

$$V(k_0) = \sum_{t=0}^{\infty} [\beta^t \ln(1 - \alpha\beta) + \beta^t \alpha \ln k_t]$$

$$= \ln(1 - \alpha\beta) \sum_{t=0}^{\infty} \beta^t + \alpha \sum_{t=0}^{\infty} \beta^t \ln k_t$$

$$= \frac{\alpha}{1 - \alpha\beta} \ln k_0 + \frac{\alpha \ln(\alpha\beta)}{1 - \alpha\beta} + \alpha \ln(\alpha\beta) \sum_{t=0}^{\infty} \beta^t$$

$$= \frac{\alpha}{1 - \alpha\beta} \ln k_0 + \frac{\alpha \ln(1 - \alpha\beta)}{1 - \alpha\beta} + \frac{\alpha\beta}{(1 - \beta)(1 - \alpha\beta)} \ln(\alpha\beta)$$



$$\text{右边} = \max \{u(f(k) - y) + \beta V(y)\}$$

Do not ask what it is. Ask what you can say about it.

$$= \ln(k^\alpha - \alpha\beta k^\alpha) + \beta \left[ \frac{\alpha}{1 - \alpha\beta} \ln \alpha\beta k^\alpha + A \right]$$

$$= \ln(k^\alpha - \alpha\beta k^\alpha) + \beta \left[ \frac{\alpha}{1 - \alpha\beta} \ln \alpha\beta k^\alpha + A \right]$$

$$= \ln(1 - \alpha\beta) + \alpha \ln k + \beta \left[ \frac{\alpha}{1 - \alpha\beta} [\ln \alpha\beta + \alpha \ln k] + k \right]$$

$$= \alpha \ln k + \frac{\alpha\beta}{1 - \alpha\beta} \alpha \ln k + \ln(1 - \alpha\beta) + \frac{\alpha\beta}{1 - \alpha\beta} \ln \alpha\beta + \beta A$$

$$= \frac{\alpha}{1 - \alpha\beta} \ln k + \ln(1 - \alpha\beta) + \frac{\alpha\beta}{1 - \alpha\beta} \ln \alpha\beta + \beta A$$

$$= \frac{\alpha}{1 - \alpha\beta} \ln k + (1 - \beta)A + \beta A$$

$$= \frac{\alpha}{1 - \alpha\beta} \ln k + A$$

Editor: Yuyang Songsheng

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Email: songshengyuyang@gmail.com

所以，左边 = 右边，证毕。

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# Chapter 1

## Approximation method



### 1.1 Time independent perturbation theory

#### 1.1.1 Brillouin-Wigner perturbation theory

We consider an unperturbed Hamiltonian  $H_0$  with eigenvalues  $\epsilon_k$  and eigenstates  $|k\alpha\rangle$ , where  $\alpha$  is an index introduced to resolve degeneracies, so that

$$H_0|k\alpha\rangle = \epsilon_k|k\alpha\rangle$$

We pick one of these levels  $\epsilon_n$  for study, so the index  $n$  will be fixed for the following discussion. We denote the eigenspace of the unperturbed system corresponding to eigenvalue  $\epsilon_n$  by  $\mathcal{H}$ , so that the unperturbed eigenkets  $\{|n\alpha\rangle, \alpha = 1, 2, \dots\}$  form a basis in this space.

We take the perturbed Hamiltonian to be  $H = H_0 + \lambda H_1$ , where  $\lambda$  is a formal expansion parameter that we allow to vary between 0 and 1 to interpolate between the unperturbed and perturbed system. When the perturbation is turned on, the unperturbed energy level  $\epsilon_n$  may split and shift. We denote one of the exact energy levels that grows out of  $\epsilon_n$  by  $E$ . We let  $|\psi\rangle$  be an exact energy eigenket corresponding to energy  $E$ , so that

$$H|\psi\rangle = (H_0 + \lambda H_1)|\psi\rangle = E|\psi\rangle$$

Both  $E$  and  $|\psi\rangle$  are understood to be functions of  $\lambda$ ; as  $\lambda \rightarrow 0$ ,  $E$  approaches  $\epsilon_n$  and  $|\psi\rangle$  approaches some state lying in  $\mathcal{H}_n$ . We break the Hilbert space into the subspace  $\mathcal{H}_n$  and its orthogonal complement which we denote by  $\mathcal{H}_n^\perp$ . The components of  $|\psi\rangle$  parallel and perpendicular to  $\mathcal{H}_n$  are conveniently expressed in terms of the projector  $P$  onto the subspace  $\mathcal{H}_n$  and the orthogonal projector  $Q$ , defined by

$$P = \sum_{\alpha} |n\alpha\rangle\langle n\alpha| \quad Q = \sum_{k \neq n, \alpha} |k\alpha\rangle\langle k\alpha|$$

These projectors satisfy

$$P^2 = P \quad Q^2 = Q \quad PQ = QP = 0 \quad P + Q = I \quad [P, H_0] = [Q, H_0] = 0$$

The component  $P|\psi\rangle$  is a linear combination of the known unperturbed eigenstates  $\{|n\alpha\rangle, \alpha = 1, 2, \dots\}$ , and is easily characterized. The orthogonal component  $Q|\psi\rangle$  is harder to find. It turns out it is possible to write a neat power series expansion for this solution. Firstly, we have

$$(E - H_0)|\psi\rangle = \lambda H_1|\psi\rangle$$

Now we define a new operator  $R$

$$R \equiv \sum_{k \neq n, \alpha} \frac{|k\alpha\rangle\langle k\alpha|}{E - \epsilon_k}$$



**Note:** If there are other unperturbed energy levels  $\epsilon_k$  lying close to  $\epsilon_n$ , then the perturbation could push the exact energy  $E$  near to or past some of these other levels, and then other small denominators would make  $R$  ill defined. This will certainly happen if the perturbation is large enough. For the time being we will assume this does not happen, so that  $R$  is free of small denominators. When this is not the case we shall refer to "nearly degenerate perturbation theory", which is discussed later.

The operator  $R$  satisfies

$$PR = RP = 0 \quad QR = RQ = R \quad R(E - H_0) = (E - H_0)R = Q$$

Then we have

$$R(E - H_0)|\psi\rangle = Q|\psi\rangle = \lambda RH_1|\psi\rangle$$

and

$$|\psi\rangle = P|\psi\rangle + \lambda RH_1|\psi\rangle$$

$|\psi\rangle$  can be solved as a series of  $P|\psi\rangle$ :

$$|\psi\rangle = \frac{1}{1 - \lambda RH_1} P|\psi\rangle = P|\psi\rangle + \lambda RH_1 P|\psi\rangle + \lambda^2 RH_1 RH_1 P|\psi\rangle + \dots$$

### 1.1.2 Nondegenerate perturbation theory

In nondegenerate perturbation theory the level  $\epsilon_n$  of  $H_0$  is nondegenerate. Then the index  $\alpha$  is not needed for the level  $\epsilon_n$ , and we can write simply  $|n\rangle$  for the corresponding eigenstate. We assume that  $P|\psi\rangle$  is normalized rather than  $|\psi\rangle$  so that

$$P|\psi\rangle = |n\rangle$$

With this normalization convention, we have

$$\langle n|\psi\rangle = 1$$

Now the series becomes

$$|\psi\rangle = |n\rangle + \lambda \sum_{k \neq n, \alpha} |k\alpha\rangle \frac{\langle k\alpha|H_1|n\rangle}{E - \epsilon_k} + \lambda^2 \sum_{k \neq n, \alpha} \sum_{k' \neq n, \alpha'} |k\alpha\rangle \frac{\langle k\alpha|H_1|k'\alpha'\rangle \langle k'\alpha'|H_1|n\rangle}{(E - \epsilon_k)(E - \epsilon_{k'})}$$

To find an equation for  $E$ , we have

$$\langle n|E - H_0|\psi\rangle = E - \epsilon_n = \lambda \langle n|H_1|\psi\rangle$$

then we can get

$$\begin{aligned} E &= \epsilon_n + \lambda \langle n|H_1|n\rangle + \lambda^2 \langle n|H_1RH_1|n\rangle + \lambda^3 \langle n|H_1RH_1RH_1|n\rangle + \dots \\ &= \epsilon_n + \lambda \langle n|H_1|n\rangle + \lambda^2 \sum_{k \neq n, \alpha} \frac{\lambda \langle n|H_1|k\alpha\rangle \langle k\alpha|H_1|n\rangle}{E - \epsilon_k} \\ &\quad + \lambda^3 \sum_{k \neq n, \alpha} \sum_{k' \neq n, \alpha'} \frac{\langle n|H_1|k\alpha\rangle \langle k\alpha|H_1|k'\alpha'\rangle \langle k'\alpha'|H_1|n\rangle}{(E - \epsilon_k)(E - \epsilon_{k'})} + \dots \end{aligned}$$



It is easy to get  $E$  up to  $O(\lambda^3)$ ,

$$E = \epsilon_n + \lambda \langle n | H_1 | n \rangle + \lambda^2 \sum_{k \neq n, \alpha} \frac{\lambda \langle n | H_1 | k \alpha \rangle \langle k \alpha | H_1 | n \rangle}{\epsilon_n - \epsilon_k} + O(\lambda^3)$$

and  $|\psi\rangle$  up to  $O(\lambda^2)$ ,

$$|\psi\rangle = |n\rangle + \lambda \sum_{k \neq n, \alpha} |k \alpha\rangle \frac{\langle k \alpha | H_1 | n \rangle}{\epsilon_n - \epsilon_k} + O(\lambda^2)$$

Higher corrections can be found on the internet.

