

# 量子力学 (II) 笔记

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# 1 Chapter 7 Time-Independent Perturbation Theory

## 1.1 Nondegenerate Perturbation Theory

### 1.1.1 General Formulation

Suppose a Schroedinger equation for some potential:

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad (1.1.1)$$

Now perturb the potential slightly and find the new eigenfunctions and eigenvalues:

$$H \psi_n = E_n \psi_n \quad (1.1.2)$$

To begin with, write the new Hamiltonian as the sum of two terms:

$$H = H^0 + \lambda H' \quad (1.1.3)$$

where  $H'$  is the perturbation.

Next we write  $\psi_n$  and  $E_n$  as power series in  $\lambda$ :

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \quad (1.1.4)$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (1.1.5)$$

$E_n^1$  is the first-order correction to the n-th eigenvalue, and  $\psi_n^1$  is the first-order correction to the n-th eigenfunction;  $E_n^2$  and  $\psi_n^2$  are the second-order corrections.

Plugging Equations (1.1.4),(1.1.5) into Equation(1.1.2):

$$(H^0 + \lambda H') [\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots) [\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] \quad (1.1.6)$$

collecting like powers of  $\lambda$ :

$$H^0 \psi_n^0 + \lambda (H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2 (H^0 \psi_n^2 + H' \psi_n^1) + \dots = E_n^0 \psi_n^0 + \lambda (E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2 (E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \dots \quad (1.1.7)$$

To lowest order:

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad (1.1.8)$$

To first order:

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \quad (1.1.9)$$

To second order:

$$H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \quad (1.1.10)$$

To k-th order:

$$(H^0 - E_n^0) \psi_n^k = (E_n^1 - H') \psi_n^{k-1} + E_n^2 \psi_n^{k-2} + \dots + E_n^k \psi_n^0 \quad (1.1.11)$$

### 1.1.2 First-Order Theory

Taking the inner product of Equation (1.1.9) with  $\psi_n^0$ :

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \quad (1.1.12)$$

$H^0$  is hermitian, so

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle \quad (1.1.13)$$

And  $\langle \psi_n^0 | \psi_n^0 \rangle = 1 \implies$

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (1.1.14)$$

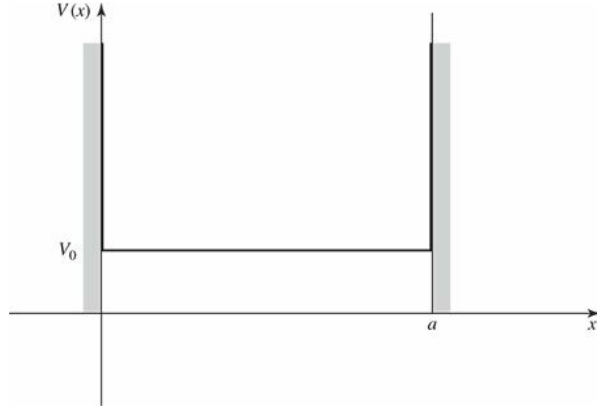
The first-order correction to the energy is the expectation value of the perturbation in the unperturbed state.

#### Example:

The unperturbed wave functions for the infinite square well are:

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad (1.1.15)$$

Perturb the system by simply raising the “floor” of the well a constant amount  $V_0$ .



#### Solution:

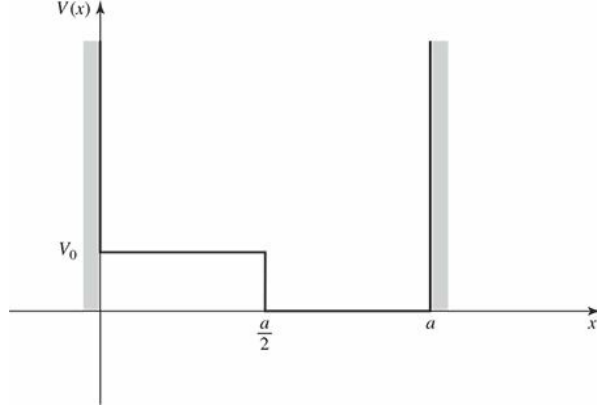
In this case  $H' = V_0$ , the first-order correction to the energy of the  $n$ th state:

$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0 \quad (1.1.16)$$

The corrected energy levels, then, are  $E_n \approx E_n^0 + V_0$ . (the first-order theory yields the exact answer)

If the perturbation extends only half-way across the well, then

$$E_n^1 = \frac{2V_0}{a} \int_0^{\frac{a}{2}} \sin^2\left(\frac{n\pi}{a}x\right) dx = \frac{V_0}{2} \quad (1.1.17)$$



In this case every energy level is lifted by  $\frac{V_0}{2}$ . (not the exact result)

To find the first-order correction to the wave function, we rewrite Equation (1.1.9):

$$(H^0 - E_n^0) \psi_n^1 = - (H' - E_n^1) \psi_n^0 \quad (1.1.18)$$

$\psi_n^0$  constitute a complete set, so  $\psi_n^1$  can be expressed as a linear combination of them:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0 \quad (1.1.19)$$

Putting Equation(1.1.19) into Equation(1.1.18), and using the fact that  $\psi_m^0$  satisfies the unperturbed Schroedinger equation, we have:

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = - (H' - E_n^1) \psi_n^0 \quad (1.1.20)$$

Taking the inner product with  $\psi_l^0$ :

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = - \langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle \quad (1.1.21)$$

If  $l = n$ , the left side is zero, and we recover Equation(1.1.14).

If  $l \neq n$ , we get

$$(E_l^0 - E_n^0) c_l^{(n)} = - \langle \psi_l^0 | H' | \psi_n^0 \rangle \quad (1.1.22)$$

or

$$c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (1.1.23)$$

so

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 \quad (1.1.24)$$

The denominator is safe as long as the unperturbed energy spectrum is nondegenerate.

**P.S.: For the k-th energy:**

Take the inner product of the k-order equation(1.1.11) with  $\psi_n^0$ :

$$\begin{aligned}\langle \psi_n^0 | \text{LHS} \rangle &= 0 = \langle \psi_n^0 | E_n^1 - H' | \psi_n^{k-1} \rangle + E_n^2 \langle \psi_n^0 | \psi_n^{k-2} \rangle + \dots \\ &= -\langle \psi_n^0 | H' | \psi_n^{k-1} \rangle + E_n^k \\ \implies E_n^k &= \langle \psi_n^0 | H' | \psi_n^{k-1} \rangle\end{aligned}\tag{1.1.25}$$

### 1.1.3 Second-Order Energies

Take the inner product of the second-order equation(1.1.10) with  $\psi_n^0$ :

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle\tag{1.1.26}$$

Exploit the hermiticity of  $H^0$ :

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle\tag{1.1.27}$$

So the first term on the left cancels the first term on the right.

Then we have:

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle\tag{1.1.28}$$

But

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0\tag{1.1.29}$$

Therefore,

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0}\tag{1.1.30}$$

or

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}\tag{1.1.31}$$

This is the fundamental result of second-order perturbation theory.

#### Remarks:

- The  $O(\lambda)$  ground state energy overestimates the true ground state energy.

$$\begin{aligned}E_0^0 + \lambda H'_{00} &= \langle \psi_0^0 | H^0 | \psi_0^0 \rangle + \lambda \langle \psi_0^0 | H' | \psi_0^0 \rangle \\ &= \langle \psi_0^0 | (H^0 + \lambda H') | \psi_0^0 \rangle \\ &= \langle \psi_0^0 | H(\lambda) | \psi_0^0 \rangle \geq E_0(\lambda)\end{aligned}\tag{1.1.32}$$

- Validity of perturbation series ( $2 \times 2$ -case):

$$\begin{aligned} H(\lambda) &= H^0 + \lambda \hat{V} = \begin{pmatrix} E_1^0 & 0 \\ 0 & E_2^0 \end{pmatrix} + \lambda \begin{pmatrix} 0 & V \\ V^* & 0 \end{pmatrix} \\ &= \begin{pmatrix} E_1^0 & \lambda V \\ \lambda V^* & E_2^0 \end{pmatrix} \end{aligned} \quad (1.1.33)$$

Eigenvalues:

$$E_{\pm}(\lambda) = \frac{E_1^0 + E_2^0}{2} \pm \frac{E_1^0 - E_2^0}{2} \sqrt{1 + \frac{\lambda^2 |V|^2}{\left(\frac{E_1^0 - E_2^0}{2}\right)^2}} \quad (1.1.34)$$

For  $f(z) = \sqrt{1+z^2} = 1 + \frac{z^2}{2} - \frac{z^4}{8} + \frac{z^6}{16} - O(z^8)$ , it converges when  $|z| < 1$ .

Therefore, we have  $E_{\pm}(\lambda)$  converges when  $|\lambda V| < \frac{|E_1^0 - E_2^0|}{2}$ .

## 1.2 Degenerate Perturbation Theory

### 1.2.1 Anharmonic oscillator

For the hamiltonian of an oscillator:

$$H^0 = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} \quad (1.2.1)$$

length scale 'd':

$$\frac{\hbar^2}{md^2} = m\omega^2 d^2 \implies d^2 = \frac{\hbar}{m\omega} \quad (1.2.2)$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a} + \hat{a}^\dagger) = \frac{d(\hat{a} + \hat{a}^\dagger)}{\sqrt{2}} \quad (1.2.3)$$

The perturbation for  $x^4$ :

$$\lambda H' = \lambda \hbar \omega \left( \frac{\hat{x}^4}{d^4} \right) = \lambda \hbar \omega \frac{(\hat{a} + \hat{a}^\dagger)^4}{4} \quad (1.2.4)$$

1-order correction for energy:

$$E_0^1 = \langle \psi_0^0 | H' | \psi_0^0 \rangle = \frac{\hbar \omega}{4} \langle \psi_0^0 | (\hat{a} + \hat{a}^\dagger)^4 | \psi_0^0 \rangle = \frac{3}{4} \hbar \omega \quad (1.2.5)$$

$$E_0(\lambda) = \frac{\hbar \omega}{2} + \lambda \frac{3}{4} \hbar \omega + O(\lambda^2) = \frac{\hbar \omega}{2} \left( 1 + \frac{3}{2} \lambda + O(\lambda^2) \right) \quad (1.2.6)$$

### 1.2.2 Two-Fold Degeneracy

**Example:**

Consider a particle of mass  $m$  in a two-dimensional oscillator potential:

$$H^0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 (x^2 + y^2) \quad (1.2.7)$$

to which is added a perturbation:

$$H' = \epsilon m\omega^2 xy \quad (1.2.8)$$

The unperturbed first-excited state ( $E^0 = 2\hbar\omega$ ) is two-fold degenerate.

One basis for those two degenerate states:

$$\begin{aligned} \psi_a^0 &= \psi_0(x)\psi_1(y) = \sqrt{\frac{2}{\pi}} \frac{m\omega}{\hbar} y e^{-\frac{m\omega}{2\hbar}(x^2+y^2)} \\ \psi_b^0 &= \psi_1(x)\psi_0(y) = \sqrt{\frac{2}{\pi}} \frac{m\omega}{\hbar} x e^{-\frac{m\omega}{2\hbar}(x^2+y^2)} \end{aligned} \quad (1.2.9)$$

Solve for the exact eigenstates of  $H = H^0 + H'$  and take their limit as  $\epsilon \rightarrow 0$ .

**Solution:**

The problem can be solved by rotating coordinates:

$$x' = \frac{x+y}{\sqrt{2}}, \quad y' = \frac{x-y}{\sqrt{2}} \quad (1.2.10)$$

In terms of the rotated coordinates, the Hamiltonian is:

$$H = \frac{1}{2m} \left( \frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} \right) + \frac{1}{2}m(1+\epsilon)\omega^2 x'^2 + \frac{1}{2}m(1-\epsilon)\omega^2 y'^2 \quad (1.2.11)$$

This amounts to two independent one-dimensional oscillators.

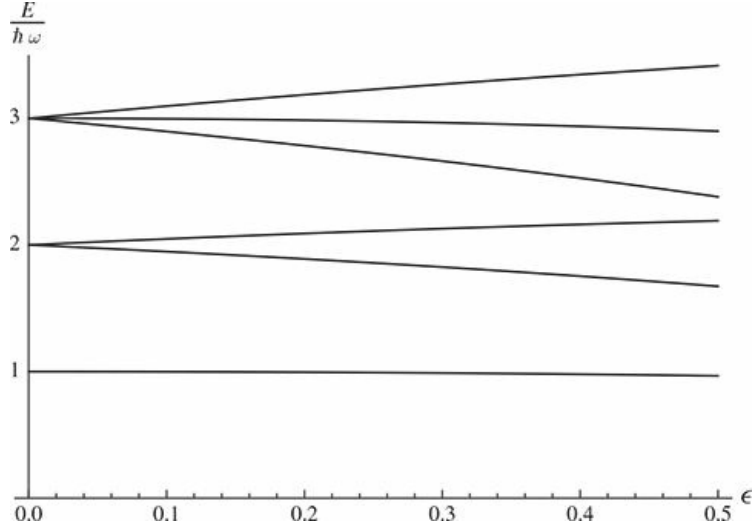
The exact solutions are:

$$\psi_{mn} = \psi_m^+(x')\psi_n^-(y') \quad (1.2.12)$$

where  $\psi_m^\pm$  are one-dimensional oscillator states with  $\omega_\pm = \sqrt{1 \pm \epsilon}\omega$  respectively.

$$E_{mn} = \left(m + \frac{1}{2}\right) \hbar\omega_+ + \left(n + \frac{1}{2}\right) \hbar\omega_- \quad (1.2.13)$$





The two states which grow out of the degenerate first-excited states as  $\epsilon$  is increased have  $m = 0, n = 1$  and  $m = 1, n = 0$ .

If we track these states back to  $\epsilon = 0$  (when  $\omega_+ = \omega_- = \omega$ ), we get:

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \psi_{01}(x) &= \lim_{\epsilon \rightarrow 0} \psi_0^+(x') \psi_1^-(y') = \psi_0 \left( \frac{x+y}{\sqrt{2}} \right) \psi_1 \left( \frac{x-y}{\sqrt{2}} \right) \\ &= \sqrt{\frac{2}{\pi}} \frac{m\omega}{\hbar} \frac{x-y}{\sqrt{2}} e^{-\frac{m\omega}{2\hbar}(x^2+y^2)} = \frac{-\psi_a^0 + \psi_b^0}{\sqrt{2}} \end{aligned} \quad (1.2.14)$$

$$\lim_{\epsilon \rightarrow 0} \psi_{10}(x) = \frac{\psi_a^0 + \psi_b^0}{\sqrt{2}} \quad (1.2.15)$$

Therefore the "good" states for this problem are:

$$\psi_{\pm}^0 \equiv \frac{1}{\sqrt{2}} (\psi_b^0 \pm \psi_a^0) \quad (1.2.16)$$

Suppose that

$$H^0 \psi_a^0 = E^0 \psi_a^0, \quad H^0 \psi_b^0 = E^0 \psi_b^0, \quad \langle \psi_a^0 | \psi_b^0 \rangle = 0 \quad (1.2.17)$$

with  $\psi_a^0$  and  $\psi_b^0$  both normalized.

Any linear combination of these states is still an eigenstate of  $H^0$ :

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 \quad (1.2.18)$$

To solve the Schreodinger equation:

$$H\psi = E\psi \quad (1.2.19)$$

with:

$$H = H^0 + \lambda H' \quad (1.2.20)$$

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots \quad (1.2.21)$$

$$\psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \dots \quad (1.2.22)$$

Plugging these into Equation(1.2.19), we find

$$H^0 \psi^0 + \lambda (H' \psi^0 + H^0 \psi^1) + \dots = E^0 \psi^0 + \lambda (E^1 \psi^0 + E^0 \psi^1) + \dots \quad (1.2.23)$$

The first terms cancel because  $H^0 \psi^0 = E^0 \psi^0$ .

At order  $\lambda^1$ :

$$H^0 \psi^1 + H' \psi^0 = E^0 \psi^1 + E^1 \psi^0 \quad (1.2.24)$$

Taking the inner product with  $\psi_a^0$ :

$$\langle \psi_a^0 | H^0 \psi^1 \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle \quad (1.2.25)$$

Because  $H^0$  is hermitian, the first term on the left cancels the first term on the right.

Putting in Equation(1.2.18), we obtain:

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1 \quad (1.2.26)$$

or, more compactly,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1 \quad (1.2.27)$$

where

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle. \quad (i, j = a, b) \quad (1.2.28)$$

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

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1 \quad (1.2.29)$$

In principle, the  $W$ s are known, which are just the matrix elements of  $H'$ , with respect to the unperturbed wave functions  $\psi_a^0$  and  $\psi_b^0$ .

Written in matrix form,

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (1.2.30)$$

Find a general solution for  $E^1$ :

$$\begin{pmatrix} W_{aa} - E^1 & W_{ab} \\ W_{ba} & W_{bb} - E^1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0 \quad (1.2.31)$$

The determinant of the matrix vanishes:

$$\begin{vmatrix} W_{aa} - E^1 & W_{ab} \\ W_{ba} & W_{bb} - E^1 \end{vmatrix} = (W_{aa} - E^1)(W_{bb} - E^1) - |W_{ab}|^2 = 0 \quad (1.2.32)$$

where we used the fact that  $W_{ba} = W_{ab}^*$ .

