1D Time-independent perturbation theory.

In QM, we need to solve Schrodinger equation.

Time-independent:

$$H_1 \psi_n = E_n \psi_n \qquad (*)$$

By now: You have seen essentially all the simple — but very important — examples that can be solved exactly:

e.g. SHO

H atom

Landau problem

susy QM

⋮

most H complicated, not solvable.
~~But most systems, are not exactly solvable.~~

⇒ need to make approximations. (art)

General strategies:

1) Ignore certain complications, reduce the problem to an exactly solvable one. (Hope essential physics remains), often not possible.

2) Develop approximate methods to solve the Schrödinger equation.

We will discuss 4 such methods.
Each method is developed for different types of Hamiltonian and suitable for different physical problems.

~~Each method tackles the equation from different perspective~~

1/4 board

10.1 perturbation theory (non-degenerate)

In many physical problems, the Hamiltonian H has the form,

$$H(\lambda) = H_0 + \lambda H'$$

where:

(1) Eigenvectors and eigenvalues of H_0 are known

$$H_0 \, |\psi_n^{(0)}\rangle = E_n^{(0)} \, |\psi_n^{(0)}\rangle, \quad n = 0, 1, 2, \cdots$$

(2) λ is a small (dimensionless) parameter.

Examples: relativistic effects, spin-orbit coupling in Hydrogen atom

Hydrogen in weak $\vec{B}$ or $\vec{E}$ fields.

(2) $\Rightarrow$ Solve (*) order by order in λ.

Strategy

- Set-up

1) $|\psi_n^{(0)}\rangle$ form a complete and orthonormal bases.

$$\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = \delta_{mn} \quad , \quad \sum_n |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}| = 1$$

2) Expand E_n and $|\psi_n\rangle$ of full Hamiltonian H in power series of λ.

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

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots$$

3) To find $|\psi_n^{(k)}\rangle$, expand them in $|\psi_n^{(0)}\rangle$ basis

e.g. $$|\psi_n^{(k)}\rangle = \sum_{m \neq n} C_{mn}^{(k)} |\psi_m^{(0)}\rangle + C_{nn}^{(k)} |\psi_n^{(0)}\rangle$$

and find $C_{mn}^{(k)}$

4) We can set $C_{nn}^{(k)} = 0$ for $k \geq 1$,

Since $|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots$

(not write)

all terms proportional to $|\psi_n^{(0)}\rangle$ can be pulled out and combined with the 0-th order term.

$\Rightarrow$ $\langle\psi_n^{(0)}|\psi_n^{(k)}\rangle = 0$

for all $k \geq 1$.

1 full board

11.1 non-degenerate perturbation

We will first assume that the spectrum of H_0 is non-degenerate, i.e.

there does not $E_n^{(0)} \neq E_m^{(0)}$ for $n \neq m$.

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

$$\Downarrow$$

$$(H_0 + \lambda H')\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right)$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right.$$

Equate coefficients before λ^n $n = 0, 1, \cdots$

Collect terms order by order in λ:

λ^0: $H_0^0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$

λ^1: $H_0 |\psi_n^{(1)}\rangle + H' |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle$

λ^2: $H_0 |\psi_n^{(2)}\rangle + H' |\psi_n^{(1)}\rangle = E_n^{(0)} |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^{(0)}\rangle$

⋮

- zero-th order: ~~with assume $\sum_m |\psi_m^{(0)}\rangle\langle\psi_m^{(0)}| = 1$~~ nothing new, ~~with assume $\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn}$~~ nothing new.
- 1st order: take ① and take inner product with $\langle\psi_n^{(0)}|$

$$\Rightarrow \langle\psi_n^{(0)}| H_0 |\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}| H' |\psi_n^{(0)}\rangle$$

$$= E_n^{(0)} \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)} \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle$$

$$\Rightarrow \boxed{E_n^{(1)} = \langle\psi_n^{(0)}| H' |\psi_n^{(0)}\rangle}$$

- 1st order: take inner product between (1) and $\langle \psi_m^{(0)} |$

$$E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle \qquad (n \neq m).$$

$$= \langle \psi_m^{(0)} | H_0 | \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle$$

$$= E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle}_{=0}$$

$$\Rightarrow \quad \langle \psi_m^{(0)} | \psi_m^{(1)} \rangle \left(E_n^{(0)} - E_m^{(0)} \right) = \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle$$

$$\Rightarrow \quad \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \qquad (m \neq n)$$

thus

$$| \psi_n^{(1)} \rangle = \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} | \psi_m^{(0)} \rangle \quad (3)$$

$$H'_{mn} = \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle$$

- 2nd order: Take inner product of ② and $\langle \psi_n^{(0)} |$

$$\Rightarrow \quad E_n^{(0)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle}_{=0} + \langle \psi_n^{(0)} | H' | \psi_n^{(1)} \rangle$$

$$= E_n^{(0)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle}_{=0} + E_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}_{=0} + E_n^{(2)}$$

$$\Rightarrow \quad E_n^{(2)} = \underline{\langle \psi_n^{(0)} | H' | \psi_n^{(1)} \rangle}$$

$$= \sum_{m \neq n} \frac{H'_{mn} \langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$= \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\boxed{E_n^{(2)} = \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}}$$

One can keep going to find $|\psi_n^{(2)}\rangle$, $E_n^{(3)}$, ...

The lowest order terms we found are often enough to extract main physics in most problem.

End of Lec. 9

Remarks:

1. Normalization: $|\psi_n\rangle$ thus constructed is not normal

$$\frac{|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \cdots}{\sqrt{1+\lambda^2\langle\psi_n^{(1)}|\psi_n^{(1)}\rangle + \cdots}} = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + O(\lambda^2) + \cdots$$

Normalization does not affect 1st order w.f.

2. Features of 2nd order energy shift:

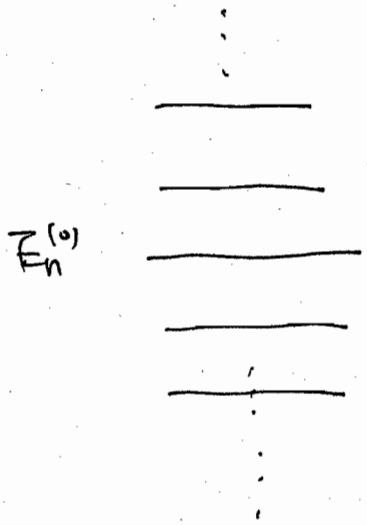
(a) 2nd order shift in ground state energy is always negative

$E_1^{(0)} - E_m^{(0)} < 0$, $\forall m \neq 1$, $E_1^{(0)}$: ground state energy