### 1.1.3 Degenerate perturbation theory

In the case that the unperturbed energy level  $\epsilon_n$  is degenerate, we have

$$P|\psi\rangle = \sum_{\alpha} |n \alpha\rangle c_{\alpha}$$

and

$$\langle n \alpha | P |\psi\rangle = \langle n \alpha | \psi\rangle = c_{\alpha}$$

Then we can obtain an equation for the  $c_{\alpha}$ ,

$$\langle n \alpha | E - H_0 | \psi\rangle = c_{\alpha} (E - \epsilon_n) = \lambda \langle n \alpha | H_1 | \psi\rangle$$

then we can get

$$\begin{aligned} (E - \epsilon_n) c_{\alpha} &= \lambda \sum_{\beta} \langle n \alpha | H_1 | n \beta\rangle c_{\beta} + \lambda^2 \sum_{\beta} \langle n \alpha | H_1 R H_1 | n \beta\rangle c_{\beta} + \dots \\ &= \lambda \sum_{\beta} \langle n \alpha | H_1 | n \beta\rangle c_{\beta} + \lambda^2 \sum_{\beta} \sum_{k \neq n, \gamma} \frac{\lambda \langle n \alpha | H_1 | k \gamma\rangle \langle k \gamma | H_1 | n \beta\rangle}{E - \epsilon_k} c_{\beta} + \dots \end{aligned} \quad (1.1)$$

This equation must be solved simultaneously for the eigenvalues  $E$  and the unknown expansion coefficients  $c_{\alpha}$ .

If we truncate the series at first order, we see that the corrections  $E - \epsilon_n$  to the energies are determined as the eigenvalues of the matrix  $\langle n \alpha | H_1 | n \beta\rangle$ , and the coefficients  $c_{\alpha}$  are the corresponding eigenvectors. This determines the energies to first order, but the coefficients  $c_{\alpha}$  only to zeroth order. Then  $P|\psi\rangle$  becomes known to zeroth order and  $Q|\psi\rangle$  to first order.

The first order matrix may or may not have degeneracies itself. If it does not, then all degeneracies are lifted at first order; if it does, the remaining degeneracies may be lifted at a higher order, or may persist to all orders. Degeneracies that persist to all orders are almost always due to some symmetry of the system, which can usually be recognized at the outset.

The higher order corrections can be calculated step by step, which will not be listed here.

Now let us consider the case in which the unperturbed levels of  $H_0$ , while not technically degenerate, are close to one another. Suppose to be specific that two levels, say,  $\epsilon_n$  and  $\epsilon_m$ , are close enough to one another that first order perturbations will push the exact level  $E$  close to



or onto the unperturbed level  $\epsilon_m$ .

In this case we choose some energy, call it  $\bar{\epsilon}$ , which is close to  $\epsilon_n$  and  $\epsilon_m$ . Then let us take the original unperturbed Hamiltonian and perturbation and rearrange them in the form,

$$H = H_0 + H_1 = H'_0 + H'_1$$

where

$$\begin{aligned} H_0 &= \sum_{k\alpha} \epsilon_k |k\alpha\rangle \langle k\alpha| \\ H'_0 &= \sum_{k \neq m,n;\alpha} \epsilon_k |k\alpha\rangle \langle k\alpha| + \sum_{k=m,n;\alpha} \bar{\epsilon} |k\alpha\rangle \langle k\alpha| \\ H'_1 &= H_1 + \sum_{k=m,n;\alpha} (\epsilon_k - \bar{\epsilon}) |k\alpha\rangle \langle k\alpha| \end{aligned}$$

Then standard degenerate perturbation theory may be applied. We will call this procedure "nearly degenerate perturbation theory."

## 1.2 Application of time independent perturbation theory in hydrogen atom

### 1.2.1 Stark effect

The Stark effect concerns the behaviour of atoms in external electric fields. We choose hydrogen atom because it is single-electron atoms. The hydrogen atom will be modelled with the central force Hamiltonian

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi r}$$

In this Hamiltonian we ignore spin and other small effects such as relativistic corrections, hyperfine effects and the Lamb shift. These effects cause a splitting and shifting of the energy levels of our simplified model, as well as the introduction of new quantum numbers and new degrees of freedom. But these effects are all small, and if the applied electric field is strong enough, it will overwhelm them and the physical consequences will be much as we shall describe them with our simplified model.

The unperturbed energy levels in hydrogen are given by

$$E_n = -\frac{1}{2n^2} \frac{e^2}{4\pi a_0}$$

where  $a_0$  is the Bohr radius. These levels are  $n^2$  degenerate.

As for the perturbation, let us write  $\mathbf{F}$  for the external electric field, and let us take it to lie in the  $z$ -direction. Thus, the perturbing potential has the form

$$V_1 = -(-e)\mathbf{F} \cdot \mathbf{x} = eFz$$

For small  $z$ , the attractive Coulomb field dominates the total potential and we have the usual Coulomb well that supports atomic bound states. However, for large negative  $z$ , the unperturbed potential goes to zero, while the perturbing potential becomes large and negative. At



intermediate values of negative  $z$ , the competition between the two potentials gives a maximum in the total potential. The electric force on the electron is zero at the maximum of the potential. Given the relative weakness of the applied field, the maximum must occur at a distance from the nucleus that is large in comparison to the Bohr radius  $a_0$ . Atomic states with small principal quantum numbers  $n$  lie well inside this radius. The perturbation analysis we shall perform applies to these states.

The bound states of the unperturbed system are able to tunnel through the potential barrier. When an external electric field is turned on, the bound states of the atom cease to be bound in the strict sense, and become resonances. Electrons that tunnel through the barrier and emerge into the classically allowed region at large negative  $z$  will accelerate in the external field, leaving behind an ion. This is the phenomenon of field ionization. This effect can be neglected if the external field is weak enough and the lifetime of the "bound state" is long enough.

In the case of hydrogen, the ground state is  $|100\rangle$ . The first order shift in the ground state energy level is given by

$$\Delta E_{gnd}^{(1)} = \langle 100 | eFz | 100 \rangle = 0$$

which vanishes because the parity of  $z$  is odd, but  $\langle 100 |$  and  $|100\rangle$  have the same parity.

For the excited states of hydrogen, according to first order degenerate perturbation theory, the shifts in the energy levels  $E_n$  are given by the eigenvalues of the  $n^2 \times n^2$  matrix,

$$\langle nlm | eFz | nl'm' \rangle$$

According to the Wigner-Eckart theorem and parity, the matrix elements vanish unless  $l - l' = \pm 1$  and  $m = m'$ . Consider, for example, the case  $n = 2$ . The four degenerate states are  $|2, 0, 0\rangle$ ,  $|2, 1, -1\rangle$ ,  $|2, 1, 0\rangle$  and  $|2, 1, 1\rangle$ . Only the states  $|2, 0, 0\rangle$  and  $|2, 1, 0\rangle$  are connected by the perturbation. Therefore of the 16 matrix elements, the only nonvanishing ones are

$$\langle 2, 0, 0 | eFz | 2, 1, 0 \rangle = -W = -3eFa_0$$

and its complex conjugate. The matrix connecting the two states  $|2, 0, 0\rangle$  and  $|2, 1, 0\rangle$  is

$$\begin{pmatrix} 0 & -W \\ -W & 0 \end{pmatrix}$$

and its eigenvalues are the first order energy shifts in the  $n = 2$  level,

$$\Delta E_2^{(1)} = \pm W$$

In addition, the two states  $|2, 1, -1\rangle$  and  $|2, 1, 1\rangle$  do not shift their energies at first order. The perturbed eigenfunctions are

$$|+W\rangle = \frac{|2, 0, 0\rangle - |2, 1, 0\rangle}{\sqrt{2}} \quad |-W\rangle = \frac{|2, 0, 0\rangle + |2, 1, 0\rangle}{\sqrt{2}}$$

This is zeroth order part of the exact eigenstates.