Solving the quadratic,

$$E_{\pm}^1 = \frac{1}{2} \left[ W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \quad (1.2.33)$$

The two roots correspond to the two perturbed energies.

**Example:**

Returning to Example above, show that diagonalizing the matrix  $W$  gives the same "good" states we found by solving the problem exactly.

**Solution:**

$$\begin{aligned} W_{aa} &= \iint \psi_a^0(x, y) H' \psi_a^0(x, y) dx dy \\ &= \epsilon m \omega^2 \int |\psi_0(x)|^2 x dx \int |\psi_0(y)|^2 y dy = 0 \end{aligned} \quad (1.2.34)$$

Similarly,  $W_{bb} = 0$ .

$$\begin{aligned} W_{ab} &= \iint \psi_a^0(x, y) H' \psi_b^0(x, y) dx dy \\ &= \epsilon m \omega^2 \int \psi_0(x) x \psi_1(x) dx \int \psi_1(y) y \psi_0(y) dy \end{aligned} \quad (1.2.35)$$

These two integrals are equal, and recalling

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a_+ + a_-) \quad (1.2.36)$$

we have:

$$\begin{aligned} W_{ab} &= \epsilon m \omega^2 \left[ \int \psi_0(x) \sqrt{\frac{\hbar}{2m\omega}} (a_+ + a_-) \psi_1(x) dx \right]^2 \\ &= \epsilon \frac{\hbar \omega}{2} \left[ \int \psi_0(x) \psi_0(x) dx \right]^2 = \epsilon \frac{\hbar \omega}{2} \end{aligned} \quad (1.2.37)$$

Therefore, the matrix  $W$  is

$$W = \epsilon \frac{\hbar \omega}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (1.2.38)$$

The (normalized) eigenvectors of this matrix are:

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix}$$

These eigenvectors tell us which linear combination of  $\psi_a^0$  and  $\psi_b^0$  are the good states:

$$\psi_{\pm}^0 = \frac{1}{\sqrt{2}} (\psi_b^0 \pm \psi_a^0) \quad (1.2.39)$$

The eigenvalues of the matrix  $W$

$$E^1 = \pm \varepsilon \frac{\hbar \omega}{2} \quad (1.2.40)$$

give the first-order corrections to the energy.

If it happens that  $W_{ab} = 0$ , then the two eigenvectors are

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and the energies

$$E_+^1 = W_{aa} = \langle \psi_a^0 | H' | \psi_a^0 \rangle, \quad E_-^1 = W_{bb} = \langle \psi_b^0 | H' | \psi_b^0 \rangle \quad (1.2.41)$$

are precisely what we would have obtained using nondegenerate perturbation theory.

### 1.2.3 "Good" States

#### Theorem:

Let  $A$  be a hermitian operator that commutes with  $H^0$  and  $H'$ . If  $\psi_a^0$  and  $\psi_b^0$  (the degenerate eigenfunctions of  $H^0$ ) are also eigenfunctions of  $A$ , with distinct eigenvalues,

$$A\psi_a^0 = \mu\psi_a^0, \quad A\psi_b^0 = \nu\psi_b^0, \quad \text{and } \mu \neq \nu \quad (1.2.42)$$

then  $\psi_a^0$  and  $\psi_b^0$  are the "good" states to use in perturbation theory.

#### Proof:

Since  $H(\lambda) = H^0 + \lambda H'$  and  $A$  commute, there exist simultaneous eigenstates  $\psi_\gamma(\lambda)$  where

$$H(\lambda)\psi_\gamma(\lambda) = E(\lambda)\psi_\gamma(\lambda) \quad \text{and} \quad A\psi_\gamma(\lambda) = \gamma\psi_\gamma(\lambda) \quad (1.2.43)$$

The fact that  $A$  is hermitian means

$$\begin{aligned} \langle \psi_a^0 | A\psi_\gamma(\lambda) \rangle &= \langle A\psi_a^0 | \psi_\gamma(\lambda) \rangle \\ \gamma \langle \psi_a^0 | \psi_\gamma(\lambda) \rangle &= \mu^* \langle \psi_a^0 | \psi_\gamma(\lambda) \rangle \\ (\gamma - \mu) \langle \psi_a^0 | \psi_\gamma(\lambda) \rangle &= 0 \end{aligned} \quad (1.2.44)$$

where we are making use of the fact that  $\mu$  is real.

This holds true for any value of  $\lambda$  and taking the limit as  $\lambda \rightarrow 0$  we have

$$\langle \psi_a^0 | \psi_\gamma(0) \rangle = 0 \quad \text{unless } \gamma = \mu \quad (1.2.45)$$

and similarly

$$\langle \psi_b^0 | \psi_\gamma(0) \rangle = 0 \quad \text{unless } \gamma = \nu \quad (1.2.46)$$

Now the good states are linear combinations of  $\psi_a^0$  and  $\psi_b^0$ .

$$\psi_\gamma(0) = \alpha\psi_a^0 + \beta\psi_b^0 \quad (1.2.47)$$

From above it follows that either  $\gamma = \mu$ , in which case

$$\beta = \langle \psi_b^0 | \psi_\gamma(0) \rangle = 0 \quad (1.2.48)$$

and the good state is simply  $\psi_a^0$ .

Or  $\gamma = \nu$  and the good state is  $\psi_b^0$ .

Once we identify the “good” states, either by solving Equation(1.2.30) or by applying this theorem, we can use these “good” states as our unperturbed states and apply ordinary non-degenerate perturbation theory.

**Example:**

Find an operator A that satisfies the requirements of the preceding theorem to construct the ”good” states in the past two examples.

**Solution:**

The perturbation  $H'$  has less symmetry than  $H^0$ .

$H^0$  had continuous rotational symmetry, but  $H = H^0 + H'$  is only invariant under rotations by integer multiples of  $\pi$ .

For A, take the operator  $R(\pi)$  that rotates a function counterclockwise by an angle  $\pi$ .

Acting on our states  $\psi_a$  and  $\psi_b$  operator  $R(\pi)$  that rotates a function counterclockwise by an angle  $\pi$ .

$$\begin{aligned} R(\pi)\psi_a^0(x, y) &= \psi_a^0(-x, -y) = -\psi_a^0(x, y) \\ R(\pi)\psi_b^0(x, y) &= \psi_b^0(-x, -y) = -\psi_b^0(x, y) \end{aligned} \quad (1.2.49)$$

That’ s no good; we need an operator with distinct eigenvalues.

How about the operator that interchanges x and y? This is a reflection about a 45° diagonal of the well.

Call this operator D.

D commutes with both  $H^0$  and  $H'$ , since they are unchanged when you switch  $x$  and  $y$ .

Now,

$$\begin{aligned} D\psi_a^0(x, y) &= \psi_a^0(y, x) = \psi_b^0(x, y) \\ D\psi_b^0(x, y) &= \psi_b^0(y, x) = \psi_a^0(x, y) \end{aligned} \quad (1.2.50)$$

So our degenerate eigenstates are not eigenstates of D.

But we can construct linear combinations that are:

$$\psi_\pm^0 \equiv \pm\psi_a^0 + \psi_b^0 \quad (1.2.51)$$

Then

$$D(\pm\psi_a^0 + \psi_b^0) = \pm D\psi_a^0 + D\psi_b^0 = \pm\psi_b^0 + \psi_a^0 = \pm(\pm\psi_a^0 + \psi_b^0) \quad (1.2.52)$$

These are ”good” states, since they are eigenstates of an operator D with distinct eigenvalues ( $\pm 1$ ), and D commutes with both  $H^0$  and  $H'$ .

### 1.2.4 Higher-Order Degeneracy

In the case of  $n$ -fold degeneracy, we look for the eigenvalues of the  $n \times n$  matrix

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle \quad (1.2.53)$$

For three-fold degeneracy (with degenerate states  $\psi_a^0$ ,  $\psi_b^0$  and  $\psi_c^0$ ) the first-order corrections to the energies  $E^1$  are the eigenvalues of  $W$ , determined by solving

$$\begin{pmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \quad (1.2.54)$$

and the "good" states are the corresponding eigenvectors:

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 + \gamma \psi_c^0 \quad (1.2.55)$$

Once again, if you can think of an operator  $A$  that commutes with  $H^0$  and  $H'$ , and use the simultaneous eigenfunctions of  $A$  and  $H^0$ , then the  $W$  matrix will automatically be diagonal, and you won't have to fuss with calculating the off-diagonal elements of  $W$  or solving the characteristic equation.

## 1.3 The Fine Structure of Hydrogen

Hamiltonian for the hydrogen atom:

$$H_{Bohr} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad (1.3.1)$$

Correction:

1. motion of the nucleus: replace  $m$  by the reduced mass
2. relativistic correction
3. spin-orbit coupling

Fine structure constant:

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137.036} \quad (1.3.2)$$

### 1.3.1 The Relativistic Correction

The kinetic energy in the relativistic formula:

$$T = \frac{mc^2}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} - mc^2 \quad (1.3.3)$$

The relativistic momentum:

$$p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \quad (1.3.4)$$

We need to express  $T$  in terms of the momentum instead of velocity.

Notice that

$$p^2 c^2 + m^2 c^4 = \frac{m^2 v^2 c^2 + m^2 c^4 \left[1 - \left(\frac{v}{c}\right)^2\right]}{1 - \left(\frac{v}{c}\right)^2} = \frac{m^2 c^4}{1 - \left(\frac{v}{c}\right)^2} = (T + mc^2)^2 \quad (1.3.5)$$

So

$$T = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \quad (1.3.6)$$

In the nonrelativistic limit  $p \ll mc$ , expanding in powers of the  $\frac{p}{mc}$ , we have:

$$\begin{aligned} T &= mc^2 \left[ \sqrt{1 + \left(\frac{p}{mc}\right)^2} - 1 \right] = mc^2 \left[ 1 + \frac{1}{2} \left(\frac{p}{mc}\right)^2 - \frac{1}{8} \left(\frac{p}{mc}\right)^4 + \cdots - 1 \right] \\ &= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \cdots \end{aligned} \quad (1.3.7)$$

The lowest-order relativistic correction to the Hamiltonian is therefore

$$H'_r = -\frac{p^4}{8m^3 c^2} \quad (1.3.8)$$

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

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3 c^2} \langle \psi | p^4 | \psi \rangle = -\frac{1}{8m^3 c^2} \langle p^2 \psi | p^2 \psi \rangle \quad (1.3.9)$$

The Schroedinger equation (for the unperturbed states) says,

$$p^2 \psi = 2m(E - V) \psi \quad (1.3.10)$$

and hence

$$E_r^1 = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = -\frac{1}{2mc^2} [E^2 - 2E \langle V \rangle + \langle V^2 \rangle] \quad (1.3.11)$$

In hydrogen,  $V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$ :

$$E_r^1 = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right] \quad (1.3.12)$$

where  $E_n$  is the Bohr energy of the state in question.

The expectation values of  $\frac{1}{r}$  and  $\frac{1}{r^2}$  in the unperturbed state  $\psi_{nlm}$ .

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a} \quad (1.3.13)$$

where  $a$  is the Bohr radius.

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(l + \frac{1}{2}\right) n^3 a^2} \quad (1.3.14)$$

It follows that

$$E_r^1 = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{\left(l + \frac{1}{2}\right) n^3 a^2} \right] \quad (1.3.15)$$

or eliminating  $a$  and expressing everything in terms of  $E_n$ :

$$E_r^1 = -\frac{(E_n)^2}{2mc^2} \left[ \frac{4n}{l + \frac{1}{2}} - 3 \right] \quad (1.3.16)$$

Evidently the relativistic correction is smaller than  $E_n$ , by a factor of about  $\frac{E_n}{mc^2} = 2 \times 10^{-5}$ .

We use non-degenerate perturbation theory in spite of the fact that the hydrogen atom is degenerate.

- The perturbation is spherically symmetric, so it commutes with  $L^2$  and  $L_z$ .
- The eigenfunctions of these operators have distinct eigenvalues for the  $n^2$  states with a given  $E_n$ . Luckily, then, the wave functions  $\psi_{nlm}$  are the "good" states for this problem. ( $n, l, m$  are the good quantum numbers).

So as it happens the use of nondegenerate perturbation theory was legitimate.

From Equation(1.3.16), we see that some of the degeneracy of the  $n$ -th energy level has lifted.

The  $2l + 1$ -fold degeneracy in  $m$  remains. (rotational symmetry)

The "accidental" degeneracy in  $l$  has disappeared, since its source is an additional symmetry unique to the  $\frac{1}{r}$  potential.



### 1.3.2 Spin-Orbit Coupling

In the electron frame, the orbiting positive charge sets up a magnetic field  $B$ , which exerts a torque on the spinning electron.

#### The Magnetic Field of the Proton

From the Biot-Savart law:

$$B = \frac{\mu_0 I}{2r} \quad (1.3.17)$$

In the rest frame of the nucleus, the orbital angular momentum of the electron:

$$L = rmv = \frac{2\pi mr^2}{T} \quad (1.3.18)$$

Moreover,  $\mathbf{B}$  and  $\mathbf{L}$  point in the same direction, so

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L} \quad (1.3.19)$$

(Use  $c = \frac{1}{\sqrt{\epsilon_0\mu_0}}$  to eliminate  $\mu_0$  in favor of  $\epsilon_0$ )

#### The Magnetic Dipole Moment of the Electron

Consider first a charge  $q$  smeared out around radius  $r$  with period  $T$ .

The magnetic dipole moment of the ring:

$$\mu = \frac{q\pi r^2}{T} \quad (1.3.20)$$

If the mass of the ring is  $m$ , its angular momentum is the moment of inertia ( $mr^2$ ) times the angular velocity:

$$S = \frac{2\pi mr^2}{T} \quad (1.3.21)$$

The gyromagnetic ratio:

$$\frac{\mu}{S} = \frac{q}{2m} \quad (1.3.22)$$

The directions of  $\boldsymbol{\mu}$  and  $\mathbf{S}$  are the same, so

$$\boldsymbol{\mu} = \frac{q}{2m} \mathbf{S} \quad (1.3.23)$$

However, the electron's magnetic moment is twice the classical value:

$$\boldsymbol{\mu}_e = -\frac{e}{m} \mathbf{S} \quad (1.3.24)$$

Putting all this together, we have

$$H = \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \quad (1.3.25)$$

Considering the Thomas precession (we are doing the analysis in the rest frame of the electron, but it's not an inertial system), it throws in a factor of 1/2:

$$H'_{SO} = \left( \frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \quad (1.3.26)$$

This is the spin-orbit interaction.

In the quantum mechanics, in the presence of spin-orbit coupling, the Hamiltonian no longer commutes with  $\mathbf{L}$  and  $\mathbf{S}$ , so the spin and orbital angular momenta are not separately conserved.

However,  $H'_{SO}$  does commute with  $L^2, S^2$  and the total angular momentum

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S} \quad (1.3.27)$$

and hence these quantities are conserved, i.e. the eigenstates of  $L_z$  and  $S_z$  are not "good" states to use in perturbation theory, but the eigenstates of  $L^2, S^2, J^2$  and  $J_z$  are.

Now

$$J^2 = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S} \quad (1.3.28)$$

so

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (J^2 - L^2 - S^2) \quad (1.3.29)$$

therefore the eigenvalues of  $\mathbf{L} \cdot \mathbf{S}$  are

$$\frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] \quad (1.3.30)$$

In this case,  $s = 1/2$ . Meanwhile, the expectation value of  $1/r^3$  is

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l + \frac{1}{2})(l+1)n^3 a^3} \quad (1.3.31)$$

and we conclude that

$$E_{SO}^1 = \langle H'_{SO} \rangle = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2} \frac{\frac{\hbar^2}{2} [j(j+1) - l(l+1) - \frac{3}{4}]}{l(l + \frac{1}{2})(l+1)n^3 a^3} \quad (1.3.32)$$

or, expressing it all in terms of  $E_n$ :

$$E_{SO}^1 = \frac{(E_n)^2}{mc^2} \left\{ \frac{n [j(j+1) - l(l+1) - \frac{3}{4}]}{l(l + \frac{1}{2})(l+1)} \right\} \quad (1.3.33)$$

It is remarkable that the relativistic correction and the spin-orbit coupling are of the same order.

Adding them together, we get the complete fine-structure formula:

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right) \quad (1.3.34)$$

Combining this with the Bohr formula, we obtain the grand result for the energy levels of hydrogen, including fine structure:

$$E_{nj} = -\frac{13.6eV}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right] \quad (1.3.35)$$

Fine structure breaks the degeneracy in  $l$ , but it still preserves degeneracy in  $j$ .

The good quantum numbers are  $n, l, s, j, m_j$ .

## 1.4 The Zeeman Effect

When an atom is placed in a uniform external magnetic field  $\mathbf{B}_{ext}$ , the energy levels are shifted, which is known as the Zeeman effect.

For a single electron, the perturbation is

$$H'_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B}_{ext}, \quad \boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S}, \quad \boldsymbol{\mu}_l = -\frac{e}{2m}\mathbf{L} \quad (1.4.1)$$

Thus

$$H'_Z = \frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{ext} \quad (1.4.2)$$

If  $B_{ext} \ll B_{int}$ , fine structure dominates, and  $H'_Z$  can be treated as a small perturbation.

If  $B_{ext} \gg B_{int}$ , then the Zeeman effect dominates, and fine structure becomes the perturbation.