$\Rightarrow$ $E_1^{(2)} < 0$

(b) More generally, < 0 $\quad$ > 0

$$E_n^{(2)} = \sum_{E_m^{(0)} > E_n^{(0)}} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \sum_{E_m^{(0)} < E_n^{(0)}} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}$$

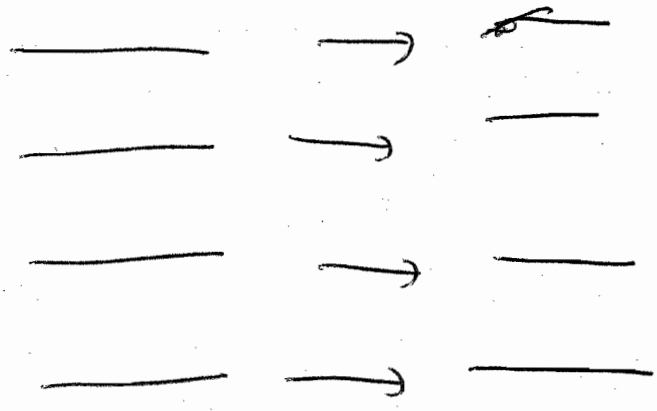


Levels repel

3. Range of validity:

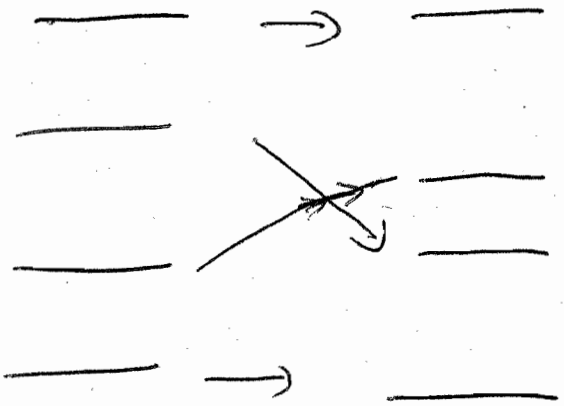
Energy levels should not cross under perturbation:

$E_n^{(2)}$, $\psi_n^{(1)}$ ... will diverge where at level crossing.



$\lambda = 0$ $\lambda \neq 0$

(good)



$\lambda = 0$ $\lambda \neq 0$

(not good)

this implies that:

$$|\lambda E_n^{(1)}|, \ |\lambda^2 E_n^{(2)}|, \ \cdots \ \ll \Delta E_n^{(0)}$$

typical energy difference between nearby levels

which roughly translates into

$$|\lambda H'_{mn}| \ll \Delta E^{(0)}$$

4. Notation:

Later, sometimes we put λ into definition of H',

i.e. $H = H_0 + H'$

In this case, set $\lambda = 1$, in all previous formulae.

10.2 Degenerate perturbation theory.

Our earlier discussion applies to non-degenerate case,

i.e. $E_n^{(0)} \neq E_m^{(0)}$ $\quad n \neq m$

or more [illegible] stringently

$$|\lambda H'_{mn}| \ll \Delta E^{(0)}$$

↑ typical matrix elements of H'

↑ typical energy level spacings

What happens if these are $E_n^{(0)} = E_m^{(0)}$, $n \neq m$?

Resolve the schrodinger equation at each

order.

Consider again the schrodinger equation at order λ:

$$H_0 |\psi_n^{(1)}\rangle + H' |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle \quad (4)$$

previously, contract (4) with: $|\psi_n^{(0)}\rangle \Rightarrow E_n^{(1)}$

$|\psi_m^{(0)}\rangle$, $m \neq n$, $E_n^{(0)} \neq E_m^{(0)} \Rightarrow \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$

$\Rightarrow |\psi_n^{(1)}\rangle$

now suppose these exist $|\psi_k^{(0)}\rangle$, $k \neq n$, $E_k^{(0)} = E_n^{(0)}$

(degenerate)

Contract (4) with such $|\psi_k^{(0)}\rangle \Rightarrow$

$$\boxed{\langle \psi_k^{(0)} | H' | \psi_n^{(0)} \rangle = 0} \quad (5)$$

Both $E_n^{(1)}$ and $|\psi_n^{(1)}\rangle$ drop out of the equation.

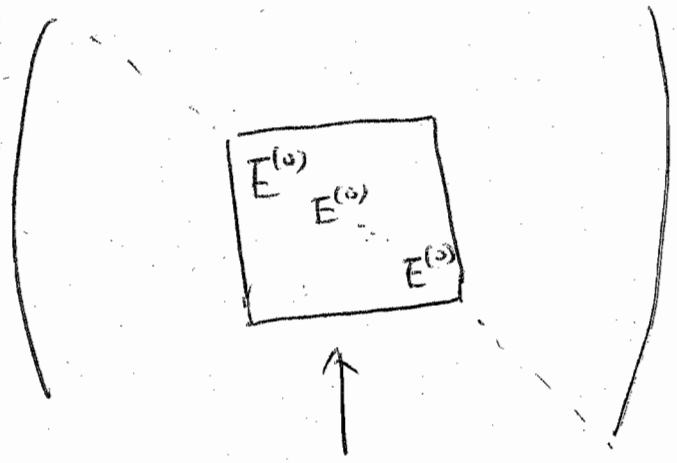
(5) is a constraint on $|\psi_k^{(0)}\rangle$ and $|\psi_n^{(0)}\rangle$:

H' is diagonal between them

- physical meaning of eq. (5):

Suppose $|\psi_k^{(0)}\rangle$ and $|\psi_n^{(0)}\rangle$ belong to a d-dimensional "degenerate subspace", i.e. d-states all with the same energy $E^{(0)}$

$H_0 =$



Call this subspace D (d-dimensional)

Note: (a) because of the degeneracy, the choice of a basis for D is not unique.

e.g. If $|\psi_i^{(0)}\rangle$, $i=1,\cdots d$

is an orthonormal basis for D,

then $|\psi_i^{(0)}\rangle = \sum_{j=1}^{d} U_{ij} |\psi_j^{(0)}\rangle$

with U_{ij} an arbitrary $d \times d$ unitary matrix

is an orthonormal basis for D in which

H_0 is diagonal, i.e. $H_0 = E_0 \mathbb{1}_{d\times d}$.

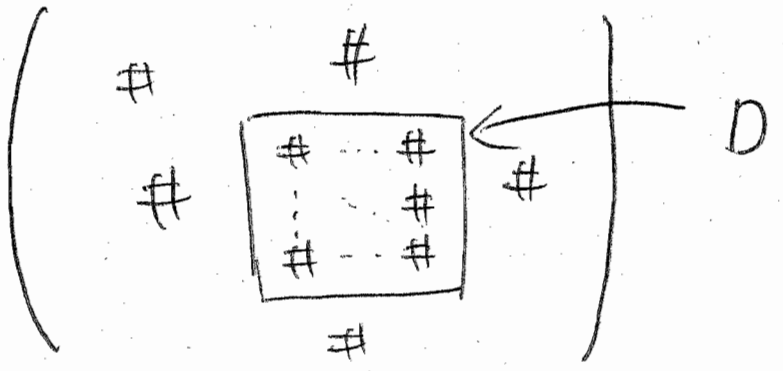
Thus in the degenerate case, these are ambiguities

in the choices of $\psi_n^{(0)}$ in the expansion

of ψ_n in λ.

