Quantum Mechanics

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VI. Approximation Methods

6.1 Perturbation Theory

6.1.1 Time-Independent Perturbation Theory: Non-Degenerate Case

The Time-independent perturbation theory is also called the Rayleigh-Schrödinger perturbation theory. Consider a time-independent Hamiltonian H split into two parts:

$$H = H_0 + V\,, \tag{6.1}$$

where the $V = 0$ case is assumed to have been solved:

$$H_0 \left| n^{(0)} \right\rangle = E_n^0 \left| n^{(0)} \right\rangle, \tag{6.2}$$

and V is the **perturbation**. We need to find the approximate solutions based on the $V = 0$ case for the full Hamiltonian:

$$\left(H_0 + V \right) \left| n \right\rangle = E_n \left| n \right\rangle. \tag{6.3}$$

It is customary to solve

$$\left(H_0 + \lambda V \right) \left| n \right\rangle_\lambda = E_n^\lambda \left| n \right\rangle_\lambda \tag{6.4}$$

with $\lambda \in [0,1]$, whose notation is simplified as

$$\left(H_0 + \lambda V \right) \left| n \right\rangle = E_n \left| n \right\rangle. \tag{6.5}$$

Define the energy shift for the nth level

$$\Delta_n \equiv E_n - E_n^{(0)}, \tag{6.6}$$

then Eq. (6.4) can be written as

$$\left(E_n^{(0)} - H_0 \right) \left| n \right\rangle = \left(\lambda V - \Delta_n \right) \left| n \right\rangle. \tag{6.7}$$

By multiplying both sides by $\left\langle n^{(0)} \right|$ on the left, we have

$$\left\langle n^{(0)} \right| \left(\lambda V - \Delta_n \right) \left| n \right\rangle = 0, \tag{6.8}$$

indicating that $\left(\lambda V - \Delta_n \right) \left| n \right\rangle$ has no component along $\left| n^{(0)} \right\rangle$. Define the complementary projection operator

$$\phi_n \equiv 1 - \left| n^{(0)} \right\rangle \left\langle n^{(0)} \right| = \sum_{k \neq n} \left| k^{(0)} \right\rangle \left\langle k^{(0)} \right|, \tag{6.9}$$

then

$$\frac{1}{E_n^{(0)} - H_0} \phi_n = \sum_{k \neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}} \left| k^{(0)} \right\rangle \left\langle k^{(0)} \right|. \tag{6.10}$$

Also from Eq. (6.8) and Eq. (6.9), it is evident that

$$\left(\lambda V - \Delta_n \right) |n\rangle = \phi_n \left(\lambda V - \Delta_n \right) |n\rangle . \tag{6.11}$$

We may therefore guess a final form of suitable solution

$$|n\rangle = c_n(\lambda) \left| n^{(0)} \right\rangle + \frac{1}{E_n^{(0)} - H_0} \phi_n \left(\lambda V - \Delta_n \right) |n\rangle , \tag{6.12}$$

where

$$c_n(\lambda) = \left\langle n^{(0)} \middle| n \right\rangle, \quad \lim_{\lambda \to 0} c_n(\lambda) = 1 . \tag{6.13}$$

If we set

$$c_n(\lambda) = \left\langle n^{(0)} \middle| n \right\rangle = 1 \tag{6.14}$$

for all λ, Eq. (6.12) becomes

$$|n\rangle = \left| n^{(0)} \right\rangle + \frac{\phi_n}{E_n^{(0)} - H_0} \left(\lambda V - \Delta_n \right) |n\rangle . \tag{6.15}$$

According to Eq. (6.8) and Eq. (6.14), we also have

$$\Delta_n = \lambda \left\langle n^{(0)} \middle| V \middle| n \right\rangle . \tag{6.16}$$

By expanding

$$\begin{aligned} |n\rangle &= \left| n^{(0)} \right\rangle + \lambda \left| n^{(1)} \right\rangle + \lambda^2 \left| n^{(2)} \right\rangle + \cdots \\ \Delta_n &= \lambda \Delta_n^{(1)} + \lambda \Delta_n^{(2)} + \cdots \end{aligned} , \tag{6.17}$$

We obtain from Eq. (6.16) the energy shifts at different levels:

$$\begin{aligned} &\mathrm{O}\left(\lambda^1\right): && \Delta_n^{(1)} = \left\langle n^{(0)} \middle| V \middle| n^{(0)} \right\rangle \\ &\mathrm{O}\left(\lambda^2\right): && \Delta_n^{(2)} = \left\langle n^{(0)} \middle| V \middle| n^{(1)} \right\rangle \\ &\quad\vdots && \qquad\vdots \\ &\mathrm{O}\left(\lambda^N\right): && \Delta_n^{(N)} = \left\langle n^{(0)} \middle| V \middle| n^{(N-1)} \right\rangle \\ &\quad\vdots && \qquad\vdots \end{aligned} . \tag{6.18}$$

Therefore, only knowing $|n\rangle$ up to order λ^{N-1} is necessary to evaluate the energy shift up to order λ^N. Moreover, we obtain from Eq. (6.15) the perturbed kets:

$$\begin{aligned} &\left| n^{(0)} \right\rangle + \lambda \left| n^{(1)} \right\rangle + \lambda^2 \left| n^{(2)} \right\rangle + \cdots = \left| n^{(0)} \right\rangle + \frac{\phi_n}{E_n^{(0)} - H_0} \left(\lambda V - \lambda \Delta_n^{(1)} - \lambda^2 \Delta_n^{(2)} - \cdots \right) \\ &\times \left(\left| n^{(0)} \right\rangle + \lambda \left| n^{(1)} \right\rangle + \cdots \right) \end{aligned} . \tag{6.19}$$

Equating the first order of λ, and using $\phi_n \Delta_n^{(1)} \left| n^{(0)} \right\rangle = 0$, we have

$$\left| n^{(1)} \right\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V \left| n^{(0)} \right\rangle , \tag{6.20}$$

which leads to

$$\Delta_n^{(2)} = \left\langle n^{(0)} \right| V \frac{\phi_n}{E_n^{(0)} - H_0} V \left| n^{(0)} \right\rangle . \tag{6.21}$$

We can then obtain

$$\begin{aligned} \left| n^{(2)} \right\rangle &= \frac{\phi_n}{E_n^{(0)} - H_0} V \frac{\phi_n}{E_n^{(0)} - H_0} V \left| n^{(0)} \right\rangle \\ &- \frac{\phi_n}{E_n^{(0)} - H_0} \left\langle n^{(0)} \right| V \left| n^{(0)} \right\rangle \frac{\phi_n}{E_n^{(0)} - H_0} V \left| n^{(0)} \right\rangle \end{aligned} . \tag{6.22}$$

