

量子力学  
Quantum mechanics

School of Physics and Information Technology  
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# Chapter 6

## Time-independent Perturbation Theory

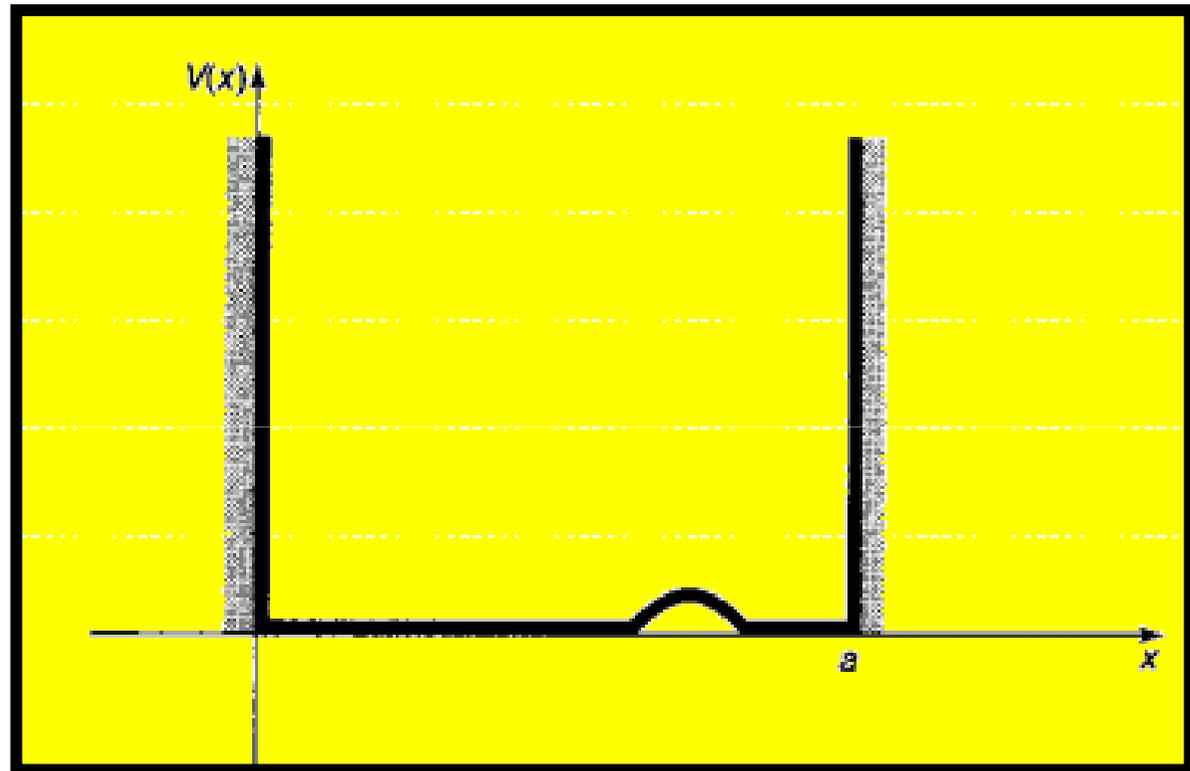
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What

&

Why



Infinite square well with small perturbation

# Problem

Suppose we have solved the (time - independent) Schrödinger equation for some potential, now we perturb the potential slightly.

## Difficulty & why

For this problem, we'd like to solve for the new eigenfunctions and eigenvalues :

$$H\Psi_n = E_n \Psi_n ,$$

But unless we are very lucky, we're unlikely to be able to solve the Schrödinger equation exactly, for this more complicated potential.

## What

Perturbation theory is a systematic procedure for obtaining approximate solutions to the perturbed problem by building on the known exact solutions to the unperturbed case.

# OUTLINE

- Non-degenerate perturbation theory
- Degenerate perturbation theory
- Some examples for application

# Non-degenerate Perturbation Theory

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- General formulation
- First-order theory
- Second-order energies

# General formulation

# The unperturbed case

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Time - independent Schrödinger equation :

$$H^0 \Psi_n^0 = E_n^0 \Psi_n^0$$

Eigenvalues:  $E_n^0$

Eigenfunctions:  $\Psi_n^0$

Requirement:

$$\langle \Psi_n^0 | \Psi_m^0 \rangle = \delta_{nm}$$

Considering the perturbed case, we should solve for the new eigenvalues and eigenfunctions.

We can write the Hamiltonian of the new system into the following two parts

$$H = H^0 + H'$$

Hamiltonian of the unperturbed system

Additional Hamiltonian of the perturbed system

Rewrite the new Hamiltonian as the sum of two terms

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

A small number ;later we will crank it up to 1, and H will be the true, exact Hamiltonian

Write the  $n^{\text{th}}$  eigenfunction and eigenvalue as power series in  $\lambda$  as follows


$$\Psi_n = \Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots$$

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

The first-order correction

The second-order correction

$$H\Psi_n = E_n\Psi_n$$



Plugging the above  $H, \psi_n$  and  $E_n$  into the time-independent equation and Collecting like powers of  $\lambda$

$$\begin{aligned} & H^0\Psi_n^0 + \lambda(H^0\Psi_n^1 + H^1\Psi_n^0) + \lambda^2(H^0\Psi_n^2 + H^1\Psi_n^1) + \dots \\ &= E_n^0\Psi_n^0 + \lambda(E_n^0\Psi_n^1 + E_n^1\Psi_n^0) + \lambda^2(E_n^0\Psi_n^2 + E_n^1\Psi_n^1 + E_n^2\Psi_n^0) + \dots \end{aligned}$$

$\lambda$  is a device to keep track of the different orders

To lowest order:

$$H^0 \Psi_n^0 = E_n^0 \Psi_n^0$$

To first order:

$$H^0 \Psi_n^1 + H^1 \Psi_n^0 = E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0$$

To second order:

$$H^0 \Psi_n^2 + H^1 \Psi_n^1 = E_n^0 \Psi_n^2 + E_n^1 \Psi_n^1 + E_n^2 \Psi_n^0$$

And so on

# First-Order Theory

- The first-order correction to the energy
- The first-order correction to the wave function

The first-order  
correction to the energy

$$H^0 \Psi_n^1 + H' \Psi_n^0 = E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0$$

Multiplying by  $(\Psi_n^0)^*$   
and integrating

$$\langle \Psi_n^0 | H^0 \Psi_n^1 \rangle + \langle \Psi_n^0 | H' \Psi_n^0 \rangle = E_n^0 \langle \Psi_n^0 | \Psi_n^1 \rangle + E_n^1 \langle \Psi_n^0 | \Psi_n^0 \rangle$$

And,

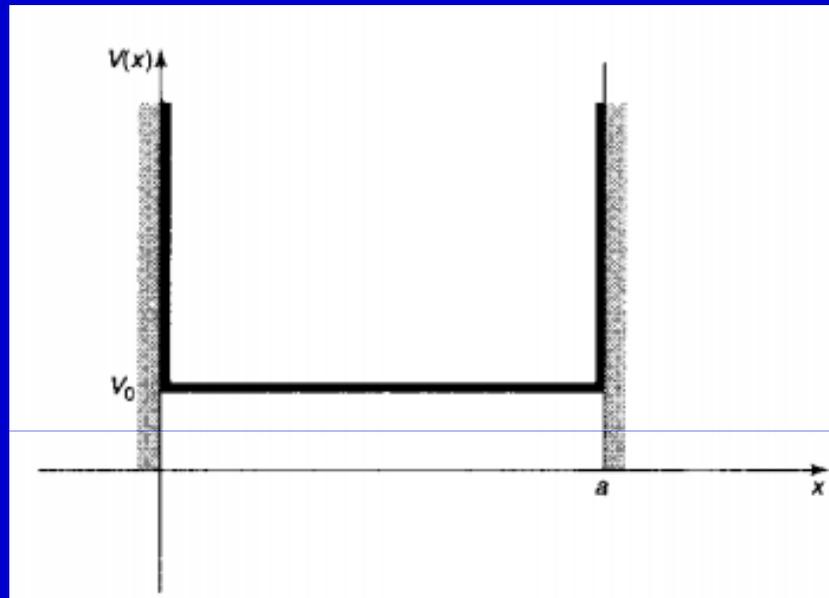
$$\begin{aligned} \langle \Psi_n^0 | \Psi_n^0 \rangle &= 1 \\ \langle \Psi_n^0 | H^0 \Psi_n^1 \rangle &= E_n^0 \langle \Psi_n^0 | \Psi_n^1 \rangle \end{aligned}$$

So,

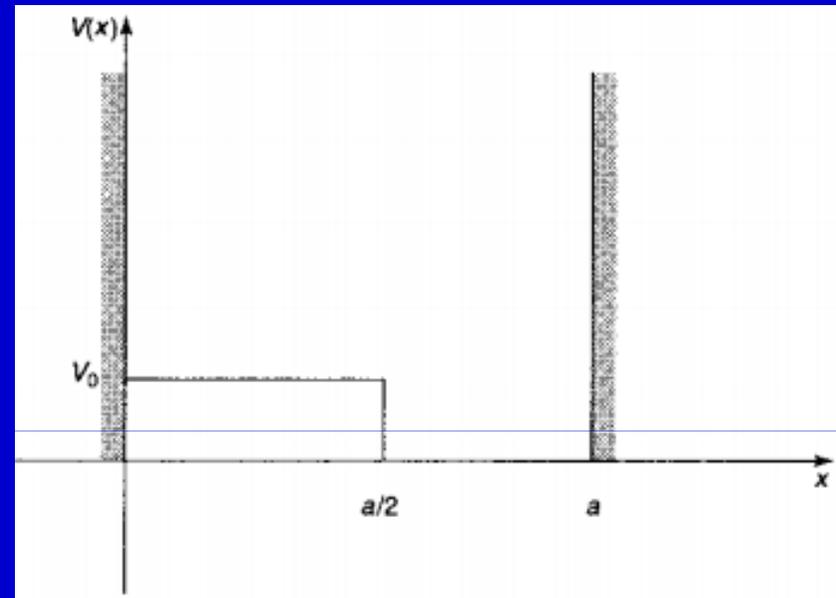
$$E_n^1 = \langle \Psi_n^0 | H' | \Psi_n^0 \rangle$$

**Results:** The first-order correction to the energy is the expectation value of the perturbation in the unperturbed state.