(b) If an arbitrarily chosen basis for D, H'

will in general not be diagonal in D.

$H' =$ 

(c) Eq (5) $\Rightarrow$ the correct basis is one in which H' is diagonal, i.e.

$$H' = \begin{pmatrix} \# & & & \\ & \# & 0 & \\ & 0 & \ddots & \# \\ & & \# & \end{pmatrix} \leftarrow D$$

Griffith: "Good states"

Once eq (5) is understood, perturbation theory can be carried out as in the non-degenerate case.

One finds: for $n \in D$

$$E_n = E_n^{(0)} + \lambda H'_{nn} + \lambda^2 \sum_{m \notin D} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \cdots$$

(H'_{nn}: eigenvalues of H')

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda \sum_{m \notin D} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle + \cdots$$

($|\psi_n^{(0)}\rangle$: H' is diagonal in D.)

- Typically, eigenvalues of H' in D will not be degenerate, i.e. H'_{nn} not equal to each other for $n \in D$.

  $\Rightarrow$ degeneracies broken by H'

- If H'_{nn} still have degeneracies for $n \in D$,

  $\Rightarrow$ further constraints on $|\psi_n^{(0)}\rangle$ from higher order equations. (more complicated, conceptually similar)

Summary:

We thus find:

When H_0 has degeneracy, to find the 0-th order wave functions in the degenerate subspace, diagonalize H' in this subspace.

After doing this, proceed as we did for non-degenerate case.

§3 A simple example:

Two-state system

$$H = H_0 + H'$$

$$H_0 = \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \qquad H' = \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix}$$

For convenience, we have absorbed λ into definition of H

λ has dimension of energy.

(a) $\varepsilon_1 \neq \varepsilon_2$, λ small (what does it mean?)

Energy perturbation:

$$E_1 = E_1^{(0)} + H'_{11} + \frac{|H'_{12}|^2}{E_1^{(0)} - E_2^{(0)}} + \cdots$$

$$= \varepsilon_1 + 0 + \frac{\lambda^2}{\varepsilon_1 - \varepsilon_2} + \cdots$$

$$E_2 = E_2^{(0)} + H'_{22} + \frac{|H'_{12}|^2}{E_2^{(0)} - E_1^{(0)}}$$

$$= \varepsilon_2 + \frac{\lambda^2}{\varepsilon_2 - \varepsilon_1} + \cdots$$

Let $|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $|2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

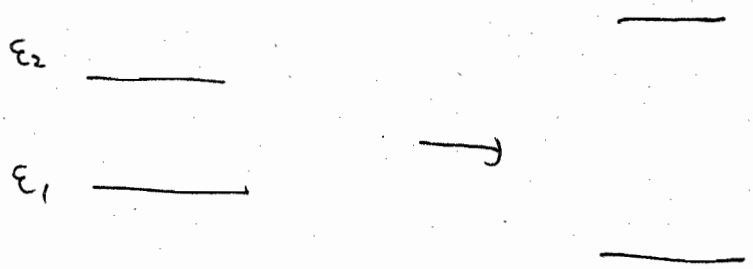
$$|\psi_1\rangle = |\psi_1^{(0)}\rangle + \frac{H_{21}'}{E_1^{(0)} - E_2^{(0)}} |\psi_2^{(0)}\rangle + \cdots$$

$$= |1\rangle + \frac{\Delta}{\varepsilon_2 - \varepsilon_1} |2\rangle + \cdots$$

} mixing.

$$|\psi_2\rangle = |2\rangle - \frac{\Delta}{\varepsilon_2 - \varepsilon_1} |1\rangle + \cdots$$

Suppose: $\varepsilon_2 > \varepsilon_1$



level repel!

Expect perturbation theory valid if

$$\boxed{\frac{\Delta}{\varepsilon_2 - \varepsilon_1} << 1}$$

(b) $\varepsilon_1 = \varepsilon_2 = \varepsilon$, to find "good states", diagonalize H'.

$$\Rightarrow \quad H' = \begin{pmatrix} -\lambda & 0 \\ 0 & \lambda \end{pmatrix}$$

$$|\psi_1^{(0)}\rangle = \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle)$$

$$|\psi_2^{(0)}\rangle = \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle)$$

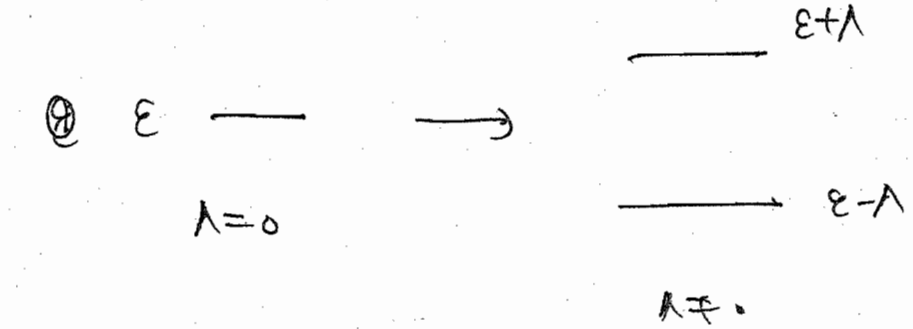
$$E_1 = \varepsilon - \lambda + O(\lambda^3)$$

(2nd order vanishes)

$$E_2 = \varepsilon + \lambda + O(\lambda^3)$$

$$|\psi_1\rangle = |\psi_1^{(0)}\rangle + O(\lambda^2)$$

$$|\psi_2\rangle = |\psi_2^{(0)}\rangle + O(\lambda^2)$$



c) Our example is exactly solvable, let us compare the results of perturbation theory to exact answer.

the full matrix

$$H = \begin{pmatrix} \varepsilon_1 & -\lambda \\ -\lambda & \varepsilon_2 \end{pmatrix}$$

is easy to diagonalize.