Overall, the explicit **expansion for the energy shift** is

$$\Delta_n \equiv E_n - E_n^{(0)} = \lambda V_{nn} + \lambda^2 \sum_{k \neq n} \frac{\left| V_{nk} \right|^2}{E_n^{(0)} - E_k^{(0)}} + \cdots , \tag{6.23}$$

where

$$V_{nk} \equiv \left\langle n^{(0)} \right| V \left| k^{(0)} \right\rangle \neq \left\langle n \right| V \left| k \right\rangle . \tag{6.24}$$

The **expansion of the perturbed ket** is:

$$\begin{aligned} \left| n \right\rangle &= \left| n^{(0)} \right\rangle + \lambda \sum_{k \neq n} \left| k^{(0)} \right\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \\ &+ \lambda^2 \left(\sum_{k \neq n} \sum_{l \neq n} \frac{\left| k^{(0)} \right\rangle V_{kl} V_{\mathrm{ln}}}{\left(E_n^{(0)} - E_k^{(0)} \right) \left(E_n^{(0)} - E_l^{(0)} \right)} - \sum_{k \neq n} \frac{\left| k^{(0)} \right\rangle V_{nn} V_{k\mathrm{n}}}{\left(E_n^{(0)} - E_k^{(0)} \right)^2} \right) + \cdots \end{aligned} \tag{6.25}$$

Due to Eq. (6.14), the perturbed ket $\left| n \right\rangle$ is not normalized. It can be renormalized by defining

$$\left| n \right\rangle_N = \sqrt{Z_n} \left| n \right\rangle , \tag{6.26}$$

where Z_n is a constant determined by ${}_N\left\langle n | n \right\rangle_N = 1$. Multiplying $\left\langle n^{(0)} \right|$ on the left, we obtain

$$\sqrt{Z_N} = \left\langle n^{(0)} \middle| n \right\rangle_N , \tag{6.27}$$

indicating that Z_n is the probability for the perturbed energy eigenstates to be found in the corresponding unperturbed energy eigenstates. Since

$${}_N\left\langle n | n \right\rangle_N = Z_N \left\langle n | n \right\rangle = 1 , \tag{6.28}$$

we have

$$
\begin{aligned}
Z_n^{-1} &= \langle n | n \rangle = \left(\langle n^{(0)} | + \lambda \langle n^{(1)} | + \lambda^2 \langle n^{(2)} | + \cdots \right) \times \left(| n^{(0)} \rangle + \lambda | n^{(1)} \rangle + \lambda^2 | n^{(2)} \rangle + \cdots \right) \\
&= 1 + \lambda^2 \langle n^{(1)} | n^{(1)} \rangle + O(\lambda^3) \\
&= 1 + \lambda^2 \sum_{k \neq n} \frac{|V_{kn}|^2}{\left(E_n^{(0)} - E_k^{(0)} \right)^2} + O(\lambda^3)
\end{aligned} \quad . \tag{6.29}
$$

Therefore, up to order λ^2, we get

$$
Z_n \simeq 1 - \lambda^2 \sum_{k \neq n} \frac{|V_{kn}|^2}{\left(E_n^{(0)} - E_k^{(0)} \right)^2} . \tag{6.30}
$$

According to Eq. (6.23), we have

$$
Z_n = \frac{\partial E_n}{\partial E_n^{(0)}} , \tag{6.31}
$$

which is a general relation not restricted to second-order perturbation theory.

Example 1: For a simple harmonic oscillator with the unperturbed Hamiltonian

$$
H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 , \tag{6.32}
$$

Suppose the spring constant $k = m\omega^2$ is changed slightly:

$$
V = \frac{1}{2} \varepsilon m\omega^2 x^2 , \tag{6.33}
$$

where $\varepsilon \ll 1$ is a dimensionless parameter. The exact solution of the new system can be easily obtained by

$$
\omega \to \sqrt{1+\varepsilon}\omega . \tag{6.34}
$$

Here just use it to show the basic procedures of the perturbation theory.

According to the perturbation theory, the new ground-state ket $|0\rangle$ and the ground-state energy shift Δ_0 are

$$
|0\rangle = |0^{(0)}\rangle + \sum_{k \neq 0} |k^{(0)}\rangle \frac{V_{k0}}{E_0^{(0)} - E_k^{(0)}} + \cdots \tag{6.35}
$$

and

$$
\Delta_0 = V_{00} + \sum_{k \neq 0} \frac{|V_{k0}|^2}{E_0^{(0)} - E_k^{(0)}} + \cdots . \tag{6.36}
$$

It can be shown that

$$
\begin{aligned}
V_{00} &= \left(\frac{\varepsilon m\omega^2}{2} \right) \langle 0^{(0)} | x^2 | 0^{(0)} \rangle = \frac{\varepsilon \hbar \omega}{4} \\
V_{20} &= \left(\frac{\varepsilon m\omega^2}{2} \right) \langle 2^{(0)} | x^2 | 0^{(0)} \rangle = \frac{\varepsilon \hbar \omega}{2\sqrt{2}}
\end{aligned} \tag{6.37}
$$

and all other V_{k0} vanish. Noting that corresponding non-vanishing $E_0^{(0)} - E_k^{(0)} = -2\hbar\omega$ in Eq. (6.35) and Eq. (6.36), we obtain

$$\left|0\right\rangle = \left|0^{(0)}\right\rangle - \frac{\varepsilon}{4\sqrt{2}}\left|2^{(0)}\right\rangle + O\left(\varepsilon^2\right) \tag{6.38}$$

and

$$\Delta_0 \equiv E_0 - E_0^{(0)} = \hbar\omega\left[\frac{\varepsilon}{4} - \frac{\varepsilon^2}{16} + O\left(\varepsilon^3\right)\right]. \tag{6.39}$$

