Perturbation Methods: Time Independent case

- Non-degenerate case: Theory
- Non-degenerate case: Examples
- Patterns of Perturbations: More examples
- Matrix view of Non-degenerate case
- Degenerate Perturbation case
- Examples of the degenerate case

Idea of perturbation theory: Generalities

You may have noticed just how few exactly solvable problems there are in QM ....

You want to solve $H|n> = E_n|n>$, but it is not possible to solve this one simply...BUT

You notice that there is a simpler part inside of H that would be exactly solvable. $H = H^0+H^1$

H^0 : the easy part. Suppose its eigenstructure is known. That is we can construct $|n^0>$ that satisfy $H^0|n^0> = E^0_n|n^0>$

H^1 : the part of the Hamiltonian that makes an exact solution of full, original problem so difficult.

Perturbation Methods: a way to solve the original equation by successive approxim
WARNING: many indices running around this business...try to stay awake!

SO: Perturbation methods are a way to relate problems that cannot be solved exactl related, simpler but exactly solvable ones.....

Non-degenerate Perturbation theory:

Want $H|n\rangle = E_n|n\rangle$ but have only $H^0|n^0\rangle = E^0_n|n^0\rangle$ with $H = H^0 + H^1$

Main Assumption of Perturbation theory: The hilbert space for H and for H^0 are the same!

(Note: this can be a spectacularly mistaken assumption...particularly in the case where the systems are in infinite volume ... phase transitions)

If they have the same Hilbert space, then we can use the known problem as an basis for expansions of the unknown problem's eigenstates.

Recall $\langle n^0|m^0\rangle = \delta_{nm}$. Note also that we can use them as a basis

$$|n\rangle = |n^0\rangle + |n^1\rangle + |n^2\rangle + \ldots$$

Where by $|n^1\rangle$, $|n^2\rangle$, etc, I simply mean linear combinations of H^0 eigenstates, th
here referring to the order of the approximation.

The order of the approximation.

We have so far talked about H^0, now we must talk about H^1

It is convenient to think of H^1 as, in a sense that will be made clear in a few slides, small relative to H^0.

As we compute the linear combinations of $|m^0\rangle$ that appear in $|n^1\rangle$, $|n^2\rangle$, e
we will count the order of a linear combination in terms of with what po
it vanishes as the perturbation H^1 is scaled away to zero.

So, at least in a formal sense, we write;

$$|n\rangle = |n^0\rangle + |n^1\rangle + |n^2\rangle + \ldots$$

Where we understand with $H = H^0 + H^1$

$$E_n = E^0_n + E^1_n + E^2_n + \ldots$$

Then, contracting both sides of the full equation
$H|n> = E_n|n>$
with $|n^0>$ then to leading order (independent of H^1)
it must be that

$$E^0_n = <n^0|H^0|n^0>$$

The next term is the so-called leading perturbative piece which reads

$$E^1_n = <n^0|H^1|n^0>$$

It is first order in the perturbation, befitting its index.

Contracting the equation with respect to another sta $\neq$ $|m^0>$ $|n^0>$
also yields the leading contribution to the overlap between the new states
(eigvects of the full problem) and the solvable problems' eigenbasis;

First contribution to the overlap:

$$<m^0|n^1> = <m^0|H^1|n^0>/(E^0_n - E^0_m)$$

Beyond 1st order

We can continue this way, collecting terms that successively contribute to the ener
linear combinations of eigenstates that contribute to the state |n>

For example, in second order, the contribution to the energy is found by contracting
the above $H|n> = E_n|n>$ equation by $<n^1|$. We find,

$E^2_n = <n^0|H^1|n^1>$

$$E_n^2 = \sum_{m \neq n} \frac{|<n^0|H^1|m^0>|^2}{E_n^0 - E_m^0}$$

Remark: Note that the second order energy shift for the ground state is always ne

Enough theory…onto some examples:

Particle in a harmonic well with linear potential – done in book

Particle in box with a delta function perturbation in the middle of the box

Particle in the box with a delta function perturbation off to one side.

