightarrow |+\rangle \to |2\rangle$ upper level

$|-\rangle \to |1\rangle$ lower "

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} = \frac{-\frac{e\hbar B_0}{2mc} - \frac{e\hbar B_0}{2mc}}{\hbar} = -\frac{eB_0}{m_e c}$$

This is just the spin-precession frequency for the $B_0 \neq 0$, $B_1 = 0$ problem.

In this case ($B_0 \neq 0$, $B_1 = 0$), $\langle S_x \rangle$ and $\langle S_y \rangle$ change due to spin-precession in the counterclockwise (seen from the positive z-side), but $|C_+|^2$ and $|C_-|^2$ remain unchanged in the absence of $V(t)$.

If $V(t)$ is present, $|C_+|^2$ and $|C_-|^2$ do change as a func. of t.

In correspondence with the previous discussion:

$$\begin{cases} -\frac{e\hbar B_1}{2mc} \equiv \gamma \\ \omega \equiv \omega \end{cases}$$

$$V(t) = -\gamma \left[+ \cos\omega t \, |+\rangle\langle -| + \cos\omega t \, |-\rangle\langle +| - i \sin\omega t \, |+\rangle\langle -| + i \sin\omega t \, |-\rangle\langle +| \right]$$

$$V(t) = -\gamma \left[e^{-i\omega t} \, |+\rangle\langle -| + e^{i\omega t} \, |-\rangle\langle +| \right]$$

$$V(t) = -\gamma \left[e^{i\omega t} \, |1\rangle\langle 2| + e^{-i\omega t} \, |2\rangle\langle 1| \right]$$

This is exactly of the form we obtained before and the discussion is the same.

Here in addition to spin-precession we have spin-flops ($|+\rangle \rightleftarrows |-\rangle$).

Semiclassically, this is due to the driving torque exerted by rotating $\vec{B}$.

Remark - Spin precession;

Consider a spin $\frac{1}{2}$ system with magnetic moment; $\mu = \frac{e\hbar}{2mc}$ subjected to uniform static magnetic field B;

$$H = -\mu \cdot B = -\frac{e}{mc} S \cdot B$$

If $\vec{B} \parallel \hat{z} \rightarrow H = -\frac{eB}{mc} S_z \rightarrow E_\pm = \mp \frac{e\hbar B}{2mc}$

We define $E_+ - E_- = \hbar\omega \rightarrow \omega \equiv \frac{|e|B}{mc}$

$\rightarrow H = \omega S_z$

The time evolution op. is $U(t,0) = e^{-i\omega S_z t/\hbar}$

Suppose at $t=0$ our state is $|\alpha\rangle = c_+|+\rangle + c_-|-\rangle$

$\rightarrow |\alpha, t_0=0; t\rangle = U(t,0)|\alpha\rangle$

$$|\alpha, t_0=0; t\rangle = c_+ e^{-\frac{i\omega t}{2}} |+\rangle + c_- e^{\frac{i\omega t}{2}} |-\rangle \quad (1)$$

where we have used $H|\pm\rangle = \pm\frac{\hbar\omega}{2}|\pm\rangle$

If at $t=0$, $c_+ = 1$, $c_- = 0$ (spin up)

eqn (1) tells us, the state $|\alpha\rangle$ remains s_z (spin up) at a later time. There is no surprise, because this is a stationary system.

Next suppose the system is in one of the following states:

since $\begin{cases} |S_x;\pm\rangle = \frac{1}{\sqrt{2}}(|+\rangle \pm |-\rangle) \\ |S_y;\pm\rangle = \frac{1}{\sqrt{2}}(|+\rangle \pm i|-\rangle) \end{cases}$

$$|B\rangle = |S_x,+\rangle = \frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}|-\rangle \rightarrow \begin{cases} c_+ = \frac{1}{\sqrt{2}} \\ c_- = \frac{1}{\sqrt{2}} \end{cases}$$

The probability of the system at t to be in the $|S_x,\pm\rangle$ is;

$$|\langle S_x,\pm|\alpha,t_0=0,t\rangle|^2 = \left|\left[\frac{1}{\sqrt{2}}\langle+| \pm \frac{1}{\sqrt{2}}\langle-|\right]\left[\frac{1}{\sqrt{2}}e^{-\frac{i\omega t}{2}}|+\rangle + \frac{1}{\sqrt{2}}e^{\frac{i\omega t}{2}}|-\rangle\right]\right|^2$$

$$= \left|\frac{1}{2}e^{-\frac{i\omega t}{2}} \pm \frac{1}{2}e^{\frac{i\omega t}{2}}\right|^2$$

$$= \begin{cases} \sin^2\frac{\omega t}{2} & \text{for } S_x+ \\ \cos^2\frac{\omega t}{2} & \text{"} \quad S_x- \end{cases}$$

Even though the spin is initially in the <u>x-positive</u> direction, the magnetic field in z-dir causes it to <u>rotate</u>.
We obtain a <u>finite</u> probability for finding $|S_x-\rangle$ at some later time.

Using $\langle A\rangle = \sum_{a'}\sum_{a''}\langle\alpha|a'\rangle\langle a''|A|a'\rangle\langle a'|\alpha\rangle = \sum_{a'} a'|\langle a'|\alpha\rangle|^2$

$$\langle S_x\rangle = \frac{\hbar}{2}\sin^2\frac{\omega t}{2} - \frac{\hbar}{2}\cos^2\frac{\omega t}{2} = \frac{\hbar}{2}\sin\omega t$$

$$\langle S_y\rangle = \frac{\hbar}{2}\sin\omega t$$

$$\langle S_z\rangle = 0$$

<u>Physically</u> ⇒ The spin precesses in the x-y plane.

5-6 Time-Dependent Perturbation Theory

Dyson Series;

Exact sols. to the differential eqn. for $C_n(t)$ are usually not available.

⟶ We must be content with approx. sol. to;

$$i\hbar \frac{d}{dt} C_n(t) = \sum_m V_{nm} e^{i\omega_{nm}t} C_m(t)$$

obtained by perturbation expansion;

$$C_n(t) = C_n^0 + C_n^1 + C_n^2 + \cdots$$

Where $C_n^1, C_n^2 \cdots$ signify amplitudes of first order, second order, and so on, in the stregth parameter of the time-dep. potential. $C_i^0 = \delta_{ni}$ (t-indep)

We use, itteration method;

The time-evolution op. in the interaction picture is defined by;

$$|\alpha, t_0, t\rangle_I = U_I(t, t_0) |\alpha, t_0, t_0\rangle_I$$

We obtained $i\hbar \frac{\partial}{\partial t} |\alpha, t_0, t\rangle_I = V_I |\alpha, t_0, t\rangle_I$

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0, t\rangle_I = i\hbar \left(\frac{\partial}{\partial t} U_I(t,t_0)\right) |\alpha, t_0, t_0\rangle_I + i\hbar U_I(t,t_0) \frac{\partial}{\partial t} |\alpha, t_0, t_0\rangle_I$$

$$\rightarrow i\hbar \frac{\partial}{\partial t} |\alpha, t_0, t\rangle_I = i\hbar \left(\frac{\partial}{\partial t} U_I(t,t_0)\right) |\alpha, t_0, t_0\rangle_I$$

$$\rightarrow i\hbar \left(\frac{\partial}{\partial t} U_I(t,t_0)\right) |\alpha, t_0, t_0\rangle_I = V_I U_I(t,t_0) |\alpha, t_0, t_0\rangle_I \quad \forall |\alpha, t_0, t_0\rangle_I$$

$$\rightarrow i\hbar \frac{d}{dt} U_I(t,t_0) = V_I(t) U_I(t,t_0)$$

We must solve this operator differential equ., subject to the initial cond.:

$$U_I(t,t_0)\Big|_{t=t_0} = \mathbb{I}$$

$$d U_I(t,t_0) = -\frac{i}{\hbar} V_I(t) U_I(t,t_0) dt$$

$$\rightarrow U_I(t,t_0) - U_I(t_0,t_0) = -\frac{i}{\hbar} \int_{t_0}^{t} V_I(t') U_I(t',t_0) dt'$$

$$U_I(t,t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} V_I(t') U_I(t',t_0) dt'$$

$$U_I(t,t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} V_I(t') \left[1 - \frac{i}{\hbar} \int_{t_0}^{t'} V_I(t'') U_I(t'',t_0) dt''\right] dt'$$

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt' V_I(t') + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' V_I(t') V_I(t'')$$

$$+ \cdots + \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \cdots \int_{t_0}^{t^{(n-1)}} dt^{(n)} V_I(t') V_I(t'') \cdots V_I(t^{(n)})$$

$$U_I(t,t_0) = 1 + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n V_I(t_1) \cdots V_I(t_n)$$

This series is known as the Dyson Series

I) $U_I = I$

II) $U_I = I - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')dt'$

III) - - - -

Transition Probability:

Once $U_I(t,t_0)$ is given $\xrightarrow{\text{we can predict}}$ time-development of any state ket.