# Example



**Figure 6.2:** Constant perturbation over the whole well.



**Figure 6.3:** Constant perturbation over half the well.

**Example.** The unperturbed wave functions for the infinite square well are (Equation 2.24)

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right).$$

Suppose first that we perturb the system by simply raising the “floor” of the well by a constant amount  $V_0$  (Figure 6.2). In that case  $H' = V_0$ , and the first-order correction to the energy of the  $n^{\text{th}}$  state is

$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0.$$

The corrected energy levels, then, are  $E_n \cong E_n^0 + V_0$ ; they are simply lifted by the amount  $V_0$ . Of *course!* The only surprising thing is that in this case the first-order theory yields the *exact* answer. Evidently, for a *constant* perturbation all the higher corrections vanish.<sup>2</sup> If, on the other hand, the perturbation extends only halfway across the well (Figure 6.3), then

$$E_n^1 = \frac{2V_0}{a} \int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right) dx = \frac{V_0}{2}.$$

In this case every energy level is lifted by  $V_0/2$ . That’s not the *exact* result, presumably, but it does seem reasonable as a first-order approximation.

The first-order correction  
to the wave function

Rewrite equation

$$H^0 \Psi_n^1 + H' \Psi_n^0 = E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0$$



$$(H^0 - E_n^0) \Psi_n^1 = -(H' - E_n^1) \Psi_n^0$$

The unperturbed wave functions constitute a complete set



$$\Psi_n^1 = \sum_{m \neq n} C_m^{(n)} \Psi_m^0$$

Additional,

$$H^0 \Psi_n^0 = E_n^0 \Psi_n^0$$



$$\sum_{m \neq n} (E_m^0 - E_n^0) C_m^{(n)} \Psi_m^0 = -(H' - E_n^1) \Psi_n^0$$

Take the inner product with  $\Psi_l^0$

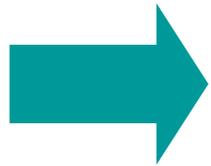


$$\sum_{m \neq n} (E_m^0 - E_n^0) C_m^{(n)} \langle \Psi_l^0 | \Psi_m^0 \rangle = -\langle \Psi_l^0 | H' | \Psi_n^0 \rangle + E_n^1 \langle \Psi_l^0 | \Psi_n^0 \rangle$$

If  $l = n$ , we get  $E_n^1$  ;

If  $l \neq n$ , we get  $C_m^{(n)}$  .

$$C_m^{(n)} = \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0}$$



$$\Psi_n^1 = \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0} \Psi_m^0$$

Notice: although perturbation theory often yields surprising by accurate energies, the wave functions are notoriously poor.

# Second-order energies

$$H^0 \Psi_n^2 + H' \Psi_n^1 = E_n^0 \Psi_n^2 + E_n^1 \Psi_n^1 + E_n^2 \Psi_n^0$$



Take the inner product with  $\Psi_n^0$

$$\langle \Psi_n^0 | H^0 \Psi_n^2 \rangle + \langle \Psi_n^0 | H' \Psi_n^1 \rangle = E_n^0 \langle \Psi_n^0 | \Psi_n^2 \rangle + E_n^1 \langle \Psi_n^0 | \Psi_n^1 \rangle + E_n^2 \langle \Psi_n^0 | \Psi_n^0 \rangle$$

$$\langle \Psi_n^0 | H^0 \Psi_n^2 \rangle = \langle H^0 \Psi_n^0 | \Psi_n^2 \rangle = E_n^0 \langle \Psi_n^0 | \Psi_n^2 \rangle$$

The Hermiticity of  $H^0$

Meanwhile,  $\langle \Psi_n^0 | \Psi_n^0 \rangle = 1$ ;

$$\langle \Psi_n^0 | \Psi_n^1 \rangle = \sum_{m \neq n} C_m^{(n)} \langle \Psi_n^0 | \Psi_m^0 \rangle$$

$$E_n^2 = \sum_{m \neq n} \frac{\left| \langle \Psi_m^0 | H' | \Psi_n^0 \rangle \right|^2}{E_n^0 - E_m^0}$$

We could proceed to calculate the second-order correction to the function, the third-order correction to the energy, and so on, but in practice, the above results is ordinarily as high as it is useful to pursue this method.

# Results

Correction to the eigenvalue:

$$E_n = E_n^0 + H'_{nn} + \sum_{m \neq n} \frac{\left| \langle \Psi_m^0 | H' | \Psi_n^0 \rangle \right|^2}{E_n^0 - E_m^0} + \dots \quad (1)$$

Correction to the eigenfunction:

$$\Psi_n = \Psi_n^0 + \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0} \Psi_m^0 + \dots \quad (2)$$

# Degenerate Perturbation Theory

- Two-fold degeneracy
- Higher-order degeneracy

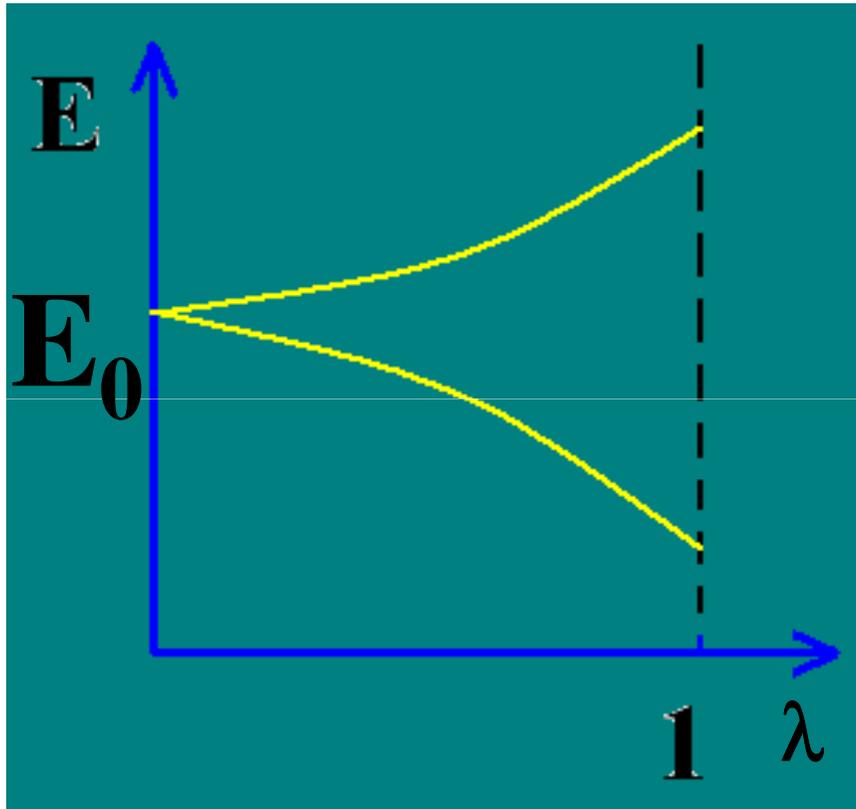
# Non-degenerate perturbation theory fail?

- In many cases, where two (or more) distinct states share the same energy, non-degenerate perturbation theory fail !
- Sometimes, two energy levels exists so near that non-degenerate perturbation theory cannot give us a satisfied answer.

So, we must look for some other way to handle the problem.

# Two-ford degeneracy

In order to see how the method generalizes, we begin with the twofold degeneracy



“Lifting of a degeneracy by a perturbation

Suppose ,

$$H^0 \Psi_a^0 = E^0 \Psi_a^0 ,$$

$$H^0 \Psi_b^0 = E^0 \Psi_b^0 ,$$

$$\langle \Psi_a^0 | \Psi_b^0 \rangle = 0 .$$

The perturbation will “break” the degeneracy

Any linear combination of the above states

$$\Psi^0 = \alpha\Psi_a^0 + \beta\Psi_b^0$$

is still an eigenstate of  $H^0$ , with the same eigenvalue  $E^0$

$$H^0\Psi^0 = E^0\Psi^0$$

**Essential problem:** When we turn off the perturbation, the “upper” state reduces down to one linear combination of  $\Psi_a^0$  and  $\Psi_b^0$ , and the “lower” state reduce to some other linear combination, but we don’t know a priori what these good linear combination will be. For this reason we can’t even calculate the first-order energy (equation 1) because we don’t know what unperturbed states to use.

As before, we write  $H$ ,  $E$ ,  $\psi$  in the following form

$$H = H^0 + \lambda H',$$

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots,$$

$$\Psi = \Psi^0 + \lambda \Psi^1 + \lambda^2 \Psi^2 + \dots$$

Plug into the stationary equation



**To lowest order,**  $H^0 \Psi_n^0 = E_n^0 \Psi_n^0$

**To first order,**  $H^0 \Psi^1 + H' \Psi^0 = E^0 \Psi^1 + E^1 \Psi^0$

$$H^0\Psi^1 + H'\Psi^0 = E^0\Psi^1 + E^1\Psi^0$$

Take the inner product with  $\Psi_a^0$

$$\langle \Psi_a^0 | H^0\Psi^1 \rangle + \langle \Psi_a^0 | H'\Psi^0 \rangle = E^0 \langle \Psi_a^0 | \Psi^1 \rangle + E^1 \langle \Psi_a^0 | \Psi^0 \rangle$$

$$H^0\Psi_a^0 = E^0\Psi_a^0 ,$$

$$H^0\Psi_b^0 = E^0\Psi_b^0 ,$$

$$\langle \Psi_a^0 | \Psi_b^0 \rangle = 0 ,$$

$$\Psi^0 = \alpha\Psi_a^0 + \beta\Psi_b^0$$

Meanwhile,  $H^0$  is Hermitian, the first term on the left cancels the first term on the right

$$\alpha \langle \Psi_a^0 | H' | \Psi_a^0 \rangle + \beta \langle \Psi_a^0 | H' | \Psi_b^0 \rangle = \alpha E^1$$

## Results

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1$$

The “matrix elements” of  $H'$

Where,  $W_{ij} \equiv \langle \Psi_i^0 | H' | \Psi_j^0 \rangle$ ,  $(i, j = a, b)$

Similarly, the inner product with  $\Psi_b^0$  yields

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1$$

Eliminate  $\beta W_{ab}$

$$\alpha \left[ W_{ab} W_{ba} - (E^1 - W_{aa})(E^1 - W_{bb}) \right] = 0$$

If  $\alpha$  is not zero, we can get the following equation

$$(E^1)^2 - E^1(W_{aa} + W_{bb}) + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0$$



$$E_{\pm}^1 = \frac{1}{2} \left[ W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \quad (3)$$

The two roots correspond to the two perturbed energies

But what if  $\alpha$  is zero?