Particle in box with a linear ramp superimposed

Matrix View of Non-degenerate perturbation theory:

In quantum mechanics you have already seen just how useful and powerfu
the matrix description is. Let us transcribe what we have done so far
in terms of the matrix description. It will be pedagogically useful to stu
some detail the case of a Hilbert space consisting of just two states, a a

So, still want to solve to find |1>, |0> and the associated energy eigenvalues G
, for example,

$$H|0\rangle = G_0|0\rangle$$

But, again $H = H^0+H^1$, and we only know the eigenvectors/eigenvalues of H^0

$$H^0|a\rangle = E^0_a|a\rangle \qquad H^0|b\rangle = E^0_b|b\rangle$$

Now, that we have set up the notation we can write these H^0 and H as matrices
the |a> |b> basis

NOTE: throughout subscripts are state labels and superscripts denote the order of the term (*i.e.* power of H^1 involved)...

Matrix View of Non-degenerate perturbation theory:

So: $$H^0 = \begin{bmatrix} E_a^0 & 0 \\ 0 & E_b^0 \end{bmatrix}$$

Now, to develop H as a matrix we need to find H^1 as a matrix. Apriori all we know is that H^1 is also Hermitean. The general form for H^1 is then,

$$H^1 = \begin{bmatrix} e_a & \Delta \\ \Delta^* & e_b \end{bmatrix}$$

Matrix View of Non-degenerate perturbation theory:

$$H^1 = \begin{bmatrix} e_a & \Delta \\ \Delta^* & e_b \end{bmatrix}$$

Where note that;

$$e_a =< a^0|H^1|a^0 >$$

Diagonal Parts

$$e_b =< b^0|H^1|b^0 >$$

Off-diagonal parts

$$\Delta =< a^0|H^1|b^0 >$$

Matrix View of Non-degenerate perturbation theory:

SO: our goal is to diagonalize with H = H^0+H^1

We can compute the eigenvalues the usual way; solving the characteristic

$$(E_a^0 + e_a - \lambda)(E_b^0 + e_b - \lambda) - |\Delta|^2 = 0$$

Let us call

$$E_a = E_a^0 + e_a$$
$$E_b = E_b^0 + e_b$$

To simplify the subsequent notation...

Matrix View of Non-degenerate perturbation theory:

Proceeding to solve this quadratic equation for the eigenvalues....

$$2\lambda = (E_a + E_b) \pm \sqrt{(E_a + E_b)^2 - 4(E_a E_b - |\Delta|^2)}$$

Note that in the limit of the case

$$|E_b - E_a| > |\Delta|$$

We can simplify this solution to the quadratic equation by Taylor expanding the squ

Matrix View of Non-degenerate perturbation theory:

Which leads to ;

$$2\lambda = (E_a + E_b) \pm \left(E_a - E_b + 2\frac{|\Delta|^2}{E_a - E_b}\right) + \ldots$$

So, for example, taking the '+' sign we arrive at an expression for G_0;

$$G_0 = E_a + \frac{|\Delta|^2}{E_a - E_b}$$

And since

$$E_a = E_a^0 + e_a \quad \text{with} \quad e_a = < a^0 | H^1 | a^0 >$$

We see that the first term contains the leading first order correction to the energy

Matrix View of Non-degenerate perturbation theory:

...while the second term corresponds to the second order result we'd already com

but here for only a 2-d vector space. Compare this second term;

$$G_0 = E_a + \frac{|\Delta|^2}{E_a - E_b}$$

But with $\Delta =< a^0|H^1|b^0 >$

To

$$E_n^2 = \sum_{m \neq n} \frac{|<n^0|H^1|m^0>|^2}{E_n^0 - E_m^0}$$

For a hilbert space with only two states. Viola!

Degenerate Perturbation Theory

Now, the reason we've developed this is not just to rederive the previous result BU
let us examine the critical assumption that went into this solution, namely that
states are so close in energy so as to invalidate the contribution on the previou
really being a second order correction. The critical assumption was ;

$$|E_b - E_a| > |\Delta|$$

Which allowed us to Taylor expand the square root. Clearly if this condition is viola
the second order contribution from this pair of terms is no longer second order

So, how are we to understand perturbations in this limit, where the spectrum is beco
degenerate? In a sense the resolution of this question is already before us in this
example;