For example, if, at $t_0 = 0$, the initial state is one of the eigenstates of H_0 (say $|i\rangle$), then;

$$|i, t_0, t\rangle_I = U_I(t,t_0)|i\rangle$$

$$|i, t_0 = 0, t\rangle_i = U_I(t,0)|i\rangle = \sum_n |n\rangle\langle n|U_I(t,0)|i\rangle$$

Comparing with $|\alpha, t_0, t\rangle_I = \sum_n C_n(t)|n\rangle$

$$C_n(t) = \langle n|U_I(t,0)|i\rangle$$

Now let us find the connection between $U_I(t,t_0)$ and $U(t,t_0)$.

$$|\alpha,t_0,t\rangle_I = e^{iH_0t/\hbar}|\alpha,t_0,t\rangle_S = e^{iH_0t/\hbar}U(t,t_0)|\alpha,t_0,t_0\rangle_S$$

$$= e^{iH_0t/\hbar}U(t,t_0)e^{-iH_0t_0/\hbar}|\alpha,t_0,t_0\rangle_I$$

$$\longrightarrow U_I(t,t_0) = e^{iH_0t/\hbar}U(t,t_0)e^{-iH_0t_0/\hbar}$$

Then;

$$\langle n|U_I(t,t_0)|i\rangle = e^{i(E_nt-E_it_0)/\hbar}\langle n|U(t,t_0)|i\rangle$$

$\langle n|U(t,t_0)|i\rangle$ is defined as <u>transition amplitude</u>.

$\langle n|U_I(t,t_0)|i\rangle$ is not quite the same as the transition amplitude defined above.

However the <u>transition probability</u> is the <u>same</u> as the analogous quantity in the interaction picture.

$$|\langle n|U_I(t,t_0)|i\rangle|^2 = |\langle n|U(t,t_0)|i\rangle|^2$$

We may remark that, <u>in general</u>;

$$|\langle b'|U_I(t,t_0)|a'\rangle| \neq |\langle b'|U(t,t_0)|a'\rangle|$$

where $|a'\rangle$ and $|b'\rangle$ are not energy eigenstates.

Remark: For example;

$|a'\rangle = a|+\rangle + b|-\rangle$

$|b'\rangle = c|+\rangle$

$\langle b'|U_I(t,t_0)|a'\rangle =$

$ae^{i(E_+t-E_+t_0)/\hbar}\langle +|U(t,t_0)|+\rangle +$

$be^{i(E_+t-E_-t_0)/\hbar}\langle +|U(t,t_0)|-\rangle$

while: $\langle b'|U(t,t_0)|a'\rangle =$

$a\langle +|U(t,t_0)|+\rangle + b\langle +|U(t,t_0)|-\rangle$

$A|a'\rangle = a'|a'\rangle$, $B|b'\rangle = b'|b'\rangle$

but $[H_0, A] \neq 0$ and/or $[H_0, B] \neq 0$

Fortunately in problems where the interaction picture is found to be useful the states are usually taken to be H_0 eigenstates.

Otherwise, we have to expand $|a'\rangle$ and $|b'\rangle$ and so on in terms of energy eigenkets of H_0.

Now, consider at $t = t_0$ the state to be $|i\rangle$;

The state ket in schrödinger picture $|i, t_0, t_0\rangle$, is equal to state $|i\rangle$ up to a phase factor.

In applying the interaction picture, it is convenient to choose the phase-factor at $t = t_0$, so that:

$$|i, t_0, t_0\rangle_S = e^{-iE_i t_0/\hbar} |i\rangle$$

then $|i, t_0, t_0\rangle_I = e^{iH_0 t_0/\hbar} |i, t_0, t_0\rangle_S = |i\rangle$

At a later time; $|i, t_0, t\rangle_I = U_I(t, t_0)|i\rangle$

Comparing with expansion:

$$|i, t_0, t\rangle_I = \sum_n C_n(t)\,|n\rangle$$

$$\longrightarrow \quad C_n(t) = \langle n|\, U_I(t,t_0)\,|i\rangle$$

Where we remember;

$$U_I(t,t_0) = I + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n\, V_I(t_1) \cdots V_I(t_n)$$

Also $\quad C_n(t) = C_n^0 + C_n^1 + C_n^2 + \cdots$

Comparing these results:

$$C_n^0(t) = \delta_{ni} \qquad (t\text{-indep.})$$

$$C_n^1(t) = -\frac{i}{\hbar}\int_{t_0}^{t} \langle n|\, V_I(t')\,|i\rangle\, dt' = -\frac{i}{\hbar}\int e^{i\omega_{ni}t'}\, V_{ni}(t')\,dt'$$

$$C_n^2(t) = \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, e^{i\omega_{nm}t'}\, V_{nm}(t')\, e^{i\omega_{mi}t''}\, V_{mi}(t'')$$

---

where $e^{i(E_n - E_i)t/\hbar} = e^{i\omega_{ni}t}$

and $\quad V_{ni}(t) = \langle n|\, V(t)\,|i\rangle$

The transition probability for $|i\rangle \longrightarrow |n\rangle$ with $n \neq i$ is obtained by

$$P(i \to n) = |C_n^1 + C_n^2 + \cdots|^2$$

Constant Perturbation:

Consider a const. Perturbation turned on at $t=0$:

$$V(t) = \begin{cases} 0 & \text{for } t<0 \\ V & " \quad t \geq 0 \end{cases} \qquad (t\text{-indep.})$$

where in general $V = V(X, P, S)$

Suppose at $t=0$, we have only state $|i\rangle$, with $t_0 = 0$

$$C_n^0 = C_n^0(0) = \delta_{ni}$$

$$C_n'(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega_{ni}t'} V_{ni}\, dt' = -\frac{i}{\hbar} V_{ni}\int_0^t e^{i\omega_{ni}t'} dt'$$

$$= -\frac{i}{\hbar} V_{ni}\,\frac{1}{i\omega_{ni}}\left[e^{i\omega_{ni}t}\right]_0^t = \frac{V_{ni}}{E_n - E_i}\left(1 - e^{i\omega_{ni}t}\right)$$

$$C_n'(t) = \frac{V_{ni}}{E_n - E_i}(-2i)\, e^{\frac{i\omega_{ni}t}{2}}\, \sin\frac{\omega_{ni}t}{2}$$

Remark:

$$1 - e^{i\omega_{ni}t} = 1 - \cos\omega_{ni}t - i\sin\omega_{ni}t$$

$$= 2\sin^2\frac{\omega_{ni}t}{2} - 2i\sin\frac{\omega_{ni}t}{2}\cos\frac{\omega_{ni}t}{2}$$

$$(-2i)\sin\frac{\omega_{ni}t}{2}\left(\cos\frac{\omega_{ni}t}{2} + i\sin\frac{\omega_{ni}t}{2}\right)$$

$$\rightarrow \quad |C_n'(t)|^2 = \frac{4\,|V_{ni}|^2}{|E_n - E_i|^2}\sin^2\left(\frac{\omega_{ni}t}{2}\right)$$

The probability of finding $|n\rangle$ depends on $\begin{cases} \text{I} - |V_{ni}|^2 \\ \text{II} - E_n - E_i \end{cases}$

In practice, we are interested of looking at $|C_n'(t)|^2$ when there are many states with:

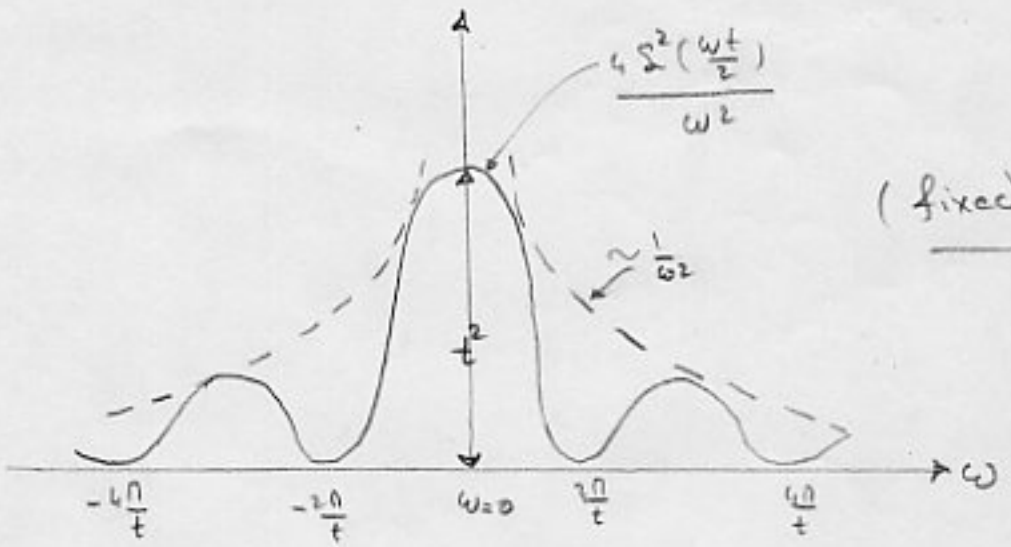
$$E \sim E_n$$

So that we can talk about a continuum of final states with nearly the same energy.
To this end we define;

$$\omega \equiv \frac{E_n - E_i}{\hbar}$$

$$|C_n^{(1)}(t)|^2 = \frac{4|V_{ni}|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega t}{2}\right)}{\omega^2}$$