$$\Delta = \frac{\varepsilon_2 - \varepsilon_1}{2}$$

we find:

$$E_1 = \frac{\varepsilon_1+\varepsilon_2}{2} - \sqrt{\Delta^2+\lambda^2}$$

$$E_2 = \frac{1}{2}(\varepsilon_1+\varepsilon_2) + \sqrt{\Delta^2+\lambda^2}$$

$$|\psi_1\rangle = \cos\theta\,|1\rangle + \sin\theta\,|2\rangle$$

$$|\psi_2\rangle = +\sin\theta\,|1\rangle - \cos\theta\,|2\rangle$$

$$\tan\theta = \frac{\lambda}{\Delta + \sqrt{\Delta^2+\lambda^2}}$$

$$\Delta = \frac{\varepsilon_2 - \varepsilon_1}{2}$$

1) When $\Delta \gg \Lambda$, we can expand the square root in E_1, E_2 and $|\psi_1\rangle, |\psi_2\rangle$ in terms of power series of $\frac{\Lambda^2}{\Delta^2}$:

$$E_1 = \frac{\varepsilon_1+\varepsilon_2}{2} - \Delta\sqrt{1+\frac{\Lambda^2}{\Delta^2}}$$

$$= \frac{\varepsilon_1+\varepsilon_2}{2} - \Delta\left(1+\frac{\Lambda^2}{2\Delta^2}+\cdots\right)$$

$$= \varepsilon_1 - \frac{\Lambda^2}{\varepsilon_2-\varepsilon_1}+\cdots$$

agree with perturbation theory. One can similarly check other quantities:

Note:

$$\frac{\Lambda^2}{\Delta^2} \sim \frac{|H_{12}|^2}{(\varepsilon_2-\varepsilon_1)^2} \ll 1$$

is needed to convergence of the power series.

3) $\lambda \gg \left|\frac{\varepsilon_1 - \varepsilon_2}{2}\right| = \Delta$

then $E_1 = \frac{1}{2}\left(\varepsilon_1 + \varepsilon_2 - 2\lambda\sqrt{1 + \frac{\Delta^2}{4\lambda^2}}\right)$

$= \frac{1}{2}(\varepsilon_1 + \varepsilon_2) - \lambda + O\left(\frac{1}{\lambda}\right)$

$E_2 = \frac{1}{2}(\varepsilon_1 + \varepsilon_2) + \lambda + O\left(\frac{1}{\lambda}\right)$

To the lowest order, degenerate perturbation theory applies, higher terms can not be obtained by perturbation theory in λ.

Higher order terms can be obtained by treating H_0 as perturbation,

$H = H_0 + \lambda H_0'$

$= H_0' + H_1'$

10.4

Perturbation theory and symmetry:

When H_0 has a symmetry, there exists an operator A which commutes with H_0

$$[A, H_0] = 0 .$$

(A and H_0 can be simultaneously diagonalized.)

Familiar example: Hydrogen atom

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

(Side)

H_0 is rotationally invariant.

$$[H_0, L^2] = [H_0, L_z] = 0$$

Now perturb $H = H_0 + \alpha H'$

Lemma!

If H' also respects the symmetry, i.e.

$$[H', A] = 0$$

Then $$H'_{ab} = \langle \psi_a^{(0)} | H' | \psi_b^{(0)} \rangle = 0$$

for $a \neq b$

for $A|\psi_a^{(0)}\rangle = a|\psi_a^{(0)}\rangle$, $A|\psi_b^{(0)}\rangle = b|\psi_b^{(0)}\rangle$, $a \neq b$

Proof:

$$0 = \langle \psi_a^{(0)} | [A, H'] | \psi_b^{(0)} \rangle$$

$$= \langle \psi_a^{(0)} | AH' - H'A | \psi_b^{(0)} \rangle$$

$$= (a-b) \langle \psi_a^{(0)} | H' | \psi_b^{(0)} \rangle$$

$$\Rightarrow \quad H'_{ab} = 0 \quad \text{for} \quad a \neq b \qquad \text{Q.E.D.}$$

~~i.e. H' can only mix states of the same eigenvalue of A.~~

(Write the table like graph)

I tell board

This simple fact has important implications, often greatly simplifying the computations: we will use it again and again, (will see examples later). P3 of pset 5

1. In the degenerate subspace of H_0, H' is automatically diagonal in the basis in which A is diagonal.

2. In the 1st order correction to wave functions, H' does not mix states of different eigenvalues of A.

10.5 The fine structure of hydrogen

We will now use perturbation theory to study a few important effects in atomic physics:

Fine structure splitting

Zeeman effect

Stark effect ...

All these effects can be understood by straightforward applying the formulae obtained in earlier lectures.

Below: focus on physical results and intuitions

not on calculation details (often tedious)

In a hydrogen atom, the characteristic velocity of an electron is:

$$v \sim \alpha c = \frac{e^2}{\hbar c} c = \frac{e^2}{\hbar}$$

$$\boxed{\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}}$$: fine structure constant

$\Rightarrow$ relativistic effect small, treat it as perturbation

Relativistic corrections:

$$H_0 = KE + PE = \frac{p^2}{2m} - \frac{e^2}{r}$$ ← non-relativistic kinetic energy

relativistic expression for kinetic energy:

$$KE = \sqrt{m^2c^4 + p^2c^2} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + O(p^6) \cdots$$

$$p^2 = \vec{p} \cdot \vec{p} \qquad p^4 = (\vec{p} \cdot \vec{p})^2$$

$\Rightarrow$ $H = H_0 + H'_{rel}$ with

$$H'_{rel} = -\frac{p^4}{8m^3c^2}$$

Recall: H_0 has degeneracies: $E_n^{(0)}$ depends on n only

not on ℓ, m.

$$[H_0, L^2] = [H_0, L_z] = 0$$

Note: p^4 is spherically symmetric $\Rightarrow$

$$[p^4, L^2] = [p^4, L_z] = 0$$

$\Rightarrow$ H'_{rel} is <u>diagonal</u> in the $|n\ell m\rangle$ basis.

Thus

$$E^{(1)}_{n\ell m} = -\frac{1}{8m^3c^2} \langle n\ell m | p^4 | n\ell m \rangle \qquad (*)$$

$$p^4 = \left(-\hbar^2 \nabla^2\right)^2$$

- Estimate (*) by dimensional analysis:

$$E_{nem}^{(1)} \sim -\frac{1}{8m^3c^2} \cdot (mv)^4$$

$$\sim -\frac{1}{8m^3c^2} 2m^3v^2 \cdot \frac{m}{2}v^2$$

Since $v \sim \alpha c$, $E_{nem}^{(0)} \sim \frac{1}{2}mv^2$

$$\Rightarrow E_{nem}^{(1)} \sim \alpha^2 E_{nem}^{(0)} \sim \underline{\underline{10^{-4} E_{nem}^{(0)}}}$$

- Evaluation of $\langle nem | p^4 | nem \rangle$ is tedious, see Griffith. (p.269)

$$\langle nem | p^4 | nem \rangle = \frac{\alpha^4 m^4 c^4}{n^4} \left(\frac{4n}{\ell + \frac{1}{2}} - 3 \right)$$

$$\Rightarrow \boxed{E_{nem}^{(1)} = -\frac{\alpha^4 mc^2}{8n^4} \left(\frac{4n}{\ell + \frac{1}{2}} - 3 \right)} \quad (*)$$

Remarks on (*):

1. Degeneacy in ℓ is broken.

2. Degeneacy in m remains, $\underline{[H', L^2] = 0}$

3. $E^{(1)}_{nem} \sim \alpha^2 E^{(0)}_{nem}$

4. 2S and 2p are not degenerate, but

   2p does <u>not</u> split.