Now let us look at the exact symmetries of the full, perturbed Hamiltonian  $H = H_0 + H_1$ , without doing perturbation theory at all. Since  $[H, L_z]$  the exact eigenstates of  $H$  can be chosen



to be eigenstates of  $L_z$  as well. Denote these by  $|\gamma m\rangle$ , where  $\gamma$  is an additional index needed to specify an energy eigenstate. Thus, we have

$$L_z|\gamma m\rangle = m|\gamma m\rangle \quad H|\gamma m\rangle = E_{\gamma m}|\gamma m\rangle$$

where  $E_{\gamma m}$  is allowed to depend on  $m$  since the full rotational symmetry is broken.

As for time reversal, the state  $T|\gamma m\rangle$  must be an eigenstate of energy with eigenvalue  $E_{\gamma m}$  since  $TH = HT$ . But because  $T^{-1}L_zT = -L_z$ , it also follows that  $T|\gamma m\rangle$  is an eigenstate of  $L_z$  with eigenvalue  $-m$ . If  $m \neq 0$ , we must have a degeneracy of at least two. The only energy levels that can be nondegenerate are those with  $m = 0$ . In the example above, even higher order corrections cannot separate  $|2, 1, -1\rangle$  and  $|2, 1, 1\rangle$ .

### 1.2.2 Fine structure

Fine structure of atoms concerns the effects of relativity and spin on the dynamics of the electron. Both these effects are of the same order of magnitude, and must be treated together in any realistic treatment of the atomic structure.

The fine structure terms account for relativistic effects through order  $v^2$ , and have the effect of enlarging the Hilbert space by the inclusion of the spin degrees of freedom, introducing new quantum numbers, and shifting and splitting the energy levels of the electrostatic model. The splitting in particular means that spectral lines that appear as singlets under low resolution become closely spaced multiplets under higher resolution.

Derivation of the exact form of relativistic corrections of Hamiltonian in quantum mechanics can be very rigorous and needs some reasonable guess. The details of derivation can be found in [lecture notes on fine structure](#) by Robert G. Littlejohn. Here we just list the result.

$$H_{FS} = H_{RKE} + H_D + H_{SO}$$

The term  $H_{RKE}$  is due to the second order term of the expansion series of  $E = \sqrt{p^2 + m^2}$ . (The first order term is just the kinetic energy in non relativistic quantum mechanics). We have

$$H_{RKE} = -\frac{p^4}{8m^3}$$

The term  $H_D$  comes out as a result of virtual process  $e^- \rightarrow e^- + e^- + e^+$  in the region whose scale is smaller than the Compton length  $\lambda_C = \frac{1}{m} = \alpha a_0$  of electrons. Such virtual states appear in perturbation theory when one sums over intermediate states, which derive ultimately from a resolution of the identity. The effect is to smear out the position of the atomic electron over a distance of order  $\lambda_C$ . We have

$$H_D = \frac{1}{8m^2} \nabla^2 V$$

The term  $H_{SO}$  arises because the electric field of nuclei generates a magnetic field in the rest frame of electron. We have

$$H_{SO} = \frac{1}{2m^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S}$$

The unperturbed energy levels in hydrogen are given by

$$E_n = -\frac{1}{2n^2} \frac{e^2}{4\pi a_0}$$





When spin of electron is taken into account, these levels are  $2n^2$  degenerate. One choice of base is  $|nlm_l s\rangle$ . It is the eigenvector of operator  $L^2$ ,  $L_z$  and  $S_z$ . However,  $L_z$  and  $S_z$  do not commute with  $H_{SO}$ . A better choice of base is  $|nljm_j\rangle$ . It is the eigenvector of operator  $L^2$ ,  $J^2$  and  $J_z$ .  $H_{SO}$ ,  $H_{RKE}$  and  $H_{SO}$  are all commute with  $L^2$ ,  $J^2$  and  $J_z$ . So

$$\langle nl'j'm'_j | H | nljm_j \rangle$$

vanishes unless  $l' = l$ ,  $j = j'$  and  $m'_j = m_j$ . The final results are

$$\langle nljm_j | H_{RKE} | nljm_j \rangle = -\alpha^2 E_n \frac{1}{n^2} \left( \frac{3}{4} - \frac{n}{l + \frac{1}{2}} \right)$$

$$\langle nljm_j | H_D | nljm_j \rangle = -\alpha^2 E_n \frac{1}{n} \delta_{l0}$$

$$\langle nljm_j | H_{SO} | nljm_j \rangle = -\alpha^2 E_n \frac{1}{2n} \frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l + \frac{1}{2})(l+1)}$$

When we add them up to get the total energy shift due to the fine structure we find

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

It is independent of the orbital angular momentum quantum number  $l$ , although each of the individual terms does depend on  $l$ . However, the total energy shift does depend on  $j$  in addition to the principal quantum number  $n$ , so when we take into account the fine structure corrections, the energy levels of hydrogen atom have the form  $E_{nj}$ .

Besides fine structure effect, the remaining important effects causing energy shift are hyperfine effects and the Lamb shift.

The Lamb shift is a shift in the energy levels due to the interaction of the electron with the vacuum fluctuations of the quantized electromagnetic field. It has small effects on the s-states ( $l = 0$ ) of hydrogen, thereby introducing a dependence of the energy levels on  $l$ . Thus, including the Lamb shift, the energy levels in hydrogen have the form  $E_{nlj}$ , and the only degeneracy is that due to rotational invariance. It will be further discussed in quantum electrodynamics. Hyperfine effects are caused by the interaction between electron spin and nuclei spin, and will be discussed later.

### 1.2.3 Zeeman effect

The Zeeman effect concerns the interaction of atomic systems with external magnetic fields. The Hamiltonian for the electron in hydrogen atom is

$$H = \frac{(\mathbf{P} + e\mathbf{A})^2}{2m} - \frac{e^2}{4\pi r} + H_{FS} + g_e \mu_B \mathbf{S} \cdot \mathbf{B}$$

where  $g_e \approx 2$  and  $\mu_B \equiv \frac{e}{2m}$ . We assume a uniform magnetic field  $\mathbf{B} = B\hat{z}$ . We take the gauge

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



which is Coulomb gauge so that  $\nabla \times \mathbf{A} = 0$ . This implies

$$\mathbf{P} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{P}$$

so the cross terms in the expansion of the kinetic energy can be written in either order. We also notice that

$$\mathbf{P} \cdot \mathbf{A} = \frac{1}{2} \mathbf{P} \cdot \mathbf{B} \times \mathbf{r} = \frac{1}{2} \mathbf{B} \cdot \mathbf{L}$$

At last, we have

$$H = H_a + H_Z + H_B + H_{FS}$$

where

$$H_a = \frac{p^2}{2m} - \frac{e^2}{4\pi r} \quad H_Z = \frac{e}{2m}(L_z + 2S_z)B \quad H_B = \frac{e^2}{8m}B^2(x^2 + y^2)$$

Suppose the typical energy of the term  $H_i$  is  $E_i$ , then we have  $E_a \sim \frac{me^4}{32n^2\pi^2\hbar^2\epsilon_0^2}$ ,  $E_z \sim \frac{nehB}{2m}$  and  $E_B \sim \frac{e^2}{8m}n^4a_0^2 = \frac{2n^4\pi^2\epsilon_0^2\hbar^4B^2}{m^3e^2}$ . So

$$\frac{E_Z}{E_a} \sim \frac{16\pi^2n^3\hbar^3\epsilon_0^2}{m^2e^3}B \sim \frac{n^3B}{2 \times 10^5T}$$

$$\frac{E_B}{E_a} \sim \left[ \frac{8\pi^2n^3\hbar^3\epsilon_0^2}{m^2e^3}B \right]^2 \sim \left[ \frac{n^3B}{4 \times 10^5T} \right]^2$$

In the previous section, we have derived that

$$\frac{E_{FS}}{E_a} \sim \frac{3\alpha^2}{4n^2} \sim \frac{1}{2.5 \times 10^4 n^2}$$

So, in the usual experimental condition, we have

$$E_B \ll E_z \ll E_a$$

So, in the following discussion, we will neglect  $E_B$  term. But whether  $\frac{E_z}{E_a}$  is much larger than 1, much smaller than 1 or close to 1 depends on the  $B$  and  $n$ .

If  $H_{FS}$  is much smaller than  $H_Z$  and can be neglected, then we have

$$H = H_a + \frac{e}{2m}(L_z + 2S_z)B$$

The eigenvector of  $H$  is  $|nlm_l m_s\rangle$  with eigenvalue  $E = E_n + \mu_B B(m_l + 2m_s)$ .