When the two fields are comparable, we need the full machinery of degenerate perturbation theory, and it is necessary to diagonalize the relevant portion of the Hamiltonian “by hand.”

### 1.4.1 Weak-Field Zeeman Effect

If  $B_{ext} \ll B_{int}$ , fine structure dominates.

Treat  $H_{Bohr} + H'_{fs}$  as the unperturbed Hamiltonian and  $H'_Z$  as the perturbation.

Unperturbed: eigenstates:  $|nljm_j\rangle$ , unperturbed energies:  $E_{nj}$

Even though fine structure has lifted some of the degeneracy in the Bohr model, these states are still degenerate. (since the energy does not depend on  $m_j$  or  $l$ )

Luckily the states  $|nljm_j\rangle$  are the “good” states for treating the perturbation  $H'_Z$  since  $H'_Z$  commutes with  $J_z$  and  $L^2$ , and each of the degenerate states is uniquely labeled by the two quantum numbers  $m_j$  and  $l$ .

In first-order perturbation theory, the Zeeman correction to the energy:

$$E_Z^1 = \langle nljm_j | H'_Z | nljm_j \rangle = \frac{e}{2m} B_{ext} \hat{k} \cdot \langle \mathbf{L} + 2\mathbf{S} \rangle \quad (1.4.3)$$

where we align  $B_{ext}$  with the z axis to eliminate the off-diagonal elements of  $\mathbf{W}$ .

Now  $\mathbf{L} + 2\mathbf{S} = \mathbf{J} + \mathbf{S}$ .

Find the expectation value of  $\mathbf{S}$ :

The total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  is constant.

$\mathbf{L}$  and  $\mathbf{S}$  precess rapidly about this fixed vector.

In particular, the time average value of  $\mathbf{S}$  is just its projection along  $\mathbf{J}$ :

$$\mathbf{S}_{ave} = \frac{(\mathbf{S} \cdot \mathbf{J})}{J^2} \mathbf{J} \quad (1.4.4)$$

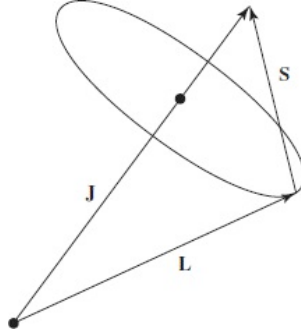
But  $\mathbf{L} = \mathbf{J} - \mathbf{S}$ , so  $L^2 = J^2 + S^2 - 2\mathbf{J} \cdot \mathbf{S}$ , and hence

$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2} (J^2 + S^2 - L^2) = \frac{\hbar^2}{2} [j(j+1) + s(s+1) - l(l+1)] \quad (1.4.5)$$

from which it follows that

$$\langle \mathbf{L} + 2\mathbf{S} \rangle = \left\langle \left( 1 + \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \right) \mathbf{J} \right\rangle = \left[ 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right] \langle \mathbf{J} \rangle \quad (1.4.6)$$

The term in square brackets is known as the Lande g-factor,  $g_J$ .



The energy corrections are then

$$E_Z^1 = \mu_B g_J B_{ext} m_j \quad (1.4.7)$$

where the Bohr magneton:

$$\mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV/T} \quad (1.4.8)$$

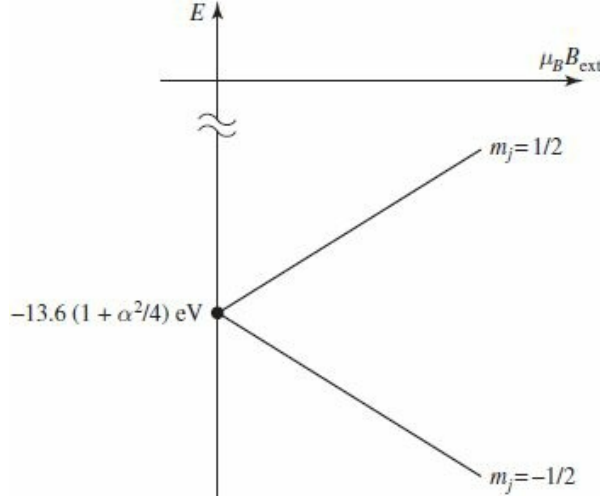
Recall that degeneracy in the quantum number  $m$  is a consequence of rotational invariance. The perturbation  $H'_Z$  picks out a specific direction in space which breaks the rotational symmetry and lifts the degeneracy in  $m$ .

The total energy is the sum of the fine-structure part (Equation 1.3.35) and the Zeeman contribution (Equation 1.4.7).

For example, the ground state ( $n = 1, l = 0, j = 1/2$ , and therefore  $g_J = 2$ ) splits into two levels:

$$-13.6 \text{ eV} \left( 1 + \frac{\alpha^2}{4} \right) \pm \mu_B B_{ext} \quad (1.4.9)$$

with the plus sign for  $m_j = 1/2$ , and minus for  $m_j = -1/2$ . These energies are plotted in Figure below:



### 1.4.2 Strong-Field Zeeman Effect

If  $B_{ext} \gg B_{int}$ , the Zeeman effect dominates and we take the unperturbed Hamiltonian to be  $H_{Bohr} + H'_Z$  and the perturbation to be  $H'_{fs}$ .

The Zeeman Hamiltonian:

$$H'_Z = \frac{e}{2m} B_{ext} (L_z + 2S_z) \quad (1.4.10)$$

To compute the unperturbed energies:

$$E_{nlm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{ext} (m_l + 2m_s) \quad (1.4.11)$$

The states used here  $|nlm_l m_s\rangle$  are degenerate, since the energy does not depend on  $l$ .

And there is an additional degeneracy due to the fact that, for example,  $m_l = 3$  and  $m_s = -1/2$  or  $m_l = 1$  and  $m_s = 1/2$  have the same energy.

Again the state  $|nlm_l m_s\rangle$  are the “good” states for treating the perturbation.

The fine structure Hamiltonian  $H'_{fs}$  commutes with both  $L^2$  and with  $J_z$ , the first operator resolves the degeneracy in  $l$  and the second resolves the degeneracy from coincidences in  $m_l + 2m_s = m_j + m_s$ .

In first-order perturbation theory the fine structure correction to these levels is:

$$E_{fs}^1 = \langle nlm_l m_s | (H'_r + H'_{SO}) | nlm_l m_s \rangle \quad (1.4.12)$$

The relativistic contribution is the same as before (Equation 1.3.16); for the spin-orbit term (Equation 1.3.26) we need:

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s \quad (1.4.13)$$

(note that  $\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle = 0$  for eigenstates of  $S_z$  and  $L_z$ ).

Putting all this together, we conclude that

$$E_{fs}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[ \frac{l(l+1) - m_l m_s}{l(l + \frac{1}{2})(l+1)} \right] \right\} \quad (1.4.14)$$

(The term in square brackets is indeterminate for  $l = 0$ ; its correct value in this case is 1).

The total energy is the sum of the Zeeman part and the fine structure contribution.

### 1.4.3 Intermediate-Field Zeeman Effect

Now neither  $H'_Z$  nor  $H'_{fs}$  dominates, the perturbations to the Bohr Hamiltonian:

$$H' = H'_Z + H'_{fs} \quad (1.4.15)$$

Focus on the case  $n = 2$ , choose basis states characterized by  $l, j, m_j$ .

Using the Clebsch-Gordan coefficients to express  $|jm_j\rangle$  as linear combinations of  $|lsm_l m_s\rangle$ , we have:

$l = 0$ :

$$\begin{aligned} \psi_1 &\equiv \left| \frac{1}{2} \frac{1}{2} \right\rangle = \left| 0 \frac{1}{2} 0 \frac{1}{2} \right\rangle \\ \psi_2 &\equiv \left| \frac{1}{2} \frac{-1}{2} \right\rangle = \left| 0 \frac{1}{2} 0 \frac{-1}{2} \right\rangle \end{aligned}$$

$l = 1$ :

$$\begin{aligned} \psi_3 &\equiv \left| \frac{3}{2} \frac{3}{2} \right\rangle = \left| 1 \frac{1}{2} 1 \frac{1}{2} \right\rangle \\ \psi_4 &\equiv \left| \frac{3}{2} \frac{-3}{2} \right\rangle = \left| 1 \frac{1}{2} -1 \frac{-1}{2} \right\rangle \\ \psi_5 &\equiv \left| \frac{3}{2} \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| 1 \frac{1}{2} 0 \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 1 \frac{1}{2} 1 \frac{-1}{2} \right\rangle \\ \psi_6 &\equiv \left| \frac{1}{2} \frac{1}{2} \right\rangle = -\sqrt{\frac{1}{3}} \left| 1 \frac{1}{2} 0 \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1 \frac{1}{2} 1 \frac{-1}{2} \right\rangle \\ \psi_7 &\equiv \left| \frac{3}{2} \frac{-1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| 1 \frac{1}{2} -1 \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1 \frac{1}{2} 0 \frac{-1}{2} \right\rangle \\ \psi_8 &\equiv \left| \frac{1}{2} \frac{-1}{2} \right\rangle = -\sqrt{\frac{2}{3}} \left| 1 \frac{1}{2} -1 \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 1 \frac{1}{2} 0 \frac{-1}{2} \right\rangle \end{aligned}$$

In this basis the nonzero matrix elements of  $H'_{fs}$  are all on the diagonal, and given by Equation (1.3.34).

$H'_Z$  has four off-diagonal elements, and the complete matrix  $W$  is:

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

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

The first four eigenvalues are already displayed along the diagonal, it remains only to find the eigenvalues of the two  $2 \times 2$  blocks.

The characteristic equation for the first of these is:

$$\lambda^2 - \lambda(6\gamma - \beta) + \left(5\gamma^2 - \frac{11}{3}\gamma\beta\right) = 0 \quad (1.4.16)$$

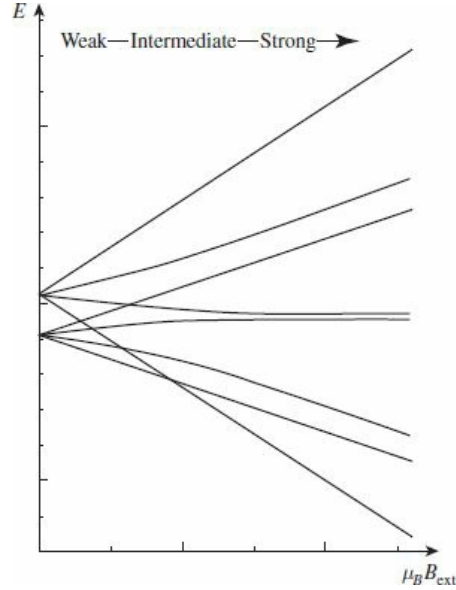
and the quadratic formula gives the eigenvalues:

$$\lambda_{\pm} = 3\gamma - \frac{\beta}{2} \pm \sqrt{4\gamma^2 + \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \quad (1.4.17)$$

The eigenvalues of the second block are the same, but with the sign of  $\beta$  reversed.

The eight energies are listed in the table below, and plotted against  $B_{ext}$  in the next Figure.

$\epsilon_1$	$= E_2 - 5\gamma + \beta$
$\epsilon_2$	$= E_2 - 5\gamma - \beta$
$\epsilon_3$	$= E_2 - \gamma + 2\beta$
$\epsilon_4$	$= E_2 - \gamma - 2\beta$
$\epsilon_5$	$= E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
$\epsilon_6$	$= E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
$\epsilon_7$	$= E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$
$\epsilon_8$	$= E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$



In the zero-field limit ( $\beta = 0$ ) they reduce to the fine structure values.

## 1.5 Hyperfine Splitting in Hydrogen

The proton itself constitutes a magnetic dipole, though its dipole moment is much smaller than the electron's because of the mass in the denominator:

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p} \mathbf{S}_p, \quad \boldsymbol{\mu}_e = -\frac{e}{m_e} \mathbf{S}_e \quad (1.5.1)$$

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

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3} [3(\boldsymbol{\mu} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} - \boldsymbol{\mu}] + \frac{2\mu_0}{3} \boldsymbol{\mu} \delta^3(\mathbf{r}) \quad (1.5.2)$$

So the Hamiltonian of the electron, in the magnetic field due to the proton's magnetic dipole moment, is

$$H'_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{[3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e]}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e} \mathbf{S}_p \cdot \mathbf{S}_e \delta^3(\mathbf{r}) \quad (1.5.3)$$

The first-order correction to the energy is the expectation value of the perturbing Hamiltonian:

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{[3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e]}{r^3} \right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle |\psi(0)|^2 \quad (1.5.4)$$

In the ground state (or any other state for which  $l = 0$ ) the wave function is spherically symmetric, and the first expectation value vanishes.

And we can find that  $|\psi_{100}(0)|^2 = \frac{1}{\pi a^3}$ , so in the ground state:

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle \quad (1.5.5)$$

This is called spin-spin coupling, because it involves the dot product of two spins.

In the presence of spin-spin coupling, the individual spin angular momenta are no longer conserved.

The "good" states are eigenvectors of the total spin,

$$\mathbf{S} \equiv \mathbf{S}_e + \mathbf{S}_p \quad (1.5.6)$$

As before, we square this out to get

$$\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2} (S^2 - S_e^2 - S_p^2) \quad (1.5.7)$$

But the electron and proton both have spin 1/2, so  $S_e^2 = S_p^2 = \frac{3}{4}\hbar^2$ .

In the triplet state, the total spin is 1, and hence  $S^2 = 2\hbar^2$ .

In the singlet state the total spin is 0, and  $S^2 = 0$ .

Thus

$$E_{hf}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a^4} \begin{cases} +1/4, & \text{(triplet);} \\ -3/4, & \text{(singlet).} \end{cases} \quad (1.5.8)$$



Spin-spin coupling breaks the spin degeneracy of the ground state, lifting the triplet configuration and depressing the singlet.

The energy gap is:

$$\Delta E = \frac{4g_p\hbar^4}{3m_p m_e^2 c^2 a^4} = 5.88 \times 10^{-6} eV \quad (1.5.9)$$

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

$$\nu = \frac{\Delta E}{\hbar} = 1420 MHz \quad (1.5.10)$$

and the corresponding wavelength is  $c/\nu = 21\text{cm}$ , which falls in the microwave region.

This famous 21cm line is among the most pervasive forms of radiation in the universe.

## 2 Chapter 8 The Variational Principle

### 2.1 Theory

The variational principle will get you an upper bound for  $E_{gs}$ .

Pick any normalized function  $\psi$  whatsoever, then:

$$E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle \quad (2.1.1)$$

**Proof:**

Since the eigenfunctions of  $H$  form a complete set, we can express  $\psi$  as a linear combination of them:

$$\psi = \sum_n c_n \psi_n, \quad \text{with } H\psi_n = E_n \psi_n \quad (2.1.2)$$

Since  $\psi$  is normalized,

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \left| \sum_n c_n \psi_n \right. \right\rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2 \quad (2.1.3)$$

Meanwhile,

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \left| H \sum_n c_n \psi_n \right. \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2 \quad (2.1.4)$$

But the ground state energy is, by definition, the smallest eigenvalue,  $E_{gs} \leq E_n$ , and hence

$$\langle H \rangle \geq E_{gs} \sum_n |c_n|^2 = E_{gs} \quad (2.1.5)$$

### Example

To find the ground state energy for the one-dimensional harmonic oscillator:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \quad (2.1.6)$$

The exact answer in this case:  $E_{gs} = \frac{\hbar\omega}{2}$ .

Pick as our “trial” wave function the gaussian:  $\psi(x) = Ae^{-bx^2}$

where  $b$  is a constant, and  $A$  is determined by normalization:

$$1 = |A|^2 \int_{-\infty}^{+\infty} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} \implies A = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}} \quad (2.1.7)$$

$\langle H \rangle = \langle T \rangle + \langle V \rangle$ , where in this case:

$$\langle T \rangle = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2} (e^{-bx^2}) dx = \frac{\hbar^2 b}{2m} \quad (2.1.8)$$

$$\langle V \rangle = \frac{1}{2} m \omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx = \frac{m \omega^2}{8b} \quad (2.1.9)$$

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m \omega^2}{8b} \quad (2.1.10)$$

To get the tightest bound, let's minimize  $\langle H \rangle$ :

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{m \omega^2}{8b^2} = 0 \implies b = \frac{m \omega}{2\hbar} \implies \langle H \rangle_{min} = \frac{\hbar \omega}{2} \quad (2.1.11)$$

In this case we happened to pick a trial function with precisely the form of the actual ground state.

### Example

To find the ground state energy of the delta function potential:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \alpha \delta(x) \quad (2.1.12)$$

We already know the exact answer:  $E_{gs} = -\frac{m\alpha^2}{2\hbar^2}$ .

We'll use a gaussian trial function, we've already determined the normalization, and calculated  $\langle T \rangle$ ,

$$\langle V \rangle = -\alpha |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} \delta(x) dx = -\alpha \sqrt{\frac{2b}{\pi}} \quad (2.1.13)$$

Evidently

$$\langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}} \quad (2.1.14)$$

Minimizing it,

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \implies b = \frac{2m^2 \alpha^2}{\pi \hbar^4} \implies \langle H \rangle_{min} = -\frac{m\alpha^2}{\pi \hbar^2} \quad (2.1.15)$$

which is indeed somewhat higher than  $E_{gs}$ .

### Example

Find an upper bound on the ground state energy of the one-dimensional infinite square well.