# How should we do in practice

Idea: It would be greatly to our advantage if we could somehow guess the “good” states right from the start.

M  
O  
R  
A  
L

1. Look around for some Hermitian operator  $A$  that commutes with  $H'$  ;
2. Pick as your unperturbed states ones that are simultaneously eigenfunctions of  $H^0$  and  $A$  ;
3. Use ordinary first-order perturbation theory.

If you can't find such an operator, you'll have to resort to Equation 3, but in practice this is seldom necessary

## Theorem

Let  $A$  be a Hermitian operator that commutes with  $H'$ . If  $\Psi_a^0$  and  $\Psi_b^0$  are eigenfunctions of  $A$  with distinct eigenvalues,  $A\Psi_a^0 = \mu\Psi_a^0$ ,  $A\Psi_b^0 = \nu\Psi_b^0$ ,  $\mu \neq \nu$ , Then  $W_{ab} = 0$  (and hence  $\Psi_a^0$  and  $\Psi_b^0$  are the "good" states to use in perturbation theory).

## Proof

By assumption,  $[A, H'] = 0$ , so

$$\begin{aligned} \langle \Psi_a^0 | [A, H'] \Psi_b^0 \rangle &= 0 \\ &= \langle \Psi_a^0 | AH' \Psi_b^0 \rangle - \langle \Psi_a^0 | H'A \Psi_b^0 \rangle \\ &= \langle A \Psi_a^0 | H' \Psi_b^0 \rangle - \langle \Psi_a^0 | H' \nu \Psi_b^0 \rangle \\ &= (\mu - \nu) \langle \Psi_a^0 | H' \Psi_b^0 \rangle = (\mu - \nu) W_{ab}. \end{aligned}$$

But  $\mu \neq \nu$ , so  $W_{ab} = 0$ . QED

## Higher-order degeneracy

**NEXT  
PAGE**

Higher-order degeneracy

$$E^0 = E_n^0, \quad \Psi^0 = \sum a_k \Psi_{nk}^0,$$

$$H^0 \Psi^1 + H' \Psi^0 = E^0 \Psi^1 + E^1 \Psi^0$$

Matrix equation

$$\sum_k (H'_{k'k} - E^1 \delta_{k'k}) a_k = 0$$

Secular equation

$$\det | H'_{k'k} - E^1 \delta_{k'k} | = 0$$

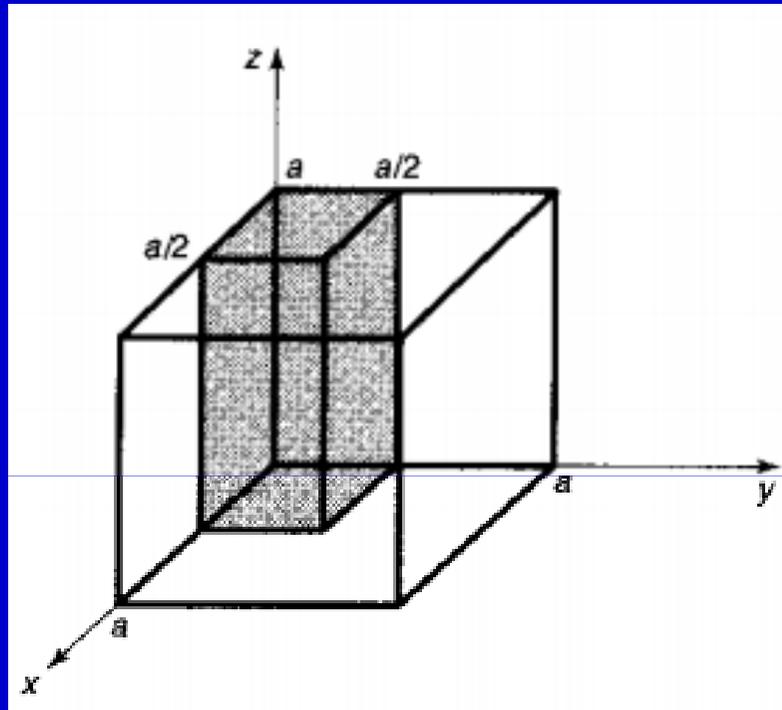
Get E'

Get  $a_k$ ,  
then  
get  $\psi^0$

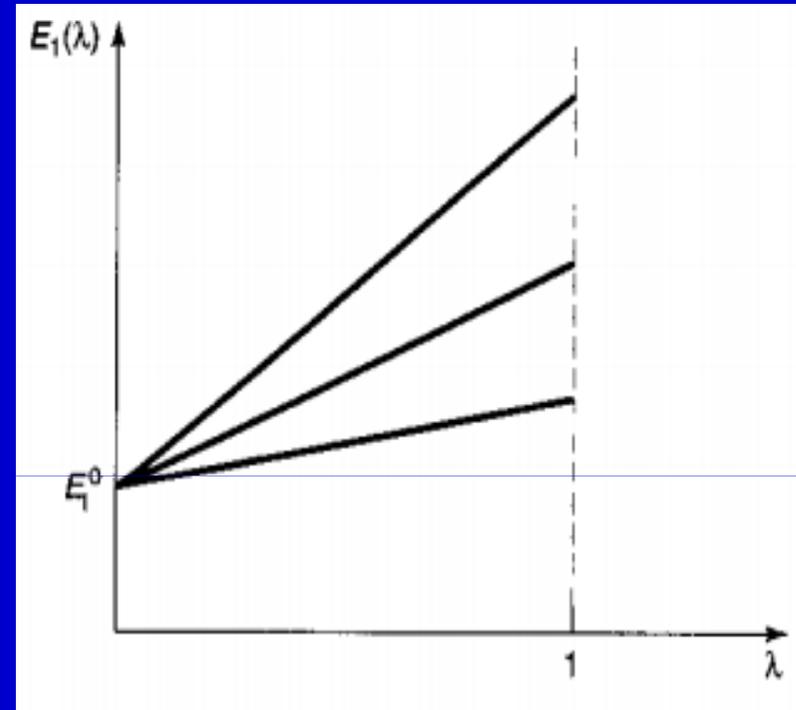
↻ Diagonalizes the perturbation H'

If you can think of an operator A that commutes with H', and use the simultaneous eigenfunctions of A and H<sup>0</sup>, then the W matrix will automatically be diagonal, and you won't have to fuss with solving the characteristic equation.

# Example



**Figure 6.5:** The perturbation increases the potential by an amount  $V_0$  in the shaded sector.



**Figure 6.6:** Lifting of the degeneracy in the example (Equation 6.38).

**Example.** Consider the three-dimensional infinite cubical well (Problem 4.2):

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < a, 0 < y < a, \text{ and } 0 < z < a; \\ \infty & \text{otherwise.} \end{cases} \quad [6.29]$$

The stationary states are

$$\psi_{n_x n_y n_z}^0(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right), \quad [6.30]$$

where  $n_x$ ,  $n_y$ , and  $n_z$  are positive integers. The corresponding allowed energies are

$$E_{n_x n_y n_z}^0 = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2). \quad [6.31]$$

Notice that the ground state ( $\psi_{111}$ ) is nondegenerate; its energy is

$$E_0^0 \equiv 3 \frac{\pi^2 \hbar^2}{2ma^2}. \quad [6.32]$$

But the first excited state is (triply) degenerate:

$$\psi_a \equiv \psi_{112}, \quad \psi_b \equiv \psi_{121}, \quad \text{and } \psi_c \equiv \psi_{211}, \quad [6.33]$$

all share the energy

$$E_1^0 \equiv 3 \frac{\pi^2 \hbar^2}{m a^2}. \quad [6.34]$$

Now let's introduce the perturbation

$$H' = \begin{cases} V_0, & \text{if } 0 < x < a/2 \text{ and } 0 < y < a/2; \\ 0, & \text{otherwise.} \end{cases} \quad [6.35]$$

This raises the potential by an amount  $V_0$  in one quarter of the box (see Figure 6.5). The first-order correction to the ground state energy is given by Equation 6.9:

$$E_0^1 = \langle \psi_{111} | H' | \psi_{111} \rangle = \left( \frac{2}{a} \right)^3 V_0 \int_0^{a/2} \sin^2 \left( \frac{\pi}{a} x \right) dx \quad [6.36]$$
$$\int_0^{a/2} \sin^2 \left( \frac{\pi}{a} y \right) dy \int_0^a \sin^2 \left( \frac{\pi}{a} z \right) dz = \frac{1}{4} V_0,$$

which is just what we would expect.

For the first excited state we need the full machinery of degenerate perturbation theory. The first step is to construct the matrix  $W$ . The diagonal elements are the same as for the ground state (except that the argument of one of the sines is doubled); you can check for yourself that

$$W_{aa} = W_{bb} = W_{cc} = \frac{1}{4}V_0.$$

The off-diagonal elements are more interesting:

$$W_{ab} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \\ \int_0^{a/2} \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right) dy \int_0^a \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right) dz.$$

But the  $z$  integral is zero (as it will be also for  $W_{ac}$ ), so

$$W_{ab} = W_{ac} = 0.$$

Finally,

$$W_{bc} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) dx \\ \int_0^{a/2} \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz = \frac{16}{9\pi^2} V_0.$$

Thus

$$W = \frac{V_0}{4} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}, \quad [6.37]$$

where  $\kappa \equiv (8/3\pi)^2 \approx 0.7205$ .