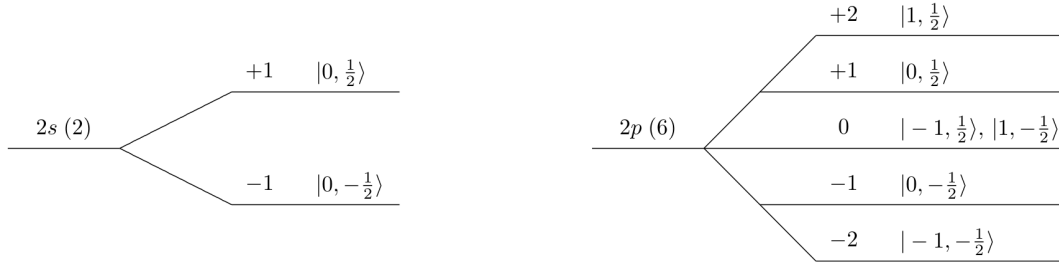
If  $H_{FS}$  is much smaller than  $H_Z$  and but cannot be neglected, we may treat it as a perturbation. For simplicity, we only take  $H_{SO}$  into account. Up to the first order, we consider the matrix element

$$\langle nlm_l m_s | f(r) \mathbf{L} \cdot \mathbf{S} | nl' m'_l m'_s \rangle$$

Since  $[H_{SO}, L^2] = 0$ , the term above vanishes unless  $l = l'$ . So we focus on the matrix in the subspace  $l = l'$ . For the  $2p$  orbit of hydrogen, there is a 2-fold degeneracy between  $|2, 1, -1, \frac{1}{2}\rangle$  and  $|2, 1, 1, -\frac{1}{2}\rangle$ . This makes one  $2 \times 2$  matrix. Let us look at the off-diagonal element,

$$\langle 2, 1, -1, \frac{1}{2} | f(r) \mathbf{L} \cdot \mathbf{S} | 2, 1, 1, -\frac{1}{2} \rangle$$



Figure 1.1: Zeeman effect for  $n = 2$  in Hydrogen atom

in which we use the identity

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(L_+S_- + L_-S_+) + L_zS_z$$

To be non-vanishing, the operator in the middle of the matrix element must connect states with  $\Delta m_l = 2$ , but in fact that operator permits only  $\Delta m_l = 0, \pm 1$ . Therefore the off-diagonal matrix element vanishes and the energy shift is determined by diagonal elements. For  $2p$  orbit, we can get

$$\Delta E = \langle nlm_l m_s | f(r) \mathbf{L} \cdot \mathbf{S} | nlm_l m_s \rangle \propto m_l m_s$$

As for the  $2s$  levels, for them  $\mathbf{L} = 0$  (that is, the operator  $\mathbf{L}$  vanishes on the  $2s$ -subspace), so  $\Delta E = 0$ .

The final case we shall examine is the weak field limit, in which  $H_z \ll H_{FS}$  and we will treat  $H_z$  as perturbation.



**Note:** In the case of hydrogen, one should also consider the Lamb shift for a realistic treatment. For example, in the  $n = 2$  levels of hydrogen, the Lamb shift is about 10 times smaller than the fine structure energy shifts, indicating that we really should question how the Lamb shift compares to the Zeeman term which is also (by our assumptions) much smaller than the fine structure term.

The eigenvector of  $H_a + H_{FS}$  are  $|nljm_j\rangle$  with eigenvalue  $E_{nj}$ . Up to the first order, the matrix elements we need have the form

$$\langle nl'jm_j' | H_z | nljm_j \rangle$$

Since  $[H_z, L^2] = 0$  and  $[H_z, J_z] = 0$ , off-diagonal matrix element vanishes automatically. The energy shift is

$$\Delta E = \mu_B B \langle nljm_j | L_z + 2S_z | nljm_j \rangle = g_{eff} \mu_B B m_j$$

where

$$g_{eff} = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

### 1.2.4 Hyperfine structure

The nucleus of an atom contains localized charge and current distributions, which produce electric and magnetic fields that can be decomposed into multipole fields much as in classical



electrostatics or magnetostatics. The first of the multipole moments, the electric monopole, is of course the Coulomb electrostatic field that holds the electrons in their orbits and produces the gross structure of the atom. The higher order multipole moments produce small corrections to the atomic structure that are known generally as hyperfine effects.

Multipole moments for a system of charges has been discussed in the part of classical electrodynamics. In quantum mechanics, we recall that the intrinsic magnetic moment operator of an electron is defined in the space of electron spin. So we may infer that multipole moments of nuclei is defined in the space of nuclear spin  $\mathbf{I}$ . We let the quantum number of the operator  $I^2$  be  $i$ , so that  $I^2$  has eigenvalues  $i(i+1)$ . The nuclear Hilbert space is a  $(2i+1)$  dimensional space in which the standard basis is  $|im_i\rangle$  with  $-i \leq m \leq i$ .

Not all the multipole fields that occur classically are allowed in the case of a nuclei. There are two rules governing the allowed multipole moments of the nucleus.

The first is that electric multipoles of odd  $k$  and magnetic multipoles of even  $k$  are forbidden. For example, if the nucleus had an electric dipole moment, the perturbing Hamiltonian would be

$$H_1 = -e \frac{\mathbf{d} \cdot \mathbf{r}}{r^3}$$

And just like  $\mu, \mathbf{d}$ , must be proportional to the spin, say  $\mathbf{d} = k\mathbf{I}$ , because all vector operators on a single irreducible subspace are proportional (Wigner-Eckart theorem). Thus,

$$H_1 = -ke \frac{\mathbf{I} \cdot \mathbf{r}}{r^3}$$

We find that  $H_1$  violates time reversal and parity

$$TH_1T^\dagger = -H_1 \quad PH_1P^\dagger = -H_1$$

The weak interactions do violate parity, and we do know that time reversal (more precisely, CP) is violated at a very small level in certain decay processes, so it is possible that the terms forbidden by this rule actually exist at a small level. For example, the neutron or the electron may have an electric dipole moment, but if such moments exist, they are certainly very small and can be neglected in our discussion.

The second rule states that a  $2^k$ -pole can occur only if  $k \leq 2i$ . For example, the proton with  $i = \frac{1}{2}$  can possess an electric monopole moment and a magnetic dipole moment, but not an electric quadrupole moment. Lying behind this rule is the fact that the operator representing the  $2^k$ -pole on the nuclear Hilbert space is, in fact, an order  $k$  irreducible tensor operator. But the maximum order of an irreducible tensor operator on the nuclear Hilbert space with spin  $i$  is  $k = 2i$ .

So for hydrogen atom, whose nuclear spin is  $i = \frac{1}{2}$ , the only term we have to concern is magnetic moment. A point magnetic dipole of moment  $\mu$  is

$$\mathbf{A}(\mathbf{r}) = \frac{\mu \times \mathbf{r}}{r^3}$$

To avoid the singularity at origin, we modify  $\mathbf{A}(\mathbf{r})$  as

$$\mathbf{A}(\mathbf{r}) = \mu \times \mathbf{r} \begin{cases} \frac{1}{a^3} & r < a \\ \frac{1}{r^3} & r > a \end{cases}$$



taking into account of the finite size of nuclei. By taking the curl we compute the magnetic field

$$\mathbf{B}(\mathbf{r}) = \begin{cases} \frac{2\boldsymbol{\mu}}{a^3} & r < a \\ \boldsymbol{\mu} \cdot \hat{T} & r > a \end{cases}$$

where  $T_{ij} = \frac{3x_i x_j - r^2 \delta_{ij}}{r^5}$ . We define

$$\Delta(r) \equiv \begin{cases} \frac{1}{a^3} & r < a \\ 0 & r > a \end{cases}$$

and

$$f(r) \equiv \begin{cases} 0 & r < a \\ 1 & r > a \end{cases}$$

Then we can write

$$\mathbf{A}(\mathbf{r}) = \boldsymbol{\mu} \times \mathbf{r} \left[ \Delta(r) + \frac{f(r)}{r^3} \right]$$

and

$$\mathbf{B}(\mathbf{r}) = \boldsymbol{\mu} \cdot [2\Delta(r)\hat{I} + f(r)\hat{T}]$$

In the limit  $a \rightarrow 0$ , we have

$$\lim_{a \rightarrow 0} \Delta(r) = \frac{4\pi}{3} \delta(\mathbf{r}) \quad \lim_{a \rightarrow 0} f(r) = 1$$

The Hamiltonian of the system is

$$H = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} - \frac{e^2}{4\pi r} + H_{FS} + H_{Lamb} + \frac{e}{m} \mathbf{S} \cdot \mathbf{B}$$