   Cannot explain fine structure splitting.

Resolution: Spin-orbit coupling (discussed in 8.05)

is of the same order magnitude as (*) and

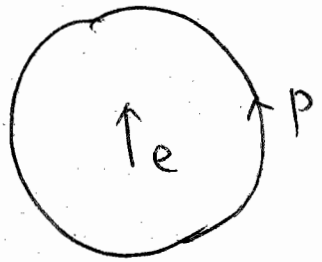
thus should be included.

<u>In fact.</u>

Dirac equation $\Rightarrow$ $H = H_0 + \underbrace{H'_{rel}}_{\text{relativistic}} + H'_{s\text{-}o}$

Spin-orbit interaction: (essentially review of 8.05)

Semi-classical picture: Consider going to rest frame of the electron.



p moves around e

$\Rightarrow$ generate a current

$\Rightarrow$ generate a magnetic field $\vec{B}$

$\Rightarrow$ Spin magnetic moment of e interacts with $\vec{B}$.

$$\Rightarrow H'_{so} = \frac{e^2}{m^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S}$$

Dirac equation: $\Rightarrow$

$$\boxed{H'_{so} = \frac{e^2}{2m^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S}}$$

$[H'_{so}, L_z] \neq 0, \quad [H'_{so}, S_z] \neq 0$

H'_{so} not diagonal in $|n\ell m_\ell m_s\rangle$ basis.

8.05: Let $\vec{J} = \vec{L} + \vec{S}$

then $[H'_{so}, J^2] = [H'_{so}, J_z] = [H'_{so}, L^2] = 0$

$\Rightarrow$ use $|n\ell j m_j\rangle$ basis, H'_{so} is diagonal.

thus $E^{(1)}_{so} = \frac{e^2}{2m^2c^2} \langle n\ell j m_j | \frac{1}{r^3} \vec{L}\cdot\vec{S} | n\ell j m_j \rangle$ (postulated in 8.05)

$= \frac{e^2}{2m^2c^2} \langle n\ell j m_j | \frac{1}{r^3} \frac{1}{2}(J^2 - L^2 - S^2) | n\ell j m_j \rangle$

$= \frac{e^2}{4m^2c^2} \hbar^2 \left(j(j+1) - \ell(\ell+1) - \frac{3}{4} \right) \langle n\ell j m_j | \frac{1}{r^3} | n\ell j m_j \rangle$

- $\langle n\ell j m_j | \frac{1}{r^3} | n\ell j m_j \rangle$ is again somewhat tedious to calculate (see Griffiths).

Order of magnitude estimate:

$$\left\langle \frac{1}{r^3} \right\rangle \sim \frac{1}{a^3}$$

a: Bohr radius.

$$a \sim \frac{\hbar}{mc}\frac{1}{\alpha}$$

$$\Rightarrow E_{SO}^{(1)} \sim \frac{e^2}{m^2c^2}\hbar^2\frac{1}{a^3}$$

$$\sim \frac{e^2\hbar^2}{m^2c^2} \cdot \frac{m^3c^3\alpha^3}{\hbar^3}$$

$$\sim \alpha^4 mc^2$$

same order as $E_{rel}^{(1)}$.

Explicit calculation: $\langle n\ell j m_j | \frac{1}{r^3} | n\ell j m_j \rangle$

$$= \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)n^3a^3}$$

$$\Rightarrow \quad E_{so}^{(1)} = \frac{\alpha^4}{4} mc^2 \; \frac{n\left(j(j+1) - \ell(\ell+1) - \frac{3}{4}\right)}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}$$

$$E_{f.s.}^{(1)} = E_{rel}^{(1)} + E_{so}^{(1)}$$

$$= \frac{\alpha^4 mc^2}{8}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) \qquad (!!)$$

Remarks: 1) Simple, all dependence on ℓ canceled, only depends on j, n.

$\Rightarrow$ degeneracy between e.g.

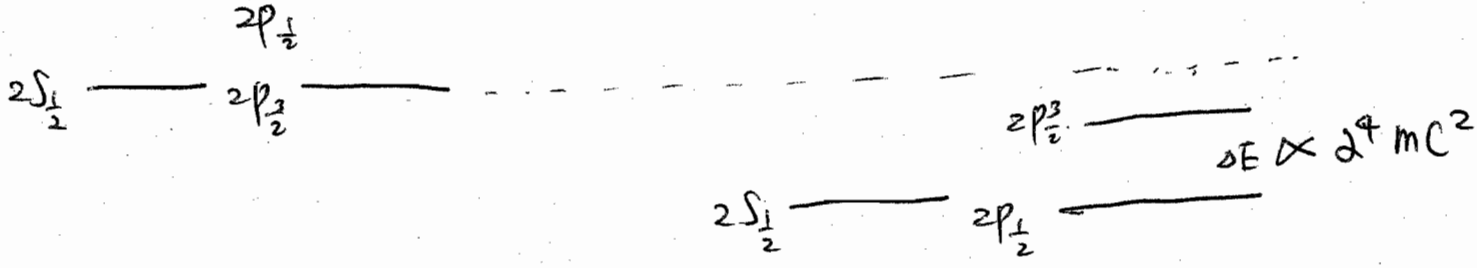
$$E_{2S_{\frac{1}{2}}} = E_{2P_{\frac{1}{2}}}$$

(j under each)

2) This feature is a consequence of specific structure of underlying Dirac equation. (see Griffith P.276) Prob. 6.19

$\ell = 0$: $j = 0 + \frac{1}{2} = \frac{1}{2}$

3) Example: $n = 2$. $\ell = 1$ $j = 1 + \frac{1}{2} = \frac{3}{2} + \frac{1}{2}$



Hydrogen

hydrogen + relativistic.

4) Splitting between $2S_{\frac{1}{2}}$ and $2p_{\frac{1}{2}}$: Lamb Shift

$$\Delta E_{2S_{\frac{1}{2}}} - \Delta E_{2p_{\frac{1}{2}}} \sim \alpha^5 mc^2$$

Need to take in account of the electro magnetic fluctuation

of the vacuum to explain Lamb Shift:

Quantum electrodynamics.