Using the "triangular" trial wave function:

$$\psi(x) = \begin{cases} Ax, & 0 \leq x \leq \frac{a}{2}, \\ A(a-x), & \frac{a}{2} \leq x \leq a, \\ 0, & \text{otherwise,} \end{cases} \quad (2.1.16)$$

where  $A$  is determined by normalization:

$$1 = |A|^2 \left[ \int_0^{\frac{a}{2}} x^2 dx + \int_{\frac{a}{2}}^a (a-x)^2 dx \right] = |A|^2 \frac{a^3}{12} \implies A = \frac{2}{a} \sqrt{\frac{3}{a}} \quad (2.1.17)$$

In this case

$$\frac{d\psi}{dx} = \begin{cases} A, & 0 \leq x \leq \frac{a}{2}, \\ -A, & \frac{a}{2} \leq x \leq a, \\ 0, & \text{otherwise,} \end{cases} \quad (2.1.18)$$

Now, the derivative of a step function is a delta function:

$$\frac{d^2\psi}{dx^2} = A\delta(x) - 2A\delta(x - \frac{a}{2}) + A\delta(x - a) \quad (2.1.19)$$

and hence

$$\begin{aligned} \langle H \rangle &= -\frac{\hbar^2 A}{2m} \int \left[ \delta(x) - 2\delta(x - \frac{a}{2}) + \delta(x - a) \right] \psi(x) dx \\ &= -\frac{\hbar^2 A}{2m} \left[ \psi(0) - 2\psi(\frac{a}{2}) + \psi(a) \right] \\ &= \frac{\hbar^2 A^2 a}{2m} = \frac{12\hbar^2}{2ma^2} \end{aligned} \quad (2.1.20)$$

The exact ground state energy is  $E_{gs} = \frac{\pi^2 \hbar^2}{2ma^2}$ , so the theorem works.

Alternatively, exploit the hermiticity of  $\hat{p}$ :

$$\begin{aligned} \langle H \rangle &= \frac{1}{2m} \langle \hat{p}^2 \rangle = \frac{1}{2m} \langle \hat{p}\psi | \hat{p}\psi \rangle \\ &= \frac{1}{2m} \int_0^a \left( -i\hbar \frac{d\psi}{dx} \right)^* \left( -i\hbar \frac{d\psi}{dx} \right) dx \\ &= \frac{\hbar^2}{2m} \left[ \int_0^{\frac{a}{2}} (A)^2 dx + \int_{\frac{a}{2}}^a (-A)^2 dx \right] \\ &= \frac{\hbar^2}{2m} A^2 a = \frac{12\hbar^2}{2ma^2} \end{aligned} \quad (2.1.21)$$

## 2.2 The Ground State of Helium

The Hamiltonian for this system (ignoring fine structure and smaller corrections) is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (2.2.1)$$

The measured ground state energy of helium:  $E_{gs} = -78.975 \text{ eV}$

Such a simple and important problem has no known exact solution.

The trouble comes from the electron-electron repulsion:

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (2.2.2)$$

If we ignore this term altogether,  $H$  splits into two independent hydrogen Hamiltonians (only with a nuclear charge of  $2e$ ); the exact solution is just the product of hydrogenic wave functions:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) \equiv \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-\frac{2(r_1+r_2)}{a}} \quad (2.2.3)$$

and the energy is  $8E_1 = -109 \text{ eV}$ .

To get a better approximation for  $E_{gs}$ , apply the variational principle, using  $\psi_0$  as the trial wave function.

$$H\psi_0 = (8E_1 + V_{ee}) \psi_0 \quad (2.2.4)$$

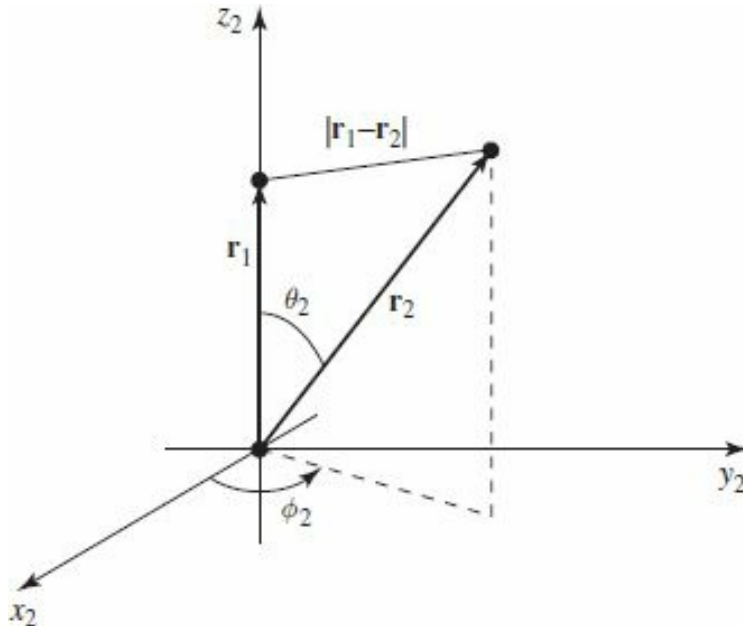
Thus

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle \quad (2.2.5)$$

where

$$\langle V_{ee} \rangle = \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{8}{\pi a^3} \right)^2 \int \frac{e^{-\frac{4(r_1+r_2)}{a}}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (2.2.6)$$

Do the  $\mathbf{r}_2$  integral first and orient the  $\mathbf{r}_2$  coordinate system so that the polar axis lies along  $\mathbf{r}_1$ .



By the law of cosines,

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2} \quad (2.2.7)$$

and hence

$$I_2 \equiv \int \frac{e^{-\frac{4r_2}{a}}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_2 = \int \frac{e^{-\frac{4r_2}{a}}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}} r_2^2 \sin\theta_2 dr_2 d\theta_2 d\phi_2 \quad (2.2.8)$$

The  $\phi_2$  integral is trivial ( $2\pi$ ); the  $\theta_2$  integral is:

$$\begin{aligned} \int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}} d\theta_2 &= \left. \frac{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}}{r_1r_2} \right|_0^\pi \\ &= \frac{1}{r_1r_2} \left( \sqrt{r_1^2 + r_2^2 + 2r_1r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1r_2} \right) \\ &= \frac{1}{r_1r_2} [(r_1 + r_2) - |r_1 - r_2|] \\ &= \begin{cases} 2/r_1, & r_2 < r_1, \\ 2/r_2, & r_2 > r_1. \end{cases} \end{aligned} \quad (2.2.9)$$

Thus

$$\begin{aligned} I_2 &= 4\pi \left( \frac{1}{r_1} \int_0^{r_1} e^{-\frac{4r_2}{a}} r_2^2 dr_2 + \int_{r_1}^\infty e^{-\frac{4r_2}{a}} r_2 dr_2 \right) \\ &= \frac{\pi a^3}{8r_1} \left[ 1 - \left( 1 + \frac{2r_1}{a} \right) e^{-\frac{4r_1}{a}} \right] \end{aligned} \quad (2.2.10)$$

It follows that  $\langle V_{ee} \rangle$  is equal to

$$\left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{8}{\pi a^3} \right) \int \left[ 1 - \left( 1 + \frac{2r_1}{a} \right) e^{-\frac{4r_1}{a}} \right] e^{-\frac{4r_1}{a}} r_1 \sin\theta_1 dr_1 d\theta_1 d\phi_1 \quad (2.2.11)$$

The angular integrals are easy ( $4\pi$ ), and the  $r_1$  integral becomes

$$\int_0^\infty \left[ r e^{-\frac{4r}{a}} - \left( r + \frac{2r^2}{a} \right) e^{-\frac{8r}{a}} \right] dr = \frac{5a^2}{128} \quad (2.2.12)$$

Finally,

$$\langle V_{ee} \rangle = \frac{5}{4a} \left( \frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5}{2} E_1 = 34eV \quad (2.2.13)$$

and therefore

$$\langle H \rangle = -109eV + 34eV = -75eV \quad (2.2.14)$$

We need to think up a more realistic trial function than  $\psi_0$ .

On the averagem each electron represents a cloud of negative charge which partially shields the nucleus, so that the other electron actually sees an effective nuclear charge ( $Z$ ) that is somewhat less than 2.

This suggests that we use a trial function of the form

$$\psi_1(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-\frac{Z(r_1+r_2)}{a}} \quad (2.2.15)$$

We'll treat  $Z$  as a variational parameter, picking the value that minimizes  $\langle H \rangle$ .

This wave function is an eigenstate of the “unperturbed” Hamiltonian (neglecting electron repulsion), only with  $Z$ , instead of 2, in the Coulomb terms.

With this in mind, we rewrite  $H$  as follows:

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (2.2.16)$$

The expectation value of  $H$  is evidently

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2) \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle \quad (2.2.17)$$

Here  $\langle 1/r \rangle$  is the expectation value of  $1/r$  in the hydrogenic ground state  $\psi_{100}$  (with nuclear charge  $Z$ ).

According to Equation  $\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}$ :

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad (2.2.18)$$

The expectation value of  $V_{ee}$  is the same as before, except that instead of  $Z = 2$  we now want arbitrary  $Z$ , so we multiply  $a$  by  $2/Z$ :

$$\langle V_{ee} \rangle = \frac{5Z}{8a} \left( \frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5Z}{4} E_1 \quad (2.2.19)$$

Putting all this together, we find:

$$\langle H \rangle = \left[ 2Z^2 - 4Z(Z-2) - \frac{5}{4}Z \right] E_1 = \left[ -2Z^2 + \frac{27}{4}Z \right] E_1 \quad (2.2.20)$$

The lowest upper bound occurs when  $\langle H \rangle$  is minimized:

$$\frac{d}{dZ} \langle H \rangle = \left[ -4Z + \frac{27}{4} \right] E_1 = 0 \implies Z = \frac{27}{16} = 1.69 \quad (2.2.21)$$

Putting in this value for  $Z$ , we find

$$\langle H \rangle = \frac{1}{2} \left( \frac{3}{2} \right)^6 E_1 = -77.5 eV \quad (2.2.22)$$

## 2.3 The Hydrogen Molecule Ion

In  $H_2^+$ , we assume for the moment that the protons are fixed in position, a specified distance  $R$  apart.

The Hamiltonian is

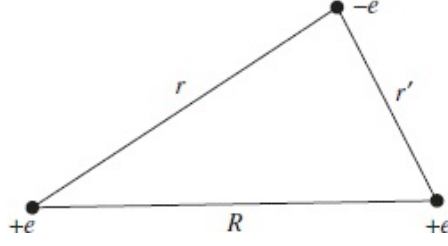
$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r} + \frac{1}{r'} \right) \quad (2.3.1)$$

where  $r$  and  $r'$  are the distances to the electron from the respective protons.

To construct the trial wave function, imagine that the ion is formed by taking a hydrogen atom in its ground state,

$$\psi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}} \quad (2.3.2)$$

bring the second proton in from infinity and nailing it down a distance  $R$  away.



Treat the case where the electron has the same probability of being associated with either one. We consider a trial function of the form:

$$\psi = A [\psi_0(r) + \psi_0(r')] \quad (2.3.3)$$

(LCAO technique: expressing the molecular wavefunction as a linear combination of atomic orbitals.)

Firstly, normalize the trial function:

$$1 = \int |\psi|^2 d^3\mathbf{r} = |A|^2 \left[ \int \psi_0(r)^2 d^3\mathbf{r} + \int \psi_0(r')^2 d^3\mathbf{r} + 2 \int \psi_0(r)\psi_0(r') d^3\mathbf{r} \right] \quad (2.3.4)$$

The first two integrals are 1, Let:

$$I \equiv \langle \psi_0(r) | \psi_0(r') \rangle = \frac{1}{\pi a^3} \int e^{-(r+r')/a} d^3\mathbf{r} \quad (2.3.5)$$

Picking coordinates so that proton 1 is at the origin and proton 2 is on the z axis at the point  $R$ :

$$r' = \sqrt{r^2 + R^2 - 2rR\cos\theta} \quad (2.3.6)$$

and therefore

$$I = \frac{1}{\pi a^3} \int e^{-r/a} e^{-\frac{\sqrt{r^2 + R^2 - 2rR\cos\theta}}{a}} r^2 \sin\theta dr d\theta d\phi \quad (2.3.7)$$

The  $\phi$  integral is trivial ( $2\pi$ ).

Let  $y \equiv \sqrt{r^2 + R^2 - 2rR\cos\theta}$ , so that  $d(y^2) = 2ydy = 2rR\sin\theta d\theta$ .

Then

$$\begin{aligned} \int_0^\pi e^{-\frac{\sqrt{r^2 + R^2 - 2rR\cos\theta}}{a}} \sin\theta d\theta &= \frac{1}{rR} \int_{|r-R|}^{r+R} e^{-y/a} y dy \\ &= -\frac{a}{rR} \left[ e^{-\frac{r+R}{a}} (r+R+a) - e^{-\frac{|r-R|}{a}} (|r-R|+a) \right] \end{aligned} \quad (2.3.8)$$

The  $r$  integral is now:

$$I = \frac{2}{a^2 R} \left[ -e^{-\frac{R}{a}} \int_0^\infty (r+R+a) e^{-\frac{2r}{a}} r dr + e^{-\frac{R}{a}} \int_0^R (R-r+a) r dr + e^{\frac{R}{a}} \int_R^\infty (r-R+a) e^{-\frac{2r}{a}} r dr \right] \quad (2.3.9)$$

Evaluating the integrals, we find

$$I = e^{-\frac{R}{a}} \left[ 1 + \left( \frac{R}{a} \right) + \frac{1}{3} \left( \frac{R}{a} \right)^2 \right] \quad (2.3.10)$$

$I$  is called an overlap integral, it measures the amount by which  $\psi_0(r)$  overlaps  $\psi_0(r')$ .  
( $I$  goes to 1 as  $R \rightarrow 0$ , and to 0 as  $R \rightarrow \infty$ )

The normalization factor:

$$|A|^2 = \frac{1}{2(1+I)} \quad (2.3.11)$$

Next we calculate the expectation value of  $H$  in the trial state  $\psi$ .

Noting that:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_0(r) = E_1 \psi_0(r) \quad (2.3.12)$$

(where  $E_1 = -13.6\text{eV}$  is the ground state energy of atomic hydrogen)

And the same with  $r'$  in place of  $r$  we have:

$$\begin{aligned} H\psi &= A \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r} + \frac{1}{r'} \right) \right] [\psi_0(r) + \psi_0(r')] \\ &= E_1 \psi - A \left( \frac{e^2}{4\pi\epsilon_0} \right) \left[ \frac{1}{r'} \psi_0(r) + \frac{1}{r} \psi_0(r') \right] \end{aligned} \quad (2.3.13)$$

It follows that

$$\langle H \rangle = E_1 - 2|A|^2 \left( \frac{e^2}{4\pi\epsilon_0} \right) \left[ \left\langle \psi_0(r) \left| \frac{1}{r'} \right| \psi_0(r) \right\rangle + \left\langle \psi_0(r) \left| \frac{1}{r} \right| \psi_0(r') \right\rangle \right] \quad (2.3.14)$$

The direct integral:

$$D \equiv a \left\langle \psi_0(r) \left| \frac{1}{r'} \right| \psi_0(r) \right\rangle = \frac{a}{R} - \left( 1 + \frac{a}{R} \right) e^{-\frac{2R}{a}} \quad (2.3.15)$$

The exchange integral:

$$X \equiv a \left\langle \psi_0(r) \left| \frac{1}{r} \right| \psi_0(r') \right\rangle = \left( 1 + \frac{a}{R} \right) e^{-\frac{R}{a}} \quad (2.3.16)$$

Putting all this together, and recalling that

$$E_1 = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2a} \quad (2.3.17)$$

We conclude:

$$\langle H \rangle = \left[ 1 + 2 \frac{(D+X)}{(1+I)} \right] E_1 \quad (2.3.18)$$

According to the variational principle, the ground state energy is less than  $\langle H \rangle$ .

There is also potential energy associated with the proton-proton repulsion:

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} = -\frac{2a}{R} E_1 \quad (2.3.19)$$

Thus the total energy of the system, in units of  $-E_1$ , and expressed as a function of  $x \equiv R/a$ , is less than

$$F(x) = -1 + \frac{2}{x} \left\{ \frac{(1 - \frac{2}{3}x^2)e^{-x} + (1+x)e^{-2x}}{1 + (1+x + \frac{1}{3}x^2)e^{-x}} \right\} \quad (2.3.20)$$



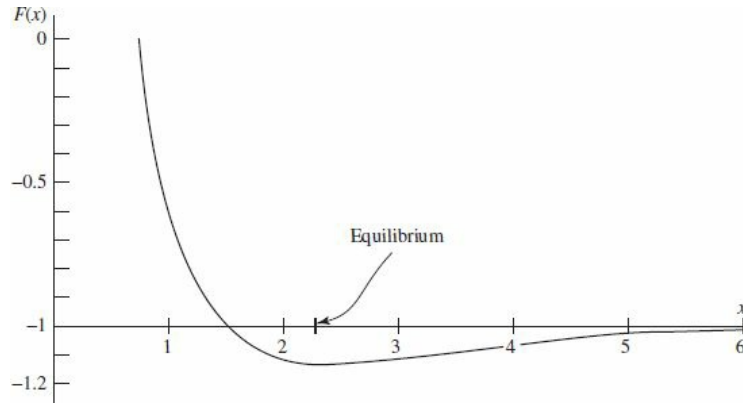


图 1: Plot of the function  $F(x)$ , showing existence of a bound state.