For the exact method, the energy shift is

$$\frac{\hbar\omega}{2} \to \frac{\hbar\omega}{2}\sqrt{1+\varepsilon} = \frac{\hbar\omega}{2}\left(1 + \frac{\varepsilon}{2} - \frac{\varepsilon^2}{8} + \cdots\right), \tag{6.40}$$

which completely agrees with Eq. (6.39); the ground-state wave function is

$$\left\langle x \middle| 0^{(0)}\right\rangle = \frac{1}{\pi^{1/4}}\frac{1}{\sqrt{x_0}}\exp\left(-\frac{x^2}{2x_0^2}\right) \tag{6.41}$$

with

$$x_0 \equiv \sqrt{\frac{\hbar}{m\omega}} \to \frac{1}{\left(1+\varepsilon^{1/4}\right)}\sqrt{\frac{\hbar}{m\omega}}, \tag{6.42}$$

so

$$\begin{aligned} \left\langle x \middle| 0^{(0)}\right\rangle &\to \frac{1}{\pi^{1/4}}\frac{1}{\sqrt{x_0}}\left(1+\varepsilon\right)^{1/8}\exp\left(-\left(\frac{x^2}{2x_0^2}\right)\left(1+\varepsilon\right)^{1/2}\right) \\ &\simeq \frac{1}{\pi^{1/4}}\frac{1}{\sqrt{x_0}}\exp\left(-\frac{x^2}{2x_0^2}\right) + \frac{\varepsilon}{\pi^{1/4}\sqrt{x_0}}\exp\left(-\frac{x^2}{2x_0^2}\right)\left(\frac{1}{8} - \frac{1}{4}\frac{x^2}{x_0^2}\right), \\ &= \left\langle x \middle| 0^{(0)}\right\rangle - \frac{\varepsilon}{4\sqrt{2}}\left\langle x \middle| 2^{(0)}\right\rangle \end{aligned} \tag{6.43}$$

where we have used

$$\left\langle x \middle| 2^{(0)}\right\rangle = \frac{1}{2\sqrt{2}}\left\langle x \middle| 0^{(0)}\right\rangle H_2\left(\frac{x}{x_0}\right) = \frac{1}{2\sqrt{2}}\frac{1}{\pi^{1/4}}\frac{1}{\sqrt{x_0}}\exp\left(-\frac{x^2}{2x_0^2}\right)\left[-2 + 4\left(\frac{x}{x_0}\right)^2\right]. \tag{6.44}$$

Example 2: The **quadratic Stark effect**. One valence electron with a negative charge of *e* outside the closed (spherically symmetrical) shell in an atom is subjected to a uniform electric field in the positive *z*-direction. The Hamiltonian

$$H = H_0 + V \tag{6.45}$$

with

$$H_0 = \frac{\mathbf{p}^2}{2m} + V_0\left(r\right) \tag{6.46}$$

and

$$V = -e\left|\mathbf{E}\right|z\,. \tag{6.47}$$

The electron spin turns out to be irrelevant in this problem and we assume that no energy level is degenerate. The energy shift is given by

$$\Delta_k = -e|\mathbf{E}| z_{kk} + e^2 |\mathbf{E}|^2 \sum_{j\neq k} \frac{|z_{kj}|^2}{E_k^{(0)} - E_j^{(0)}} + \cdots . \qquad (6.48)$$

With no degeneracy, $\left|k^{(0)}\right\rangle$ is a parity eigenstate, so

$$z_{kk} = 0 . \qquad (6.49)$$

Physically speaking, there can be no linear Stark effect—that is, there is no term in the energy shift proportional to $|\mathbf{E}|$ because the atom possesses a vanishing permanent electric dipole. So the energy shift is *quadratic* in $|\mathbf{E}|$ if terms of order $e^3|\mathbf{E}|^3$ or higher is ignored.

Let us now look at z_{kj}, where *k* or *j* is the collective index standing for (n,l,m). L_z is still a good quantum number since *V* is still invariant under rotation around the *z*-axis. Because the selection rule from angular momentum is

$$\langle n', l', m' | z | n, l, m \rangle = 0 \qquad (6.50)$$

unless $l' = l \pm 1$ and $m' = m$, and the second-order energy shift is obtained from the first-order ket (see Eq. (6.21)), only the $m = 0$ terms contribute to the sum.

The polarizability α of an atom is defined as

$$\Delta = -\frac{1}{2}\alpha|\mathbf{E}|^2 . \qquad (6.51)$$

Since the ground state $\left|0^{(0)}\right\rangle = |n=1, l=0, m=0\rangle$ with spin ignored is nondegenerate, we have

$$\alpha = -2e^2 \sum_{k\neq 0}^{\infty} \frac{\left|\left\langle k^{(0)} \right| z |1,0,0\rangle\right|^2}{E_0^{(0)} - E_k^{(0)}} , \qquad (6.52)$$

where the sum over *k* includes not only all bound states but also the positive-energy continuum states of hydrogen.

If the denominator in the above equation were constant, we could obtain the sum by applying the completeness relation:

$$\sum_{k\neq 0}^{\infty} \left|\left\langle k^{(0)} \right| z |1,0,0\rangle\right|^2 = \sum_{\text{all } k} \left|\left\langle k^{(0)} \right| z |1,0,0\rangle\right|^2 = \langle 1,0,0| z^2 |1,0,0\rangle . \qquad (6.53)$$

For the ground state, we have

$$\langle z^2 \rangle = \langle x^2 \rangle = \langle y^2 \rangle = \frac{1}{3}\langle r^2 \rangle , \qquad (6.54)$$

and

$$\langle r^2 \rangle = 3a_0^2 . \qquad (6.55)$$

where a_0 is the Bohr radius. Put the inequality

$$-E_0^{(0)} + E_k^{(0)} \geq -E_0^{(0)} + E_1^{(0)} = \frac{3e^2}{8a_0} \qquad (6.56)$$

into Eq. (6.52), we obtain the upper limit for the polarizability of the ground state

$$\alpha < \frac{16a_0^3}{3} \simeq 5.3a_0^3. \tag{6.57}$$

Other methods can give the exact value agreeing with the experimental value:

$$\alpha = \frac{9a_0^3}{2} = 4.5a_0^3. \tag{6.58}$$

6.1.2 Time-Independent Perturbation Theory: Degenerate Case

For the degenerate case, the term

$$\frac{V_{nk}}{E_n^{(0)} - E_k^{(0)}} \tag{6.59}$$

in Eq. (6.23) and Eq. (6.25) becomes singular if V_{nk} is nonvanishing and $E_n^{(0)}$ and $E_k^{(0)}$ are equal.

Suppose there are *g* different eigenkets $\left\{\left|m^{(0)}\right\rangle\right\}$ with the same unperturbed energy $E_D^{(0)}$ before the perturbation *V* is switched on. Generally the perturbation removes the degeneracy by generating *g* perturbed eigenkets $\{|l\rangle\}$ with different energies. However, $\left\{\left|l^{(0)}\right\rangle\right\}$ corresponding to $\lambda \to 0$ need not coincide with $\left\{\left|m^{(0)}\right\rangle\right\}$ even though they span the same degenerate subspace *D*. We can write

$$\left|l^{(0)}\right\rangle = \sum_{m\in D} \left\langle m^{(0)} \middle| l^{(0)} \right\rangle \left|m^{(0)}\right\rangle. \tag{6.60}$$