5) Hyperfine splitting:

proton spin magnetic moment can interacts with the magnetic moment ($\hat{Spin}$) of the electron.

$$E_{h.f.}^{(1)} \propto \langle \vec{S}_p \cdot \vec{S}_e \rangle$$

most significant for <u>1s state.</u>

need $\vec{S} = \vec{S}_p + \vec{S}_e$

$$\tfrac{1}{2} \otimes \tfrac{1}{2} = 1 \oplus 0$$

↑ triplet ↑ singlet.

$\Delta E = 5.9 \times 10^{-6} eV \sim \frac{m_e}{m_p} \alpha^4 mc^2$

$\nu = 1420\ Hz$

$\lambda = 21\ cm$ ∴ important in astrophys.

10.6 Zeeman effect:

In an external magnetic field $\vec{B}$,

$$H_Z' = -(\vec{\mu}_e + \vec{\mu}_S)\cdot\vec{B}$$

where $\vec{\mu}_e = -\frac{e}{2m}\vec{L}$: orbital magnetic moment

$\vec{\mu}_S = -\frac{e}{m}\vec{S}$: spin magnetic moment

Take $\vec{B} = (0, 0, B)$

$$\Rightarrow H_Z' = \frac{eB}{2m}(L_z + 2S_z) = \frac{eB}{2m}(J_z + S_z)$$

Thus we now have:

$$H = H_0 + H_{f.s.}' + H_Z'$$

Depending on the strength of B, we can have the following three possibilities:

A: Strong-field Zeeman effect:

$$H_z' \gg H'_{f.s.}$$

One can ignore $H'_{f.s.}$ when considering the effect of an external B-field.

B: Weak-field Zeeman effect.

$$H_z' \ll H'_{f.s.}$$

in which case, we can write H as:

$$H = H_0 + H'_{f.s.} + H'_z = \underline{\underline{\tilde{H}_0}} + H_z'$$

$$\tilde{H}_0 = H_0 + H'_{fs}$$

C: Intermediate field Zeeman effect:

$$H_z' \approx H'_{f.s.}$$

need to treat both terms on equal footing.

10.6.1 Strong-field Zeeman effect:

$$H_Z^{(1)} = \frac{e}{2m} B (L_z + 2S_z)$$

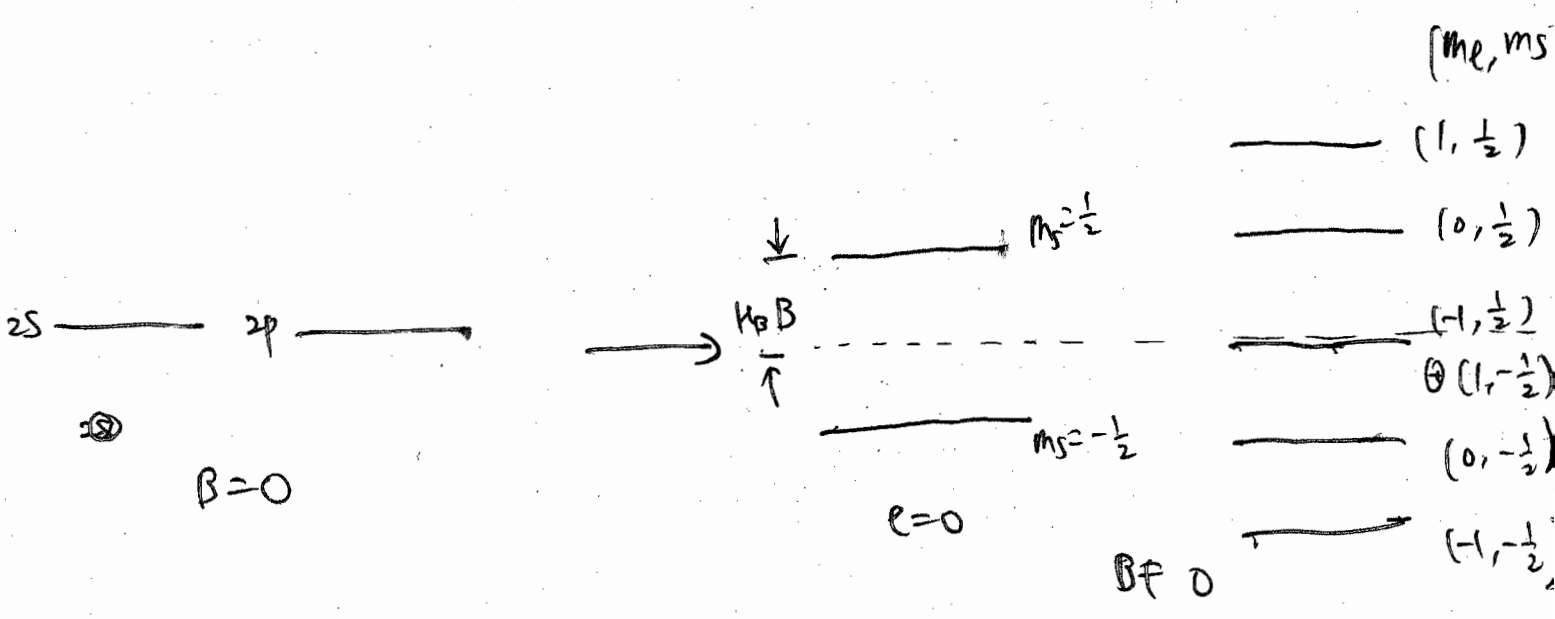
$H_Z^{(1)}$ is diagonal in the basis $|n\ell m_\ell m_s\rangle$.

$$\Rightarrow \quad E^{(1)}_{n\ell m_\ell m_s} = \frac{e\hbar}{2m} B (m_\ell + 2m_s)$$

$$= \mu_B B (m_\ell + 2m_s)$$

with $\mu_B = \frac{e\hbar}{2m}$ (Bohr magneton)

Example: $n=2$ states:



Compare with fine structure splitting

$$E^{(1)}_{f.s.} = \frac{\alpha^4 mc^2}{8n^4}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)$$

n=2 levels:

$$E^{(1)}_{f.s.}\Big|_{2s_{1/2}} = E^{(1)}_{f.s.}\Big|_{2p_{1/2}} = -\frac{13.6}{4}\text{eV}\,\frac{5\alpha^2}{16} \sim 5.7 \times 10^{-5}\ \text{eV}$$

$$E^{(1)}_{f.s.}\Big|_{2p_{3/2}} = -\frac{13.6\,\text{eV}}{4}\,\frac{\alpha^2}{16} \sim 1.1 \times 10^{-5}\ \text{eV}$$

$$E^{(1)}_{\text{zeeman}} \sim \mu_B B$$

$$\mu_B = 5.8 \times 10^{-5}\ \frac{\text{eV}}{\text{Tesla}}$$

$$E^{(1)}_{\text{zeeman}} \sim E^{(1)}_{f.s.} \Rightarrow B \sim 1\ \text{Tesla}$$

Thus strong-field approximation when $B \gg 1$ Tesla.