Evidently bonding does occur, for there exists a region in which the graph goes below  $-1$ , indicating that the energy is less than that of a neutral atom plus a free proton.

It's a covalent bond, with the electron shared equally by the two protons.

The equilibrium separation of the protons is about 2.4 Bohr radii. The calculated binding energy is 1.8eV, whereas the experimental value is 2.8eV.

## 2.4 The Hydrogen Molecule

Taking the two protons to be at rest, the Hamiltonian is:

$$\hat{H} = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_1} - \frac{1}{r'_1} - \frac{1}{r_2} - \frac{1}{r'_2} \right) \quad (2.4.1)$$

where  $r_1$  and  $r'_1$  are the distances of electron 1 from each proton and  $r_2$  and  $r'_2$  are the distances of electron 2 from each proton.

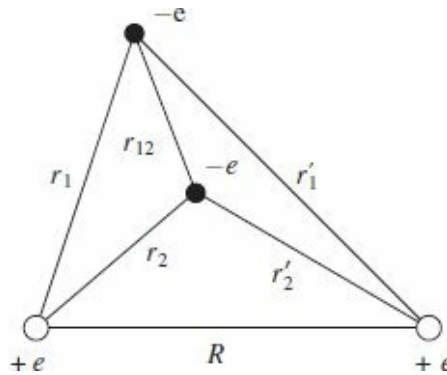


图 2: Diagram of  $H_2$  showing the distances on which the potential energy depends.

For the variational wave function, associate one electron with each proton, and symmetrize:

$$\psi_+(\mathbf{r}_1, \mathbf{r}_2) = A_+ [\psi_0(r_1)\psi_0(r'_2) + \psi_0(r'_1)\psi_0(r_2)] \quad (2.4.2)$$

Since this spatial wave function is symmetric under interchange, the electrons must occupy the antisymmetric spin state.

We could also choose the trial wave function:

$$\psi_{-}(\mathbf{r}_1, \mathbf{r}_2) = A_{-} [\psi_0(r_1)\psi_0(r'_2) - \psi_0(r'_1)\psi_0(r_2)] \quad (2.4.3)$$

in which case the electrons would be in a symmetric (triplet) spin state.

These two variational wave functions constitute the Heitler-London approximation.

Calculate the energy of each one, first we need to normalize the wave functions.

Note that

$$|\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2)|^2 = A_{\pm}^2 [\psi_0(r_1)^2\psi_0(r'_2)^2 + \psi_0(r'_1)^2\psi_0(r_2)^2 \pm 2\psi_0(r_1)\psi_0(r'_2)\psi_0(r'_1)\psi_0(r_2)] \quad (2.4.4)$$

Normalization requires

$$\begin{aligned} 1 &= \iint |\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\ &= A_{\pm}^2 \left[ \int \psi_0(r_1)^2 d^3\mathbf{r}_1 \int \psi_0(r'_2)^2 d^3\mathbf{r}_2 + \int \psi_0(r'_1)^2 d^3\mathbf{r}_1 \int \psi_0(r_2)^2 d^3\mathbf{r}_2 \right. \\ &\quad \left. \pm 2 \int \psi_0(r_1)\psi_0(r'_1) d^3\mathbf{r}_1 \int \psi_0(r'_2)\psi_0(r_2) d^3\mathbf{r}_2 \right] \end{aligned} \quad (2.4.5)$$

The individual orbitals are normalized and the overlap integral was given the symbol  $I$  and calculated in Equation(2.3.10). Thus

$$A_{\pm} = \frac{1}{\sqrt{2(1 \pm I^2)}} \quad (2.4.6)$$

To calculate the expectation value of the energy, we will start with the kinetic energy of particle 1.

Since  $\psi_0$  is the ground state of the hydrogen Hamiltonian, the same trick that brought us to Equation(2.3.14) gives

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla_1^2 \psi_{\pm} &= A_{\pm} \left[ \left( -\frac{\hbar^2}{2m} \nabla_1^2 \psi_0(r_1) \right) \psi_0(r'_2) \pm \left( -\frac{\hbar^2}{2m} \nabla_1^2 \psi_0(r'_1) \right) \psi_0(r_2) \right] \\ &= A_{\pm} \left[ \left( E_1 + \frac{e^2}{4\pi\epsilon_0 r_1} \right) \psi_0(r_1)\psi_0(r'_2) \pm \left( E_1 + \frac{e^2}{4\pi\epsilon_0 r'_1} \right) \psi_0(r'_1)\psi_0(r_2) \right] \\ &= E_1 \psi_{\pm} + \frac{e^2}{4\pi\epsilon_0 a} A_{\pm} \left( \frac{a}{r_1} \psi_0(r_1)\psi_0(r'_2) \pm \frac{a}{r'_1} \psi_0(r'_1)\psi_0(r_2) \right) \end{aligned} \quad (2.4.7)$$

Taking the inner product with  $\psi_{\pm}$  then gives:

$$\begin{aligned} \left\langle -\frac{\hbar^2}{2m} \nabla_1^2 \right\rangle &= E_1 + \left( \frac{e^2}{4\pi\epsilon_0 a} \right) A_{\pm}^2 \left[ \left\langle \psi_0(r_1) \left| \frac{a}{r_1} \right| \psi_0(r_1) \right\rangle \langle \psi_0(r'_2) | \psi_0(r'_2) \rangle \right. \\ &\quad \pm \left\langle \psi_0(r'_1) \left| \frac{a}{r'_1} \right| \psi_0(r_1) \right\rangle \langle \psi_0(r_2) | \psi_0(r'_2) \rangle \pm \left\langle \psi_0(r_1) \left| \frac{a}{r'_1} \right| \psi_0(r'_1) \right\rangle \langle \psi_0(r'_2) | \psi_0(r_2) \rangle \\ &\quad \left. + \left\langle \psi_0(r'_1) \left| \frac{a}{r'_1} \right| \psi_0(r'_1) \right\rangle \langle \psi_0(r_2) | \psi_0(r_2) \rangle \right] \end{aligned} \quad (2.4.8)$$

These inner products were calculated in Section 8.3 and the kinetic energy of particle 1 is:

$$\left\langle -\frac{\hbar^2}{2m} \nabla_1^2 \right\rangle = E_1 + \left( \frac{e^2}{4\pi\epsilon_0 a} \right) \frac{1 \pm IX}{1 \pm I^2} \quad (2.4.9)$$

The kinetic energy of particle 2 is the same, so the total kinetic energy is simply twice Equation(2.4.9).

The calculation of the electron-proton potential energy is similar:

$$\left\langle -\frac{e^2}{4\pi\epsilon_0 r_1} \right\rangle = -\frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0 a} \right) \frac{1 + D \pm 2IX}{1 \pm I^2} \quad (2.4.10)$$

and the total electron-proton potential energy is four times this amount.

The electron-electron potential energy is given by

$$\begin{aligned} \langle V_{ee} \rangle &= \left( \frac{e^2}{4\pi\epsilon_0 a} \right) \iint |\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2)|^2 \frac{a}{r_{12}} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\ &= \left( \frac{e^2}{4\pi\epsilon_0 a} \right) A_{\pm}^2 \left[ \iint \psi_0(r_1)^2 \frac{a}{r_{12}} \psi_0(r'_2)^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 + \iint \psi_0(r'_1)^2 \frac{a}{r_{12}} \psi_0(r_2)^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \right. \\ &\quad \left. \pm 2 \iint \psi_0(r_1) \psi_0(r'_1) \frac{a}{r_{12}} \psi_0(r_2) \psi_0(r'_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \right] \end{aligned} \quad (2.4.11)$$

The first two integrals are equal, as you can see by interchanging the labels 1 and 2.

We will name the two remaining integrals:

$$D_2 = \iint |\psi_0(r_1)|^2 \frac{a}{r_{12}} |\psi_0(r'_2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (2.4.12)$$

$$X_2 = \iint \psi_0(r_1) \psi_0(r'_1) \frac{a}{r_{12}} \psi_0(r_2) \psi_0(r'_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (2.4.13)$$

so that

$$\langle V_{ee} \rangle = \left( \frac{e^2}{4\pi\epsilon_0 a} \right) \frac{D_2 \pm X_2}{1 \pm I^2} \quad (2.4.14)$$

Note that the integral  $D_2$  is just the electrostatic potential energy of two charge distributions

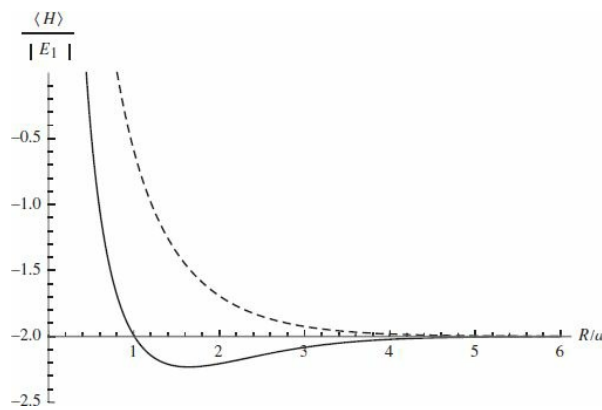
$$\rho_1 = |\psi_0(r_1)|^2, \quad \rho_2 = |\psi_0(r_2)|^2 \quad (2.4.15)$$

The exchange term  $X_2$  has no such classical counterpart.

When we add all of the contributions to the energy:

$$\langle H \rangle_{\pm} = 2E_1 \left[ 1 - \frac{a}{R} + \frac{2D - D_2 \pm (2IX - X_2)}{1 \pm I^2} \right] \quad (2.4.16)$$

A plot of  $\langle H \rangle_+$  and  $\langle H \rangle_-$  is shown in the following picture.



According to the figure, bonding only occurs if the two electrons are in a singlet configuration. Again, it's a covalent bond.

Locating the minimum on the plot, our calculation predicts a bond length of 1.64 Bohr radii (1.40 Bohr radii for experimental value), and suggests a binding energy of 3.15eV (4.75eV for experimental value).

The difference between the singlet and triplet energies is called the exchange splitting  $J$ .

In the Heitler-London approximation:

$$J = \langle H \rangle_+ - \langle H \rangle_- = 4E_1 \frac{(D_2 - 2D)I^2 - (X_2 - 2IX)}{1 - I^4} \quad (2.4.17)$$

which is roughly  $-10\text{eV}$  at the equilibrium separation. This means a strong preference for having the electron spins anti-aligned.

In this treatment of  $H_2$  we've left out completely the (magnetic) spin-spin interaction between the electrons.

Applying Equation(1.5.4) to two electrons a distance  $R$  apart, the energy of the spin-spin interaction is something like  $10^{-4}\text{eV}$  in this system, five orders of magnitude smaller than the exchange splitting.

This calculation shows us that different spin configurations can have very different energies, even when the interaction between the spins is negligible.

## 3 Chapter 11 Quantum Dynamics

### 3.1 Two-Level Systems

Suppose that there are just two states of the (unperturbed) system  $\psi_a$  and  $\psi_b$ .

They are eigenstates of the unperturbed Hamiltonian  $\hat{H}^0$ :

$$\hat{H}^0\psi_a = E_a\psi_a, \quad \text{and} \quad \hat{H}^0\psi_b = E_b\psi_b \quad (3.1.1)$$

and they are orthonormal:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}, \quad (i, j = a, b) \quad (3.1.2)$$

Any state can be expressed as a linear combination of them; in particular,

$$\Psi(0) = c_a \psi_a + c_b \psi_b \quad (3.1.3)$$

In the absence of any perturbation, each component evolves with its characteristic wiggly factor:

$$\Psi(t) = c_a \psi_a e^{-iE_a t/\hbar} + c_b \psi_b e^{-iE_b t/\hbar} \quad (3.1.4)$$

Normalization of  $\Psi$  requires that

$$|c_a|^2 + |c_b|^2 = 1 \quad (3.1.5)$$

### 3.1.1 The Perturbed System

Now we turn on a time-dependent perturbation  $\hat{H}'(t)$ .

Since  $\psi_a$  and  $\psi_b$  constitute a complete set,  $\Psi(t)$  can still be expressed as a linear combination of them:

$$\Psi(t) = c_a(t) \psi_a e^{-\frac{iE_a t}{\hbar}} + c_b(t) \psi_b e^{-\frac{iE_b t}{\hbar}} \quad (3.1.6)$$

We solve for  $c_a(t)$  and  $c_b(t)$  by demanding that  $\Psi(t)$  satisfy the time-dependent Schrodinger equation:

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad \text{where } \hat{H} = \hat{H}^0 + \hat{H}'(t) \quad (3.1.7)$$

From Equations(3.1.6) and (3.1.7), we find:

$$\begin{aligned} LHS &= RHS \\ LHS &= c_a \left( \hat{H}^0 \psi_a \right) e^{-\frac{iE_a t}{\hbar}} + c_b \left( \hat{H}^0 \psi_b \right) e^{-\frac{iE_b t}{\hbar}} + c_a \left( \hat{H}' \psi_a \right) e^{-\frac{iE_a t}{\hbar}} + c_b \left( \hat{H}' \psi_b \right) e^{-\frac{iE_b t}{\hbar}} \\ RHS &= i\hbar \left[ \dot{c}_a \psi_a e^{-\frac{iE_a t}{\hbar}} + \dot{c}_b \psi_b e^{-\frac{iE_b t}{\hbar}} + c_a \psi_a \left( -\frac{iE_a}{\hbar} \right) e^{-\frac{iE_a t}{\hbar}} + c_b \psi_b \left( -\frac{iE_b}{\hbar} \right) e^{-\frac{iE_b t}{\hbar}} \right] \end{aligned} \quad (3.1.8)$$

The first two terms on the left cancel the last two terms on the right, and hence:

$$c_a \left( \hat{H}' \psi_a \right) e^{-\frac{iE_a t}{\hbar}} + c_b \left( \hat{H}' \psi_b \right) e^{-\frac{iE_b t}{\hbar}} = i\hbar \left( \dot{c}_a \psi_a e^{-\frac{iE_a t}{\hbar}} + \dot{c}_b \psi_b e^{-\frac{iE_b t}{\hbar}} \right) \quad (3.1.9)$$

To isolate  $\dot{c}_a$ : Take the inner product with  $\psi_a$  (exploit the orthogonality):

$$c_a \left\langle \psi_a | \hat{H}' | \psi_a \right\rangle e^{-\frac{iE_a t}{\hbar}} + c_b \left\langle \psi_a | \hat{H}' | \psi_b \right\rangle e^{-\frac{iE_b t}{\hbar}} = i\hbar \dot{c}_a e^{-\frac{iE_a t}{\hbar}} \quad (3.1.10)$$

For short, we define:

$$H'_{ij} \equiv \left\langle \psi_i | \hat{H}' | \psi_j \right\rangle \quad (3.1.11)$$

Note the hermiticity of  $\hat{H}'$  entails  $H'_{ji} = (H'_{ij})^*$ .

Multiplying through by  $-\frac{i}{\hbar} e^{\frac{iE_a t}{\hbar}}$ , we conclude that:

$$\dot{c}_a = -\frac{i}{\hbar} \left[ c_a H'_{aa} + c_b H'_{ab} e^{-\frac{i(E_b - E_a)t}{\hbar}} \right] \quad (3.1.12)$$

Similarly, the inner product with  $\psi_b$  picks out  $\dot{c}_b$ :

$$c_a \left\langle \psi_b | \hat{H}' | \psi_a \right\rangle e^{-\frac{iE_a t}{\hbar}} + c_b \left\langle \psi_b | \hat{H}' | \psi_b \right\rangle e^{-\frac{iE_b t}{\hbar}} = i\hbar \dot{c}_b e^{-\frac{iE_b t}{\hbar}} \quad (3.1.13)$$

$$\dot{c}_b = -\frac{i}{\hbar} \left[ c_b H'_{bb} + c_a H'_{ba} e^{\frac{i(E_b - E_a)t}{\hbar}} \right] \quad (3.1.14)$$

Equations(3.1.12) and (3.1.14) determine  $c_a(t)$  and  $c_b(t)$ ; taken together, they are completely equivalent to the (time-dependent) Schroedinger equation for a two-level system.

Typically, the diagonal matrix elements of  $\hat{H}'$  vanish.

$$H'_{aa} = H'_{bb} = 0 \quad (3.1.15)$$

If so, the equations simplify:

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b, \quad \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{-i\omega_0 t} c_a \quad (3.1.16)$$

where

$$\omega_0 \equiv \frac{E_b - E_a}{\hbar} \quad (3.1.17)$$

(Assuming that  $E_b \geq E_a$ , so  $\omega_0 \geq 0$ .)

### 3.1.2 Time-Dependent Perturbation Theory

If  $\hat{H}'$  is small, we can solve Equation(3.1.16) by a process of successive approximations.