The characteristic equation for  $W$  (or rather, for  $4W/V_0$ , which is easier to work with) is

$$(1 - w)^3 - \kappa^2(1 - w) = 0,$$

and the eigenvalues are

$$w_1 = 1; \quad w_2 = 1 + \kappa \approx 1.7205; \quad w_3 = 1 - \kappa \approx 0.2795.$$

To first order in  $\lambda$ , then,

$$E_1(\lambda) = \begin{cases} E_1^0 + \lambda V_0/4, \\ E_1^0 + \lambda(1 + \kappa)V_0/4, \\ E_1^0 + \lambda(1 - \kappa)V_0/4, \end{cases} \quad [6.38]$$

where  $E_1^0$  is the (common) unperturbed energy (Equation 6.34). The perturbation lifts the degeneracy, splitting  $E_1^0$  into three distinct energy levels (see Figure 6.6). Notice that if we had naively applied *nondegenerate* perturbation theory to this problem, we would have concluded that the first-order correction (Equation 6.9) is the

same for all three states, and equal to  $V_0/4$ —which is actually correct only for the middle state.

Meanwhile, the “good” unperturbed states are linear combinations of the form:

$$\psi^0 = \alpha\psi_a + \beta\psi_b + \gamma\psi_c, \quad [6.39]$$

where the coefficients ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) form the eigenvectors of the matrix  $W$ :

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}.$$

For  $w = 1$  we get  $\alpha = 1$ ,  $\beta = \gamma = 0$ ; for  $w = 1 \pm \kappa$  we get  $\alpha = 0$ ,  $\beta = \pm\gamma = 1/\sqrt{2}$ . (I normalized them as I went along.) Thus the “good” states are<sup>4</sup>

$$\psi^0 = \begin{cases} \psi_a, \\ (\psi_b + \psi_c)/\sqrt{2}, \\ (\psi_b - \psi_c)/\sqrt{2}. \end{cases} \quad [6.40]$$

# Some Examples For Application

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- The fine structure of hydrogen
- The zeeman effect
- Hyperfine splitting

# The Fine Structure of Hydrogen

- The relativistic correction
- Spin-orbit coupling

The simplest  
Hamiltonian of  
the hydrogen

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

Replace  $m$  by the  
reduced mass

Correct for the motion  
of the nucleus

Relativistic correction

Spin-orbit coupling

Fine structure

Quantization of the Coulomb field

Lamb shift

The magnetic interaction  
between the dipole moments of  
the electron and the proton

Hyperfine structure

# Hierarchy of correction to the Bohr energies of hydrogen

Bohr energies:	of order	$\alpha^2 mc^2$
Fine structure:	of order	$\alpha^4 mc^2$
Lamb shift :	of order	$\alpha^5 mc^2$
Hyperfine splitting:	of order	$\left(\frac{m}{m_p}\right) \alpha^4 mc^2$

An application of time-independent perturbation theory

# The relativistic correction

## General discussion

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

Represent  
kinetic energy

The total  
relativistic  
energy

## Classical formula

$$T = \frac{p^2}{2m}$$

## The relativistic formula

$$T = \frac{mc^2}{\sqrt{1 - (v/c)^2}} - mc^2$$

The rest energy

# Express T in terms of the relativistic momentum

The relativistic momentum:  $p = \frac{mv}{\sqrt{1 - (v/c)^2}}$

$$p^2 c^2 + m^2 c^4 = \frac{m^2 v^2 c^2 + m^2 c^4 \left[ 1 - (v/c)^2 \right]}{1 - (v/c)^2} = (T + mc^2)^2$$

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

The nonrelativistic  
limit  $p \ll mc$

$$T = mc^2 \left[ 1 + \frac{1}{2} \left( \frac{p}{mc} \right)^2 - \frac{1}{8} \left( \frac{p}{mc} \right)^4 \dots - 1 \right] = \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots$$

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

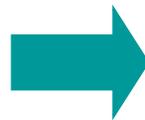
The classical result

The lowest-order relativistic contribution to the Hamiltonian

In first-order perturbation theory, the correction to  $E_n$  is given by the expectation value of  $H'$  in the unperturbed state

$$\rightarrow E_r^1 = -\frac{1}{8m^3c^2} \langle \psi | \hat{p}^4 \psi \rangle = -\frac{1}{8m^3c^2} \langle \hat{p}^2 \psi | \hat{p}^2 \psi \rangle$$

$$\text{And, } \left( \frac{\hat{p}^2}{2m} + V \right) \psi = E \psi$$



$$\hat{p}^2 \psi = 2m(E - V) \psi$$



$$E_r^1 = -\frac{1}{2mc^2} \left[ E^2 - 2E \langle V \rangle + \langle V^2 \rangle \right]$$

# In the case of hydrogen

$$E_r^1 = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right]$$

Where  $E_n$  is the Bohr energy of the state in question

$$\text{And, } \left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}, \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(l + \frac{1}{2}\right) n^3 a^2}$$



$$E_r^1 = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{\left(l + \frac{1}{2}\right) n^3 a^2} \right]$$

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

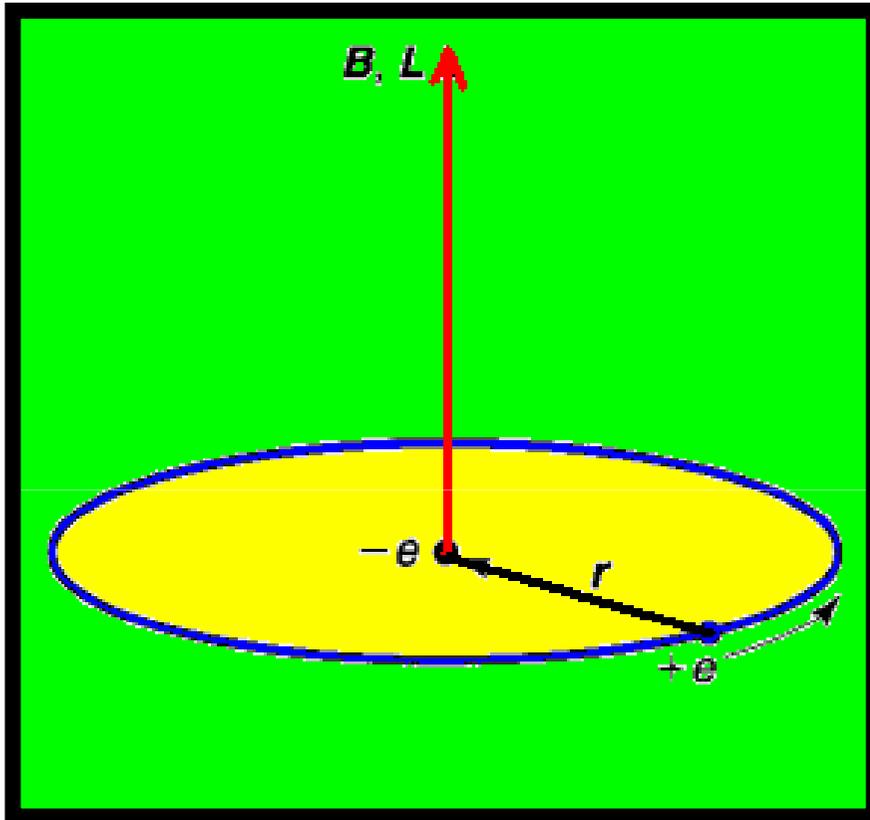
$$E_n = - \left[ \frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}$$

↓ **P l u g g i n g** ↓

$$E_r^1 = - \frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{\left( l + \frac{1}{2} \right) n^3 a^2} \right]$$

$$E_r^1 = - \frac{E_n^2}{2mc^2} \left[ \frac{4n}{l + \frac{1}{2}} - 3 \right]$$

# Spin-Orbit Coupling



Hydrogen atom, from the electron's perspective.

The orbiting positive charge sets up a magnetic field  $\mathbf{B}$  in the electron frame, which exerts a torque on the spinning electron, tending to align its magnetic moment ( $\boldsymbol{\mu}$ ) along the direction of the field.

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}$$

# The Magnetic Field of the Proton

According to the Biot - Savart law :  $B = \frac{\mu_0 I}{2r}$

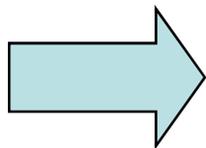
An effective current  $I = \frac{e}{T}$

The charge of proton

The period of the orbit

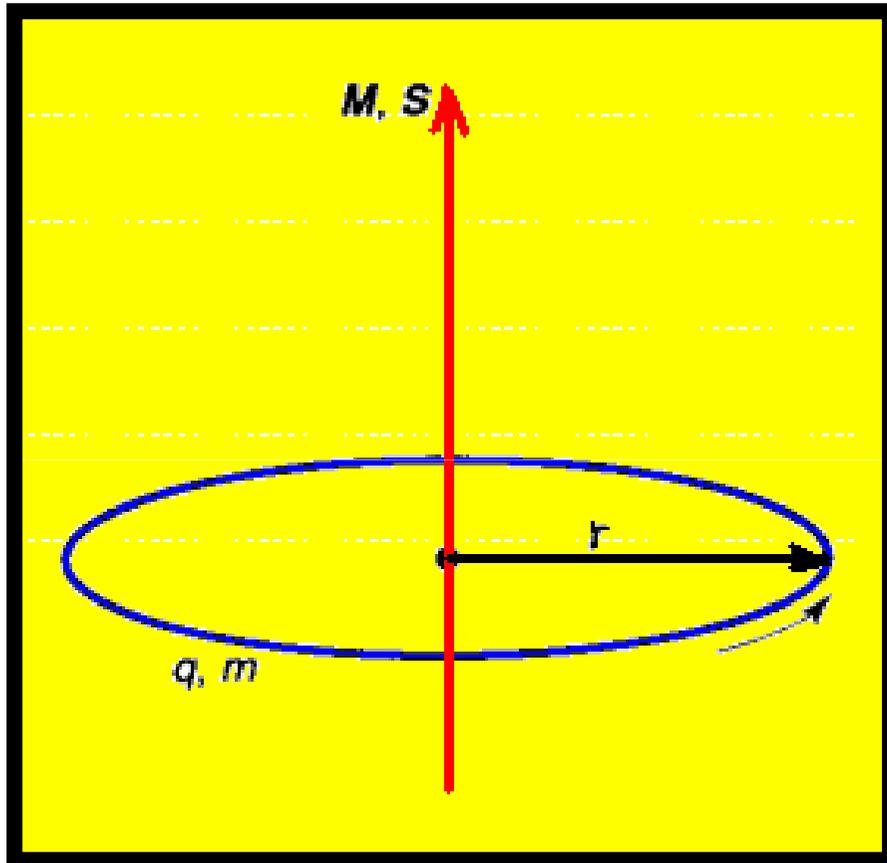
The orbital angular momentum of the electron :  $L = rmv = \frac{2\pi mr^2}{T}$

Additional, **B** and **L** point in the same direction



$$\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L}$$

# The Magnetic Dipole Moment of the Electron



A ring of charge, rotating about its axis

Classical  
electrodynamics

$$\mu = \frac{q \pi r^2}{T}$$

$$S = \frac{2\pi m r^2}{T}$$

$$\boldsymbol{\mu} = \left( \frac{q}{2m} \right) \mathbf{S}$$

Classical  
result



However, as it turns out, the electron's magnetic moment is twice the classical answer

$$\boldsymbol{\mu}_e = -\frac{e}{m} \mathbf{S}$$

The “extra” factor of 2 was explained by Dirac in his relativistic theory of the electron. For a related discussion, see V.Namias, *Am.J.Phys.*, **57**, 171 (1989).