One can consider further corrections due to fine structure split by adding $H'_{rel} + H'_{SO}$ to $H_0 + H'_z$. See e.g. Griffith P.280.

10.6.2 Weak field Zeeman effect.

When $B \ll 1$ Tesla. $H'_z \ll H'_{f.s.}$,

treat H'_z as small perturbations around

$$\tilde{H_0} = H_0 + H'_{f.s.}$$

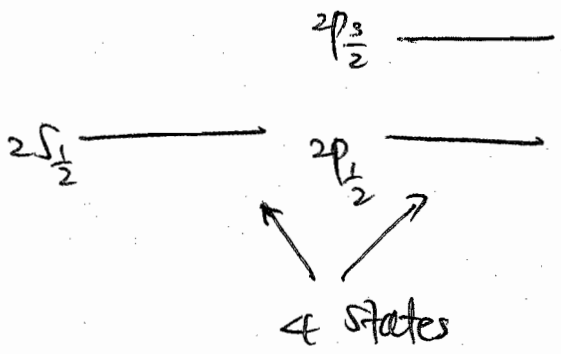
Thus we use the basis $|nejm_j\rangle$ in which $\tilde{H_0}$ is diagonalized.

Zeeman

Since $E_{f.s.}^{(1)}$ only depend on j and n, at first

sight we need degenerate perturbation theory.

E.g. $n=2$



Given $H_z' = \frac{e}{2m} B (J_z + S_z)$. we need to

compute $\frac{\langle n\ell j m_j | J_z + S_z | n\ell' j m_j' \rangle}{M}$

Note: 1) M is zero for $\ell \neq \ell'$, since J_z, S_z do not change ℓ. $\Rightarrow$ states of different ℓ don't mix. e.g. $2s_{\frac{1}{2}}$, $2p_{\frac{1}{2}}$ do not mix.

2) $\langle n e j m_j | J_z | n e j m_j' \rangle = m_j \delta_{m_j m_j'}$ ①

3) $\langle n e j m_j | S_z | n e j m_j' \rangle \propto \delta_{m_j m_j'}$

Since $[S_z, J_z] = 0$. (applying lemma of (0.4)

($|n e j m_j\rangle$ are eigenstates of J_z)

$\Rightarrow$ H_z' is automatically diagonal in $|n e j m_j\rangle$ basis,

no need for diagonalization.

- Computation of $\langle n e j m_j | S_z | n e j m_j \rangle$

One method: use C-G coefficients to express $|j m_j\rangle$

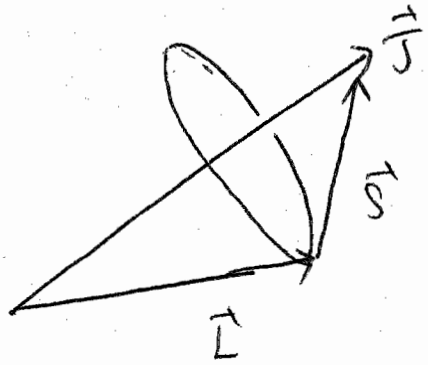
in terms of $|m_e m_s\rangle$.

We use a different method.

In the presence of $H'_{s\cdot o}$ (spin-orbit coupling),

$\vec{L}$ and $\vec{S}$ are not conserved, they precess around ↑ as in NMR

$\vec{J} = \vec{L} + \vec{S}$ (conserved).



Since $\langle n_e j m_j | S_z | n_e j m_z \rangle$ is time-independent, we can replace S_z by its average value.

$$\vec{S}_{ave} = \frac{(\vec{S}\cdot\vec{J})}{J^2}\vec{J}$$

(i.e. project $\vec{S}$ to $\vec{J}$-direction.)

Note: $\vec{S}\cdot\vec{J} = \frac{1}{2}\left(J^2 + S^2 - (\vec{J}-\vec{S})^2\right)$

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

Thus

$$\langle n e j m_j | S_z | n e j m_j \rangle$$

$$= \langle n e j m_j | \frac{J^2 + S^2 - L^2}{2J^2} J_z | n e j m_j \rangle$$

$$= m_j \hbar \frac{j(j+1) + \frac{3}{4} - e(e+1)}{2 j (j+1)} \qquad (2)$$

Using (1) and (2), we find that

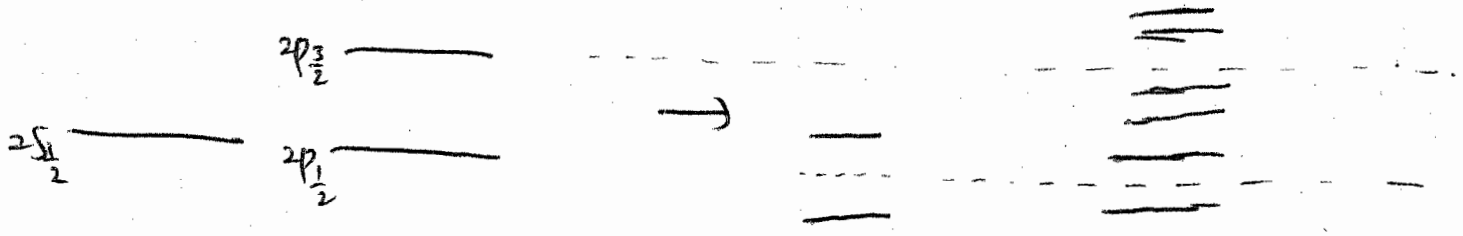
$$E_z^{(1)} = \frac{eB}{2m} \langle n e j m_j | J_z + S_z | n e j m_j \rangle$$

$$= \frac{e\hbar}{2m} B m_j g_J$$

$$\Rightarrow \boxed{E_z^{(1)} = \mu_B B m_j g_J}$$

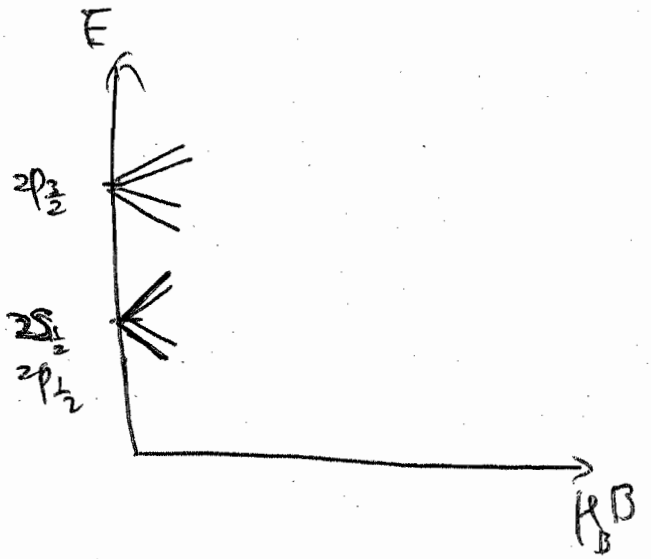
where $g_J = 1 + \frac{j(j+1) + \frac{3}{4} - e(e+1)}{2j(j+1)}$ (Lande g- factor)

Example: $n=2$.