Suppose the particle starts out in the lower state:

$$c_a(0) = 1, \quad c_b(0) = 0 \quad (3.1.18)$$

If there were no perturbation at all, they would stay this way forever (Zeroth Order):

$$c_a^{(0)}(t) = 1, \quad c_b^{(0)}(t) = 0 \quad (3.1.19)$$

To calculate the first-order approximation, we insert the zeroth-order values on the right side of Equation(3.1.16):

First Order:

$$\frac{dc_a^{(1)}}{dt} = 0 \implies c_a^{(1)}(t) = 1 \quad (3.1.20)$$

$$\frac{dc_b^{(1)}}{dt} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \implies c_b^{(1)} = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \quad (3.1.21)$$

Now insert these expressions on the right side of Equation(3.1.16) to obtain the second-order approximation:

Second Order:

$$\begin{aligned} \frac{dc_a^{(2)}}{dt} &= -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left(-\frac{i}{\hbar}\right) \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \Rightarrow \\ c_a^{(2)}(t) &= 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[ \int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' \right] dt' \end{aligned} \quad (3.1.22)$$

while  $c_b$  is unchanged ( $c_b^{(2)}(t) = c_b^{(1)}(t)$ ).

In principle, we could continue this ritual indefinitely.

The zeroth order contains no factors of  $\hat{H}'$ , the first-order correction contains one factor of  $\hat{H}'$  and so on.

The error in the first-order approximation is evident in the fact that:

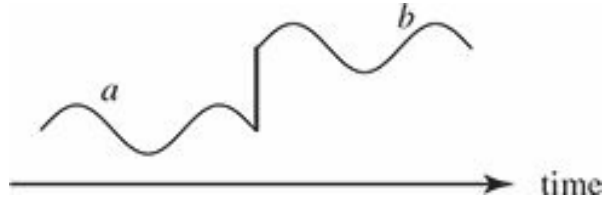
$$|c_a^{(1)}(t)|^2 + |c_b^{(1)}(t)|^2 \neq 1 \quad (3.1.23)$$

However,  $|c_a^{(1)}(t)|^2 + |c_b^{(1)}(t)|^2$  is equal to 1 to first order in  $\hat{H}'$ . And the same goes for the higher orders. Equation(3.1.21) can be written in the form:

$$c_b^{(1)}(t) e^{-\frac{iE_b t}{\hbar}} = -\frac{i}{\hbar} \int_0^t e^{-\frac{iE_b(t-t')}{\hbar}} H'_{ba}(t') e^{-\frac{iE_a t'}{\hbar}} dt' \quad (3.1.24)$$

This suggests: reading from right to left, the system remains in state  $a$  from time 0 to time  $t'$  (picking up the “wobble factor”  $e^{-\frac{iE_a t'}{\hbar}}$ ), makes a transition from state  $a$  to state  $b$  at time  $t'$ , and then remains in state  $b$  until time  $t$ .

This process is represented in the following Figure.



Consider Equation(3.1.22), which can be written:

$$c_a^{(2)}(t) e^{-\frac{iE_a t}{\hbar}} = e^{-\frac{iE_a t}{\hbar}} + \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t'} e^{-\frac{iE_a(t-t')}{\hbar}} \times H'_{ab}(t') e^{-\frac{iE_b(t'-t'')}{\hbar}} H'_{ba}(t'') e^{-\frac{iE_a t''}{\hbar}} dt'' dt' \quad (3.1.25)$$

The two terms here describe a process where the system remains in state  $a$  for the entire time, and a second process where the system transitions from  $a$  to  $b$  at time  $t''$  and then back to  $a$  at time  $t'$ .

This is shown in the following figure.



With the insight provided by these pictures, the general result for a multilevel system:

$$c_n^{(2)}(t)e^{-\frac{iE_n t}{\hbar}} = \delta_{ni}e^{-\frac{iE_i t}{\hbar}} + \left(-\frac{i}{\hbar}\right) \int_0^t e^{-\frac{iE_n(t-t')}{\hbar}} H_{ni}(t')e^{-\frac{iE_i t'}{\hbar}} dt' \\ + \sum_m \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t'} e^{-\frac{iE_n(t-t')}{\hbar}} H_{nm}(t')e^{-\frac{iE_m(t'-t'')}{\hbar}} \times H_{mi}(t'')e^{-\frac{iE_i t''}{\hbar}} dt'' dt' \quad (3.1.26)$$

For  $n \neq i$ , this is represented by the diagram in the following figure.

The first-order term describes a direct transition from  $i$  to  $n$ , and the second-order term describes a process where the transition occurs via an intermediate (or "virtual") state  $m$ .



### 3.1.3 Sinusoidal Perturbations

Suppose the perturbation has sinusoidal time dependence:

$$\hat{H}'(\mathbf{r}, t) = V(\mathbf{r})\cos(\omega t) \quad (3.1.27)$$

so that

$$H'_{ab} = V_{ab}\cos(\omega t) \quad (3.1.28)$$

where

$$V_{ab} \equiv \langle \psi_a | V | \psi_b \rangle \quad (3.1.29)$$

(As before, we assume the diagonal matrix elements vanish.)

To first order we have:

$$c_b(t) \approx -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{iV_{ba}}{2\hbar} \int_0^t \left[ e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt' \\ = -\frac{V_{ba}}{2\hbar} \left[ \frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \right] \quad (3.1.30)$$

Things simplify substantially if we restrict our attention to driving frequencies ( $\omega$ ) that are very close to the transition frequency ( $\omega_0$ ), so that the second term in the square brackets dominates.

Specifically, we assume:

$$\omega_0 + \omega \gg |\omega_0 - \omega| \quad (3.1.31)$$

This is not much of a limitation, since perturbations at other frequencies have a negligible probability of causing a transition anyway.



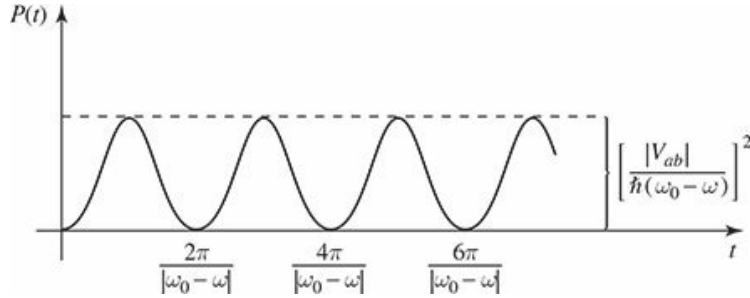
Dropping the first term, we have

$$\begin{aligned}
 c_b(t) &\approx -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0-\omega)t/2}}{\omega_0 - \omega} [e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2}] \\
 &= -i \frac{V_{ba}}{\hbar} \frac{\sin \left[ \frac{(\omega_0-\omega)t}{2} \right]}{\omega_0 - \omega} e^{i(\omega_0-\omega)t/2}
 \end{aligned} \tag{3.1.32}$$

The transition probability—the probability that a particle which started out in the state  $\psi_a$  will be found, at time  $t$ , in the state  $\psi_b$  is:

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \approx \frac{|V_{ab}|^2}{\hbar^2} \frac{\sin^2 \left[ \frac{(\omega_0-\omega)t}{2} \right]}{(\omega_0 - \omega)^2} \tag{3.1.33}$$

As a function of time, the transition probability oscillates sinusoidally.



After rising to a maximum of  $\frac{|V_{ab}|^2}{\hbar^2(\omega_0 - \omega)^2}$  (necessarily much less than 1, else the assumption that the perturbation is “small” would be invalid)—it drops back down to zero!

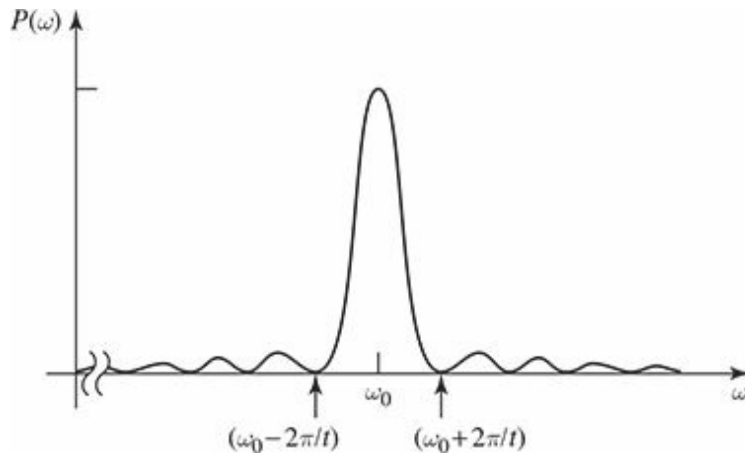
At times  $t_n = \frac{2n\pi}{|\omega_0 - \omega|}$ , where  $n = 1, 2, 3, \dots$ , the particle is certain to be back in the lower state.

The probability of a transition is greatest when the  $\omega$  is close to the natural frequency  $\omega_0$ .

The peak has a height of  $(\frac{|V_{ab}|t}{2\hbar})^2$  and a width  $\frac{4\pi}{t}$ .

Evidently it gets higher and narrower as time goes on.

(The perturbation assumption breaks down before it gets close to 1.)

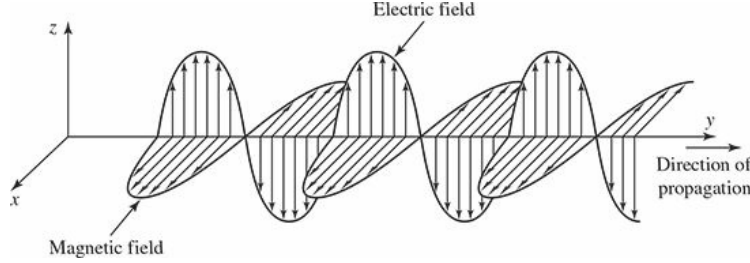


## 3.2 Emission and Absorption of Radiation

### 3.2.1 Electromagnetic Waves

An electromagnetic wave consists of transverse oscillating electric and magnetic fields.

An atom, in the presence of a passing light wave, responds primarily to the electric component.



If the wavelength is long (compared to the size of the atom), we can ignore the spatial variation in the field; the atom then, is exposed to a sinusoidally oscillating electric field:

$$\mathbf{E} = E_0 \cos(\omega t) \hat{k} \quad (3.2.1)$$

The perturbing Hamiltonian is

$$H' = -qE_0 z \cos(\omega t) \quad (3.2.2)$$

where  $q$  is the charge of the electron. Evidently

$$H'_{ba} = -\wp E_0 \cos(\omega t), \quad \text{where } \wp \equiv q \langle \psi_b | z | \psi_a \rangle \quad (3.2.3)$$

Typically,  $\psi$  is an even or odd function of  $z$ ; in either case  $z|\psi|^2$  is odd, and integrates to zero.

This licenses our usual assumption that the diagonal matrix elements of  $\hat{H}'$  vanish.

Thus the interaction of light with matter is governed by the kind of oscillatory perturbation we studied in Section 11.1.3, with

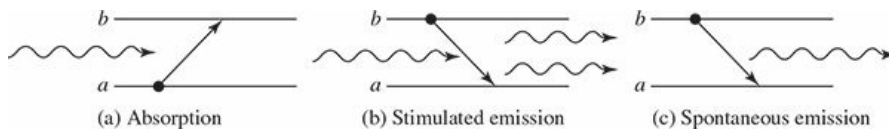
$$V_{ba} = -\wp E_0 \quad (3.2.4)$$

### 3.2.2 Absorption, Stimulated Emission, and Spontaneous Emission

If an atom starts out in the lower state  $\psi_a$ , and we shine a polarized monochromatic beam of light on it, the probability of a transition to the upper state  $\psi_b$  is given by Equation(3.1.33), which takes the form:

$$P_{a \rightarrow b}(t) = \left( \frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2 \left[ \frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} \quad (3.2.5)$$

In this process, the atom absorbs energy  $E_b - E_a = \hbar\omega_0$ , so it's called absorption.



For a system that starts off in the upper state, it comes out exactly the same:

$$P_{b \rightarrow a}(t) = \left( \frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2 \left[ \frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} \quad (3.2.6)$$

(We are switching  $a \leftrightarrow b$ , which substitutes  $-\omega_0$  for  $\omega_0$ .)

The probability is exactly the same as for a transition upward from the lower state.

This process, which was first predicted by Einstein, is called stimulated emission.

There is a third mechanism by which radiation interacts with matter— “spontaneous emission” .

An atom in the excited state makes a transition downward, with the release of a photon, but without any applied electromagnetic field to initiate the process.

This is the mechanism that accounts for the normal decay of an atomic excited state.

In quantum electrodynamics the fields are nonzero even in the ground state.

It is the “zero point” radiation that serves to catalyze spontaneous emission. When you come right down to it, there is really no such thing as truly spontaneous emission. it’ s all stimulated emission.

### 3.2.3 Incoherent Perturbations

The energy density in an electromagnetic wave is:

$$u = \frac{\epsilon_0}{2} E_0^2 \quad (3.2.7)$$

where  $E_0$  is the amplitude of the electric field.

So the transition probability is proportional to the energy density of the fields:

$$P_{b \rightarrow a}(t) = \frac{2u}{\epsilon_0 \hbar^2} |\wp|^2 \frac{\sin^2 \left[ \frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} \quad (3.2.8)$$

But this is for a monochromatic wave, at a single frequency  $\omega$ .

If the system is exposed to electromagnetic waves at a whole range of frequencies,  $u \rightarrow \rho(\omega)d\omega$ , where  $\rho(\omega)d\omega$  is the energy density in the frequency range  $d\omega$ , and the net transition probability takes the form of an integral:

$$P_{b \rightarrow a}(t) = \frac{2}{\epsilon_0 \hbar^2} |\wp|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2 \left[ \frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} \right\} d\omega \quad (3.2.9)$$

The term in curly brackets is sharply peaked about  $\omega_0$ , whereas  $\rho(\omega)$  is ordinarily quite broad.

So we may as well replace  $\rho(\omega)$  by  $\rho(\omega_0)$ , and take it outside the integral:

$$P_{b \rightarrow a}(t) \approx \frac{2|\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \int_0^\infty \frac{\sin^2 \left[ \frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} d\omega \quad (3.2.10)$$

Changing variables to  $x \equiv \frac{(\omega_0 - \omega)t}{2}$ , extending the limits of integration to  $x = \pm\infty$  (since the integrand is essentially zero out there anyway), and looking up the definite integral

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi \quad (3.2.11)$$

we find

$$P_{b \rightarrow a}(t) \approx \frac{\pi |\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t \quad (3.2.12)$$

This time the transition probability is proportional to  $t$ .

In particular, the transition rate ( $R \equiv \frac{dP}{dt}$ ) is now a constant:

$$P_{b \rightarrow a} = \frac{\pi}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0) \quad (3.2.13)$$

We've assumed that the perturbing wave is coming in along the  $y$  direction, and polarized in the  $z$  direction.

But we are interested in the case of an atom bathed in radiation coming from all directions, and with all possible polarizations; the energy in the fields ( $\rho(\omega)$ ) is shared equally among these different modes. What we need, in place of  $|\wp|^2$ , is the average of  $|\wp \cdot \hat{n}|^2$ , where

$$\wp \equiv q \langle \psi_b | \mathbf{r} | \psi_a \rangle \quad (3.2.14)$$

and the average is over all polarizations and all incident directions.

The averaging can be carried out as follows:

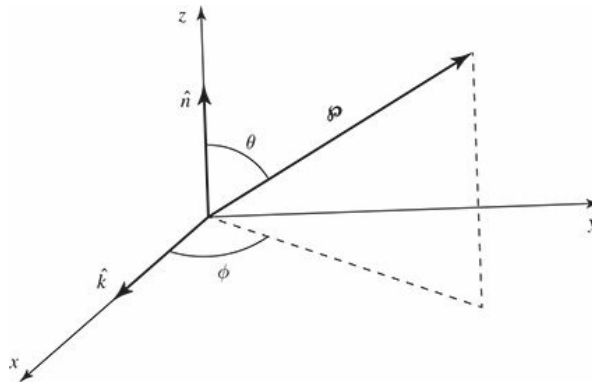
Choose spherical coordinates such that the direction of propagation ( $\hat{k}$ ) is along  $x$ , the polarization ( $\hat{n}$ ) is along  $z$ , and the vector  $\wp$  defines the spherical angles  $\theta$  and  $\phi$ .

Then

$$\wp \cdot \hat{n} = \wp \cos \theta \quad (3.2.15)$$

and

$$\begin{aligned} |\wp \cdot \hat{n}|_{ave}^2 &= \frac{1}{4\pi} \int |\wp|^2 \cos^2 \theta \sin \theta d\theta d\phi \\ &= \frac{|\wp|^2}{4\pi} \left( -\frac{\cos^3 \theta}{3} \right) \Big|_0^\pi (2\pi) = \frac{1}{3} |\wp|^2 \end{aligned} \quad (3.2.16)$$



Conclusion: The transition rate for stimulated emission from state  $b$  to state  $a$ , under the influence of incoherent, unpolarized light incident from all directions is

$$R_{b \rightarrow a} = \frac{\pi}{3\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0) \quad (3.2.17)$$

where  $\wp$  is the matrix element of the electric dipole moment between the two states, and  $\rho(\omega_0)$  is the energy density in the fields, per unit frequency, evaluated at  $\omega_0 = \frac{E_b - E_a}{\hbar}$ .

### 3.3 Spontaneous Emission

#### 3.3.1 Einstein's A and B Coefficients

Picture a container of atoms:  $N_a$  of them in the lower state ( $\psi_a$ ), and  $N_b$  of them in the upper state ( $\psi_b$ ).

Let  $A$  be the spontaneous emission rate, so that the number of particles leaving the upper state by this process, per unit time, is  $N_b A$ .