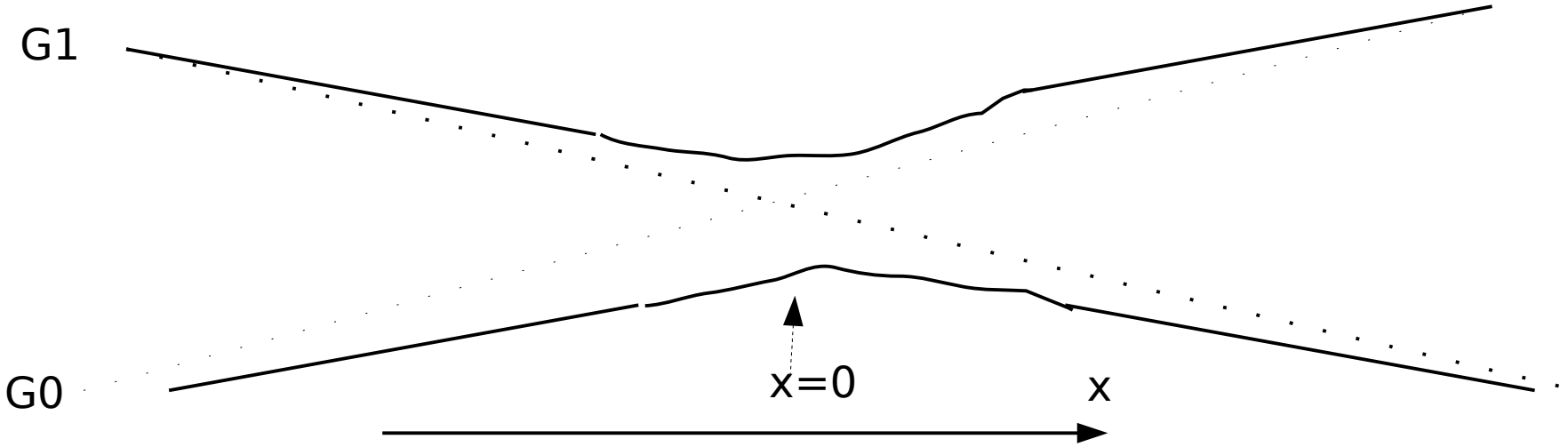
ANSWER: go back to the matrix formulation of quantum mechanics and treat the per
as mixing the states in the subspace of Hilbert space formed out of all eigenvecto
nearly degenerate eigenvalues.

Degenerate Perturbation Theory

Thus, in our 2-d Hilbert space example, let $x = E_a - E_b$

be a 'co-ordinate' representing the progression of a perturbation whose 1st order terms would tend to make the eigenvalues of the states 'collide'. Then our more complete version of the diagonalization of the 2x2 matrix for H reads

$$2\lambda = (E_a + E_b) \pm \sqrt{x^2 + 4|\Delta|^2}$$



Degenerate Perturbation Theory

$$< \phi | k >= e^{ik\phi}$$

$$E_k^0 = \frac{\hbar^2 k^2}{2m}$$

A Simple Example:

1) Particle on a ring. +\- k have the same energy, k is discrete

Symmetry is (translation) x (reflection)

$|-k>$ $|k>$

$$H^0 = \begin{bmatrix} E_k^0 & 0 \\ 0 & E_k^0 \end{bmatrix}$$

2) Put in a delta function spike on the ring. Breaks down (reduces) the sy

3) Must use degenerate perturbation theory in the +/- k subspace

cos sin

$$H^1 = \Gamma \delta(\phi - \phi_0)$$

$$H^0+H^1 = \begin{bmatrix} E_k^0+\Gamma & \Gamma \\ \Gamma & E_k^0+\Gamma \end{bmatrix}$$

Find Eigenvectors and Eigenvalues: two Eigenvectors

Symmetric State

$$(1,1)/\sqrt{2}$$

means

($|k> + |-k>$)/sqrt(2)

Anti-symmetric State

$$(1,\text{-}1)/\sqrt{2}$$

means

($|k> - |-k>$)/sqrt(2)

$$E_{(1,1)} = E_k^0 + 2\Gamma$$

$$E_{(1,-1)} = E_k^0$$

Perturbations of the Hydrogen Atom

We want to study the spectrum of the Hydrogen atom in more detail in order to develop a deeper understanding of the optical structure of other atoms and wit 'wink' towards understanding real-world applications of this deeper understand

1) Finite Size Effect: example of non-degenerate perturbation theory

Non-degenerate perturbation theory

2) Fine Structure corrections: Relativity breaks the n^2 degeneracy

Degenerate perturbation theory

3) Hyperfine structure

Degenerate Perturbation theory and spin

These lift much (but not all!) of the degeneracy in the original hydrogen spectrum..