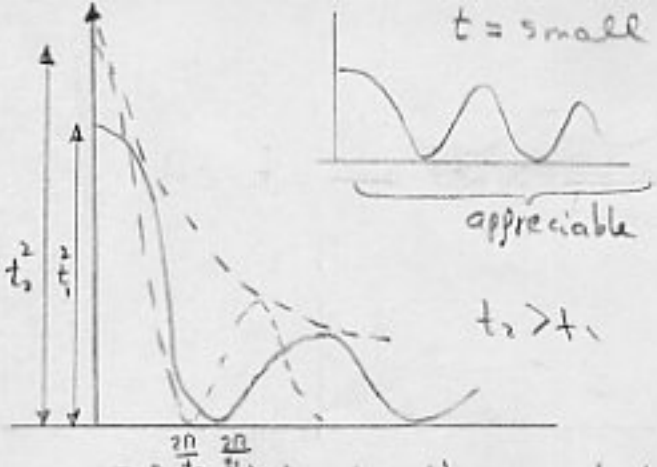
We plot $|C_n^{(1)}(t)|^2$ for a fixed t as a func. of ω ($E_n \sim E$)



$$\frac{4\sin^2\left(\frac{\omega t}{2}\right)}{\omega^2} = t^2 \frac{\sin^2\left(\frac{\omega t}{2}\right)}{\left(\frac{\omega t}{2}\right)^2}$$

As can be seen from the Fig.

The width $\sim \frac{1}{t}$ $\left(\frac{2\pi}{t} - \left(-\frac{2\pi}{t}\right) = \frac{4\pi}{t} \sim \frac{1}{t}\right)$



As $t \to \infty$

$|C_n^{(1)}(t)|^2 \simeq$ small

except:

$|C_n^{(1)}(t)|^2 \not\to$ small for those final states that satisfy $t \sim \frac{2\pi}{|\omega|} = \frac{2\pi\hbar}{|E_n - E_i|}$

(i.e. within $t = 0, \frac{2\pi}{|\omega|}$)

If Δt is the perturbation duration; (turn on time of $V(t)$),

a transition with appreciable probability is possible only if:

$$\Delta t \, \Delta E \sim \hbar$$

where ΔE is the energy change involved in a transition with appreciable probability.

If Δt = small $\to \Delta E$ = large (Γ = large) (energy non conservation)

Now;

I) When the energy is exactly conserved (i.e. $E_n = E_i$)

$$|C_n^{(1)}(t)|^2 = \frac{1}{\hbar^2} |V_{ni}|^2 t^2$$

(due to $\left(\frac{\sin \frac{\omega t}{2}}{\frac{\omega t}{2}} \right) \to 1$ as $\omega \to 0$)

The probability of finding $|n\rangle$ after a time interval t is quadratic, not linear, in the time interval during which $V(t)$ has been on!.

This may appear intuitively unreasonable.

There is no cause for alarm, however.

In a realistic situation, there is usually a group of final states all with nearly the same energy of the initial states $|i\rangle$.

In other words, a final state forms a continuous energy spectrum in the neighborhood of E_i.
(See examples on P269).

Remark:

If Δt = small (Perturbation time) ⟶ we have broader peak

⟶ we can tolerate a fair amount of energy nonconservation.

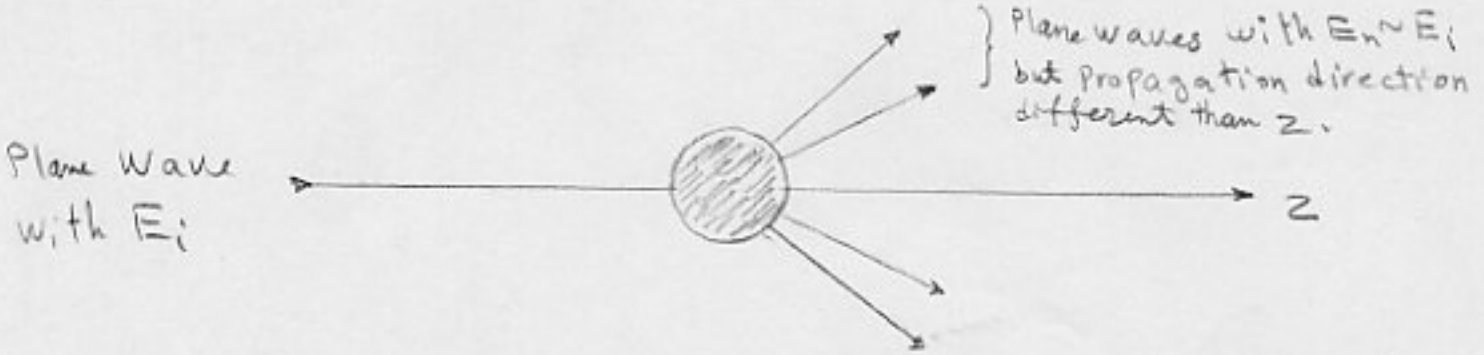
$\Delta t \, \Delta E \sim \hbar$ ⟶ Δt = small ⟶ $\Delta E = E_n - E_i$ = large

On the other hand if Δt = long ⟶ we have narrow peak

⟶ an approximate energy conservation is required for a transition with appreciable probability.

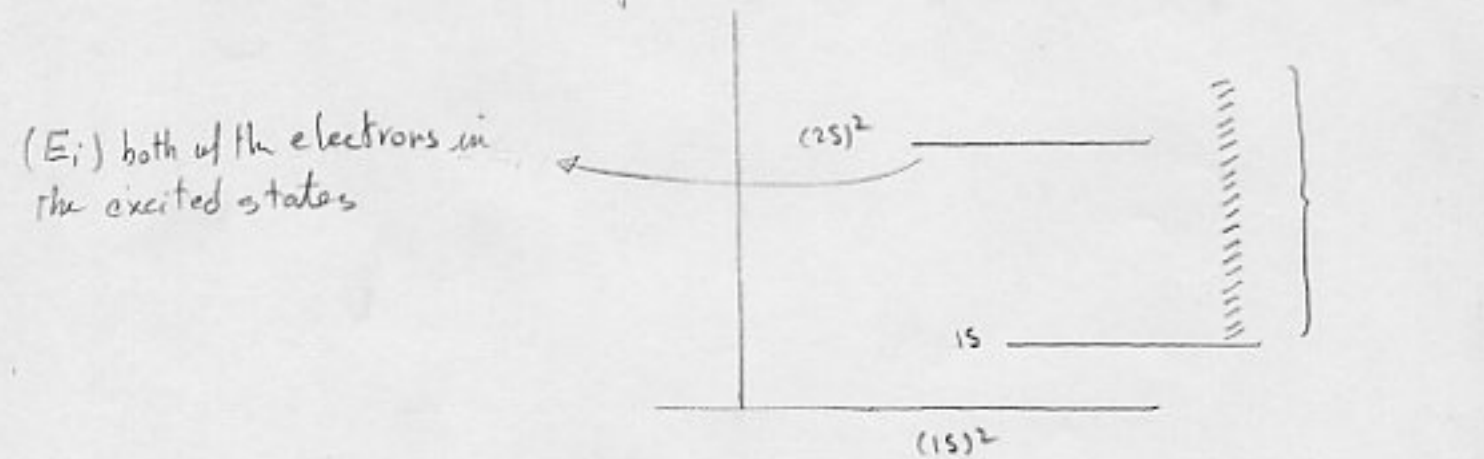
We give two examples along

a) Consider elastic scattering by some finite range potential;



b) Consider de-excitation of an excited atomic state via the emission of an Auger electron.

The simplest example is helium atom.



Initial state: $(2S)^2$ ——→ final state $(1S)$ of He^+ ion + Auger electron with positive energy E (i.e. second electron escapes)

Remark; Auger electron:

An electron in de-excitation instead of emission of a photon gives its energy to an other electron and the electron is ejected.