Let P_0 be a projection operator onto the space defined by $\left\{\left|m^{(0)}\right\rangle\right\}$ and $P_1 = 1 - P_0$ be the projection on the remaining states, The Schrödinger equation for $|l\rangle$ can be written as

$$\begin{aligned} 0 &= \left(E - H_0 - \lambda V\right)|l\rangle \\ &= \left(E - E_D^{(0)} - \lambda V\right) P_0 |l\rangle + \left(E - H_0 - \lambda V\right) P_1 |l\rangle \end{aligned}, \tag{6.61}$$

which becomes two equations by projecting from the left with P_0 and P_1:

$$\left(E - E_D^{(0)} - \lambda P_0 V\right) P_0 |l\rangle - \lambda P_0 V P_1 |l\rangle = 0 \tag{6.62}$$

and

$$-\lambda P_1 V P_0 |l\rangle + \left(E - H_0 - \lambda P_1 V\right) P_1 |l\rangle = 0. \tag{6.63}$$

From Eq. (6.63), we obtain

$$P_1 |l\rangle = P_1 \frac{\lambda}{E - H_0 - \lambda P_1 V P_1} P_1 V P_0 |l\rangle. \tag{6.64}$$

By expanding $|l\rangle = \left|l^{(0)}\right\rangle + \lambda \left|l^{(1)}\right\rangle + \cdots$, we have

$$P_1\left|l^{(1)}\right\rangle = \sum_{k\notin D}\frac{\left|k^{(0)}\right\rangle V_{kl}}{E_D^{(0)}-E_k^{(0)}}. \tag{6.65}$$

To calculate $P_0\left|l\right\rangle$, we substitute Eq. (6.64) into Eq. (6.62) to obtain

$$\left(E-E_D^{(0)}-\lambda P_0VP_0-\lambda^2P_0VP_1\frac{P_1VP_0}{E-H_0-\lambda V}\right)P_0\left|l\right\rangle = 0, \tag{6.66}$$

which for $\left|l^{(0)}\right\rangle$ leads to

$$\left(E-E_D^{(0)}-\lambda P_0VP_0\right)P_0\left|l^{(0)}\right\rangle = 0. \tag{6.67}$$

Therefore, the eigenvectors are just the eigenvectors of the $g\times g$ matrix P_0VP_0 and the eigenvalues $E^{(1)}$ are just the roots of the secular equation

$$\det\left[V-\left(E-E_D^{(0)}\right)\right]=0. \tag{6.68}$$

Explicitly, in matrix form we have

$$\begin{pmatrix} V_{11} & V_{12} & \cdots \\ V_{21} & V_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix}\left\langle 1^{(0)}\middle|l^{(0)}\right\rangle \\ \left\langle 2^{(0)}\middle|l^{(0)}\right\rangle \\ \vdots\end{pmatrix} = \Delta_l^{(1)}\begin{pmatrix}\left\langle 1^{(0)}\middle|l^{(0)}\right\rangle \\ \left\langle 2^{(0)}\middle|l^{(0)}\right\rangle \\ \vdots\end{pmatrix}, \tag{6.69}$$

where $V_{mm'}=\left\langle m^{(0)}\right|V\left|m'^{(0)}\right\rangle$. From the above equation we simultaneously obtain $\Delta_l^{(1)}$ and $\left|l^{(0)}\right\rangle$, and

$$\Delta_l^{(1)}=\left\langle l^{(0)}\right|V\left|l^{(0)}\right\rangle. \tag{6.70}$$

Now Eq. (6.66) can be written as

$$\left(E-E_D^{(0)}-\lambda P_0VP_0-\lambda^2P_0VP_1\frac{P_1VP_0}{E_D^{(0)}-H_0}\right)P_0\left|l\right\rangle = 0. \tag{6.71}$$

Denote the eigenvalues of the $g\times g$ matrix P_0VP_0 to be $\{v_i\}$ and the eigenvectors to be $\left\{P_0\left|l_i^{(0)}\right\rangle\right\}$. The eigen energies to the first order are

$$E_i^{(1)}=E_D^{(0)}+\lambda v_i, \tag{6.72}$$

and we assume that the degeneracy is completely revolved so that $E_i^{(1)}-E_j^{(1)}=\lambda\left(v_i-v_j\right)$ are all nonzero. We can now apply the nondegenerate result of Eq. (6.20) to obtain

$$P_0\left|l_i^{(1)}\right\rangle=\sum_{j\neq i}\lambda\frac{P_0\left|l_j^{(0)}\right\rangle}{v_j-v_i}\left\langle l_j^{(0)}\right|VP_1\frac{1}{E_D^{(0)}-H_0}P_1V\left|l_i^{(0)}\right\rangle \tag{6.73}$$

or more explicitly

$$P_0\left|l_i^{(1)}\right\rangle = \sum_{j\neq i}\lambda \frac{P_0\left|l_j^{(0)}\right\rangle}{v_j - v_i}\sum_{k\notin D}\left\langle l_j^{(0)}\right|V\left|k\right\rangle \frac{1}{E_D^{(0)} - E_k^{(0)}}\left\langle k\right|V\left|l_i^{(0)}\right\rangle. \tag{6.74}$$

Together with Eq. (6.65), the above equation give the eigenvector accurate to order λ.

It is convenient to adopt the normalization convention

$$\left\langle l^{(0)}\middle| l\right\rangle = 1. \tag{6.75}$$

According to Eq. (6.62) and Eq. (6.63), we have

$$\lambda\left\langle l^{(0)}\right|V\left|l\right\rangle = \Delta_l = \lambda\Delta_l^{(1)} + \lambda^2\Delta_l^{(2)} + \cdots, \tag{6.76}$$

where the λ-term is just Eq. (6.70), and the λ^2-term is

$$\Delta_l^{(2)} = \left\langle l^{(0)}\right|V\left|l^{(1)}\right\rangle = \left\langle l^{(0)}\right|V\left|P_1 l^{(1)}\right\rangle + \left\langle l^{(0)}\right|V\left|P_0 l_i^{(1)}\right\rangle. \tag{6.77}$$

Since $\left|P_0 l_i^{(1)}\right\rangle$ are eigenvectors of *V*, the correction in Eq. (6.74) gives no contribution to the second-order energy shift, so by using Eq. (6.65), we find

$$\Delta_l^{(2)} = \sum_{k\notin D}\frac{\left|V_{kl}\right|^2}{E_D^{(0)} - E_k^{(0)}}. \tag{6.78}$$

In summary, the basic procedure of degenerate perturbation theory is:

(1) Construct the $g\times g$ perturbation matrix *V*.

(2) Diagonalize the perturbation matrix by solving the appropriate secular equation.

(3) Identify the roots of the secular equation with the first-order energy shifts; the base kets that diagonalize the *V* matrix are the zeroth-order kets in the limit $\lambda\to 0$.

(4) For higher orders, use the formulas of the corresponding nondegenerate perturbation theory except in the summations, where all contributions from the unperturbed kets in the degenerate subspace *D* are excluded.