The expressions for  $\mathbf{A}$  and  $\mathbf{B}$  are given above and  $\boldsymbol{\mu}$  in the expression are given by

$$\boldsymbol{\mu} = g_p \mu_p \mathbf{I}$$

where  $g_p$  is g-factor of proton and  $\mu_p \equiv \frac{e}{2m_p}$ . Thus, the Hamiltonian must be interpreted as an operator acting the total Hilbert space

$$\mathcal{H} = \mathcal{H}_{elec} \otimes \mathcal{H}_{nucl}$$

For  $\mathcal{H}_{elec}$  the obvious basis is  $|nljm_j\rangle$  with energies  $E_{nlj}$  when there is no hyperfine terms. In hydrogen energies depend on  $l$  because of the Lamb shift. The obvious basis in  $\mathcal{H}_{nucl}$  is  $|im_i\rangle$ . Thus we define the basis states in  $\mathcal{H}$  as  $|nljm_jm_i\rangle$  (we suppress the index  $i$  since it is a constant). It is called uncoupled basis. Now we expand the Hamiltonian and neglect the term  $A^2$ , writing the result as  $H = H_0 + H_1$ , where

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi r} + H_{FS} + H_{Lamb}$$

and

$$H_1 = 2\mu_B(\mathbf{p} \cdot \mathbf{A} + \mathbf{S} \cdot \mathbf{B})$$



Since

$$\mathbf{p} \cdot (\mathbf{I} \cdot \mathbf{r}) = \mathbf{I} \cdot (\mathbf{r} \cdot \mathbf{P}) = \mathbf{I} \cdot \mathbf{L}$$

we have

$$H_{1,orbi} \equiv 2\mu_B(\mathbf{p} \cdot \mathbf{A}) = k(\mathbf{I} \cdot \mathbf{L}) \left[ \Delta(r) + \frac{f(r)}{r^3} \right]$$

where  $k \equiv g_e g_p \mu_B \mu_p$ . On the other hand, we have

$$H_{1,spin} \equiv 2\mu_B \mathbf{S} \cdot \mathbf{B} = k \left[ 2\Delta(r) \mathbf{I} \cdot \mathbf{S} + f(r) \mathbf{I} \cdot \hat{\mathbf{T}} \cdot \mathbf{S} \right]$$

In the limit  $a \rightarrow 0$ , we have

$$H_{1,orbi} = k(\mathbf{I} \cdot \mathbf{L}) \left[ \frac{4\pi}{3} \delta(\mathbf{r}) + \frac{1}{r^3} \right]$$

and

$$H_{1,spin} = k \left[ \frac{8\pi}{3} \delta(\mathbf{r}) \mathbf{I} \cdot \mathbf{S} + \mathbf{I} \cdot \hat{\mathbf{T}} \cdot \mathbf{S} \right]$$

Since the coupling term (e.g.  $\mathbf{I} \cdot \mathbf{S}$ ) are not invariant under either electronic rotations alone or under nuclear rotations alone. The uncoupled basis is not the best one for carrying out the perturbation calculation. The total angular momentum of the system are defined by

$$\mathbf{F} \equiv \mathbf{I} + \mathbf{J} = \mathbf{I} + \mathbf{L} + \mathbf{S}$$

The new coupled basis is  $|nljm_f\rangle$ . Since  $[\mathbf{F}, H] = 0$ ,  $|nljm_f\rangle$  is the eigenvector of  $H$ . The energy shift caused by  $H_1$  is

$$\Delta E = \langle nljm_f | H_1 | nljm_f \rangle$$

After a lengthy calculation, we can get

$$\Delta E = \frac{g_e g_p \mu_B \mu_p}{4\pi a_0^3} \frac{1}{n^3} \frac{f(f+1) - j(j+1) - i(i+1)}{j(j+1)(2l+1)}$$

The energy levels were  $E_{nlj}$  before the hyperfine interactions were turned on, but since  $\Delta E$  depends on  $f$ , they now have the form  $E_{nljf}$ . The energy eigenstates are  $|nljm_f\rangle$ , and are  $(2f+1)$ -fold degenerate, causing the fine structure levels of hydrogen to split, giving rise to hyperfine multiplets.

For example, the ground state  $|1, 0, \frac{1}{2}\rangle$  splits into two levels  $f=0$  and  $f=1$ . This  $f=0$  level is the true ground state of hydrogen. It is nondegenerate. The  $f=1$  level is 3-fold degenerate, and lies above the ground state by an energy of approximately  $1.42GHz$  in frequency units, or  $21cm$  in wave length units.

### 1.3 Time dependent perturbation theory

Time-dependent perturbation theory applies to Hamiltonians of the form

$$H = H_0 + H_1(t)$$



where  $H_0$  is solvable and  $H_1$  is treated as a perturbation. In time-dependent perturbation theory, we are usually interested in time-dependent transitions between eigenstates of the unperturbed system induced by the perturbation  $H_1$ . Time-dependent transitions are usually described by the transition amplitude, defined as the quantity

$$\langle f|U(t)|i\rangle$$

where  $U(t)$  is the exact time evolution operator for the Hamiltonian, and where  $|i\rangle$  and  $|f\rangle$  are two eigenstates of the unperturbed Hamiltonian  $H_0$ . Let us denote the unperturbed time-evolution operator by  $U_0(t)$  and the exact one by  $U(t)$ . These operators satisfy the evolution equations

$$i\frac{\partial U_0(t)}{\partial t} = H_0 U_0(t) \quad i\frac{\partial U(t)}{\partial t} = H U(t)$$

Since  $H_0$  is independent of time, we have  $U_0 = e^{-iH_0 t}$ .

Suppose the state in Schrödinger picture is  $|\psi_S(t)\rangle$ , then we define the state in interaction picture as

$$|\psi_I(t)\rangle \equiv U_0^\dagger(t)|\psi_S(t)\rangle$$

Similarly, we define the operator in interaction picture as

$$A_I(t) \equiv U_0^\dagger(t)A_S(t)U_0(t)$$

Let us define  $W(t)$  as the operator that evolves kets in the interaction picture forward from time 0 to final time  $t$ , i.e.

$$|\psi_I(t)\rangle = W(t)|\psi_I(0)\rangle$$

We can verify that

$$W(t) = U_0^\dagger(t)U(t)$$

And we can get the time evolution of  $W(t)$

$$i\frac{\partial W}{\partial t} = H_{1I}(t)W(t)$$

The formal solution is

$$W(t) = I + (-i)^n \sum_{n=1}^{\infty} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n H_{1I}(t_1) H_{1I}(t_2) \cdots H_{1I}(t_n)$$

Let us assume for simplicity that  $H_0$  has a discrete spectrum  $H_0|n\rangle = E_n|n\rangle$ . We assume that the system is initially in an eigenstate of the unperturbed system, what we will call the "initial" state  $|i\rangle$  with energy  $E_i$ . Then

$$|\psi_I(t)\rangle = W(t)|i\rangle$$

Let us expand the exact solution of the Schrödinger equation in the interaction picture in the unperturbed eigenstates

$$|\psi_I(t)\rangle = \sum_n c_n(t)|n\rangle$$



We then have

$$c_n(t) = \langle n|W(t)|i\rangle = \langle n|U_0^\dagger U(t)|i\rangle = e^{iE_n t} \langle n|U(t)|i\rangle$$

So the transition amplitudes in the interaction picture and those in the Schrödinger picture are related by a simple phase factor. The transition probabilities are the squares of the amplitudes and are the same in either case. The perturbation expansion of the transition amplitude  $c_n(t)$  is

$$c_n(t) = \delta_{ni} + c_n^{(1)}(t) + \dots$$

where

$$c_n^{(1)}(t) = \frac{1}{i} \int_0^t dt' \langle n|H_1(t')|i\rangle = \frac{1}{i} \int_0^t dt' e^{i(E_n - E_i)t'} \langle n|H_1(t')|i\rangle$$

If  $H_1$  is time-independent, we have

$$c_n^{(1)}(t) = \frac{2}{i} e^{i\omega_{ni}t/2} \left( \frac{\sin \omega_{ni}t/2}{\omega_{ni}} \right) \langle n|H_1|i\rangle$$

Up to the first order, the transition probability is

$$P_n(t) = 4 \left( \frac{\sin^2 \omega_{ni}t/2}{\omega_{ni}^2} \right) |\langle n|H_1|i\rangle|^2 \quad (n \neq i)$$

Another case that is important in practice is when  $H_1$  has a periodic time dependence of the form

$$H_1(t) = K e^{-i\omega_0 t} + K^\dagger e^{i\omega_0 t}$$

We can get

$$c_n^{(1)}(t) = \frac{2}{i} \left[ e^{i(\omega_{ni} - \omega_0)t/2} \left( \frac{\sin(\omega_{ni} - \omega_0)t/2}{\omega_{ni} - \omega_0} \right) \langle n|K|i\rangle + e^{i(\omega_{ni} + \omega_0)t/2} \left( \frac{\sin(\omega_{ni} + \omega_0)t/2}{\omega_{ni} + \omega_0} \right) \langle n|K^\dagger|i\rangle \right]$$

Often, we are most interested in those final states to which most of the probability goes, which are the states for which one or the other of the two denominators is small. For these states we have

$$E_n \approx E_i \pm \omega_0$$

We call these two cases absorption and stimulated emission, respectively. Taking the case of absorption, and looking only at final states that are near resonance, we can write the transition probability to first order of perturbation theory as

$$P_n(t) = 4 \left( \frac{\sin^2(\omega_{ni} - \omega_0)t/2}{(\omega_{ni} - \omega_0)^2} \right) |\langle n|K|i\rangle|^2$$

Let us fix the final state and examine how the probability develops as a function of time in first order time-dependent perturbation theory. Obviously  $P_n(0) = 0$ . At later times we see that  $P_n(t)$  oscillates at frequency  $\omega_{ni}$  between 0 and a maximum proportional to  $\frac{1}{\omega_{ni}}$ . The frequency  $\omega_{ni}$  measures how far the final state is off resonance, that is, how much it fails to conserve energy. If this frequency is large, the probability oscillates rapidly between zero and





a small maximum. But as we move the state closer to the initial state in energy,  $\omega_{ni}$  gets smaller, the period of oscillations becomes longer, and the amplitude grows.