# The Spin-Orbit Interaction

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L}$$

$$\boldsymbol{\mu}_e = -\frac{e}{m} \mathbf{S}$$

$$H = \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

**FR  
A  
U  
D**

We did the analysis in the rest frame of the electron, but that's not an inertial system—it accelerates as the electron orbits around the nucleus.

**S O L U T I O N**

Make an appropriate kinematic correction, known as the **Thomas precession**.

# The Spin-Orbit Interaction

The modified  
gyromagnetic ratio  
for the electron

**Exactly  
cancel one  
another**

the Thomas  
precession  
factor

**D I S R E G A R D**

Safely, on the basis of a naive classical model

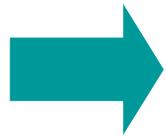
$$H'_{so} = \left( \frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

$$\begin{aligned} [H'_{SO}, \mathbf{L}] &\neq 0 \\ [H'_{SO}, \mathbf{S}] &\neq 0 \end{aligned}$$



The spin and orbital angular momenta are not conserved

**Put it another way**



$$\begin{aligned} \text{The total angular momentum } \mathbf{J} &\equiv \mathbf{L} + \mathbf{S} \\ [H'_{SO}, L^2] &= 0 \quad [H'_{SO}, S^2] = 0 \end{aligned}$$



$L^2, S^2, J^2, J_z$  are conserved, and the eigenstates of these quantities are good states to use in perturbation theory.

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$$



$$J^2 = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S}$$



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



The eigenvalue  $s$  of  $\mathbf{L} \cdot \mathbf{S}$  :

$$\frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)]$$

Meanwhile,

$$H'_{so} = \left( \frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l + \frac{1}{2})(l+1)n^3 a^3}$$

$$E_{so}^1 = \left( \frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2} \frac{\hbar^2 / 2 [j(j+1) - l(l+1) - 3/4]}{l(l + \frac{1}{2})(l+1)n^3 a^3}$$

Express in  
terms of  $E_n$



$$E_{so}^1 = \frac{E_n^2}{mc^2} \left\{ \frac{n [j(j+1) - l(l+1) - 3/4]}{l(l + \frac{1}{2})(l+1)} \right\}$$

Fine structure

## The relativistic correction

$$E_r^1 = -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{l + \frac{1}{2}} - 3 \right]$$

## The spin-orbit coupling

$$E_{so}^1 = \frac{E_n^2}{mc^2} \left\{ \frac{n \left[ j(j+1) - l(l+1) - \frac{3}{4} \right]}{l \left( l + \frac{1}{2} \right) (l+1)} \right\}$$

The correction to the Bohr formula

$$E_{fs}^1 = \frac{E_n^2}{2mc^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right)$$

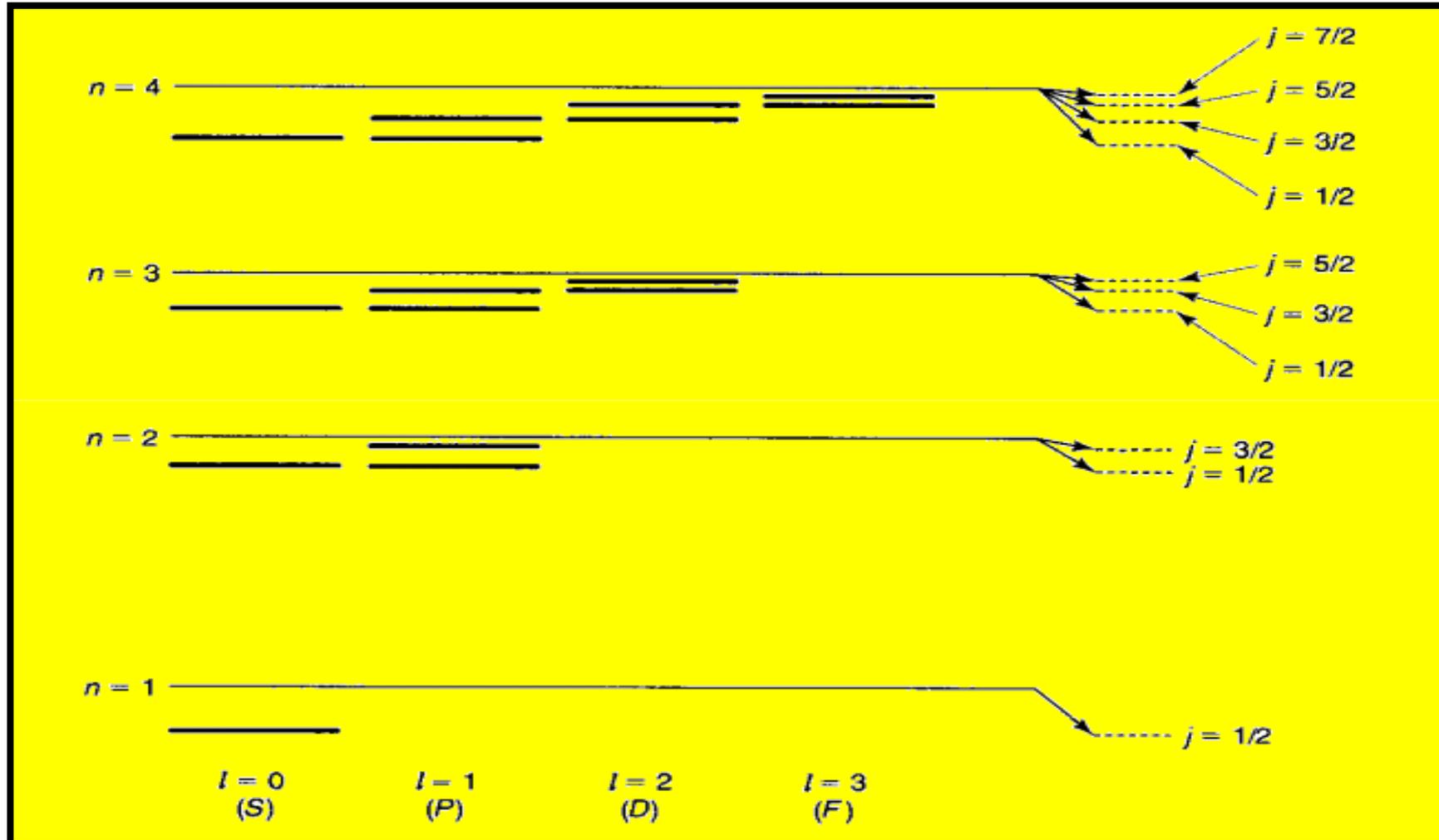
Combine with the Bohr formula

The complete fine-structure formula

$$E_{nj} = -\frac{13.6eV}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right]$$

- Fine structure breaks the degeneracy in  $l$
- The energies are determined by  $n$  and  $j$

# The Fine Structure of Hydrogen



Energy levels of hydrogen, including fine structure (not to scale)

# The Zeeman Effect

- Weak-field zeeman effect
- Strong-field zeeman effect
- Intermediate-field zeeman effect

# General discussion

Consider an atom placed in a uniform external magnetic field  $\mathbf{B}_{\text{ext}}$

What  
&  
How

For a single electron

$$H'_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B}_{\text{ext}}$$

Associated with  
orbital motion

Associated with  
electron spin

$$H'_Z = \frac{e}{2m} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{\text{ext}}$$

# New phenomenon

# Zeeman Effect

The energy levels are shifted when an atom is placed in a uniform external magnetic field

H

Depend on the strength of the external field in comparison with the internal field that gives rise to spin-orbit coupling

O

Weak-field

Intermediate

Strong-field



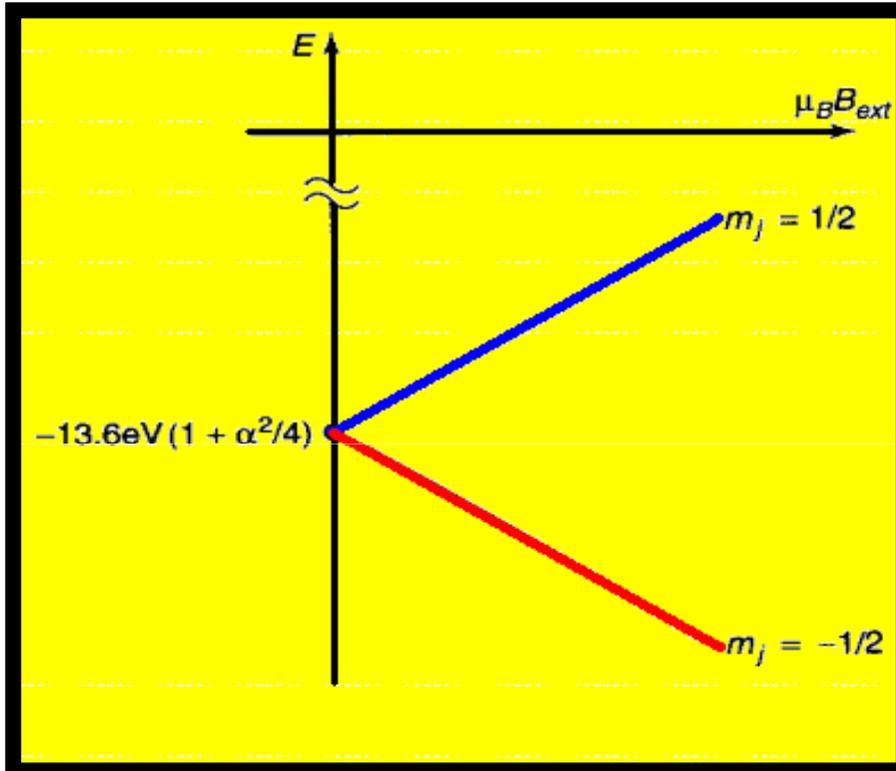
W

$B_{\text{ext}} \ll B_{\text{int}}$

Comparable

$B_{\text{ext}} \ll B_{\text{int}}$

# Weak-field Zeeman Effect



Weak-field Zeeman splitting of the ground state; the upper line ( $m_j=1/2$ ) has slope 1, the lower line ( $m_j=-1/2$ ) has slope -1

$$B_{\text{ext}} \ll B_{\text{int}}$$

Fine structure  
dominates

$H_Z$  as a small  
perturbation

$$\begin{aligned} [H'_{SO}, \mathbf{L}] &\neq 0 \\ [H'_{SO}, \mathbf{S}] &\neq 0 \end{aligned}$$