Perturbations of the Hydrogen Atom

1) Finite Nuclear Size effect:

The fact that the nucleus has a finite size means that the electrons don't actual
quite see a 1/r-potential all the way down to r=0. Instead, assuming that the pr
charge is smeared out uniformly across the nuclear radius R, we expect (by Ga
law)

$$V(r) = \frac{-3e^2}{2R} + \frac{e^2 r^2}{2R^3} \qquad r<R$$

$$V(r) = -\frac{e^2}{r} \qquad r>R$$

We now use the fact that the nuclear radius R is so much smaller than the typical length scale in an atomic wave function; when we compute the leading contribution to the energy (i.e., $E^1_n = \langle n|H^1|n\rangle$), only the s-wave (l=0) receive the largest contribution...the other l<>0 wavefunctions vanish at the o

Finite Nuclear Size effect: (con't)

...in the oft-used parlance, only l=0 wave functions have 'penetration at the nu

Note that the wave function's value at r=0 is;

$$\Psi_{n0}(0) = \left(\frac{2Z}{na_o}\right)^{3/2} \frac{1}{\sqrt{2}} \frac{1}{\sqrt{4\pi}}$$

Where we are keeping track of the Z-dependence for use later...

The overall difference between the coulombic and the smeared-out coulombic p

is;

$$\delta V(r) = -\frac{3e^2}{2R} + \frac{e^2 r^2}{2R^3} + \frac{e^2}{r} \qquad \text{when } r < R$$

And computing the first order shift, because it is over so short a range, we find,

$$< n, l = 0 | \delta V | n, l = 0 >$$

$$\sim |\Psi_{n0}(0)|^2 \int_0^R \mathrm{d}^3 r \delta V(r)$$

Which gives immediately,

$$< n, l = 0 | \delta V | n, l = 0 > = \frac{4}{5} \mathbf{Ry} \left(\frac{Z}{n} \right)^3 \left(\frac{R}{a_0} \right)^2$$

Where:

$$\mathrm{Ry} = mc^2 \frac{\alpha^2}{2}$$

So that we can write of the unperturbed levels (here for Z=1),

$$E_n^0 = -mc^2 \frac{\alpha^2}{2n^2}$$

We pause to note a few things about the finite nuclear size effect ....

Finite Nuclear Size effect: (con't)

$$E^{1}_{n0} = \frac{4}{5}\mathbf{Ry}\left(\frac{Z}{n}\right)^{3}\left(\frac{R}{a_0}\right)^{2}$$

Summary:

0) Only shifts the l=0 levels.

1) Grows rapidly with Z

2) falls off rapidly with increasing n

For Hydrogen (Z=1), using typical values, R = 1.2 x 10^{-15} m,
and a_0 = .529 x 10^{-10} m we arrive at