If there is a final state degenerate in energy with the initial state, then  $\omega_{ni} = 0$  and the time-dependent factor takes on its limiting value  $\frac{t^2}{4}$ . In this case, first order perturbation theory predicts that the probability grows without bound. This is an indication of the fact that at sufficiently long times first order perturbation theory breaks down and we must take into account higher order terms in the perturbation expansion. But at short times it is correct that  $P_n$  for a state on resonance grows as  $t^2$ .

Now let us fix the time  $t$  and examine how the expression for  $P_n(t)$  in first order perturbation theory depends on the energy of the final state. To do this we focus on  $\frac{\sin^2(\omega t/2)}{\omega^2}$  as a function of  $\omega$ .

The curve of the function consists of oscillations under the envelope  $\frac{1}{\omega^2}$ , with zeroes at  $\omega = \frac{2n\pi}{t}$ . The central lobe has height  $\frac{t^2}{4}$  and width that is proportional to  $\frac{1}{t}$ , so the area of the central lobe is proportional to  $t$ . We can derive that

$$\lim_{t \rightarrow \infty} \frac{1}{t} \frac{\sin^2 \omega t/2}{\omega^2} = \frac{\pi}{2} \delta(\omega)$$

The  $\delta$ -function enforces energy conservation in the limit  $t \rightarrow \infty$ . But at finite times, transitions take place to states in a range of energies about the initial energy. This width is of order  $\frac{1}{t}$ . This is an example of the energy-time uncertainty relation,  $\Delta t \Delta E = 1$ , indicating that a system that is isolated (not subjected to a measurement) over a time interval  $\Delta t$  has an energy that is uncertain by an amount  $\Delta E \geq \frac{1}{\Delta t}$ .

## 1.4 Atomic Radiation

## 1.5 Variational Method



# Chapter 2

## Many body problem



### 2.1 Identical particles

If two particles are identical, their exchange must not change physical quantities, so we have

$$|\cdots \psi_j \cdots \psi_i \cdots\rangle = E_{ij} |\cdots \psi_i \cdots \psi_j \cdots\rangle = e^{i\theta} |\cdots \psi_i \cdots \psi_j \cdots\rangle$$

where  $E_{ij}$  is the operator to exchange particle  $i$  and  $j$  and  $psi_i$  is the quantum number to describe the state of particle  $i$ . In coordinate representation, it can be expressed as

$$\Psi(\cdots \mathbf{x}_j \cdots \mathbf{x}_i \cdots) = e^{i\theta} \Psi(\cdots \mathbf{x}_i \cdots \mathbf{x}_j \cdots)$$

In three dimension space, the value of  $e^{i\theta}$  can only be  $\pm 1$ . If the spin of the particle is integer, then the phase factor must be 1 and the particle is called boson. If the spin of the particle is half-integer, then the phase factor must be  $-1$  and the particle is called fermion. This is called spin-statistics theorem and can only be proved by relativistic quantum field theory. Here, we will take it for granted.



**Note:** In two dimension space, the phase  $e^{i\theta}$  can be anything, and the particles that obey quantum statistics of this sort are called anyons. There is a brief introduction in chapter 12.1 and 12.2 of the book *Quantum Field Theory and the Standard Model* (Matthew D. Schwartz).

So not all vectors in the space  $\mathcal{H}_1 \otimes \cdots \otimes \mathcal{H}_n$  are physical state. The physical states must be the eigenvectors of all  $E_{ij}$  with eigenvalue 1 ( $-1$ ) for bosons (fermions). The space composed of physical states is the so-called Fock space. For example, suppose there are three particles with different state  $a, b, c$ .  $|abc\rangle$  is not a physical state. The physical state for bosons is

$$\frac{1}{\sqrt{3!}} (|abc\rangle + |acb\rangle + |bca\rangle + |bac\rangle + |cab\rangle + |cba\rangle)$$

The physical state for fermions is

$$\frac{1}{\sqrt{3!}} (|abc\rangle - |acb\rangle + |bca\rangle - |bac\rangle + |cab\rangle - |cba\rangle)$$

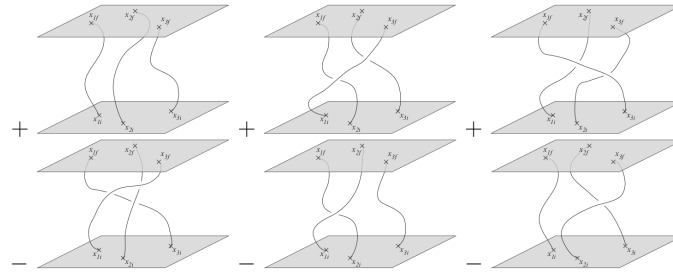
In general, for  $N$  particles filling  $N$  distinct states, there are  $N!$  states to start with, but there is only one totally symmetric state and one totally anti-symmetric state, and the rest of  $N! - 2$  states are thrown out. Therefore quantum statistics reduces the size of the Hilbert space quite dramatically.

Further more, not all Hermitian operators are physical observables. A nonphysical operator is one that takes a state in the physical subspace of the Hilbert space (one that satisfies the right

symmetry under exchange), and maps it into a nonphysical state (one that does not have the right symmetry). An example is the operator  $\mathbf{X}_1$ . We might call this the operator corresponding to the measurement of the position of particle 1. The problem with this operator from a physical standpoint is that you cannot measure the position of particle 1. You can select a region of space, and ask whether there is a particle in that region. But if you find one, you cannot say whether it is particle 1 or particle 2, since they are identical. If  $O$  is a physical observable, we must have

$$[E_{ij}, O] = 0$$

for all  $ij$ .



**Figure 2.1:** The path integral for three identical fermions

In path integral formulation of quantum mechanics, we calculate the transition amplitudes

$$\langle \mathbf{x}_f, t_f | \mathbf{x}_i, t_i \rangle = \int \mathcal{D}\mathbf{x}(t) e^{i \int_{t_i}^{t_f} dt L(t)}$$

The generalization to the  $N$ -particle case is

$$\langle \mathbf{x}_{1f} \cdots \mathbf{x}_{Nf}, t_f | \mathbf{x}_{1i} \cdots \mathbf{x}_{Ni}, t_i \rangle = \int \mathcal{D}\mathbf{x}_1(t) \cdots \mathcal{D}\mathbf{x}_N(t) e^{i \int_{t_i}^{t_f} dt L(t)}$$

Here, the particle 1 at the initial position  $\mathbf{x}_{1i}$  moves to the final position  $\mathbf{x}_{1f}$ , the particle 2 at the initial position  $\mathbf{x}_{2i}$  to  $\mathbf{x}_{2f}$ , etc, and you sum over all possible paths. When the particles are identical, however, we need to introduce proper (anti-)symmetry of the state. For fermions (The case for bosons can be obtained easily by dropping all minus signs), we introduce the anti-symmetrized position bra

$$\langle [\mathbf{x}_1 \cdots \mathbf{x}_N] | = \frac{1}{\sqrt{N!}} \sum_{\sigma} (-1)^{\sigma} \langle \mathbf{x}_{\sigma(1)} \cdots \mathbf{x}_{\sigma(N)} |$$

We now consider path integral representation of the transition amplitudes

$$\langle [\mathbf{x}_{1f} \cdots \mathbf{x}_{Nf}], t_f | [\mathbf{x}_{1i} \cdots \mathbf{x}_{Ni}], t_i \rangle$$

On the other hand, the Lagrangian for identical particles must be invariant under the exchange of particles, we can prove that

$$\langle [\mathbf{x}_{1f} \cdots \mathbf{x}_{Nf}], t_f | [\mathbf{x}_{1i} \cdots \mathbf{x}_{Ni}], t_i \rangle = \sum_{\sigma} \langle \mathbf{x}_{\sigma(1)f} \cdots \mathbf{x}_{\sigma(N)f}, t_f | \mathbf{x}_{1i} \cdots \mathbf{x}_{Ni}, t_i \rangle$$

In other words, the path integral sums over all possible paths allowing the positions at the final time slice are interchanged in all possible ways starting from the positions at the initial time slice.