The transition rate for stimulated emission is proportional to the energy density of the electromagnetic field:  $B_{ba} \rho(\omega_0)$ , where  $B_{ba} = \frac{\pi |\wp|^2}{3\epsilon_0 \hbar^2}$ .

The number of particles leaving the upper state by this mechanism, per unit time, is  $N_b B_{ba} \rho(\omega_0)$ .

The absorption rate is likewise proportional to  $\rho(\omega_0)$ - call it  $B_{ab} \rho(\omega_0)$ .

The number of particles per unit time joining the upper level is therefore  $N_a B_{ab} \rho(\omega_0)$ .

All told, then,

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba} \rho(\omega_0) + N_a B_{ab} \rho(\omega_0) \quad (3.3.1)$$

Suppose these atoms are in thermal equilibrium with the ambient field, so that the number of particles in each level is constant.

In that case  $\frac{dN_b}{dt} = 0$ , and it follows that

$$\rho(\omega_0) = \frac{A}{\left(\frac{N_a}{N_b}\right) B_{ab} - B_{ba}} \quad (3.3.2)$$

On the other hand, we know from statistical mechanics that the number of particles with energy  $E$ , in thermal equilibrium at temperature  $T$ , is proportional to the Boltzmann factor,  $\exp(-E/k_B T)$ , so

$$\frac{N_a}{N_b} = \frac{e^{-E_a/k_B T}}{e^{-E_b/k_B T}} = e^{\frac{\hbar \omega_0}{k_B T}} \quad (3.3.3)$$

and hence

$$\rho(\omega_0) = \frac{A}{e^{\frac{\hbar \omega_0}{k_B T}} B_{ab} - B_{ba}} \quad (3.3.4)$$

But Planck's blackbody formula tells us the energy density of thermal radiation:

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar \omega}{k_B T}} - 1} \quad (3.3.5)$$

comparing the two expressions, we conclude that

$$B_{ab} = B_{ba} \quad (3.3.6)$$

and

$$A = \frac{\omega_0^3 \hbar}{\pi^2 c^3} B_{ba} \quad (3.3.7)$$

Equation(3.3.6) confirms: the transition rate for stimulated emission is the same as for absorption.

From Equation(3.2.17) we read off:

$$B_{ba} = \frac{\pi}{3\epsilon_0 \hbar^2} |\wp|^2 \quad (3.3.8)$$

and it follows that the spontaneous emission rate is:

$$A = \frac{\omega_0^3 |\wp|^2}{3\pi \epsilon_0 \hbar c^3} \quad (3.3.9)$$

### 3.3.2 The Lifetime of an Excited State

Suppose now we have somehow pumped a large number of atoms into the excited state. As a result of spontaneous emission, this number will decrease as time goes on.

Specifically, in a time interval  $dt$  we will lose a fraction  $A dt$  of them:

$$dN_b = -AN_b dt \quad (3.3.10)$$

(assuming there is no mechanism to replenish the supply.)

Solving for  $N_b(t)$ , we find:

$$N_b(t) = N_b(0)e^{-At} \quad (3.3.11)$$

The number remaining in the excited state decreases exponentially with a time constant:

$$\tau = \frac{1}{A} \quad (3.3.12)$$

We call this the lifetime of the state.

Equation(3.3.9) gives the transition rate for  $\psi_b \rightarrow \psi_a$  regardless of what other states may be accessible.

Typically, an excited atom has many different decay modes ( $\psi_b \rightarrow \psi_{a_1}, \psi_{a_2}, \dots$ )

In that case the transition rates add, and the net lifetime is

$$\tau = \frac{1}{A_1 + A_2 + A_3 + \dots} \quad (3.3.13)$$

#### Example

Suppose a charge  $q$  is attached to a spring and constrained to oscillate along the  $x$  axis.

Say it starts out in the state  $|n\rangle$ , and decays by spontaneous emission to state  $|n'\rangle$ .

From Equation(3.2.14) we have:

$$\wp = q \langle n|x|n'\rangle \hat{i} \quad (3.3.14)$$

We calculated the matrix elements of  $x$ :

$$\langle n|x|n'\rangle = \sqrt{\frac{\hbar}{2m\omega}} \left( \sqrt{n'}\delta_{n,n'-1} + \sqrt{n}\delta_{n',n-1} \right) \quad (3.3.15)$$

where  $\omega$  is the natural frequency of the oscillator.

But we're talking about emission, so  $n'$  must be lower than  $n$ ; then,

$$\wp = q\sqrt{\frac{n\hbar}{2m\omega}}\delta_{n',n-1}\hat{i} \quad (3.3.16)$$

Evidently transitions occur only to states one step lower on the “ladder” , and the frequency of the photon emitted is:

$$\omega_0 = \frac{E_n - E_{n'}}{\hbar} = \frac{(n + \frac{1}{2})\hbar\omega - (n' + \frac{1}{2})\hbar\omega}{\hbar} = (n - n')\omega = \omega \quad (3.3.17)$$

The system radiates at the classical oscillator frequency.

The transition rate (Equation(3.3.9)) is:

$$A = \frac{nq^2\omega^2}{6\pi\epsilon_0 mc^3} \quad (3.3.18)$$

and the lifetime of the  $n$ th stationary state is

$$\tau_n = \frac{6\pi\epsilon_0 mc^3}{nq^2\omega^2} \quad (3.3.19)$$

Meanwhile, each radiated photon carries an energy  $\hbar\omega$ , so the power radiated is  $A\hbar\omega$ :

$$P = \frac{q^2\omega^2}{6\pi\epsilon_0 mc^3}(n\hbar\omega) \quad (3.3.20)$$

or, since the energy of an oscillator in the  $n$ th state is  $E = (n + \frac{1}{2})\hbar\omega$ :

$$P = \frac{q^2\omega^2}{6\pi\epsilon_0 mc^3} \left( E - \frac{1}{2}\hbar\omega \right) \quad (3.3.21)$$

This is the average power radiated by a quantum oscillator with (initial) energy  $E$ .

For comparison, let's determine the average power radiated by a classical oscillator with the same energy.

According to classical electrodynamics, the power radiated by an accelerating charge  $q$  is given by the Larmor formula:

$$P = \frac{q^2 a^2}{6\pi\epsilon_0 c^3} \quad (3.3.22)$$

For a harmonic oscillator with amplitude  $x_0$ ,  $x(t) = x_0 \cos(\omega t)$ , and the acceleration is  $a = -x_0 \omega^2 \cos(\omega t)$ .

Averaging over a full cycle, then,

$$P = \frac{q^2 x_0^2 \omega^4}{12\pi\epsilon_0 c^3} \quad (3.3.23)$$

But the energy of the oscillator is  $E = \frac{1}{2}m\omega^2 x_0^2$ , so  $x_0^2 = \frac{2E}{m\omega^2}$ , and hence

$$P = \frac{q^2 \omega^2}{6\pi\epsilon_0 m c^3} E \quad (3.3.24)$$

In the classical limit ( $\hbar \rightarrow 0$ ) the classical and quantum formulas agree.

However, the quantum formula (Equation(3.3.21)) protects the ground state: If  $E = \frac{\hbar\omega}{2}$  the oscillator does not radiate.

### 3.3.3 Selection Rules

The calculation of spontaneous emission rates has been reduced to evaluate matrix elements of the form

$$\langle \psi_b | \mathbf{r} | \psi_a \rangle \quad (3.3.25)$$

These quantities are very often zero, and it would be helpful to know in advance.

Suppose we are interested in systems like hydrogen, for which the Hamiltonian is spherically symmetrical. In that case we can specify the states with the usual quantum numbers  $n, l, m$ , and the matrix elements are

$$\langle n'l'm' | \mathbf{r} | nlm \rangle \quad (3.3.26)$$

$\mathbf{r}$  is a vector operator, and we can invoke the results of Chapter 6 to obtain the selection rules:

$$\Delta l \equiv l' - l = \pm 1, \quad \Delta m \equiv m' - m = 0 \text{ or } \pm 1 \quad (3.3.27)$$

These conditions follow from symmetry alone. If they are not met, then the matrix element is zero, and the transition is said to be forbidden.

Moreover, it follows:

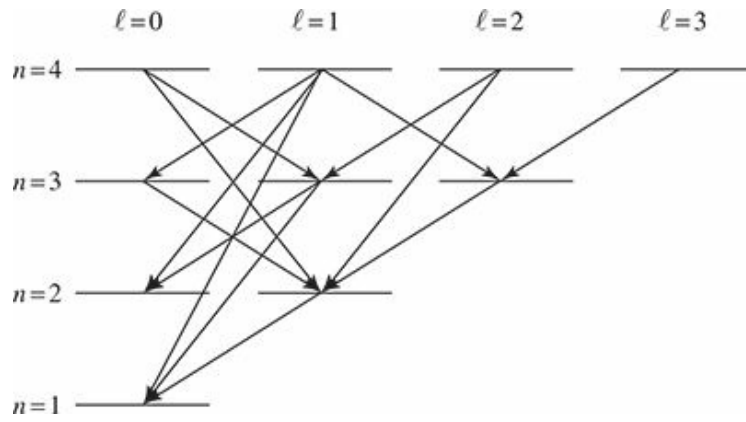
$$\begin{cases} \text{if } m' = m, & \text{then } \langle n'l'm' | x | nlm \rangle = \langle n'l'm' | y | nlm \rangle = 0, \\ \text{if } m' = m \pm 1, & \text{then } \langle n'l'm' | x | nlm \rangle = \pm i \langle n'l'm' | y | nlm \rangle \text{ and } \langle n'l'm' | z | nlm \rangle = 0. \end{cases} \quad (3.3.28)$$

So it is never necessary to compute the matrix elements of both  $x$  and  $y$ ; we can always get one from the other.

Evidently not all transitions to lower-energy states can proceed by electric dipole radiation.

The scheme of allowed transitions for the first four Bohr levels in hydrogen is shown in the following figure.





Notice that the  $2S$  state ( $\psi_{200}$ ) is "stuck": it cannot decay, because there is no lower energy state with  $l = 1$ .

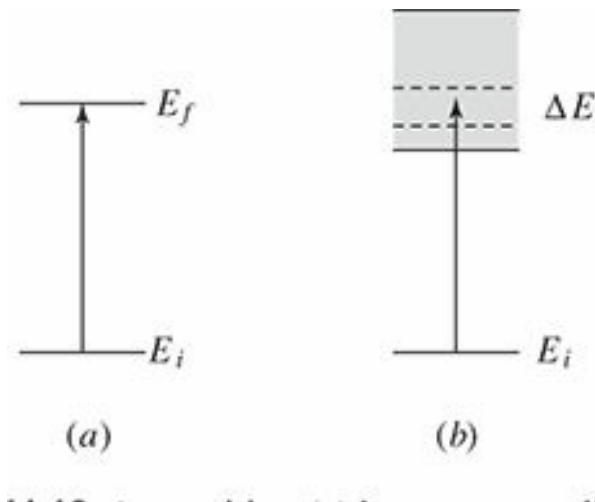
It is called a metastable state, and its lifetime is indeed much longer than that of, for example, the  $2P$  states ( $\psi_{211}, \psi_{210}$ , and  $\psi_{21-1}$ ).

Metastable states do eventually decay, by collisions, or by "forbidden" transitions, or by multiphoton emission.

### 3.4 Fermi's Golden Rule

In the previous sections, we saw that a transition between two discrete energy states was most likely when the final energy satisfied the resonance condition:  $E_f = E_i + \hbar\omega$ , where  $\omega$  is the frequency associated with the perturbation.

Now look at the case where  $E_f$  falls in a continuum of states.



We can't talk about a transition to a precise state in that continuum, but we can compute the probability that the system makes a transition to a state with an energy in some finite range  $\Delta E$  about  $E_f$ .

That is given by the integral of Equation(3.1.33) over all the final states:

$$P = \int_{E_f - \frac{\Delta E}{2}}^{E_f + \frac{\Delta E}{2}} \frac{|V_{in}|^2}{\hbar^2} \left\{ \frac{\sin^2 \left[ \frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} \right\} \rho(E_n) dE_n \quad (3.4.1)$$

where  $\omega_0 = \frac{(E_n - E_i)}{\hbar}$ , the quantity  $\rho(E)dE$  is the number of states with energy between  $E$  and  $E + dE$ ;  $\rho(E)$  is called the density of states.

At short times, Equation(3.4.1) leads to a transition probability proportional to  $t^2$ , just as for a transition between discrete states.

At long times the quantity in curly brackets in Equation(3.4.1) is sharply peaked: as a function of  $E_n$  its maximum occurs at  $E_f = E_i + \hbar\omega$  and the central peak has a width of  $\frac{4\pi\hbar}{t}$ .

For sufficiently large  $t$ , we can therefore approximate Equation(3.4.1) as

$$P = \frac{|V_{if}|^2}{\hbar^2} \rho(E_f) \int_{-\infty}^{\infty} \frac{\sin^2 \left[ \frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} dE_n \quad (3.4.2)$$

The remaining integral was already evaluated in Section 11.2.3:

$$P = \frac{2\pi}{\hbar} \left| \frac{V_{if}}{2} \right|^2 \rho(E_f) t \quad (3.4.3)$$

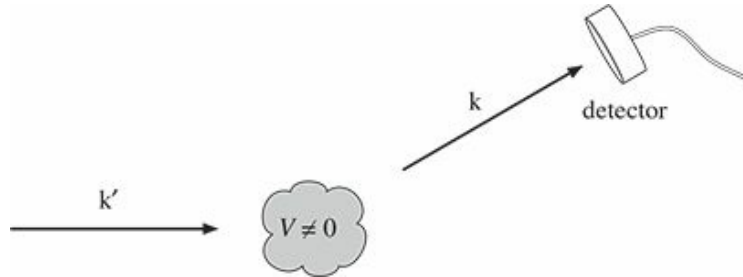
The oscillatory behavior of  $P$  has again been “washed out”, giving a constant transition rate:

$$R = \frac{2\pi}{\hbar} \left| \frac{V_{if}}{2} \right|^2 \rho(E_f) \quad (3.4.4)$$

Equation(3.4.4) is known as Fermi’s Golden Rule.

### Example:

Use Fermi’ s Golden Rule to obtain the differential scattering cross-section for a particle of mass  $m$  and incident wave vector  $\mathbf{k}'$  scattering from a potential  $V(\mathbf{r})$ .



### Solution:

Take our initial and final states to be plane waves:

$$\psi_i = \frac{1}{\sqrt{l^3}} e^{i\mathbf{k}' \cdot \mathbf{r}} \text{ and } \psi_f = \frac{1}{\sqrt{l^3}} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (3.4.5)$$

Here we've used box normalization.

We place the whole setup inside a box of length  $l$  on a side. This makes the free-particle states normalizable and countable. Formally, we want the limit  $l \rightarrow \infty$ ; in practice  $l$  will drop out of our final expression.

Using periodic boundary conditions, the allowed values of  $\mathbf{k}$  are

$$\mathbf{k} = \frac{2\pi}{l} (n_x \hat{i} + n_y \hat{j} + n_z \hat{k}) \quad (3.4.6)$$

for integers  $n_x, n_y$  and  $n_z$ .

The perturbation is the scattering potential,  $\hat{H}' = V(\mathbf{r})$ , and the relevant matrix element is

$$V_{fi} = \int \psi_f^*(\mathbf{r}) V(\mathbf{r}) \psi_i(\mathbf{r}) d^3\mathbf{r} = \frac{1}{l^3} \int e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} V(\mathbf{r}) d^3\mathbf{r} \quad (3.4.7)$$

We need to determine the density of states.

In a scattering experiment we measure the number of particles scattered into a solid angle  $d\Omega$ .

We want to count the number of states with energies between  $E$  and  $E + dE$ , with wave vectors  $\mathbf{k}$  lying inside  $d\Omega$ .

In  $k$  space these states occupy a section of a spherical shell of radius  $k$  and thickness  $dk$  that subtends a solid angle  $d\Omega$ ; it has a volume  $k^2 dk d\Omega$  and contains a number of states

$$\rho(E) dE = \frac{k^2 dk d\Omega}{(2\pi/l)^3} = \left(\frac{l}{2\pi}\right)^3 k^2 \frac{dk}{dE} dE d\Omega \quad (3.4.8)$$

Since  $E = \frac{\hbar^2 k^2}{2m}$  this gives

$$\rho(E) = \left(\frac{l}{2\pi}\right)^3 \frac{\sqrt{2m^3 E}}{\hbar^3} d\Omega \quad (3.4.9)$$

From Fermi's Golden Rule, the rate at which particles are scattered into the solid angle  $d\Omega$  is

$$R_{i \rightarrow d\Omega} = \frac{2\pi}{\hbar} \frac{1}{l^6} \left| \int e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} V(\mathbf{r}) d^3\mathbf{r} \right|^2 \left(\frac{l}{2\pi}\right)^3 \frac{\sqrt{2m^3 E_f}}{\hbar^3} d\Omega \quad (3.4.10)$$

This is closely related to the differential scattering cross section:

$$\frac{d\sigma}{d\Omega} = \frac{R_{i \rightarrow d\Omega}}{J_i d\Omega} \quad (3.4.11)$$

where  $J_i$  is the flux of incident particles. For an incident wave of the form  $\psi_i = A e^{i\mathbf{k}' \cdot \mathbf{r}'}$ , the probability current is

$$J_i = |A|^2 v = \frac{1}{l^3} \frac{\hbar k'}{m} \quad (3.4.12)$$

and

$$\frac{d\sigma}{d\Omega} = \left| -\frac{m}{2\pi\hbar^2} \int e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} V(\mathbf{r}) d^3\mathbf{r} \right|^2 \quad (3.4.13)$$

This is exactly what we got from the first Born approximation.