In such a case we are interested in the Total Probability,

Total transition probability for:

$$|i\rangle \longrightarrow \{|n\rangle\}_{E_n \sim E_i}$$

is $$\sum_{\substack{n \\ E_n \sim E_i}} |C_n'(t)|^2$$

Define the density of final states as a number of states within energy interval $(E, E+dE)$ as

$$\rho(E)\,dE$$

$$\sum_{\substack{n \\ E_n \sim E_i}} |C_n'(t)|^2 \longrightarrow \int dE_n\, \rho(E_n)\, |C_n'(t)|^2$$

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

Since $\lim_{\alpha \to \infty} \frac{1}{\pi} \frac{\Sigma^2 \alpha x}{\alpha x^2} = \delta(x)$

$$\longrightarrow \lim_{t\to\infty} \frac{1}{|E_n - E_i|^2}\, \Sigma^2\left[\frac{(E_n - E_i)t}{2\hbar}\right] = \lim_{t\to\infty} \frac{\Sigma^2\left[\frac{(E_n - E_i)t}{2\hbar}\right]}{\left[\frac{(E_n - E_i)}{2\hbar}\right]^2 t} \frac{t}{(2\hbar)^2}$$

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

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

It is now possible to take the average of $|V_{in}|^2$ outside the integral sign and perform the integration with the δ-func.

$\overline{|V_{ni}|^2}$ → { due to $t \to$ large not ∞ and also all $|n\rangle$ despite have $E_n \simeq E_i$ but can be different }

$$\lim_{t\to\infty} \int dE_n\, \rho(E_n)\, |C_n^{(1)}(t)|^2 = \left(\frac{2\pi}{\hbar}\right) \overline{|V_{ni}|^2}\, \rho(E_n)\, t \Big|_{E \simeq E_i}$$

$\longrightarrow$ Total transition probability $\sim t$

Also from the Fig.:

Probability $\sim$ (area under the Peak) $\sim$ (the height) $\times$ (the width)

$\sim (t^2) \times \left(\frac{1}{t}\right) = t$

The total transition rate $= \frac{d}{dt}\left(\sum_n |C_n^{(1)}(t)|^2\right)$

$$\frac{d}{dt}\left(\sum_n |C_n^{(1)}(t)|^2\right) = \omega_{i\to[n]} = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2}\, \rho(E)_{E_n \simeq E_i}$$

This is Fermi's Golden rule

It is indep. of t, provided the first-order time-dep. perturbation theory is valid.

This is sometimes written as:

$$\omega_{i\to[n]} = \left(\frac{2\pi}{\hbar}\right)|V_{ni}|^2\,\delta(E_n - E_i)$$

Remark: when $t \to$ large, $\delta(E_n - E_i)$ may be chosen to be broader.

where, it must be understood that this expression is integrated with $\int dE_n\,\rho(E_n)$

What is the meaning of $\overline{|V_{ni}|^2}$?

If the final states $|n\rangle$ $\xrightarrow{\text{form}}$ quasi-continuum the matrix elements V_{ni} are often similar if $|n\rangle$ are similar.

However, it may happen that all energy eigekets with the same E_n do not necessarily have similar matrix elements.

For example, in elastic scattering, the $|V_{ni}|^2$ that determines the scattering cross-section, may depend on the final momentum direction.

In such a case the group of final states, we should consider, must have not only approximately the same energy, but they must also have approximately the same momentum direction. (Photoelectric effect)

Second order term:

$$C_n^2(t) = \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \; e^{i\omega_{nm}t'} V_{nm}(t') \, e^{i\omega_{mi}t''} V_{mi}(t'')$$

$$C_n^2(t) = \left(-\frac{i}{\hbar}\right)^2 \sum_m V_{nm} V_{mi} \int_0^t dt' \, e^{i\omega_{nm}t'} \int_0^{t'} dt'' \, e^{i\omega_{mi}t''}$$

$$= \left(-\frac{i}{\hbar}\right)^2 \sum_m V_{nm} V_{mi} \int_0^t dt' \, e^{i\omega_{nm}t'} \left[\frac{1}{i\omega_{mi}}\left(e^{i\omega_{mi}t'} - 1\right)\right]$$

$$= \left(-\frac{i}{\hbar}\right)^2 \sum_m V_{nm} V_{mi} \frac{1}{i\omega_{mi}} \int_0^{t'} dt' \left(e^{i\omega_{ni}t'} - e^{i\omega_{nm}t'}\right)$$

$$= \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \int_0^t dt' \left(e^{i\omega_{ni}t'} - e^{i\omega_{nm}t'}\right)$$

$$= -\sum_m \frac{V_{nm} V_{mi}}{(E_n - E_i)(E_n - E_i)} \left(1 - e^{i\omega_{ni}t}\right) - \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \int e^{i\omega_{nm}t'} dt'$$

Where we have considered const. Perturbation,

$$V(t) = \begin{cases} 0 & t < 0 \\ V & t \geq 0 \end{cases} \qquad (V = V(x, p, s))$$

a) The first term is like $C_n^1(t)$, the only important contribution arises from $E_n \approx E_i$ as $t \longrightarrow \infty$

(it has the same t-dependence as $C_n^1(t)$)

b) Consider the term $\frac{1}{E_m - E_i}\int_0^t dt' e^{i\omega_{nm}t'}$

1- When E_m differs from E_n and E_i, rapid oscillation kills the expression. (gives no contribution to the sum)

2- When $E_m \approx E_i$, the expression dominates the sum. (gives contribution to the sum).

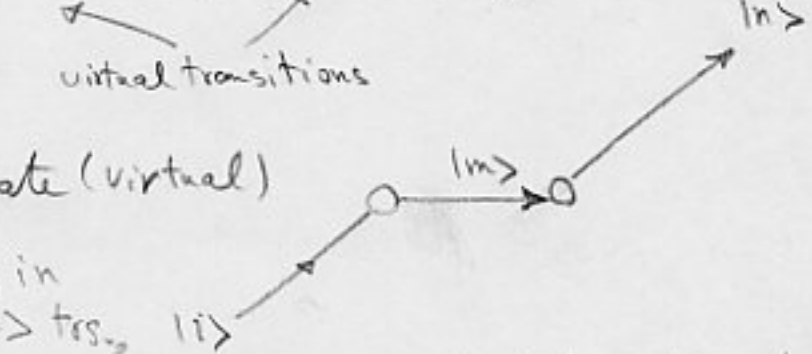
$$\omega_{i\to[n]} = \frac{d}{dt}\left|C_n^1(t) + C_n^2(t)\right|^2$$

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar}\left|V_{ni} + \sum_m \frac{V_{nm}V_{mi}}{E_i - E_m}\right|^2 \rho(E)\Big|_{E_n \approx E_i}$$

$C_n^1(t)$: $|i\rangle \longrightarrow |n\rangle$ $(E_n \approx E_i)$

$C_n^2(t)$: $|i\rangle \xrightarrow{\frac{V_{mi}}{E_i - E_m}} |m\rangle \xrightarrow{V_{nm}} |n\rangle$

virtual transitions



$|m\rangle$: is intermediate state (virtual)

There is energy nonconserving in $|i\rangle \to |m\rangle$ and $|m\rangle \to |n\rangle$ trs., (virtual trs.), but overall energy conservation exsits between $|i\rangle$ and $|n\rangle$.

A special treatment is needed if $V_{nm}V_{mi} \neq 0$ with $E_i \approx E_m$, ($\frac{V_{nm}V_{mi}}{E_i - E_m} \to \infty$). The best way is to use slow turn-on method ($V \to e^{\eta t}V$), (the net result is $E_i - E_n \to E_i - E_n + i\epsilon$).

Harmonic Perturbation;

$$V(t) = V e^{i\omega t} + V^{+} e^{-i\omega t}$$

where in general $V = V(x, P, S)$

{ V(t) may be written in the form like as we did in two-state prob. (P251), but this depends on the nature of V. (i.e. $V = V(x,P,S)$)

Again assume that only one of the eigenstates of H_0 is populated initially.

Assume $V(t)$ is turned on at $t = 0$,

$$C_n'(t) = -\frac{i}{\hbar} \int_0^t e^{i\omega_{ni} t'} \cdot V_{ni}(t')\, dt'$$

$$C_n'(t) = -\frac{i}{\hbar} \int_0^t \left(V_{ni} e^{i\omega t'} + V_{ni}^{+} e^{-i\omega t'} \right) e^{i\omega_{ni} t'} dt'$$

$$= \frac{1}{\hbar} \left[\frac{1 - e^{i(\omega_{ni} + \omega)t}}{\omega_{ni} + \omega} V_{ni} + \frac{1 - e^{i(\omega_{ni} - \omega)t}}{\omega_{ni} - \omega} V_{ni}^{+} \right]$$

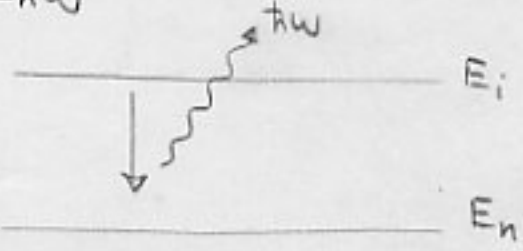
This is similar to const. Perturbation Case.