The spin and orbital angular momenta are not conserved

**Put it another way**

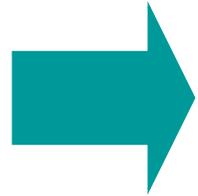


$$\begin{aligned} \text{The total angular momentum } \mathbf{J} &\equiv \mathbf{L} + \mathbf{S} \\ [H'_{SO}, L^2] &= 0 \quad [H'_{SO}, S^2] = 0 \end{aligned}$$



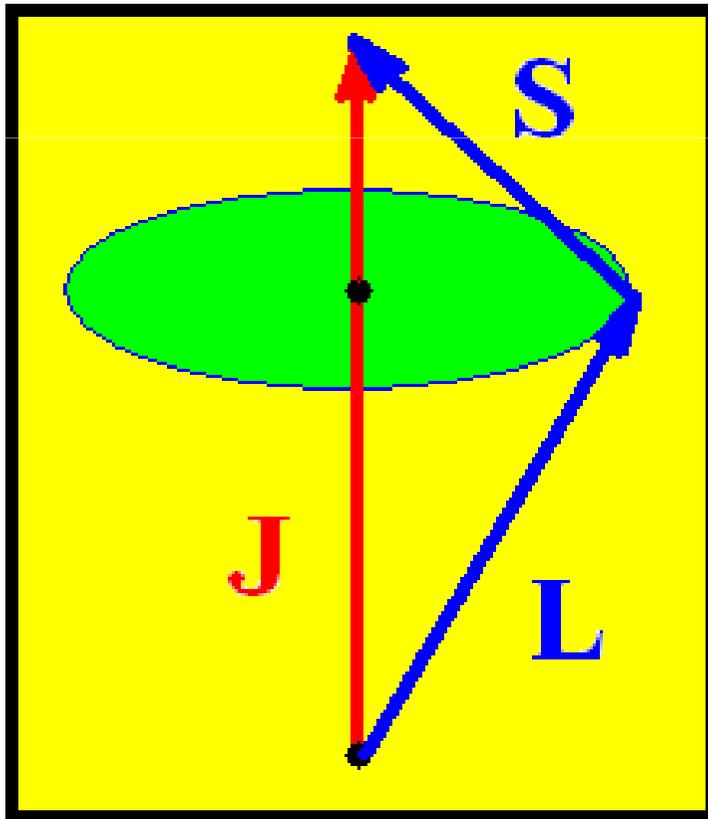
$L^2, S^2, J^2, J_z$  are conserved, and the eigenstates of these quantities are good states to use in perturbation theory.

$n, l, j$  and  $m_j$  are the "good" quantum numbers



The zeeman correction to the energy

$$E_Z^1 = \langle n l j m_j | H'_Z | n l j m_j \rangle = \frac{e}{2m} B_{\text{ext}} \cdot \langle \mathbf{L} + 2\mathbf{S} \rangle$$



The expectation  
value of  $\mathbf{S}$  ?

In the presence of spin-orbit coupling,  $\mathbf{L}$  and  $\mathbf{S}$  are not separately conserved; they precess about the fixed total angular momentum,  $\mathbf{J}$ .



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

$$\mathbf{L} = \mathbf{J} - \mathbf{S}$$



$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)]$$

Meanwhile,

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



$$\begin{aligned} \langle \mathbf{L} + 2\mathbf{S} \rangle &= \left\langle \left( 1 + \frac{(\mathbf{S} \cdot \mathbf{J})}{J^2} \right) \mathbf{J} \right\rangle \\ &= \left[ 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \langle \mathbf{J} \rangle \end{aligned}$$

The  
landé  
g-factor,  
 $g_J$

Choose the z-axis to lie along  $\mathbf{B}_{\text{ext}}$

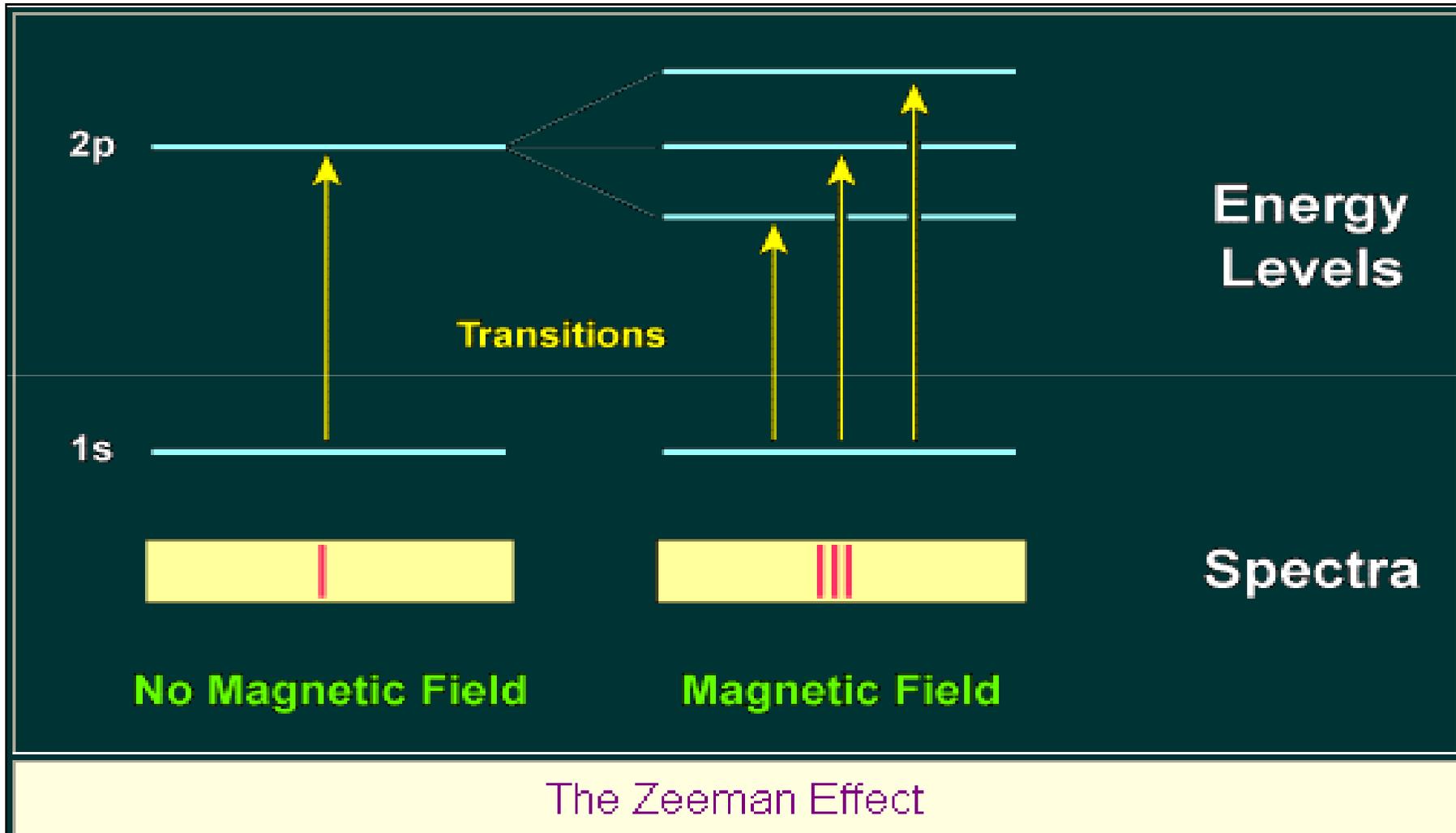


$$E_Z^1 = \mu_B g_J B_{\text{ext}} m_j$$

Bohr  
magneton

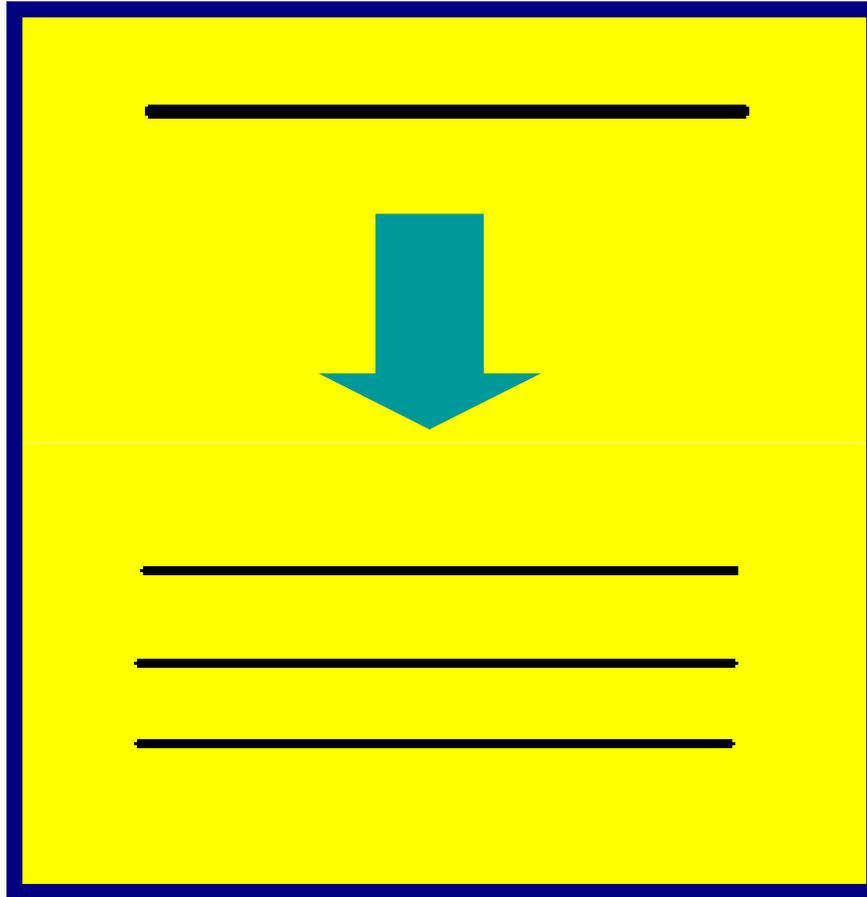
$$\text{Where, } \mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV/T}$$