## 3.5 The Adiabatic Approximation

### 3.5.1 The Adiabatic Theorem

Suppose the Hamiltonian changes gradually from some initial form  $\hat{H}(0)$  to some final form  $\hat{H}(T)$ .

The adiabatic theorem:

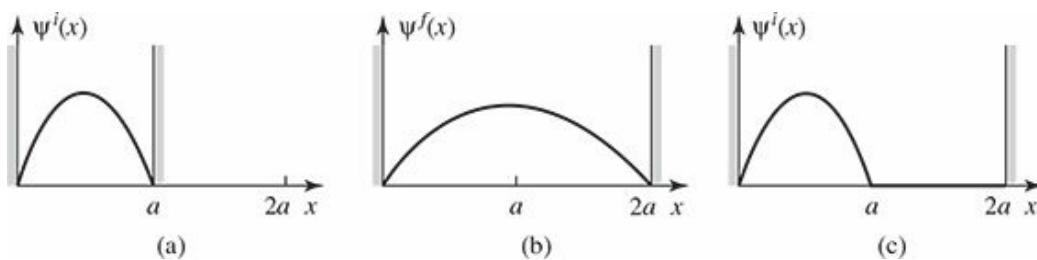
If the particle was initially in the  $n$ th eigenstate of  $\hat{H}(0)$ , it will be carried (under the Schroedinger equation) into the  $n$ th eigenstate of  $\hat{H}(T)$ .

(Assume that the spectrum is discrete and nondegenerate throughout the transition, so there is no ambiguity about the ordering of the states.)

#### Example

Suppose we prepare a particle in the ground state of the infinite square well:

$$\psi^i(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) \quad (3.5.1)$$



If we now gradually move the right wall out to  $2a$ , the adiabatic theorem says that the particle will end up in the ground state of the expanded well:

$$\psi^f(x) = \sqrt{\frac{1}{a}} \sin\left(\frac{\pi}{2a}x\right) \quad (3.5.2)$$

Notice that this is not a small change in the Hamiltonian but a huge one(happen slowly).

Energy is not conserved here:

Whoever is moving the wall is extracting energy from the system.

By contrast, if the well expands suddenly, the resulting state is still  $\psi^i(x)$ , which is a complicated linear combination of eigenstates of the new Hamiltonian. In this case energy is conserved; as in the free expansion of a gas (into a vacuum) when the barrier is suddenly removed; no work is done.

For a constant Hamiltonian it would pick up the standard “wobble factor”  $e^{-iE_n t/\hbar}$ , but the eigenvalue  $E_n$  may now itself be a function of time, so the wobble factor naturally generalizes to  $e^{i\theta_n(t)}$ , where

$$\theta_n(t) \equiv -\frac{1}{\hbar} \int_0^t E_n(t') dt' \quad (3.5.3)$$

This is called the dynamic phase.

There may be an additional phase factor  $\gamma_n(t)$ , the so-called geometric phase.

In the adiabatic limit, the wave function at time  $t$  takes the form

$$\Psi_n(t) = e^{i\theta_n(t)} e^{i\gamma_n(t)} \psi_n(t) \quad (3.5.4)$$

where  $\psi_n(t)$  is the  $n$ th eigenstate of the instantaneous Hamiltonian,

$$\hat{H}(t)\psi_n(t) = E_n(t)\psi_n(t) \quad (3.5.5)$$

Equation(3.5.4) is the formal statement of the adiabatic theorem.

The phase of  $\psi_n(t)$  is itself arbitrary, so the geometric phase itself carries no physical significance. But what if we carry the system around a closed cycle, so that the Hamiltonian at the end is identical to the Hamiltonian at the beginning?

Then the net phase change is a measurable quantity. The dynamic phase depends on the elapsed time, but the geometric phase, around an adiabatic closed cycle, depends only on the path taken. It is called Berry's phase:

$$\gamma_B \equiv \gamma(T) - \gamma(0) \quad (3.5.6)$$

### Example

Imagine an electron at rest at the origin, in the presence of a magnetic field whose magnitude ( $B_0$ ) is constant, but whose direction sweeps out a cone, of opening angle  $\alpha$ , at constant angular velocity  $\omega$ :

$$\mathbf{B}(t) = B_0 [\sin\alpha\cos(\omega t)\hat{i} + \sin\alpha\sin(\omega t)\hat{j} + \cos\alpha\hat{k}] \quad (3.5.7)$$

The Hamiltonian is:

$$\begin{aligned} \hat{H}(t) &= \frac{e}{m} \mathbf{B} \cdot \mathbf{S} = \frac{e\hbar B_0}{2m} [\sin\alpha\cos(\omega t)\sigma_x + \sin\alpha\sin(\omega t)\sigma_y + \cos\alpha\sigma_z] \\ &= \frac{\hbar\omega_1}{2} \begin{pmatrix} \cos\alpha & e^{-i\omega t}\sin\alpha \\ e^{i\omega t}\sin\alpha & -\cos\alpha \end{pmatrix} \end{aligned} \quad (3.5.8)$$

where

$$\omega_1 \equiv \frac{eB_0}{m} \quad (3.5.9)$$

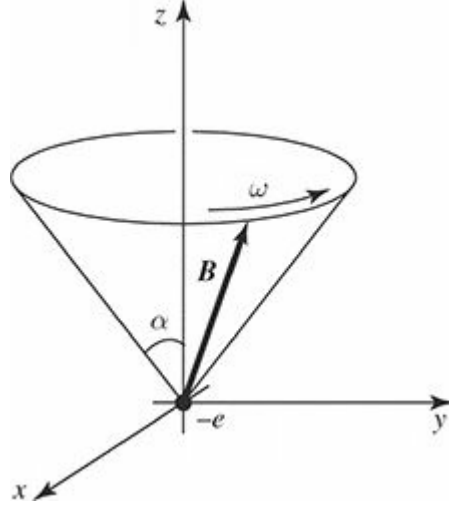
The normalized eigenspinors of  $\hat{H}(t)$  are

$$\chi_+(t) = \begin{pmatrix} \cos(\alpha/2) \\ e^{i\omega t}\sin(\alpha/2) \end{pmatrix} \text{ and } \chi_-(t) = \begin{pmatrix} e^{-i\omega t}\sin(\alpha/2) \\ -\cos(\alpha/2) \end{pmatrix} \quad (3.5.10)$$

They represent spin up and spin down, respectively, along the instantaneous direction of  $\mathbf{B}(t)$ .

The corresponding eigenvalues are

$$E_{\pm} = \pm \frac{\hbar\omega_1}{2} \quad (3.5.11)$$



Suppose the electron starts out with spin up, along  $\mathbf{B}(0)$ :

$$\chi(0) = \begin{pmatrix} \cos(\alpha/2) \\ \sin(\alpha/2) \end{pmatrix} \quad (3.5.12)$$

The exact solution to the time-dependent Schroedinger equation is:

$$\chi(t) = \begin{pmatrix} \left[ \cos\left(\frac{\lambda t}{2}\right) - i\frac{(\omega_1 - \omega)}{\lambda} \sin\left(\frac{\lambda t}{2}\right) \right] \cos(\alpha/2) e^{-i\omega t/2} \\ \left[ \cos\left(\frac{\lambda t}{2}\right) - i\frac{(\omega_1 + \omega)}{\lambda} \sin\left(\frac{\lambda t}{2}\right) \right] \sin(\alpha/2) e^{+i\omega t/2} \end{pmatrix} \quad (3.5.13)$$

where

$$\lambda \equiv \sqrt{\omega^2 + \omega_1^2 - 2\omega\omega_1 \cos\alpha} \quad (3.5.14)$$

or, expressing it as a linear combination of  $\chi_+$  and  $\chi_-$ :

$$\chi(t) = \left[ \cos\left(\frac{\lambda t}{2}\right) - i\frac{(\omega_1 - \omega \cos\alpha)}{\lambda} \sin\left(\frac{\lambda t}{2}\right) \right] e^{-i\omega t/2} \chi_+(t) + i \left[ \frac{\omega}{\lambda} \sin\alpha \sin\left(\frac{\lambda t}{2}\right) \right] e^{+i\omega t/2} \chi_-(t) \quad (3.5.15)$$

Evidently the (exact) probability of a transition to spin down (along the current direction of  $\mathbf{B}$ ) is

$$|\langle \chi(t) | \chi_-(t) \rangle|^2 = \left[ \frac{\omega}{\lambda} \sin\alpha \sin\left(\frac{\lambda t}{2}\right) \right]^2 \quad (3.5.16)$$

The adiabatic theorem says that this transition probability should vanish in the limit  $T_e \gg T_i$ , where  $T_e$  is the characteristic time for changes in the Hamiltonian and  $T_i$  is the characteristic time for changes in the wave function.

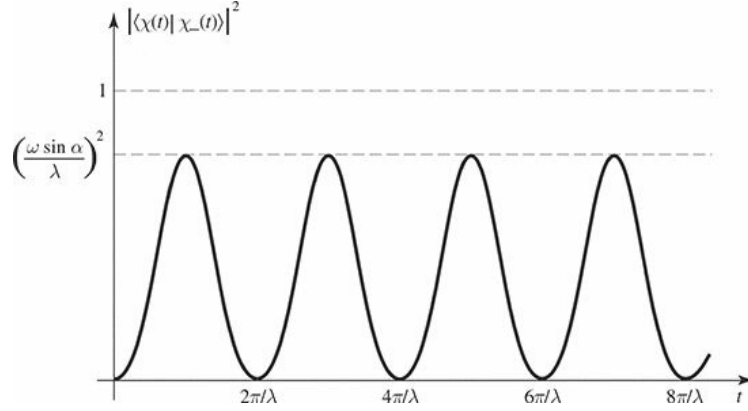
Thus the adiabatic approximation means  $\omega \ll \omega_1$ :

The field rotates slowly, in comparison with the phase of the (unperturbed) wave functions.

In the adiabatic regime  $\lambda \approx \omega_1$  (Equation(3.5.14)), and therefore

$$|\langle \chi(t) | \chi_-(t) \rangle|^2 \approx \left[ \frac{\omega}{\omega_1} \sin\alpha \sin\left(\frac{\lambda t}{2}\right) \right]^2 \rightarrow 0 \quad (3.5.17)$$

The magnetic field leads the electron around by its nose, with spin always pointing in the direction of  $\mathbf{B}$ . By contrast, if  $\omega \gg \omega_1$  then  $\lambda \approx \omega$ , and the system bounces back and forth between spin up and spin down.



## 4 Chapter 11B Quantum Dynamics

### 4.1 Dynamics of a perturbed system: General Framework

**Problem:** System subjected to  $\hat{H}(t) = \hat{H}_0 + \hat{W}(t)$ ,  
where  $\hat{W}(t)$  is a time-dependent perturbation, and we know:

$$\hat{H}_0 = \sum_n \hbar \omega_n |\psi_n\rangle \langle \psi_n| \quad (\psi_n \text{ are unperturbed energy eigenbasis}) \quad (4.1.1)$$

**Goal:** Given  $|\psi(0)\rangle = \sum_n a_n |\psi_n\rangle$ , we want to understand the time-dependent state  $|\psi(t)\rangle$ , which satisfies:

$$i\hbar \partial_t |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \quad (4.1.2)$$

For  $\hat{W} = 0$ :

$$|\psi(t)\rangle = e^{\frac{\hat{H}_0 t}{i\hbar}} |\psi(0)\rangle = \sum_n e^{-i\omega_n t} a_n |\psi_n\rangle \quad (4.1.3)$$

where  $e^{\frac{\hat{H}_0 t}{i\hbar}} \equiv \hat{u}_0(t)$ , which is called time-evolution operator.

For  $\hat{W} \neq 0$ :

$$|\psi(t)\rangle = \sum_n e^{-i\omega_n t} c_n(t) |\psi_n\rangle, \quad c_n(0) = a_n \quad (4.1.4)$$

Substituting this into the evolution equation:

$$\begin{aligned} i\hbar \partial_t |\psi(t)\rangle &= \hat{H}_0 |\psi(t)\rangle + \hat{W}(t) |\psi(t)\rangle \\ &= \hat{H}_0 |\psi(t)\rangle + \sum_n e^{-i\omega_n t} c_n(t) \hat{W}(t) |\psi_n\rangle \end{aligned} \quad (4.1.5)$$

but also

$$\begin{aligned}
i\hbar\partial_t |\psi(t)\rangle &= \sum_n i\hbar(-i\omega_n)e^{-i\omega_n t}c_n(t) |\psi_n\rangle + \sum_n i\hbar\dot{c}_n(t)e^{-i\omega_n t} |\psi_n\rangle \\
&= \sum_n \hbar\omega_n e^{-i\omega_n t}c_n(t) |\psi_n\rangle + \sum_n i\hbar\dot{c}_n(t)e^{-i\omega_n t} |\psi_n\rangle \\
&= \hat{H}_0 |\psi(t)\rangle + \sum_n i\hbar\dot{c}_n(t)e^{-i\omega_n t} |\psi_n\rangle
\end{aligned} \tag{4.1.6}$$

which leads:

$$\sum_n e^{-i\omega_n t}c_n(t)\hat{W}(t) |\psi_n\rangle = \sum_n i\hbar\dot{c}_n(t)e^{-i\omega_n t} |\psi_n\rangle \tag{4.1.7}$$

Projecting on  $\langle\psi_{n'}|$ :

$$i\hbar\dot{c}_{n'}(t)e^{-i\omega_{n'} t} = \sum_n e^{-i\omega_n t}c_n(t) \langle\psi_{n'}| \hat{W}(t) |\psi_n\rangle \tag{4.1.8}$$

We can define:

$$\hbar\Omega_{n'n}(t) = \langle\psi_{n'}| \hat{W}(t) |\psi_n\rangle \tag{4.1.9}$$

Then

$$\dot{c}_n = -i \sum_{n'} e^{i\Delta_{nn'}t} \Omega_{nn'}(t) c_{n'}, \quad \Delta_{nn'} = \omega_n - \omega_{n'} \tag{4.1.10}$$

P.S. Generalization to degenerate & continuous spectra:

For degenerate case: eigenenergies  $\hbar\omega_n$  labeled by an index 'n', eigenstates by an additional index 'm'.

For continuous case: eigenenergies  $\hbar\omega(\beta_0)$  labeled by a continuous index  $\beta_0$ ; eigenstates labeled by a set of continuous indices  $\beta \equiv (\beta_0, \beta_1, \dots, \beta_N)$  and possibly a discrete one 'm' too.

$$\hat{H}_0 = \sum_n \hbar\omega_n \sum_{m=1}^{g_n} |\psi_{nm}\rangle \langle\psi_{nm}| + \sum_m \int d\beta \hbar\omega(\beta_0) |\psi_m(\beta)\rangle \langle\psi_m(\beta)| \tag{4.1.11}$$

with  $\langle\psi_{nm}|\psi_{n'm'}\rangle = \delta_{nn'}\delta_{mm'}$ ,  $\langle\psi_{nm}|\psi_{m'}(\beta)\rangle = 0$ ,  $\langle\psi_m(\beta)|\psi_{m'}(\beta')\rangle = \delta_{mm'}\delta(\beta - \beta')$

Then

$$|\psi(t)\rangle = \sum_n \sum_{m=1}^{g_n} e^{-i\omega_n t} c_{nm}(t) |\psi_{nm}\rangle + \sum_m \int d\beta e^{-i\omega(\beta_0)t} c_m(\beta; t) |\psi_m(\beta)\rangle \tag{4.1.12}$$

Under  $\hat{H} = \hat{H}_0 + \hat{W}(t)$ , denoting:

$$\begin{aligned}
\langle\psi_{nm}|\hat{W}(t)|\psi_{n'm'}\rangle &\equiv \hbar\Omega_{nm;n'm'}(t) \\
\langle\psi_m(\beta)|\hat{W}(t)|\psi_{m'}(\beta')\rangle &\equiv \hbar\Omega_{mm'}(\beta, \beta'; t) \\
\langle\psi_{nm}|\hat{W}(t)|\psi_{m'}(\beta)\rangle &\equiv \hbar\Omega_{nm;m'}(\beta; t)
\end{aligned} \tag{4.1.13}$$

we get:

$$\dot{c}_{nm} = -i \sum_{n'm'} e^{i\Delta_{nn'}t} \Omega_{nm;n'm'}(t) C_{n'm'} - i \sum_{m'} \int d\beta e^{i\Delta_{n(\beta_0)}t} \Omega_{nm;m'}(\beta; t) C_{m'}(\beta) \tag{4.1.14}$$

$$\dot{c}_m(\beta) = -i \sum_{m'} \int d\beta' e^{i\Delta_{( \beta_0, \beta'_0 )}t} \Omega_{mm'}(\beta, \beta'; t) C_{m'}(\beta') - i \sum_{nm'} e^{-i\Delta_{n(\beta_0)}t} \Omega_{nm';m}^*(\beta; t) C_{nm'} \tag{4.1.15}$$



## 4.2 Time-dependent perturbation theory