Example: Linear Stark Effect. For a hydrogen atom, all excited states are degenerate because

$$0\le l < n. \tag{6.79}$$

For $n=2$, there are one 2*s* state ($l=0, m=0$) and three 2*p* states ($l=1, m=0,\pm1$), all with the same energy $-e^2/8a_0$. As a uniform electric field is applied in the *z*-direction:

$$V = -ez\left|\mathbf{E}\right|, \tag{6.80}$$

the matrix elements are nonvanishing only between states of opposite parity—$l=1$ and $l=0$, and also $m=0$ because of the symmetry of *z*. The only nonvanishing terms are

$$\left\langle 2s\right|V\left|2p, m=0\right\rangle = \left\langle 2p, m=0\right|V\left|2s\right\rangle = 3ea_0\left|\mathbf{E}\right|, \tag{6.81}$$

so the matrix is

$$V = \begin{array}{c} \\ \\ \\ \\ \end{array} \begin{matrix} 2s & 2p,m=0 & 2p,m=1 & 2p,m=-1 \end{matrix}$$

$$V = \begin{pmatrix} 0 & 3ea_0|\mathbf{E}| & 0 & 0 \\ 3ea_0|\mathbf{E}| & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} . \tag{6.82}$$

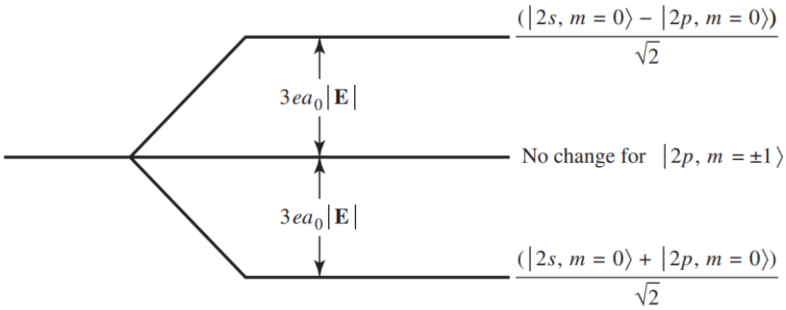
The energy shifts are then

$$\Delta_{\pm}^{(1)} = \pm 3ea_0|\mathbf{E}| , \tag{6.83}$$

where

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(|2s, m=0\rangle \pm |2p, m=0\rangle\right) . \tag{6.84}$$

The schematic energy-level diagram is shown below.



Schematic energy-level diagram for the linear Stark effect as an example of degenerate perturbation theory.

Generally, for an energy state which can be written as a superposition of opposite parity states, it is permissible to have a nonvanishing permanent electric dipole moment, which gives rise to the **linear Stark effect**.

6.2 Hydrogen-Like Atoms

6.2.1 The Relativistic Correction to the Kinetic Energy

A hydrogen-like atom with a single electron has the nonrelativistic Hamiltonian

$$H_0 = \frac{\mathbf{p}^2}{2m_e} - \frac{Ze^2}{r} . \tag{6.85}$$

For the relativistic case, the kinetic energy changes to

$$K = \sqrt{\mathbf{p}^2c^2 + m_e^2c^4} - m_ec^2 \approx \frac{\mathbf{p}^2}{2m_e} - \frac{\left(\mathbf{p}^2\right)^2}{8m_e^3c^2} . \tag{6.86}$$

Therefore, we may treat it with the perturbation

$$V = -\frac{\left(\mathbf{p}^2\right)^2}{8m_e^3c^2} . \tag{6.87}$$

Because $\left[\mathbf{L},\mathbf{p}^2\right]=0$, we also have

$$\left[\mathbf{L},V\right]=0, \tag{6.88}$$

so V is rotationally symmetrical and already diagonal in the $|nlm\rangle$ basis. Following Eq. (6.18), we write

$$\Delta_{nl}^{(1)}=\langle nlm|V|nlm\rangle=-\langle nlm|\frac{\left(\mathbf{p}^2\right)^2}{8m_e^3c^2}|nlm\rangle. \tag{6.89}$$

Because

$$\frac{\left(\mathbf{p}^2\right)^2}{8m_e^3c^2}=\frac{1}{2m_ec^2}\left(\frac{\mathbf{p}^2}{2m_e}\right)^2=\frac{1}{2m_ec^2}\left(H_0+\frac{Ze^2}{r}\right)^2, \tag{6.90}$$

Eq. (6.89) can be written as

$$\Delta_{nl}^{(1)}=-\frac{1}{2m_ec^2}\left[\left(E_n^{(0)}\right)^2+2E_n^{(0)}\langle nlm|\frac{Ze^2}{r}|nlm\rangle+\langle nlm|\left(\frac{Ze^2}{r}\right)^2|nlm\rangle\right]. \tag{6.91}$$

The second term at the RHS is just the potential term in Eq. (6.85). According to the virial theorem for the Coulomb potential ($\langle E_{\mathrm{k}}\rangle=-\frac{1}{2}\langle E_{\mathrm{p}}\rangle$), we have

$$\langle nlm|\frac{Ze^2}{r}|nlm\rangle=-2E_n^{(0)}. \tag{6.92}$$

Considering $\left(\frac{Ze^2}{r}\right)^2$ as a perturbation to the Hamiltonian Eq. (6.85), which can be also solved exactly, from the first-order correction, we then obtain

$$\langle nlm|\frac{\left(Ze^2\right)^2}{r^2}|nlm\rangle=\frac{4n}{l+\frac{1}{2}}\left(E_n^{(0)}\right)^2. \tag{6.93}$$

Since $E_n^{(0)}=-\frac{1}{2}mc^2\frac{Z^2\alpha^2}{n^2}$, Eq. (6.91) can be rewritten as

$$\Delta_{nl}^{(1)}=E_n^{(0)}\left[\frac{Z^2\alpha^2}{n^2}\left(-\frac{3}{4}+\frac{n}{l+\frac{1}{2}}\right)\right]=-\frac{1}{2}m_ec^2Z^4\alpha^4\left[-\frac{3}{4n^4}+\frac{1}{n^3\left(l+\frac{1}{2}\right)}\right]. \tag{6.94}$$

6.2.2 Spin-Orbit Interaction and Fine Structure

The general hydrogen-like atoms have one valence electron outside the closed shell. Due to the electron cloud, the electrostatic potential

$$V_{\mathrm{c}}(r)=e\phi(r) \tag{6.95}$$

is no longer $e|Z|$, and the higher l states lie higher for a given n. We discuss the effect of the spin-orbit ($\mathbf{L}\cdot\mathbf{S}$) interaction that gives rise to *fine structure*.