## 2.2 Homonuclear Molecule

## 2.3 Non-relativistic quantum field theory

There are some limitations of multi-body Schrödinger wave function. Firstly, when the number of particles is large, multi-body Schrödinger wave function would be cumbersome. Secondly, it is incapable of describing processes where the number of particles changes.

The aim of the quantum field theory is to come up with a formalism which is completely equivalent to multi-body Schrödinger equations but just better: it allows you to consider a variable number of particles all within the same framework and can even describe the change in the number of particles. It also gives totally symmetric or anti-symmetric multi-body wave function automatically. It also allows a systematic way of organizing perturbation theory in terms of Feynman diagrams. It is particularly suited to multi-body problems.

In quantum mechanics, you start with classical particle Hamiltonian mechanics, with no concept of wave or interference. After quantizing it, we introduce Schrödinger wave function and there emerges concepts of wave and its interference. In quantum field theory, you start with classical wave equation, with no concept of particle. After quantizing it, we find particle interpretation of excitations in the system.

Let us consider a classical field equation

$$\left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m}\right)\psi(\mathbf{x}, t) = 0$$

A solution to this field equation is that of a plane wave

$$\psi(\mathbf{x}, t) = e^{i\mathbf{k}\cdot\mathbf{x} - i\omega t}$$

where  $\omega = \frac{k^2}{2m}$ . This classical field equation can be derived from the action

$$S = \int dt d\mathbf{x} \mathcal{L} \quad \mathcal{L} = \psi^* \left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m}\right) \psi$$

We can even add a non-linear term in the action, for instance

$$\mathcal{L} = \psi^* \left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m}\right) \psi - \frac{1}{2}\gamma\psi^{*2}\psi^2$$

Variation method gives a non-linear field equation

$$\left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m} - \gamma\psi^*\psi\right)\psi(\mathbf{x}, t) = 0$$

Now we quantize the Schrödinger field by canonical quantization method. A more formal discussion on the motivation and validity of canonical quantization will be discussed in relativistic quantum field theory.

The canonically conjugate momenta is

$$\pi(\mathbf{x}) = \frac{\partial \mathcal{L}}{\partial \dot{\psi}(\mathbf{x})} = i\psi^\dagger(\mathbf{x})$$



We now introduce canonical commutation relation

$$[\psi(\mathbf{x}), \pi(\mathbf{y})] = i\delta(\mathbf{x} - \mathbf{y})$$

so

$$[\psi(\mathbf{x}), \psi^\dagger(\mathbf{y})] = \delta(\mathbf{x} - \mathbf{y})$$

We now regard  $\psi(\mathbf{x})$  as annihilation operator and  $\psi^\dagger(\mathbf{x})$  creation operator of a particle at position  $\mathbf{x}$ .

The Hamiltonian of the system is

$$H = \int d^3\mathbf{x} \left( -\psi^\dagger \frac{\nabla^2}{2m} \psi + \frac{1}{2} \gamma \psi^\dagger{}^2 \psi^2 \right)$$

We define the "vacuum"  $|0\rangle$  which is annihilated by the annihilation operator

$$\psi(\mathbf{x})|0\rangle = 0$$

and construct the Fock space by

$$|\mathbf{x}_1 \cdots \mathbf{x}_N\rangle = \psi^\dagger(\mathbf{x}_1) \cdots \psi^\dagger(\mathbf{x}_N)|0\rangle$$

The state  $|\mathbf{x}_1 \cdots \mathbf{x}_N\rangle$  is an n-particle state of identical bosons in the position eigenstate at  $\mathbf{x}_1 \cdots \mathbf{x}_N$ . We will verify this interpretation below explicitly.



# Chapter 3

## Scattering theory



### 3.1 Lippmann–Schwinger equation

Imagine a particle coming in and getting scattered by a short-ranged potential  $V(x)$  located around the origin  $x \sim 0$ . The time-independent Schrödinger equation is simply

$$(H_0 + V)|\psi\rangle = E|\psi\rangle$$

Here,  $H_0 = \frac{p^2}{2m}$  is the free-particle Hamiltonian operator. We can write the solution as

$$|\psi^{(\pm)}\rangle = \frac{1}{E - H_0 \pm i\epsilon} V |\psi^{(\pm)}\rangle + |\phi\rangle$$

Here,  $H_0|\phi\rangle = E|\phi\rangle$ . In coordinate representation,

$$\psi^{(\pm)}(\mathbf{x}) = \phi(\mathbf{x}) + \int d^3x' \langle \mathbf{x} | \frac{1}{E - H_0 \pm i\epsilon} | \mathbf{x}' \rangle V(\mathbf{x}') \psi^{(\pm)}(\mathbf{x}')$$

Here,  $\phi(\mathbf{x}) = \frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{(2\pi)^{\frac{3}{2}}}$ . Define the Green function as

$$G_{\pm}(\mathbf{x}, \mathbf{x}') \equiv \frac{1}{2m} \langle \mathbf{x} | \frac{1}{E - H_0 \pm i\epsilon} | \mathbf{x}' \rangle$$

We can derive that

$$G_{\pm}(\mathbf{x}, \mathbf{x}') = -\frac{1}{4\pi} \frac{e^{\pm ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x} - \mathbf{x}'|}$$

where  $k = \sqrt{2mE}$ . And it is easy to show that

$$(\nabla^2 + k^2)G_{\pm}(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}')$$

So, we have

$$\psi^{(\pm)}(\mathbf{x}) = \frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{(2\pi)^{\frac{3}{2}}} - 2m \int d^3x' \frac{1}{4\pi} \frac{e^{\pm ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x} - \mathbf{x}'|} V(\mathbf{x}') \psi^{(\pm)}(\mathbf{x}')$$

We now can interpret  $\psi^+(\mathbf{x})$  as a superposition of incident plane wave and scattered wave which propagate from scatterer to outside region. From now on, we will denote it as  $\psi(\mathbf{x})$ .

The experiment is done typically by placing the detector far away from the scatterer  $|\mathbf{x}| \ll a$  where  $a$  is the "size" of the scatterer. The integration over  $\mathbf{x}'$ , on the other hand, is limited within the "size" of the scatterer because of the  $V(\mathbf{x}')$  factor. Therefore, we are in the situation  $|\mathbf{x}| \ll |\mathbf{x}'|$ , and hence can use the approximation

$$|\mathbf{x} - \mathbf{x}'| \approx |\mathbf{x}| - \frac{\mathbf{x}' \cdot \mathbf{x}}{|\mathbf{x}|}$$

Under this limit,

$$\psi(\mathbf{x}) = \frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{(2\pi)^{\frac{3}{2}}} - 2m \frac{e^{ikr}}{4\pi r} \int d^3x' e^{-\mathbf{k}'\cdot\mathbf{x}'} V(\mathbf{x}') \psi(\mathbf{x}')$$

Here,  $r = |\mathbf{x}|$  and  $\mathbf{k}' = k \frac{\mathbf{x}}{r}$ . It is customary to write this equation in the form

$$\psi(\mathbf{x}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \left( e^{i\mathbf{k}\cdot\mathbf{x}} + f(\mathbf{k}, \mathbf{k}') \frac{e^{ikr}}{r} \right)$$

Here,

$$f(\mathbf{k}, \mathbf{k}') \equiv -\frac{m}{2\pi} (2\pi)^3 \langle \mathbf{k}' | V | \psi \rangle$$

Recall the definition of cross section

$$\sigma \equiv \frac{\text{Number of Events}}{\text{Time} \times \text{Incident Flux}}$$

So, the differential cross section for particles being scattered into the solid angle is

$$d\sigma = \frac{|\mathbf{j}_{\text{scatt}}| r^2 d\Omega}{|\mathbf{j}_{\text{inc}}|} = |f(\mathbf{k}, \mathbf{k}')|^2 d\Omega$$

In a more realistic situation, we should use wave packets to describe the scattering process. The basic picture is a free wave packet approaches the scattering center. After a long time, we have both the original wave packet moving in the original direction plus a spherical wave front that moves outward. The details can be found in the section 3 of the lecture notes *Scattering Theory I (Hitoshi Murayama)*.

Furthermore, if we require that the normalization of the wave function should always satisfy  $\int dx^3 |\psi(\mathbf{x})|^2$  for any  $t$ , as guaranteed by the unitarity of time evolution operator. This requirement leads to a special requirement on the scattered wave, and hence  $f(\mathbf{k}, \mathbf{k}')$ , from which we can derive the optical theorem.