# Strong-field Zeeman Effect



From [csep10.phys.utk.edu/.../light/zeeman-split.html](http://csep10.phys.utk.edu/.../light/zeeman-split.html)

# Strong-field Zeeman Effect



The splitting of spectrum

$$B_{\text{ext}} \gg B_{\text{int}}$$

The zeeman  
effect dominates

Fine structure  
as the  
perturbation

# Strong-field Zeeman Effect

$n, l, m_l$  and  $m_s$  are now the "good" quantum numbers

Choose the z-axis to lie along  $\mathbf{B}_{\text{ext}}$

Proof!

The zeeman Hamiltonian

$$H'_Z = \frac{e}{2m} B_{\text{ext}} (L_z + 2S_z)$$



The "unperturbed" energies

$$E_{n m_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{\text{ext}} (m_l + 2m_s)$$

## The fine structure correction:

$$E_{fs}^1 = \langle n l m_l m_s | H'_r + H'_{so} | n l m_l m_s \rangle$$

$H'_r$ : The same as before

$$\langle \mathbf{S} \cdot \mathbf{J} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s$$



$$E_{fs}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[ \frac{l(l+1) - m_l m_s}{l(l + \frac{1}{2})(l+1)} \right] \right\}$$

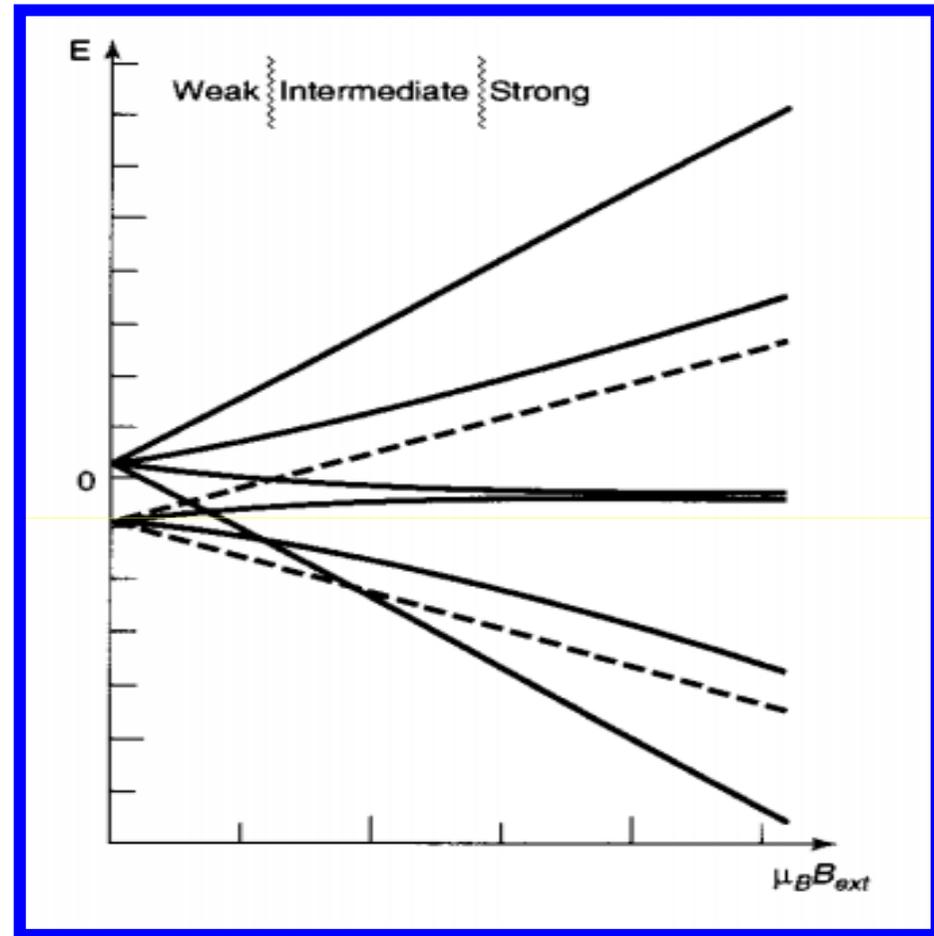
What  
if  $l=0$ ?

# Intermediate-field Zeeman Effect

Neither  $H'_Z$  nor  $H'_{fs}$  dominates

Treat them on an equal footing

As perturbation to Bohr Hamiltonian



$$H' = H'_Z + H'_{fs}$$

# Intermediate-field Zeeman Effect

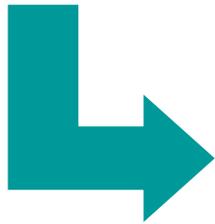
**My  
choice**

The case :  $n = 2$ ; The basis : the states characterized by  $l$ ,  $j$ , and  $m_j$

Using the Clebsch-Gordan coefficients



$$l = 0 \begin{cases} \Psi_1 \equiv \left| \frac{1}{2} \frac{1}{2} \right\rangle = \left| 0 0 \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle, \\ \Psi_2 \equiv \left| \frac{1}{2} \frac{-1}{2} \right\rangle = \left| 0 0 \right\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle, \end{cases}$$



$$l = 1 \begin{cases} \Psi_3 \equiv \left| \frac{3}{2} \frac{3}{2} \right\rangle = \left| 1 1 \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle, \\ \Psi_4 \equiv \left| \frac{3}{2} \frac{-3}{2} \right\rangle = \left| 1 -1 \right\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle, \\ \Psi_5 \equiv \left| \frac{3}{2} \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| 1 0 \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 1 1 \right\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle, \\ \Psi_6 \equiv \left| \frac{1}{2} \frac{1}{2} \right\rangle = -\sqrt{\frac{1}{3}} \left| 1 0 \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1 1 \right\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle, \\ \Psi_7 \equiv \left| \frac{3}{2} \frac{-1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| 1 -1 \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1 0 \right\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle, \\ \Psi_8 \equiv \left| \frac{1}{2} \frac{-1}{2} \right\rangle = -\sqrt{\frac{2}{3}} \left| 1 -1 \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 1 0 \right\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle. \end{cases}$$

# Matrix of H'

$$\begin{pmatrix}
 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta & 0
 \end{pmatrix}$$

Where ,  $\gamma \equiv \left(\frac{\alpha}{8}\right)^2 13.6 eV$  and  $\beta \equiv \mu_B B_{ext}$  .

# Energy levels for the n=2 states of hydrogen, with fine structure and zeeman splitting

$$\varepsilon_1 = E_2 - 5\gamma + \beta$$

$$\varepsilon_2 = E_2 - 5\gamma - \beta$$

$$\varepsilon_3 = E_2 - \gamma + 2\beta$$

$$\varepsilon_4 = E_2 - \gamma - 2\beta$$

$$\varepsilon_5 = E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$$

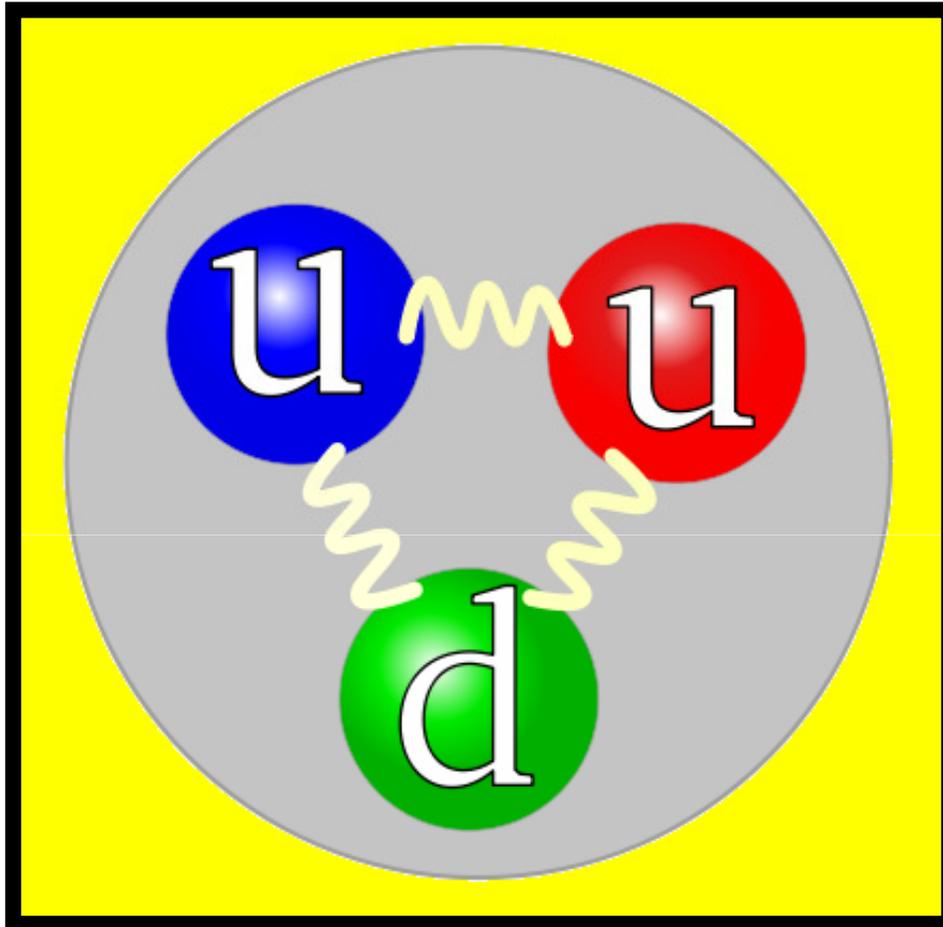
$$\varepsilon_6 = E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$$

$$\varepsilon_7 = E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$$

$$\varepsilon_8 = E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$$

# Hyperfine splitting

# Brief introduction to proton



Made by [Arpad Horvath](https://commons.wikimedia.org/wiki/Image:Quark_struct...).  
[commons.wikimedia.org/wiki/  
Image:Quark\\_struct...](https://commons.wikimedia.org/wiki/Image:Quark_struct...)