The only change needed is;

$$\omega_{ni} = \frac{E_n - E_i}{\hbar} \longrightarrow \omega_{ni} \pm \omega$$

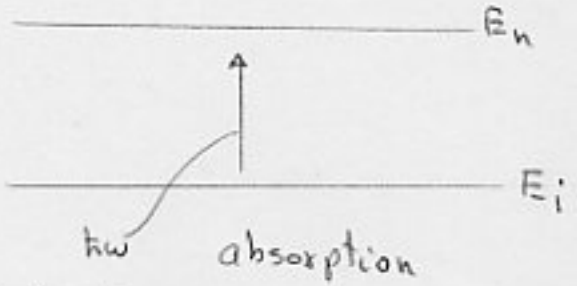
So, as $t \to \infty$, $|C_n'(t)|^2$ is appreciable only if.

1) $\omega_{ni} + \omega \approx 0$ or $E_n \simeq E_i - \hbar\omega$



stimulated emission

2) $\omega_{ni} - \omega \simeq 0$ or $E_n \simeq E_i + \hbar\omega$



Clearly, whenever the first term is important, the second one is unimportant and vice versa.

We see that there is no energy conservation, rather the appearent lack of energy conservation is compensated by the energy given out to - or energy taken away from - the external potential $V(t)$.

In complete analogy with the previous case;

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2}\, \rho(E_n)\Big|_{E_n = E_i - \hbar\omega} \qquad (1)$$

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar} \overline{|V_{ni}^+|^2}\, \rho(E_n)\Big|_{E_n = E_i + \hbar\omega} \qquad (2)$$

or

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar} \begin{Bmatrix} |V_{ni}|^2 \\ |V_{ni}^+|^2 \end{Bmatrix} \delta(E_n - E_i \pm \hbar\omega)$$

Where the expression is integrated with $\int dE_n \rho(E_n)$

Since $\langle i|V^\dagger|n\rangle = \langle n|V|i\rangle^*$

$$\longrightarrow \quad |V_{ni}|^2 = |V_{ni}^\dagger|^2 \qquad (3)$$

$$(1)(2)(3) \longrightarrow \frac{\text{emission rate for } i \to [n]}{\text{density of final states for } [n]} = \frac{\text{absorption rate for } n \to [i]}{\text{density of final states for } [i]}$$

Where in the absorption case we let i stand for final states.

This eqn is known as <u>detailed balancing</u>.

Absorption and Stimulated Emission:

The interaction Hamiltonian between the atomic electrons and the radiation field is assumed to be obtainable from the standard prescription:

$$\bar{P} \rightarrow \bar{P} - \frac{e\bar{A}}{c} \qquad (e<0)$$

where A: classical radiation field.

$$H = \frac{(P - \frac{eA}{c})^2}{2m_e} + V(r)$$

$$H = \frac{P^2}{2m_e} + V(r) - \frac{e}{2m_e c}(P\cdot A + A\cdot P) + \frac{e^2A^2}{2m_e c^2}$$

$$P\cdot A = P_x A_x + P_y A_y + P_z A_z$$

Consider the x-component:

$$P_x(A_x f) = \frac{\hbar}{i}\frac{\partial}{\partial x}(A_x f) = \frac{\hbar}{i}\left(A_x \frac{\partial f}{\partial x} + f\frac{\partial A_x}{\partial x}\right)$$

But if $\frac{\partial A}{\partial x} + \frac{\partial A}{\partial y} + \frac{\partial A}{\partial z} = \nabla\cdot A = 0$

$$\rightarrow \quad P\cdot(Af) = A\cdot(Pf) \quad \text{i.e.} \rightarrow P\cdot A = A\cdot P$$

Also $V(r) = e\varphi(r)$

$$\rightarrow H = \underbrace{\frac{p^2}{2m_e} + e\varphi(r)}_{H_0} - \underbrace{\frac{e}{m_e c} A\cdot P}_{V(t)} + O(e^2A^2)$$

$$A = A_0 \hat{\varepsilon}\, e^{\pm [ik\cdot x - i\omega t]} \qquad \text{(monochromatic field)}$$

when $\frac{\omega}{c}\hat{n} \equiv \hat{k}$ $\qquad (\bar{x} \equiv \bar{r})$

$$-\left(\frac{e}{mc}\right) A\cdot P = -\left(\frac{e}{mc}\right) A_0 \left[e^{\pm [ik\cdot x - i\omega t]} \right] \hat{\varepsilon}\cdot P$$

+ sign : Emission

− " : Absorption

Compare with;

$$V(t) = V e^{i\omega t} + V^{\dagger} e^{-i\omega t}$$

Absorption: $V_{ni}^{\dagger} = -\frac{e A_0}{mc} \left[e^{ik\cdot x}\, \hat{\varepsilon}\cdot P \right]_{ni}$

$$\omega_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i) \qquad \text{Golden rule}$$

$$\omega_{i\to n} = \frac{2\pi}{\hbar} \left(\frac{e^2}{m_e^2 c^2}\right) |A_0|^2 |\langle n| e^{ik\cdot x}\, \hat{\varepsilon}\cdot p |i\rangle|^2 \delta(E_n - E_i - \hbar\omega)$$

If $|n\rangle$ forms a continuum we simply integrate with $g(E_n)\, dE_n$.

Even in the case that $|n\rangle$ is discrete, since it is not a groundstate (because it is excited state but of course it is bound state energy level)

its energy is not infinitely sharp,

there may be → a natural broading due to a finite liftime,

There can also be a mechanism for broading due to collisions.

In such cases: we regard $\delta(\omega-\omega_{ni})$ as;

$$\delta(\omega-\omega_{ni}) = \lim_{\gamma\to 0} \left(\frac{\gamma}{2\pi}\right) \frac{1}{\left[(\omega-\omega_{ni})^2 + \frac{\gamma^2}{4}\right]}$$

Finally, the incident electromagnetic wave itself is not perfectly monochromatic

→ There is always a finite frequency width.

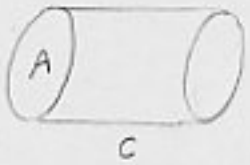
The absorption cross-section is given;

$$\alpha_{abs.} = \frac{\left(\frac{\text{Energy}}{\text{unit time}}\right) \text{absorbed by the atom } (i\to n)}{\text{Energy flux of A}}$$

$$\text{Energy flux} = \frac{\text{Energy}}{(\text{unit area})(\text{unit time})}$$

From the classical electromagnetic theory:

$$c\mathcal{U} = \frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2$$



where we have used:

$$u = \frac{1}{2}\left(\frac{E^2_{max}}{8\pi} + \frac{B^2_{max}}{8\pi}\right)$$

energy density
or = Per unit volume

with $E = -\frac{1}{c}\frac{\partial}{\partial t}A \qquad B = \nabla \times A$ (Source free fields $\rho = 0 \quad J = 0$)

(remember $\nabla \times E = -\frac{1}{c}\frac{\partial B}{\partial t}$)

$$\alpha_{abs} = \frac{(\hbar\omega)\left\{\frac{2\pi}{\hbar}\left(\frac{e^2}{m^2c^2}\right)|A_0|^2|\langle n|e^{ik\cdot x}\hat{\epsilon}\cdot p|i\rangle|^2\,\delta(E_n - E_i - \hbar\omega)\right\}}{\frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2}$$

Where $\{\ldots\}$ is absorption rate.

$$\alpha_{abs} = \frac{4\pi^2\hbar}{m^2\omega}\left(\frac{e^2}{\hbar c}\right)|\langle n|e^{ik\cdot x}\hat{\epsilon}\cdot p|i\rangle|^2\,\delta(E_n - E_i - \hbar\omega)$$

Electric Dipole Approx. –

If $K \longrightarrow$ small (i.e. $|K| = \frac{\omega}{c} = \frac{1}{\lambda}$ $\lambda \rightarrow$ large)

in $e^{ik\cdot x}$ expansion;

$$e^{ikx} = 1 + ik\cdot x + \cdots$$

the leading term is the first term (i.e. 1)

This is called <u>electric dipole approx.</u> E1.

The reason for this nominating will be clear soon.