The valence electron experiences the inner electric field

$$\mathbf{E} = -\left(\frac{1}{e}\right)\nabla V_{\mathrm{c}}\left(r\right) \tag{6.96}$$

and "feels" an effective magnetic field

$$\mathbf{B}_{\text{eff}} = -\left(\frac{\mathbf{v}}{c}\right)\times\mathbf{E}. \tag{6.97}$$

Because the electron has a magnetic moment

$$\boldsymbol{\mu} = \frac{e\mathbf{S}}{m_e c}, \tag{6.98}$$

according to Dirac's relativistic theory, a spin-orbit potential V_{LS} contribute to *H* by

$$\begin{aligned} V_{LS} &= -\frac{1}{2}\boldsymbol{\mu}\cdot\mathbf{B}_{\text{eff}} = \frac{1}{2}\boldsymbol{\mu}\cdot\left(\frac{\mathbf{v}}{c}\times\mathbf{E}\right) = \left(\frac{e\mathbf{S}}{m_e c}\right)\cdot\left[\frac{\mathbf{p}}{m_e c}\times\left(\frac{\mathbf{x}}{r}\right)\frac{1}{\left(-e\right)}\frac{\mathrm{d}V_{\mathrm{c}}}{\mathrm{d}r}\right] \\ &= \frac{1}{m_e^2c^2}\frac{1}{r}\frac{\mathrm{d}V_{\mathrm{c}}}{\mathrm{d}r}\left(\mathbf{L}\cdot\mathbf{S}\right) \end{aligned}, \tag{6.99}$$

as a perturbation to the unperturbed Hamiltonian

$$H_0 = \frac{\mathbf{p}^2}{2m} + V_{\mathrm{c}}\left(r\right). \tag{6.100}$$

Because $\mathbf{L}\cdot\mathbf{S}$ commute with $\mathbf{J}^2$ and J_z, but not with L_z and S_z, we choose the base kets of $\left(\mathbf{L}^2, \mathbf{S}^2, \mathbf{J}^2, J_z\right)$ rather than $\left(\mathbf{L}^2, L_z, \mathbf{S}^2, S_z\right)$.

Since this choice of the base kets has the perturbation already diagonal, we only need to take the expectation value for the first-order energy shift. The wave function is

$$\psi_{nlm} = R_{nl}\left(r\right)\mathscr{Y}^{j=l\pm1/2,m}, \tag{6.101}$$

where the spin-angular function

$$\mathscr{Y}^{j=l\pm1/2,m} = \frac{1}{\sqrt{2l+1}}\begin{pmatrix} \pm\sqrt{l\pm m+\frac{1}{2}}Y_l^{m-1/2}\left(\theta,\phi\right) \\ \sqrt{l\mp m+\frac{1}{2}}Y_l^{m+1/2}\left(\theta,\phi\right) \end{pmatrix}. \tag{6.102}$$

By using the *m*-independent identity

$$\int\mathscr{Y}^{\dagger}\mathbf{S}\cdot\mathbf{L}\,\mathscr{Y}\,\mathrm{d}\Omega = \frac{1}{2}\left[j\left(j+1\right)-l\left(l+1\right)-\frac{3}{4}\right]\hbar^2 = \frac{\hbar^2}{2}\begin{cases} l, & j = l+\frac{1}{2} \\ -\left(l+1\right), & j = l-\frac{1}{2} \end{cases}, \tag{6.103}$$

the first-order energy shift becomes

$$\Delta_{nlj} = \frac{1}{2m_e^2c^2}\left\langle\frac{1}{r}\frac{\mathrm{d}V_{\mathrm{c}}}{\mathrm{d}r}\right\rangle_{nl}\frac{\hbar^2}{2}\begin{cases} l, & j = l+\frac{1}{2} \\ -\left(l+1\right), & j = l-\frac{1}{2} \end{cases} \tag{6.104}$$

with

$$\left\langle \frac{1}{r}\frac{\mathrm{d}V_c}{\mathrm{d}r} \right\rangle_{nl} = \int_0^\infty R_{nl}\frac{1}{r}\frac{\mathrm{d}V_c}{\mathrm{d}r}R_{nl}r^2\mathrm{d}r \,, \tag{6.105}$$

which is known as the **Lande's interval rule**.

6.2.3 The Zeeman Effect

The Zeeman effect takes place when a uniform magnetic field **B** applied to a hydrogen or hydrogen-like (one-electron) atoms, sometimes called the *anomalous Zeeman effect* with the electron spin taken into account. The vector potential

$$\mathbf{A} = \frac{1}{2}(\mathbf{B}\times\mathbf{r}). \tag{6.106}$$

For $\mathbf{B} = B\hat{\mathbf{z}}$, it becomes

$$\mathbf{A} = -\frac{1}{2}(By\hat{\mathbf{x}} - Bx\hat{\mathbf{y}}). \tag{6.107}$$

Apart from the spin term, the interaction Hamiltonian is generated by

$$\mathbf{p} \to \mathbf{p} - \frac{e\mathbf{A}}{c} \tag{6.108}$$

to have

$$H = \frac{\mathbf{p}^2}{2m_e} + V_c(r) - \frac{e}{2m_e c}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2A^2}{2m_e c^2}. \tag{6.109}$$

Because

$$\begin{aligned}\langle \mathbf{x}'|\mathbf{p}\cdot\mathbf{A}(\mathbf{x})|\alpha\rangle &= -i\hbar\nabla'\cdot\left[\mathbf{A}(\mathbf{x}')\langle\mathbf{x}'|\alpha\rangle\right] \\ &= \langle\mathbf{x}'|\mathbf{A}(\mathbf{x})\cdot\mathbf{p}|\alpha\rangle + \langle\mathbf{x}'|\alpha\rangle\left[-i\hbar\nabla'\cdot\mathbf{A}(\mathbf{x}')\right],\end{aligned} \tag{6.110}$$

$\mathbf{p}\cdot\mathbf{A}$ can be replaced by $\mathbf{A}\cdot\mathbf{p}$ whenever

$$\nabla\cdot\mathbf{A}(\mathbf{x}) = 0, \tag{6.111}$$

which is the case of Eq. (6.107). Since

$$\mathbf{A}\cdot\mathbf{p} = |\mathbf{B}|\left(-\frac{1}{2}yp_x + \frac{1}{2}xp_y\right) = \frac{1}{2}|\mathbf{B}|L_z \tag{6.112}$$

and

$$\mathbf{A}^2 = \frac{1}{4}|\mathbf{B}|^2\left(x^2+y^2\right), \tag{6.113}$$

Eq. (6.109) becomes

$$H = \frac{\mathbf{p}^2}{2m_e} + V_c(r) - \frac{e}{2m_e c}|\mathbf{B}|L_z + \frac{e^2}{8m_e c^2}|\mathbf{B}|^2\left(x^2+y^2\right). \tag{6.114}$$