The quark structure of the proton. There are two up quark in it and one down quark. The strong force is mediated by gluons (wavey). The strong force has three types of charges, the so called red, green and the blue. cut is a d o u c h e b a g g

magnetic

## Brief introduction to proton

The <sup>field</sup>proton itself constitutes a magnetic dipole, smaller than the electron's

$$\boldsymbol{\mu}_p = \frac{ge}{2m_p} \mathbf{S}_p ; g = 5.59 \text{ (measured value)}$$

According to classical electrodynamics, a dipole  $\boldsymbol{\mu}$  sets up a magnetic field.

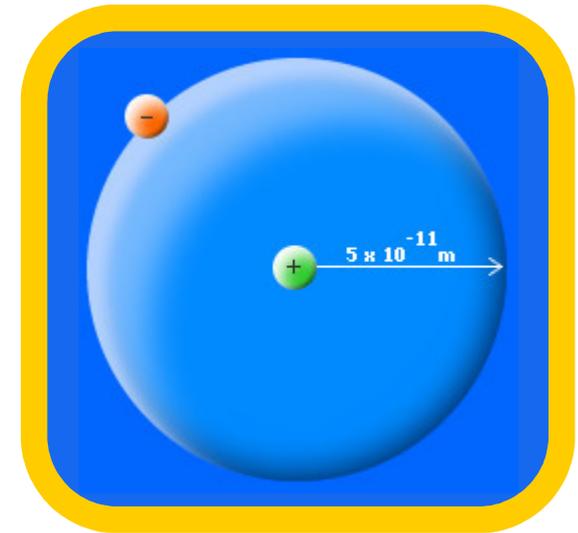
$$\mathbf{B} = \frac{\mu_0}{4\pi r^3} [3(\boldsymbol{\mu} \cdot \mathbf{r})\mathbf{r} - \boldsymbol{\mu}] + \frac{2\mu_0}{3} \boldsymbol{\mu} \delta^3(\mathbf{r})$$

For a related discussion, see D.J.Griffiths,Am.J.Phys.,**50**,698(1982).

# The electron near proton

The Hamiltonian of the electron, due to the proton's magnetic dipole moment

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}$$



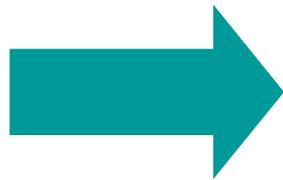
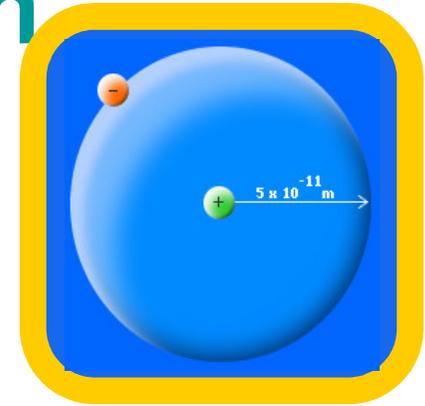
$$H'_{hf} = \frac{\mu_0 g e^2}{8\pi m_p m_e} \frac{[3(\mathbf{S}_p \cdot \mathbf{r})(\mathbf{S}_e \cdot \mathbf{r}) - \mathbf{S}_p \cdot \mathbf{S}_e]}{r^3} + \frac{\mu_0 g e^2}{3m_p m_e} \mathbf{S}_p \cdot \mathbf{S}_e \delta^3(\mathbf{r})$$

According to perturbation theory, we can get the first-order correction to the energy

$$E_{hf}^1 = \frac{\mu_0 g e^2}{8\pi m_p m_e} \left\langle \frac{3(\mathbf{S}_p \cdot \mathbf{r})(\mathbf{S}_e \cdot \mathbf{r}) - \mathbf{S}_p \cdot \mathbf{S}_e}{r^3} \right\rangle + \frac{\mu_0 g e^2}{3m_p m_e} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle |\Psi(0)|^2$$

# For the ground state hydrogen

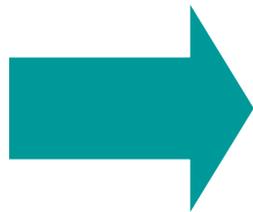
The wave function is spherically symmetrical



$$\left\langle \frac{3(\mathbf{S}_p \cdot \mathbf{r})(\mathbf{S}_e \cdot \mathbf{r}) - \mathbf{S}_p \cdot \mathbf{S}_e}{r^3} \right\rangle = 0$$

Meanwhile,  $|\psi_{100}(0)|^2 = \frac{1}{\pi a^3}$

**Spin-spin coupling**



$$E_{hf}^1 = \frac{\mu_0 g e^2}{3\pi m_p m_e a^3} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle$$

# Spin-spin coupling

The individual spin angular momenta are no longer conserved; the “good” states are eigenvectors of the total spin.

$$\mathbf{S} \equiv \mathbf{S}_e + \mathbf{S}_p$$



$$\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2} (S^2 - S_e^2 - S_p^2)$$

The electron and proton both have spin 1/2 .



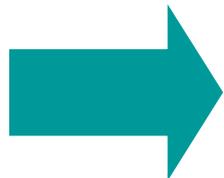
$$S_e^2 = S_p^2 = \left(\frac{3}{4}\right) \hbar^2$$

In the triplet state,

$$S^2 = 2 \hbar^2$$

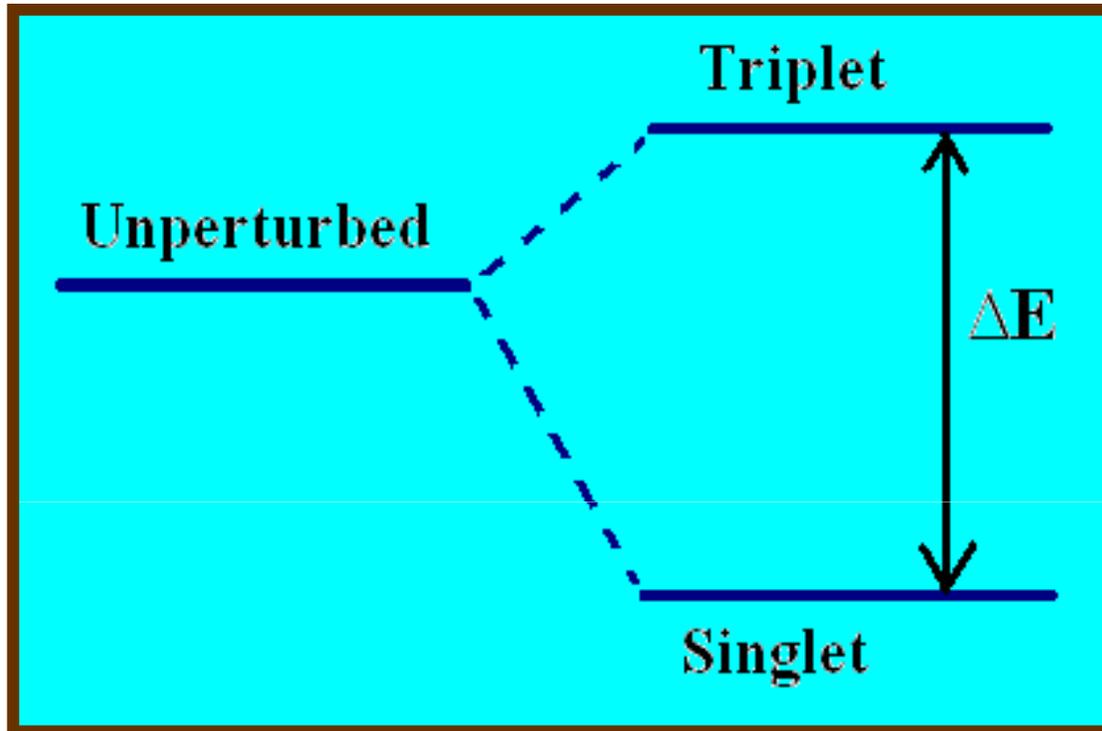
In the singlet state,

$$S^2 = 0 .$$



$$E_{hf}^1 = \frac{4g\hbar^2}{3m_p m_e^2 c^2 a^4} \begin{cases} + \frac{1}{4}, & \text{(triplet);} \\ - \frac{3}{4}, & \text{(singlet).} \end{cases}$$

# Effect of spin-spin coupling



Hyperfine splitting in the ground state of hydrogen

- Lifting the triplet configuration
- Depressing the singlet configuration

# The energy gap as a result of spin-spin coupling

$$\Delta E = \frac{4g\hbar^2}{3m_p m_e^2 c^2 a^4} = 5.88 \times 10^{-6} \text{ eV}$$



$$\nu = \frac{\Delta E}{h} = 1420 \text{ MHz}$$

The frequency of the photon emitted in a transition from the triplet to the singlet state

Corresponding wavelength :  $\frac{c}{\nu} = 21 \text{ cm}$

**Fall in the microwave region**

This famous “21-centimeter line” is among the most pervasive and ubiquitous forms of radiation in the universe.

**21-  
centimeter  
line**