$B=0$ $\qquad\qquad$ $B\neq 0$

all degeneracy removed.



For intermediate field, $H'_Z \sim H'_{SO}$, treat them on equal footing.

degenerate perturbation theory in 8-dim subspace ($n=2$)

See Griffith P. 281.

10.7

Stark effect: Atom in an electric field

$$\vec{E} = (0, 0, \mathcal{E}), \quad \phi = -\mathcal{E}z, \quad \vec{B} = 0$$

Consider

$$H = H^0_{Bohr} + H'_{Stark}$$

$$H'_{Stark} = -q\mathcal{E}z = e\mathcal{E}z$$

Ignore fine structure, spin etc.

Intuitively, what can happen when we apply an electric field to a neutral object?

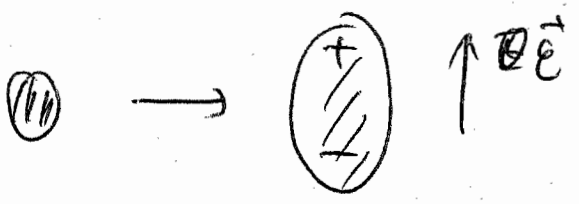
(1) If the object has an dipole $\vec{d}$, then energy shift will be

$$\Delta E = -\vec{\mathcal{E}} \cdot \vec{d}$$

$\vec{d}$ can be found by

$$d = -\frac{\partial \Delta E}{\partial \mathcal{E}}.$$

(2) If the object does not have a dipole moment, then the electric field can induce a dipole



for small $\vec{E}$, the induced dipole. $\vec{d} \propto \vec{\mathcal{E}}$

$$\Rightarrow \quad \Delta E = -\vec{d}\cdot\vec{\mathcal{E}} = -\frac{\beta}{2}\mathcal{E}^2$$

β: polarizability.

Now: energy shifts of various levels.

$n=1$: Ground state ψ_{100}.

$$E^{(1)}_{Stark} = e\mathcal{E}\langle 100|z|100\rangle$$

$$= e\mathcal{E}\int d^3x\, |\psi_{100}|^2 z = 0$$

Thus ground state does not have a permanent dipole.

$$E^{(2)}_{Stark} = e^2\mathcal{E}^2 \sum_{nem} \frac{|\langle 100|z|nem\rangle|^2}{E^{(0)}_{100} - E^{(0)}_{nem}} \qquad (*)$$

Complicated, ~~sure~~ since e.g.

$\langle 100|z|n10\rangle \neq 0$ for all n.

need to an infinite sum, which cannot be done exactly.

Alternatively, one can find $E^{(2)}_{stark}$ by

(1) Solving

$$(H_0 - E^{(0)}_{100})\,\psi^{(1)}_{100} = -(H'_{stark} - \overset{0}{\cancel{E^{(1)}_{100}}})\,\psi^{(0)}_{100}$$

directly in coordinate space.

(2) find $E^{(2)}$ using

$$E^{(2)}_{100} = \langle \psi^{(1)}_{100} \mid H' \mid \psi^{(0)}_{100} \rangle$$

see prob. 6.40 of Griffiths (p. 291)

We will not do it here. Estimate (*) from dimensional analysis:

$$E^{(2)} \sim e^2\mathcal{E}^2 \cdot \frac{a^2}{E^{(0)}}$$

$$\sim e^2\mathcal{E}^2 \frac{a^2}{\frac{e^2}{a}}$$

$$\sim e^2 a^3$$

$$\Rightarrow \quad \underline{\beta \sim a^3}$$

Exact calculation yields: $\beta = \frac{9}{2} a^3$ (polarizability of g.s.)

$n=2$: 4-fold degenerate. need to do degenerate perturbation.

$$|1\rangle = |200\rangle$$

$$|2\rangle = |210\rangle$$

$$|3\rangle = |211\rangle$$

$$|4\rangle = |21{-1}\rangle$$

Since $[L_z, H'_{stark}] = 0$

$\Rightarrow$ $\langle nem | H'_{stark} | nem' \rangle \propto \delta_{m,m'}$

$\Rightarrow$ $$H'_{stark} = \begin{pmatrix} \# & \# & 0 & 0 \\ \# & \# & 0 & 0 \\ 0 & 0 & \# & 0 \\ 0 & 0 & 0 & \# \end{pmatrix}$$

Also recall $\psi_{nem} = f_n(r)\, Y_{em}(\theta, \phi)$

and Y_{em} has parity $(-1)^e$

$\Rightarrow$ $\langle nem | \hat{z} | nem \rangle = \int d^3x \, |\psi_{nem}|^2 \, z = 0$

↑ even parity

$\Rightarrow$ $H'_{Stark} = \begin{pmatrix} 0 & \# & 0 & 0 \\ \# & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$

$\langle 200 | H'_{Stark} | 210 \rangle = \mathcal{E}e \langle 200 | z | 210 \rangle$

$= -3 \mathcal{E} e a$ (from explicit calculation)

$\Rightarrow$ $n=2$ ——— → ——— $\frac{1}{\sqrt{2}}(|200\rangle - |210\rangle)$

——— $|2,1,1\rangle, |2,1,-1\rangle$

——— $\frac{1}{\sqrt{2}}(|200\rangle + |210\rangle)$

$E = 0$

dipole $\underline{\underline{d = 3ea}}$ for $|200\rangle$ and $|210\rangle$

Summary:

Hydrogen spectral.

$E_n^{(0)} \sim \alpha^2 mc^2$ $\quad 2n^2$ degenerate

$E_{f.s.}^{(1)} \sim \alpha^4 mc^2$ depend on $\underline{j}$ and $\underline{n}$

↑ (fine structure)

$E_{rel}^{(1)} + E_{s-o}^{(1)}$

e.g $E^{(1)}_{2S_{\frac{1}{2}}} = E^{(2)}_{2P_{\frac{1}{2}}}$

Lamb shift $\sim \alpha^5 mc^2$. Splitting between $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$

Hyperfine structure $\sim \frac{m_e}{m_p} \alpha^4 mc^2$. Splitting of $\underline{\text{ground state}}$.

(spin-spin interaction between proton and electron)

Zeeman $\sim \mu_B B$

Stark $\sim e\mathcal{E}a$ (linear)

$\sim e^2 a^3$ (quadratic)