This is valid in <u>light</u> atoms;

The reason:

$\hbar\omega$ must be of order of <u>atomic level spacing</u>
(because of δ-func.)

i.e. $\hbar\omega \sim \frac{Ze^2}{\frac{a_0}{Z}} = \frac{Ze^2}{R_{atom}}$

$\frac{c}{\omega} = \lambda \sim \frac{c\hbar R_{atom}}{Ze^2} \simeq \frac{137 R_{atom}}{Z}$ $\left(\lambda = \frac{\lambda}{2\pi}\right)$

$\frac{1}{\lambda} R_{atom} \sim \frac{Z}{137} \ll 1$ (for light atoms Z: small)

Since $K \cdot x \sim \frac{\text{Rad}}{\lambda}$

$(K \cdot x)^2 \sim \left(\frac{\text{Rad}}{\lambda}\right)^2 \rightarrow (k \cdot x)^2 << 1$

Now;

$$\langle n | e^{ik \cdot x} \hat{\varepsilon} \cdot p | i \rangle = \langle n | (1 + ik \cdot x + \cdots) \hat{\varepsilon} \cdot p | i \rangle$$

$$\simeq \langle n | \hat{\varepsilon} \cdot p | i \rangle = \hat{\varepsilon} \cdot \langle n | \bar{p} | i \rangle$$

Since $[\bar{p}^2, \bar{x}] = -2i\hbar \bar{p}$

and $H_0 = \frac{\bar{p}^2}{2m} + V(x)$

$$\bar{p} = \frac{im}{\hbar} [H_0, \bar{x}]$$

$$\rightarrow \langle n | \bar{p} | i \rangle = \frac{im}{\hbar} \langle n | [H_0, x] | i \rangle$$

$$= \frac{im}{\hbar} (E_n - E_i) \langle n | \bar{x} | i \rangle = im \omega_{ni} \langle n | \bar{x} | i \rangle$$

Since $\bar{x}$ is electric dipole op. ($\bar{\varepsilon} = e\bar{x}$),
this approx. scheme is called electric dipole approx.

Angular momentum selection rule in E1 -

$\overline{X}$ is a vector (spherical tensor op. of rank $k=1$)

$$X_1^{\pm 1} = \mp \frac{1}{\sqrt{2}} (x \pm iy) = r \sqrt{\frac{4\pi}{3}}\, Y_1^{\pm 1}$$

$$X_1^{0} = z = r \sqrt{\frac{4\pi}{3}}\, Y_1^{0}$$

$\longrightarrow$ $m_n - m_i = \pm 1, 0$

$|J_n - J_i| = 1, 0$

No $0 \rightarrow 0$ transition ($|J_i - 1| \leq J_n \leq J_i + 1$)

By Wigner-Eckart theorem:

$$\langle J_n m_n | X_1^q | J_i m_i \rangle = \frac{1}{\sqrt{2J_i+1}} \langle J_i \underset{\uparrow k}{1}\, m_i\, q | J_n m_n \rangle \langle n \| X_1 \| i \rangle$$

where $k=1$

The clebsch-Gorda coeffs. are <u>non-zero</u> only for the mentioned selection rules.

Physically this is the consequence of the fact that <u>one unit</u> of angular momentum is carried away by the spin of photon.

Parity selection rule in E1 -

$$\langle n|\bar{x}|i\rangle = -\langle n|\Pi^{-1}\bar{x}\Pi|i\rangle = -\Pi_n\Pi_i\langle n|\bar{x}|i\rangle$$

⟶ The parity is changed.

With E1 approx.:

$$\sigma_{abs} = \frac{4\pi^2\hbar}{mc^2\omega}\left(\frac{e^2}{\hbar c}\right)|2m_e\omega_{ni}\langle n|x|i\rangle|^2\,\delta(\hbar(\omega_{ni}-\omega))$$

$$\sigma_{abs} = 4\pi^2\alpha\,\omega_{ni}\,|\langle n|x|i\rangle|^2\,\delta(\omega_{ni}-\omega)$$

If $|i\rangle$ is the ground state, then ω_{ni} is necessarily positive, integrating we get:

$$\int \sigma_{abs}(\omega)\,d\omega = \sum_n 4\pi^2\alpha\,\omega_{ni}\,|\langle n|x|i\rangle|^2$$

→ (due to δ-func.: $\omega=\omega_{ni}, \omega'=\omega_{n'i}$ --!

In atomic physics the oscillation strength f_{ni} is defined as:

$$f_{ni} = \frac{2m\,\omega_{ni}}{\hbar}\,|\langle n|x|i\rangle|^2$$

It is easy to show the Thomas-Reiche-Kuhn sum rule:

$$\sum_n f_{ni} = 1$$

Proof. :

$$[x, H_0] = \left[x, \frac{p^2}{2m} + V(x)\right] = \left[x, \frac{p_x^2}{2m}\right]$$

$$= \frac{1}{2m}\left[x, p_x^2\right] = \frac{1}{2m}\left\{ [x, p_x] p_x + p_x [x, p_x] \right\} = \frac{i\hbar}{m} p_x$$

$$\left[x, [x, H_0]\right] = \left[x \ \frac{i\hbar}{m} p_x\right\} = \frac{i\hbar}{m} [x, p_x] = \frac{-\hbar^2}{m} \quad (1)$$

Also $\left[x, [x, H_0]\right] = H_0 x^2 + x^2 H_0 - 2x H_0 x \quad (2)$

$$\langle i | [x, [x, H_0]] | i \rangle = \frac{-\hbar^2}{m} \quad (3)$$

(1)(2)(3) $\rightarrow \langle i | H_0 x^2 | i \rangle + \langle i | x^2 H_0 | i \rangle - 2\langle i | x H_0 x | i \rangle = \frac{-\hbar^2}{m}$

$$2E_i \langle i | x^2 | i \rangle - 2\langle i | x H_0 x | i \rangle = \frac{-\hbar^2}{m}$$

$$\sum_n \langle i | x | n \rangle \langle n | x | i \rangle E_i - \sum_n \langle i | x H_0 | n \rangle \langle n | x | i \rangle = \frac{-\hbar^2}{2m}$$

$$\sum_n |\langle n | x | i \rangle|^2 E_i - \sum_n |\langle n | x | i \rangle|^2 E_n = \frac{-\hbar^2}{2m}$$

$$\sum_n |\langle n | x | i \rangle|^2 (E_i - E_n) = \frac{-\hbar^2}{2m}$$

$$\sum_n |\langle n | x | i \rangle|^2 \frac{2\omega_{ni} m}{\hbar} = +1 \longrightarrow \sum_n f_{ni} = 1$$

$$\longrightarrow \int \alpha_{abs}(\omega)\, d\omega = \frac{4\pi^2 \alpha \hbar}{2mc} = 2\pi^2 c \left(\frac{e^2}{mc^2}\right)$$

Photoelectric Effect:

That is the ejection of an electron when an atom is placed in the radiation field.

If we consider Hydrogen-like atom:

$$\psi_i(r) = \langle x | i \rangle = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$ bound electron $E < 0$

$$\psi_f(r) = \langle x | f \rangle \equiv \langle x | k_f \rangle = \frac{1}{L^{3/2}} e^{i k_f \cdot x}$$ free $\Rightarrow$ $E > 0$ (continuum)

Plane wave approx. of $\psi_f(r)$ is true if the final electron is not too slow.

In this example the matrix element depends not only the final state energy (E), but also on the momentum direction ($\bar{P}$).

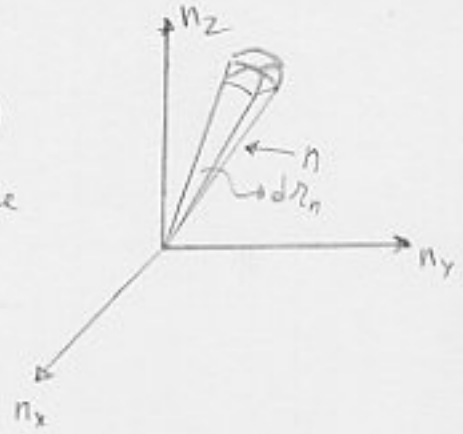
To find the number of final states per unit energy interval we use box normalization.

For the plane-wave $\psi_f(r)$, we have:

$$k_x = \frac{2\pi}{L} n_x, \; - \; - \; -$$

As $L \to \infty$ $\quad k_x, k_y, k_z \to$ Continuous variables

{ The number of states with definite P and with definite dir of P } $\sim$ { The number of dots in lattice space }



$$n^2 = n_x^2 + n_y^2 + n_z^2$$

As $L \to \infty$, $n_x, n_y, n_z \to$ continuous variables

$$dV_n = n^2 dn\, d\Omega_n$$

$$E = \frac{p_f^2}{2m_e} = \frac{\hbar^2 k_f^2}{2me} = \frac{\hbar^2}{2me}\left(\frac{2\pi}{L}\right)^2 n^2$$

Furthermore $\hat{n} \parallel \bar{p}_f$

$$dE = \frac{\hbar^2}{m_e} k_f\, dk_f \qquad \frac{dk_f}{dE} = \frac{me}{\hbar^2 k_f}$$

$n^2 d\Omega_n \frac{dn}{dE} dE$: The number of states in the interval between E and $E+dE$ with dir. into $d\Omega_n$ (Ω $d\Omega_{k_f}$), being k_f.

$$n^2 d\Omega_n \frac{dn}{dE} dE = \left[\left(\frac{L}{2\pi}\right)^2 k_f^2\right] d\Omega_n \left(\frac{L}{2\pi}\frac{dk_f}{dE}\right) dE$$

$$= \left(\frac{L}{2\pi}\right)^3 k_f^2 \frac{dk_f}{dE} d\Omega_n dE = \left(\frac{L}{2\pi}\right)^3 \frac{me}{\hbar^2} k_f\, dE\, d\Omega_n$$

$$\equiv g(E)\, dE\, d\Omega$$

We had:

$$\alpha = \frac{4\pi^2 \hbar \alpha}{m_e^2 \omega} \left| \langle k_f | e^{i\left(\frac{\omega}{c}\right)\hat{n}\cdot\bar{x}} \hat{\varepsilon}\cdot\bar{p} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

(α must be integrated with $\int dE_n g(E_f)$)

$\frac{\omega}{c}\hat{n} \equiv \bar{k}$

(This must be integrated over $\int dk^3$ or $\int d\Omega$ $\int dn^3 \equiv \int dV_n$ in order to take into account all momentum dirs.)