The spin magnetic-moment interaction is

$$-\boldsymbol{\mu}\cdot\mathbf{B} = -\frac{e}{m_e c}\mathbf{S}\cdot\mathbf{B} = -\frac{e}{m_e c}|\mathbf{B}|S_z. \tag{6.115}$$

For a one-electron atom, the quadratic term $|\mathbf{B}|^2\left(x^2+y^2\right)$ is unimportant, so the total Hamiltonian is made up of the following three terms:

$$
\begin{aligned}
H_0 &= \frac{\mathbf{p}^2}{2m_e} + V_c(r) \\
H_{LS} &= \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{\mathrm{d}V_c(r)}{\mathrm{d}r}\mathbf{L}\cdot\mathbf{S}\,. \\
H_B &= \frac{-e|\mathbf{B}|}{2m_ec}\left(L_z + 2S_z\right)
\end{aligned}
\tag{6.116}
$$

Below we consider two limiting cases:

(1) The magnetic field is so small that H_B can be treated as a small perturbation. Choosing the eigenkets of $H_0 + H_{LS}$ ($\mathbf{J}^2, J_z$) as the base kets. Noting that

$$
L_z + 2S_z = J_z + S_z\,, \tag{6.117}
$$

the first-order shift can be written as

$$
\frac{-e|\mathbf{B}|}{2m_ec}\left\langle J_z + S_z\right\rangle_{j=l\pm1/2,m} = \frac{-e|\mathbf{B}|}{2m_ec}\left(m\hbar + \langle S_z\rangle\right). \tag{6.118}
$$

Since

$$
\begin{aligned}
&\left|j = l\pm\frac{1}{2}, m\right\rangle = \pm\sqrt{\frac{l\pm m+\frac{1}{2}}{2l+1}}\left|m_l = m-\frac{1}{2}, m_s = \frac{1}{2}\right\rangle \\
&+\sqrt{\frac{l\mp m+\frac{1}{2}}{2l+1}}\left|m_l = m+\frac{1}{2}, m_s = -\frac{1}{2}\right\rangle
\end{aligned}
, \tag{6.119}
$$

we have

$$
\begin{aligned}
\left\langle S_z\right\rangle_{j=l\pm1/2,m} &= \frac{\hbar}{2}\left(|c_+|^2 - |c_-|^2\right) \\
&= \frac{\hbar}{2}\frac{1}{(2l+1)}\left[\left(l\pm m+\frac{1}{2}\right) - \left(l\mp m+\frac{1}{2}\right)\right] = \pm\frac{m\hbar}{2l+1}
\end{aligned}
. \tag{6.120}
$$

So we obtain the Lande's formula for the energy shift

$$
\Delta E_B = \frac{-e\hbar B}{2m_ec}m\left[1\pm\frac{1}{2l+1}\right]. \tag{6.121}
$$

(2) **The Paschen-Back limit**: the magnetic field is so tense that H_{LS} can be treated as a perturbation. The spherical symmetry is completed destroyed by the strong **B** and only a cylindrical symmetry about the *z*-direction is conserved, so the good quantum numbers are L_z and S_z with eigenkets $\left|l, s = \frac{1}{2}, m_l, m_s\right\rangle$ as the base kets. Then

$$
\left\langle H_B\right\rangle_{m_lm_s} = \frac{-e|\mathbf{B}|\hbar}{2m_ec}\left(m_l + 2m_s\right) \tag{6.122}
$$

and

$$\langle \mathbf{L}\cdot\mathbf{S}\rangle = \left\langle L_z S_z + \frac{1}{2}\left(L_+ S_- + L_- S_+\right)\right\rangle_{m_l m_s} = \hbar^2 m_l m_s , \tag{6.123}$$

where we have used $\langle L_\pm \rangle_{m_l} = 0, \quad \langle S_\pm \rangle_{m_s} = 0$. Hence,

$$\langle H_{LS} \rangle_{m_l m_s} = \frac{\hbar^2 m_l m_s}{2m_e^2 c^2}\left\langle \frac{1}{r}\frac{\mathrm{d}V_\mathrm{c}}{\mathrm{d}r}\right\rangle . \tag{6.124}$$

6.2.4 The Van der Waals Interaction

The Rayleigh-Schrödinger perturbation theory can be applied to calculating the van der Waals interaction between two hydrogen atoms in their ground states. The two protons are fixed at a distance r with $\mathbf{r}_1, \mathbf{r}_2$ the two vectors from the proton to its electron. The Hamiltonian can be written as

$$\begin{aligned} H &= H_0 + V \\ H_0 &= -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{r_1} - \frac{e^2}{r_2} \\ V &= \frac{e^2}{r} + \frac{e^2}{|\mathbf{r}+\mathbf{r}_2-\mathbf{r}_1|} - \frac{e^2}{|\mathbf{r}_1+\mathbf{r}_2|} - \frac{e^2}{|\mathbf{r}-\mathbf{r}_1|} \end{aligned} . \tag{6.125}$$

The lowest-energy solution of H_0 is simply the product of the ground-state wave functions of the noninteracting hydrogen atoms:

$$U_0^{(0)} = U_{100}^{(0)}(\mathbf{r}_1)U_{100}^{(0)}(\mathbf{r}_2). \tag{6.126}$$

For large $r \gg a_0$, the perturbation V can be expanded in powers of $\mathbf{r}_1/\mathbf{r}$:

$$V = \frac{e^2}{r^3}\left(x_1x_2 + y_1y_2 - 2z_1z_2\right) + O\left(\frac{1}{r^4}\right) + \cdots , \tag{6.127}$$

whose lowest order with the r^{-3} term corresponds to the interaction of two electric dipoles. The first-order perturbation energy matrix element $V_{00} \simeq 0$ because the ground-state wave function has the spherical symmetry. The second-order perturbation

$$E^{(2)}(r) = \frac{e^4}{r^6}\sum_{k\neq 0}\frac{\left|\left\langle k^{(0)}\right| x_1x_2 + y_1y_2 - 2z_1z_2 \left|0^{(0)}\right\rangle\right|^2}{E_0^{(0)} - E_k^{(0)}} \tag{6.128}$$

varies as $\sim -\dfrac{1}{r^6}$.

6.3 Variational Methods

The variational method estimates the ground-state energy E_0 when exact solutions are not available. Starting with a trial ket $|\tilde{0}\rangle$ imitating the true ground-state ket $|0\rangle$, we define

$$\bar{H} \equiv \frac{\langle\tilde{0}|H|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle}. \tag{6.129}$$

Theorem. $\bar{H} \geq E_0$.