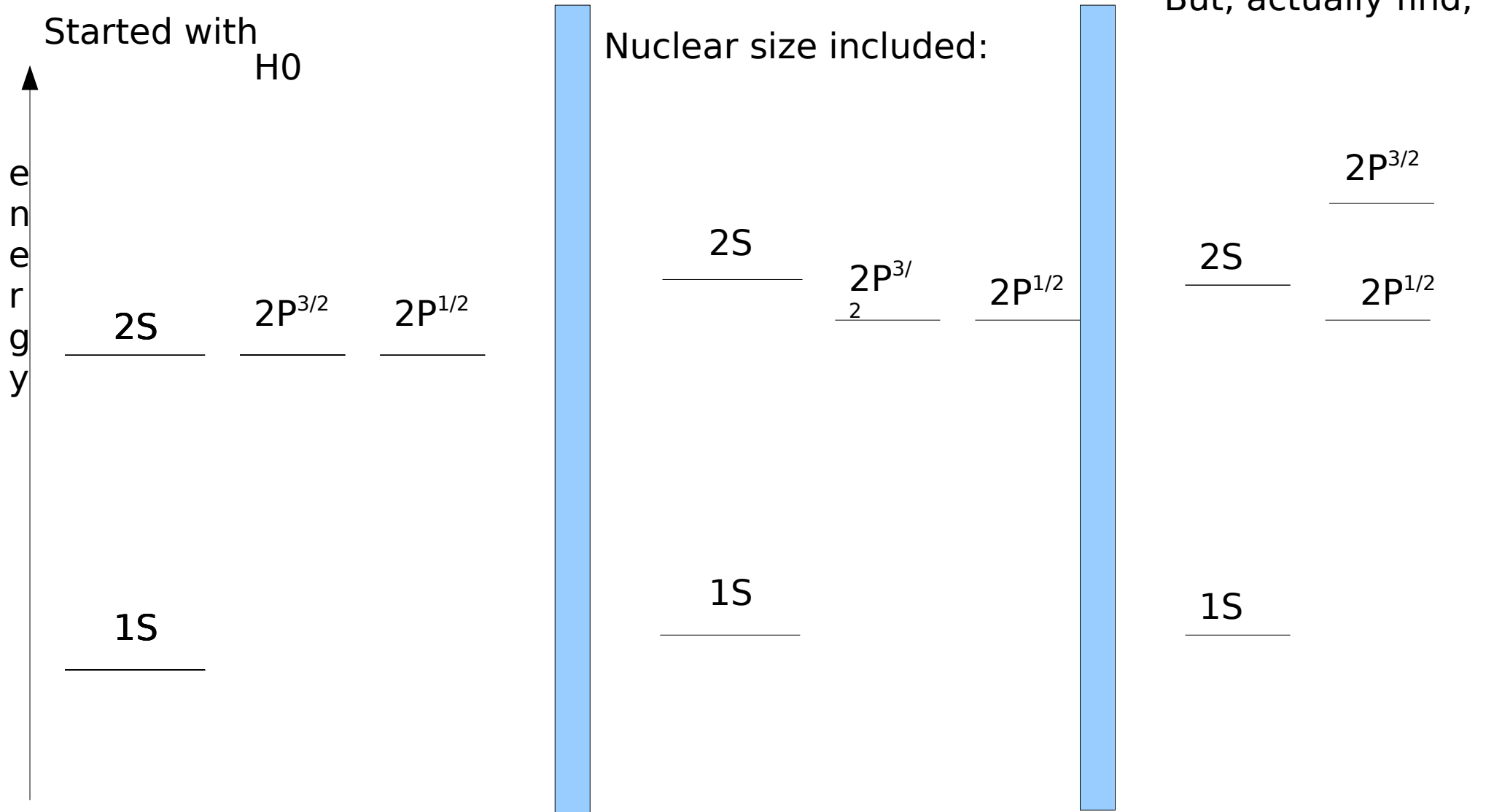
3) Leads to a ground state shift upwards of 5.6 x 10^{-9} eV (about 1.35 MHz).

4) Would lead to shift between 2S (going up) and 2P of about 170 KHz.

Plus...

Hydrogen Spectrum: Closer look at low levels

nl^j -notation with j = l+s



Hydrogen Spectrum: Fine Structure Splitting

SO...something else must be going on. We need to understand this 'fine splitting'

In the ground state of hydrogen the electrons are going about 1/137th the spe light. We need to be a little cautious about the use of the non-relativistic v equation.

We will do a much better job of understanding this when we solve the Hydrog problem using the fully relativistic Dirac equation next semester. But for n we treat relativistic corrections as a perturbation. Idea is recall the that th total kinetic energy is just the difference of the relativistic energy and the mass energy;

$$E_{kin} = \sqrt{p^2 + m^2c^4} - mc^2$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots$$

The perturbation on the naïve hydrogen spectrum from the earlier chapter reads;

$$H^1 = -\frac{p^4}{8m^3c^2}$$

And so the first order energy shift can be written;

$$< nlm|H^1|nlm >$$
$$= -\frac{1}{8m^3c^2} < nlm|p^4|nlm >$$

Note that this perturbation is again diagonal! Anyways, it reads,

$$E_n^1 = -\frac{1}{8m^3c^2}$$
$$< nlm|(2m(H^0 - e^2/r))^2|nlm >$$

Which we can break up into parts as

$$E^1_{n0} = -\frac{1}{2mc^2}\left[(E^0_n)^2 - E^0_n < \frac{e^2}{r} > + e^4 < \frac{1}{r^2} >\right]$$

Factor of 2 missing here!

And we can compute the matrix elements there straightforwardly in the basis of (unperturbed, naïve zeroth order) eignestate of the hydrogen atom.

They are;

$$< e^2/r >= -2E^0_n$$

$$< e^4/r^2 >= \frac{4(E^0_n)^2 n}{l+1/2}$$

And so, finally fastening it all together, we have,

$$E^1_n = -\frac{1}{2}mc^2\alpha^4\left(\frac{-3}{4n^4} + \frac{1}{n^3(l+1/2)}\right)$$

$$E_n^1 = -\frac{1}{2}mc^2\alpha^4\left(\frac{-3}{4n^4} + \frac{1}{n^3(l+1/2)}\right)$$

Good Thing: as l increases the E1n is more positive (less negative) ... that is, under this perturbation the 2P would shift up more than the 2S.