### Theorem 3.1 Optical theorem

$$\text{Im} f(\theta = 0) = \frac{k\sigma_{\text{tot}}}{4\pi}$$

where

$$f(\theta = 0) \equiv f(\mathbf{k}, \mathbf{k}),$$

the setting of  $\mathbf{k} \equiv \mathbf{k}'$  imposes scattering in the forward direction, and

$$\sigma_{\text{tot}} = \int \frac{d\sigma}{d\Omega} d\Omega$$

The meaning of this theorem is clear. Because the scattered wave takes the probability away to different directions, the total probability for the particle to go to the forward direction (unscattered) should decrease. This decrease is caused by the interference between the unscattered and scattered waves and hence is proportional to  $f(0)$ . On the other hand, the amount of decrease in the forward direction should equal the total probability at other directions, which is proportional to the total cross section. The proof can be found in the section 4 of the lecture notes *Scattering Theory I (Hitoshi Murayama)*.



## 3.2 Born approximation

If  $|\psi\rangle = |\phi\rangle + O(V)$  is close to  $|\phi\rangle$ , we can solve the Lippmanmn-Schwinger equation by perturbation theory. The lowest order approximation in  $V$  is

$$|\psi\rangle = \frac{1}{E - H_0 + i\epsilon} V |\phi\rangle + |\phi\rangle$$

This is called Born approximation. In coordinate representation,

$$f^{(1)}(\mathbf{k}, \mathbf{k}') = -\frac{m}{2\pi} \int d^3x V(\mathbf{x}) e^{i\mathbf{q}\cdot\mathbf{x}}$$

Here,  $\mathbf{q} = |\mathbf{k} - \mathbf{k}'|$ . If the potential is central, we can derive that

$$f^{(1)}(\mathbf{k}, \mathbf{k}') = -\frac{2m}{q} \int_0^\infty dr r V(r) \sin(qr)$$

### Yukawa potential

$$V = \frac{\alpha}{r} e^{-\mu r}$$

So, we can derive

$$f(\theta) = -\frac{2m\alpha}{q^2 + \mu^2}$$

Different cross section is therefore given by

$$\frac{d\sigma}{d\Omega} = (2m\alpha)^2 \frac{1}{[2k^2(1 - \cos\theta) + \mu^2]^2}$$

The total cross section is obtained by integrating over  $d\Omega$ ,

$$\sigma = (2m\alpha)^2 \frac{4\pi}{4k^2\mu^2 + \mu^4}$$

### Coulomb potential

$$V = \frac{\alpha}{r}$$

Take the limit  $\mu \rightarrow 0$ , we can get

$$f(\theta) = -\frac{2m\alpha}{q^2}$$

Different cross section is given by

$$\frac{d\sigma}{d\Omega} = \left(\frac{\alpha}{4E}\right)^2 \frac{1}{\sin^4 \frac{\theta}{2}}$$

The total cross section diverges. The divergence is in the  $\cos\theta$  integral when  $\theta \rightarrow 0$ . In other words, the divergence occurs for the small momentum transfer  $q \rightarrow 0$ , which corresponds to large distances. The reason why the total cross section diverges is because the Coulomb potential is actually a long-range force. No matter how far the incident particles are from the charge, there is always an effect on the motion of the particles and they get scattered.





### Form factor

If the source of Coulomb potential has an distribution  $\rho_N(\mathbf{x})$ , then

$$V(\mathbf{x}) = \int d^3x' \frac{\alpha}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}')$$

Note that the potential is mathematically a convolution of the Coulomb potential and the probability density. Since the first Born amplitude is nothing but the Fourier transform of the potential, the convolution becomes a product of Fourier transforms, one for the Coulomb potential and the other for the probability density. So

$$f(\theta) = f(\theta)_{\text{pointlike}} F(q)$$

Here,

$$F(q) \equiv \int d^3x \rho_N(\mathbf{x}) e^{i\mathbf{q} \cdot \mathbf{x}},$$

being called form factor.

### Born expansion

Define T-matrix by

$$V|\psi\rangle = T|\phi\rangle$$

Using the definition of the T-matrix, we find

$$f(\mathbf{k}, \mathbf{k}') = -\frac{m}{2\pi} (2\pi)^3 \langle \mathbf{k}' | T | \mathbf{k} \rangle$$

Using the Lippmann–Schwinger equation and multiplying the both sides by  $V$  from left, we find

$$T|\phi\rangle = V \frac{1}{E - H_0 + i\epsilon} T|\phi\rangle + V|\phi\rangle$$

A formal solution to the T-matrix is

$$T = \frac{1}{1 - V \frac{1}{E - H_0 + i\epsilon}} V$$

By Taylor expanding this operator in geometric series, we find

$$T = V + V \frac{1}{E - H_0 + i\epsilon} V + V \frac{1}{E - H_0 + i\epsilon} V \frac{1}{E - H_0 + i\epsilon} V + \dots$$

So,

$$|\psi\rangle = \left( 1 + \frac{1}{E - H_0 + i\epsilon} V + \frac{1}{E - H_0 + i\epsilon} V \frac{1}{E - H_0 + i\epsilon} V + \dots \right) |\phi\rangle$$

The first term is the wave which did not get scattered. The second term is the wave that gets scattered at a point in the potential and then propagates outwards by the propagator. In the third term, the wave gets scattered at a point in the potential, propagates for a while, and gets scattered again at another point in the potential, and propagates outwards. In the  $n + 1$ -th term, there are  $n$  times scattering of the wave before it propagates outwards.



### 3.3 Partial wave analysis

#### Partial wave expansion

When the potential is **central**, angular momentum is conserved due to Noether's theorem. Therefore, we can expand the wave function in the eigenstates of the angular momentum. Obtained waves with definite angular momenta are called partial waves. We can solve the scattering problem for each partial wave separately, and then in the end put them together to obtain the full scattering amplitude. The plane wave can be expanded as follows.

$$e^{ikz} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\cos \theta)$$

Here,  $j_l(kr)$  is spherical Bessel functions of first kind. The asymptotic behaviour of  $j_l(kr)$  at large  $r$  can be written as

$$j_l(kr) \sim \frac{\sin(kr - \frac{l\pi}{2})}{kr}$$

so,

$$e^{ikz} \sim \frac{1}{2ikr} \sum_{l=0}^{\infty} (2l+1) (e^{ikr} - (-1)^l e^{-ikr}) P_l(\cos \theta)$$

Meanwhile, the  $f$  factor can be expanded as

$$f(\theta) = \sum_{l=0}^{\infty} f_l (2l+1) P_l(\cos \theta)$$

#### Optical theorem constraint

The cross section can be represented by expansion coefficient of  $f$  factor as

$$\sigma = 4\pi \sum_l (2l+1) |f_l|^2$$

On the other hand,

$$\text{Im} f(0) = \sum_l (2l+1) \text{Im} f_l$$

From optical theorem we can derive that

$$|f_l|^2 = \frac{1}{k} \text{Im} f_l$$

This constraint can be rewritten as

$$|1 + 2ikf_l|^2 = 1$$

So we can define a phase  $\delta_l$  as

$$1 + 2ikf_l = e^{i\delta_l}$$

or equivalently,

$$f_l = \frac{1}{k} e^{i\delta_l} \sin(\delta_l)$$



### Phase shifts

We can derive the asymptotic behaviour of the wave function as

$$\psi(\mathbf{x}) \sim \frac{1}{2ikr} \sum_l (2l+1) P_l(\cos \theta) [e^{ikr} e^{2i\delta_l} - (-1)^l e^{-ikr}]$$

Compare it to the case of the plane wave without scattering. What this equation says is that the wave converging on the scatterer has the well-defined phase factor  $-(-1)^l$ , the same as in the case without scattering. On the other hand, the wave that emerges from the scatterer has an additional phase factor  $e^{2i\delta_l}$ . All what scattering did is to shift the phase of the emerging wave by  $2\delta_l$ . The reason why this is merely a phase factor is the conservation of probability. What converged to the origin must come out with the same strength. But this shift in the phase causes the interference among all partial waves different from the case without the phase shifts, and the result is not a plane wave but contains the scattered wave.

In terms of the phase shifts, the cross section is given by

$$\sigma = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \delta_l$$

Actual calculation of phase shifts is basically to solve the Schrödinger equation for each partial waves,

$$\left[ -\frac{1}{r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{r^2} + 2mV(r) \right] R_l(r) = k^2 R_l(r)$$

After solving the equation, we take the asymptotic limit  $r \rightarrow \infty$ , and write  $R_l(r)$  as a linear combination of  $j_l(kr) \cos \delta_l + n_l(kr) \sin \delta_l$ . The relative coefficients of  $j_l$  and  $n_l$  determines the phase shift  $\delta_l$ , and hence the cross section.