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2 \alpha \hbar}{mc^2 \omega} \left| \langle k_f | e^{i(\frac{\omega}{c})\hat{n}\cdot x} \hat{\varepsilon}\cdot\bar{p} | i \rangle \right|^2 \left(\frac{L}{2\pi}\right)^3 \frac{mc}{\hbar^2} k_f$$

(Because of dir. dependence of α $\alpha \to d\sigma$)

Ex. Ejection of a K-shell ($n=1$) electron caused by absorption of light.

$\psi_i(r)$ is essentially the same as the ground state Hydrogen atom wave-func. except that the Bohr radius a_0 is replaced by $\frac{a_0}{Z}$

$$\langle k_f | e^{i(\frac{\omega}{c})\hat{n}\cdot x} \hat{\varepsilon}\cdot\bar{p} | i \rangle = \hat{\varepsilon}\cdot \int d^3x \frac{e^{-ik_f\cdot x}}{L^{3/2}} e^{i(\frac{\omega}{c})\hat{n}\cdot x} \cdot(-i\hbar\nabla)\left[\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}\right]$$

Integrating by parts we can pass ∇ to the left side;

Furthermore $\hat{\varepsilon}\cdot\left[\nabla e^{i(\omega/c)\hat{n}\cdot\bar{x}}\right] = 0$ (because $\hat{\varepsilon} \perp \hat{n}$)

$$\nabla e^{-ik_f\cdot x} = -i\bar{k}_f e^{-ik_f\cdot x}$$

Alternatively;

$$\langle k_f | e^{i(\omega/c)\hat{n}\cdot\bar{x}} \hat{\varepsilon}\cdot\bar{p} | i \rangle = \langle k_f | \hat{\varepsilon}\cdot p\, e^{i(\frac{\omega}{c})\hat{n}\cdot x} | i \rangle$$

$$= \hat{\varepsilon}\cdot\bar{p}_f \langle k_f | e^{i(\omega/c)\hat{n}\cdot\bar{x}} | i \rangle \quad \text{(because } A\cdot P = P\cdot A\text{)}$$

$$\rightarrow \langle k_f | e^{i(\omega/c)\hat{n}\cdot\bar{x}} | i \rangle = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{L^{3/2}} \int d^3x \; e^{i(k-k_f)\cdot\bar{x}} \; e^{-Zr/a_0}$$

$$= \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{L^{3/2}} \int d^3x \; e^{-iq\cdot x} \; e^{-Zr/a_0} \qquad \left(\text{Fourier tr. of } e^{-Zr/a_0}\right)$$

$$q \equiv k_f - k \qquad k = \frac{\omega}{c}\hat{n}$$

Now;

$$\int d^3r \; e^{-i\bar{q}\cdot\bar{r}} \frac{e^{-\mu r}}{r} = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} r^2 dr \; e^{-iqr\cos\theta} \frac{e^{-\mu r}}{r}$$

$$= 2\pi \int_0^{\infty} r\,dr \; e^{-\mu r} \int_{-1}^{1} d(\cos\theta) \; e^{-iqr\cos\theta}$$

$$= \frac{2\pi}{iq} \int_0^{\infty} dr \; e^{-\mu r} \left(e^{iqr} - e^{-iqr}\right) = \frac{2\pi}{iq}\left[\frac{1}{\mu - iq} - \frac{1}{\mu + iq}\right]$$

$$= \frac{4\pi}{\mu^2 + q^2}$$

By differentiating w.r.t μ;

$$\int d^3r \; e^{-iq\cdot r} \; e^{-\mu r} = \frac{8\pi\mu}{(\mu^2 + q^2)^2}$$

$$\rightarrow \langle k_f | e^{i(\omega/c)\hat{n}\cdot x} | i \rangle = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{L^{3/2}} \frac{8\pi\left(\frac{Z}{a_0}\right)}{\left[\left(\frac{Z}{a_0}\right)^2 + q^2\right]^2}$$

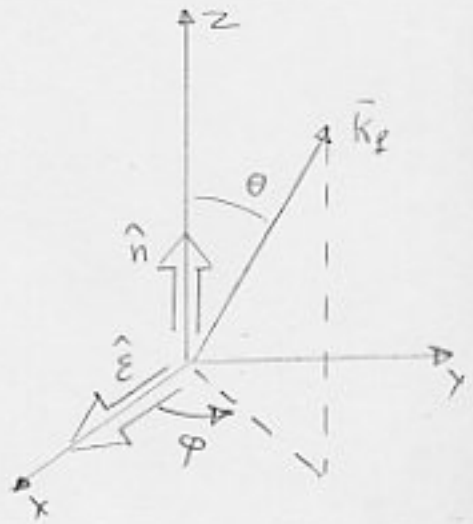
$$\frac{d\omega}{d\Omega} = \frac{4\pi^2 \alpha \hbar}{mc^2\omega} \left(\frac{Z}{a_0}\right)^5 \frac{64\pi^2}{L^3} \frac{(\hat{\varepsilon}\cdot\hat{p}_f)^2}{\left[\left(\frac{Z}{a_0}\right)^2 + q^2\right]^4} \left(\frac{L}{2\pi}\right)^3 \frac{mc}{\hbar^2} k_f$$

$$\frac{d\sigma}{d\Omega} = 32 e^2 k_f \frac{(\hat{\varepsilon}\cdot k_f)^2}{m_e c \omega} \frac{Z^5}{a_0^5} \frac{1}{\left[\left(\frac{Z}{a_0}\right)^2 + q^2\right]^4}$$

where $\alpha = \frac{e^2}{\hbar c}$ $\quad p_f = \hbar k_f$

$$(\hat{\varepsilon}\cdot k_f)^2 = k_f^2 \sin^2\theta \cos^2\varphi$$

$$q^2 = k_f^2 - 2 k_f \frac{\omega}{c} \cos\theta + \left(\frac{\omega}{c}\right)^2$$



$\hat{n}$: dir. of the photon momentum.

$\hat{\varepsilon}$: dir of $A(x,t)$

$\bar{k}_f$: ejected ectron dir.

5-8 Energy Shift and Decay Width

Our consideration so far have been restricted to the poulation of states n other than i $(i \neq n)$

i.e. $C_n(t)$ $\quad n \neq i$

Now we consider $C_i(t)$ itself.

To avoid any sudden change in H, we propose to increase the perturbation very slowly.

$$\rightarrow V(t) = e^{\eta t} V \qquad 0 < \eta << 1$$

V: assumed to be const.

At the end of calculation we let $\eta \rightarrow 0$

$$\rightarrow V(t) \rightarrow V \quad \forall t \qquad \text{(const. perturb.)}$$

In the remote past $t = -\infty$; $|i\rangle$ our state in the int. picture

Our aim is to evaluate $C_i(t)$.