Bad Thing: does not lead to shift that depends on the J-values and not just the l-values.

There must be some additional spin-dependent effect that is responsible for the observed level spacings.

B – field due to motion and the spin-orbit coupling

The point is that we have forgotten something else about relativity...namely that wh
particle moves in an electric field it sees a magnetic field arise.

$$\vec{B} = -\frac{e}{cr^3}\vec{v} \times \vec{r}$$

The electron's spin responds to this and contributes a total energy

$$H = -\vec{\mu} \cdot \vec{B}$$

So that in terms of the spin-magnetic moment of an electron (assume g=2) we ha

$$H = \frac{e^2}{m^2c^2r^3}\vec{S} \cdot \vec{L}$$

This, for obvious reasons, is called a spin-orbit coupling...

Note that we can rewrite this entirely in terms of J as

$$\vec{J} = \vec{L} + \vec{S}$$

using

$$2\vec{S} \cdot \vec{L} = J^2 - L^2 - S^2$$

+ Thomas Precession Factor

$$H_{s.o.} = \frac{e^2}{4m^2c^2r^3}(J^2 - L^2 - S^2)$$

$$E^1_{s.o.} = < j', m'_j, l, s | H_{s.o.} | j, m_j, l, s$$

$$< \frac{1}{r^3} >= \frac{1}{a_0^3} \frac{1}{n^3 l(l+1/2)(l+1)}$$

So

$$E^1_{s.o.} = \frac{1}{4} \frac{mc^2\alpha^4}{n^3 l(l+1/2)(l+1)} \times (l \text{ or } -(l+1))$$

Recall

$$\alpha = \frac{e^2}{\hbar c} \qquad\qquad mc^2\alpha^2/2 = 13.6 \text{ eV}$$

Good even for *l=0* !

$$E^1 = -\frac{mc^2\alpha^4}{2n^3}\left[\frac{1}{j+1/2} - \frac{3}{4n}\right] + \frac{e^1_{nucle}}{n^3}$$

So;

$$E^1_{2S} = -\frac{mc^2\alpha^4}{16}(5/8) + e^1_{nuclear}$$

$$E^1_{2P^{1/2}} = -\frac{mc^2\alpha^4}{16}(5/8)$$

$$E^1_{2P^{3/2}} = -\frac{mc^2\alpha^4}{16}(1/8)$$

Run the numbers.... $\frac{mc^2\alpha^4}{16} = 9.06 \text{ x } 10^{-5} \text{ eV}$

Other Applications of perturbation theory:

Intrinsic to atoms:

1) Hyperfine Splitting: Interaction between nuclear and electron spin
   typically varies from Mhz to GHz
2) Lamb Shift: Additional relativistic corrections to the Schroedinger Eqn.
   4.37 x 10-6 eV ~ 1057 Mhz. Also much larger than the nuclear size e

Atom in External Fields

1) Stark Effect: Atom in an electric field
2) Zeeman Effect: Atom in a Magnetic Field
3) AC stark effect: atom in a time-varying electric field

$$|E_b - E_a| > |\Delta| \qquad \Delta =< a^0|H^1|b^0 >$$

$$E_a = E_a^0 + e_a \qquad e_a =< a^0|H^1|a^0 >$$

$$E_b = E_b^0 + e_b \qquad e_b =< b^0|H^1|b^0 >$$

$$(E_a^0 + e_a - \lambda)(E_b^0 + e_b - \lambda) - |\Delta|^2 = 0$$

$$2\lambda = (E_a + E_b) \pm \sqrt{(E_a + E_b)^2 - 4(E_a E_b - |\Delta|^2)}$$

$$2\lambda = (E_a + E_b) \pm (E_a - E_b + 2\frac{|\Delta|^2}{E_a - E_b})$$

$$\lambda = E_a + \frac{|\Delta|^2}{E_a - E_b}$$

$$H^0 = \begin{bmatrix} E_a^0 & 0 \\ 0 & E_b^0 \end{bmatrix}$$

$$H^1 = \begin{bmatrix} e_a & \Delta \\ \Delta^* & e_b \end{bmatrix}$$

$$x = E_a - E_b$$