But let first to be sure that the old formula of Golden rule can be reproduced using slow-turn-on method.

$$C_n^0(t) = \delta_{in} = 0 \qquad (i \neq n)$$

$$C_n^1(t) = -\frac{i}{\hbar} V_{ni} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} e^{i\omega_{ni} t'} dt' = -\frac{i}{\hbar} V_{ni} \frac{e^{\eta t + i\omega_{ni} t}}{\eta + i\omega_{ni}}$$

To lowest nonvanishing order:

$$|C_n(t)|^2 \simeq \frac{|V_{ni}|^2}{\hbar^2} \frac{e^{2\eta t}}{\eta^2 + \omega_{ni}^2}$$

$$\rightarrow \frac{d}{dt}|C_n(t)|^2 \simeq \frac{2|V_{ni}|^2}{\hbar^2} \left(\frac{\eta e^{2\eta t}}{\eta^2 + \omega_{ni}^2} \right)$$

Now, we let $\eta \to 0$

$$\lim_{\eta \to 0} \frac{\eta}{\eta^2 + \omega_{ni}^2} = \pi \delta(\omega_{ni}) = \pi \hbar \, \delta(E_n - E_i)$$

$$\rightarrow \omega_{i \to n} \simeq \left(\frac{2\pi}{\hbar} \right) |V_{ni}|^2 \delta(E_n - E_i) \qquad \text{(ok)}$$

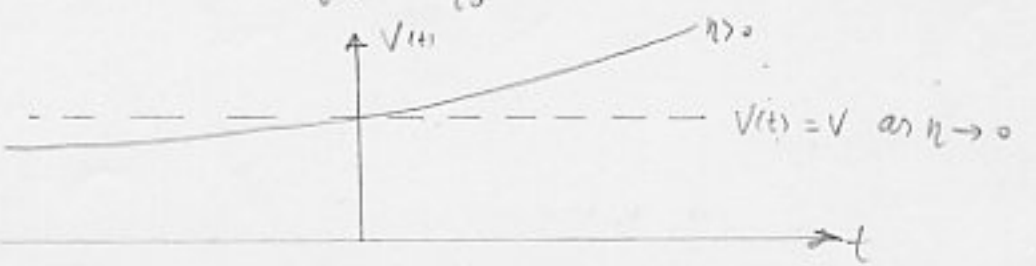
Remark: if $e^{\eta t'}$ term is absent
then $\int_{t_0}^{t} dt' = t - t_0$
$|C_i^1(t)|^2 \sim t^2$

Now;

$$C_i^0(t) = \delta_{ii} = 1$$

$$C_i^1(t) = -\frac{i}{\hbar} V_{ii} \lim_{t_0 \to -\infty} \int_{t_0}^{t} (1) e^{\eta t'} dt' = -\frac{i}{\hbar \eta} V_{ii} e^{\eta t}$$

$$C_i^{(2)}(t) = \left(-\frac{i}{\hbar}\right)^2 |V_{ii}|^2 \lim_{t_0 \to -\infty} \int_{t_0}^{t} dt' \, e^{i\omega_{im} t' + \eta t'} \frac{e^{i\omega_{mi} t' + \eta t'}}{i(\omega_{mi} - i\eta)}$$



$$C_i^{(2)}(t) = \left(-\frac{i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} + \left(-\frac{i}{\hbar}\right) \sum_{m\neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta (E_i - E_m + i\hbar\eta)}$$

Up to second order;

$$C_i(t) = 1 - \frac{i}{\hbar\eta} V_{ii} e^{\eta t} + \left(\frac{i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} + \left(\frac{i}{\hbar}\right) \sum_{m\neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta (E_i - E_m + i\hbar\eta)}$$

$$\text{lim}_{\eta\to 0} \frac{\dot{C}_i}{C_i} \simeq \frac{-\frac{i}{\hbar} V_{ii} + \left(-\frac{i}{\hbar}\right)^2 \frac{|V_{ii}|^2}{\eta} + \left(-\frac{i}{\hbar}\right)^2 \sum_{m\neq i} \frac{|V_{mi}|^2}{(E_i - E_m + i\hbar\eta)}}{1 - \frac{i}{\hbar}\frac{V_{ii}}{\eta} + \underbrace{\mathcal{O}}_{\text{second order}}}$$

where appropriate

$$\simeq -\frac{i}{\hbar} V_{ii} + \left(-\frac{i}{\hbar}\right)^2 \sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta} \quad \text{(up to second order in } V\text{)} \qquad (1)$$

where $\dot{C}_i \equiv \frac{dC_i}{dt}$

Note that $\frac{\dot{C}_i(t)}{C_i(t)}$ is now indep. of t

It is convenient to renormalize C_i, so that $C_i(0) = 1$

We now try the ansatz;

$$C_i(t) = e^{-i\Delta_i t/\hbar} \rightarrow \frac{\dot{C}_i(t)}{C_i(t)} = -\frac{i}{\hbar}\Delta_i \qquad (2)$$

Δ_i: const. in t, but in general complex.

Physical meaning of Δ_i:

$e^{-i\Delta_i t/\hbar}|i\rangle$ The state in the int. picture $\longrightarrow e^{-i\Delta_i t/\hbar - iE_i t/\hbar}|i\rangle$ The state in the Schrodinger picture

In other words; $E_i \longrightarrow E_i + \Delta_i$ as a result of perturbation

This is <u>level shift</u> using time-dep pert theory.

Now expand as usual:

$$\Delta_i = \left(-\frac{i}{\hbar}\right)^0 \Delta_i^{(1)} + \left(-\frac{i}{\hbar}\right)^1 \Delta_i^{(2)} + \cdots \qquad (3)$$

$(1)(2)(3) \longrightarrow \Delta_i^{(1)} = V_{ii}$

But this is <u>just</u> what we expect from time-indep. pert. theory.

Now, Since; $\lim_{\epsilon \to 0} \frac{1}{x+i\epsilon} = Pr.\left(\frac{1}{x}\right) - i\pi\delta(x)$ $\left\{ Pr.\left(\frac{1}{x}\right) = \frac{1}{2}\left[\frac{1}{x+i\epsilon} + \frac{1}{x-i\epsilon}\right] \right.$

$$\Delta_i^{(2)} = \sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta}$$

$$\Delta_i^{(2)} = \left[Pr. \sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m} - i\pi \sum_{m \neq i} |V_{mi}|^2 \, \delta(E_i - E_m) \right]$$

$$Re(\Delta_i^{(2)}) = Pr. \sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m} \qquad (4)$$

$$\mathrm{Im}(\Delta_i^{(2)}) = -\pi \sum_{m \neq i} |V_{mi}|^2 \delta(E_i - E_m) \qquad (5)$$

From the Golden rule;

$$\sum_{m \neq i} w_{i \to m} = \frac{2\pi}{\hbar} \sum_{m \neq i} |V_{mi}|^2 \delta(E_i - E_f) = -\frac{2}{\hbar} \mathrm{Im}[\Delta_i^{(2)}].$$

Now; $C_i(t) = e^{-i\Delta_i t/\hbar} = e^{-\frac{i}{\hbar}[\mathrm{Re}(\Delta_i)t] + \frac{1}{\hbar}[\mathrm{Im}(\Delta_i)t]}$

If we define $\frac{\Gamma_i}{\hbar} = -\frac{2}{\hbar}\mathrm{Im}(\Delta_i)$

$$\rightarrow |C_i(t)|^2 = e^{2\mathrm{Im}(\Delta_i)t/\hbar} = e^{-\Gamma_i t/\hbar}$$

Therefore; Γ_i : the rate at which state $|i\rangle$ disappears

Let us check the probability conservation up to second order in V for small t.

$$\sum_{m \neq i} w_{i \to m} = -\frac{2}{\hbar}\mathrm{Im}(\Delta_i^{(2)})$$

on the other hand $w_{i \to [m]} = \sum_{i \neq m} w_{i \to m} \equiv \frac{d}{dt} \sum_{i \neq m} |C_m|^2$

$$\sum_{i \neq m} |C_m|^2 = \sum_{i \neq m} w_{i \to m} t$$

$$|C_i|^2 + \sum_{m \neq i} |C_m|^2 = (1 - \Gamma_i t/\hbar + \cdots) + \sum_{m \neq i} \omega_{i \to m} t = 1$$

$$\longrightarrow \quad -\frac{\Gamma_i}{\hbar} t + \sum_{m \neq i} \omega_{i \to m} t = 0$$

$\longrightarrow$ Depletion of $|i\rangle$ $\xrightarrow{\text{is compensated by}}$ the growth of states other than $|i\rangle$

To summarize;

The <u>real</u> part of the <u>energy shift</u> is what we usually associate with the <u>level shift</u>.

The <u>imaginary</u> part of the <u>energy shift</u> is (apart from -2) the decay width -

Note that $\frac{\hbar}{\Gamma_i} = \tau_i$ mean life of $|i\rangle$

because, $|C_i|^2 = e^{-t/\tau_i}$

To see why Γ_i is called width, we look at the Fourier decomposition

$$\int f(E)\, e^{-iEt/\hbar}\, dE = C \qquad e^{-i\Delta_i t/\hbar - i E_i t/\hbar} \quad e^{-i[E_i + \mathrm{Re}(\Delta_i)]t/\hbar - \Gamma_i t/2\hbar} = C$$

$\downarrow$ (P295)

$$|f(E)|^2 \sim \frac{1}{\{E - [E_i + \mathrm{Re}(D_i)]\}^2 + \Gamma_i^2/4}$$

Therefore, Γ_i has the usual meaning of <u>full</u> width at half max.

Also, $\frac{\hbar}{\Gamma_i} = \tau_i \longrightarrow \Delta t \, \Delta E \sim \hbar$

We can generalize our considerations to the harmonic perturbation case as below;

$$E_n - E_i \longrightarrow E_n - E_i \pm \hbar\omega$$
$$E_m - E_i \longrightarrow E_m - E_i \pm \hbar\omega$$