Proof. The trial ket can be expanded by the exact energy eigenkets $\{|k\rangle\}$ as

$$|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle \tag{6.130}$$

with

$$H|k\rangle = E_k|k\rangle. \tag{6.131}$$

Putting Eq. (6.130) into Eq. (6.129), we have

$$\bar{H} = \frac{\sum_{k=0} \left|\langle k|\tilde{0}\rangle\right|^2 E_k}{\sum_{k=0} \left|\langle k|\tilde{0}\rangle\right|^2} = \frac{\sum_{k=0} \left|\langle k|\tilde{0}\rangle\right|^2 (E_k - E_0)}{\sum_{k=0} \left|\langle k|\tilde{0}\rangle\right|^2} + E_0 \geq E_0. \tag{6.132}$$

The equality sign holds only if $|\tilde{0}\rangle = |0\rangle$.

A relatively poor trial ket can give a fairly good estimation because if

$$\langle k|\tilde{0}\rangle \sim O(\varepsilon) \tag{6.133}$$

for $k \neq 0$, then

$$\bar{H} - E_0 \sim O(\varepsilon^2). \tag{6.134}$$

The trial kets are usually characterized by one or more parameters λ_i, whose optimum values are determined by

$$\frac{\partial \bar{H}}{\partial \lambda_i} = 0. \tag{6.135}$$

Example: One-dimensional infinite-well. Suppose we do not know the ground state of

$$V = \begin{cases} 0, & |x| < a \\ \infty, & |x| > a \end{cases}. \tag{6.136}$$

By the requirements that the wave function (1) must vanish at $x = \pm a$, and (2) cannot have any wiggles, the simplest analytic function is

$$\langle x|\tilde{0}\rangle = a^2 - x^2, \quad -a \leq x \leq a. \tag{6.137}$$

Then

$$\bar{H}=\frac{\frac{-\hbar^2}{2m}\int_{-a}^{a}\left(a^2-x^2\right)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(a^2-x^2\right)\mathrm{d}x}{\int_{-a}^{a}\left(a^2-x^2\right)^2\mathrm{d}x}=\left(\frac{10}{\pi^2}\right)\left(\frac{\pi^2\hbar^2}{8a^2m}\right)\simeq 1.0132E_0 \,. \tag{6.138}$$

A much better trial function is

$$\langle x|\tilde{0}\rangle=|a|^{\lambda}-|x|^{\lambda}\,,\quad -a\le x\le a\,, \tag{6.139}$$

where λ is a variational parameter. Then

$$\bar{H}=\left[\frac{(\lambda+1)(2\lambda+1)}{(2\lambda-1)}\right]\left(\frac{\hbar^2}{4ma^2}\right), \tag{6.140}$$

which has a minimum value at

$$\lambda=\frac{1+\sqrt{6}}{2}\simeq 1.72 \tag{6.141}$$

corresponding to

$$\bar{H}_{\min}=\left(\frac{5+2\sqrt{6}}{\pi^2}\right)E_0=1.00298E_0\,. \tag{6.142}$$

6.4 Time-Dependent Potentials

The time-dependent Hamiltonian can be split into two parts:

$$H=H_0+V(t) \tag{6.143}$$

with H_0 does not depend on time and the solution for $V(t)=0$ is known:

$$H_0|n\rangle=E_n|n\rangle\,. \tag{6.144}$$

Supposing at $t=0$, the state ket is given by

$$|\alpha\rangle=\sum_n c_n(0)|n\rangle\,, \tag{6.145}$$

we wish to find $c_n(t)$ for $t>0$ such that

$$|\alpha,t_0=0;t\rangle=\sum_n c_n(t)\exp(-iE_nt/\hbar)|n\rangle \tag{6.146}$$

6.4.1 The Interaction Picture

Define the state ket in the *interaction picture* to be

$$|\alpha,t_0;t\rangle_{\mathrm{I}}=\exp(iH_0t/\hbar)|\alpha,t_0;t\rangle_{\mathrm{S}}\,, \tag{6.147}$$

where $|\alpha,t_0;t\rangle_{\mathrm{S}}$ is the same state ket in the Schrödinger picture. An observable in the interaction picture is defined as

$$A_{\mathrm{I}} \equiv \exp\left(iH_0 t/\hbar\right) A_{\mathrm{S}} \exp\left(-iH_0 t/\hbar\right). \tag{6.148}$$

In particular,

$$V_{\mathrm{I}} \equiv \exp\left(iH_0 t/\hbar\right) V(t) \exp\left(-iH_0 t/\hbar\right). \tag{6.149}$$

Taking the time derivative of Eq. (6.147), we have

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left|\alpha,t_0;t\right\rangle_{\mathrm{I}} &= i\hbar\frac{\partial}{\partial t}\left(\exp\left(iH_0 t/\hbar\right)\left|\alpha,t_0;t\right\rangle_{\mathrm{S}}\right) \\ &= -H_0\exp\left(iH_0 t/\hbar\right)\left|\alpha,t_0;t\right\rangle_{\mathrm{S}} + \exp\left(iH_0 t/\hbar\right)\left(H_0+V\right)\left|\alpha,t_0;t\right\rangle_{\mathrm{S}}, \\ &= \exp\left(iH_0 t/\hbar\right)V\exp\left(-iH_0 t/\hbar\right)\exp\left(iH_0 t/\hbar\right)\left|\alpha,t_0;t\right\rangle_{\mathrm{S}} \end{aligned} \tag{6.150}$$

which is a Schrödinger-like equation with the total H replaced by V_{I}:

$$i\hbar\frac{\partial}{\partial t}\left|\alpha,t_0;t\right\rangle_{\mathrm{I}} = V_{\mathrm{I}}\left|\alpha,t_0;t\right\rangle_{\mathrm{I}}. \tag{6.151}$$

For an observable, we obtain the Heisenberg-like equation with H replaced by H_0:

$$\frac{\mathrm{d}A_{\mathrm{I}}}{\mathrm{d}t} = \frac{1}{i\hbar}\left[A_{\mathrm{I}}, H_0\right]. \tag{6.152}$$

A state ket can be expanded as

$$\left|\alpha,t_0;t\right\rangle_{\mathrm{I}} = \sum_n c_n(t)\left|n\right\rangle. \tag{6.153}$$

Multiplying Eq. (6.151) by $\left\langle n\right|$ from the left, we obtain

$$i\hbar\frac{\partial}{\partial t}\left\langle n|\alpha,t_0;t\right\rangle_{\mathrm{I}} = \sum_m \left\langle n\right|V_{\mathrm{I}}\left|m\right\rangle\left\langle m|\alpha,t_0;t\right\rangle_{\mathrm{I}}, \tag{6.154}$$

which can also be written as

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_n(t) = \sum_m V_{nm}\exp\left(i\omega_{nm}t\right)c_m(t) \tag{6.155}$$

with

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar} = -\omega_{mn}. \tag{6.156}$$

The matrix form of this differential equation is

$$i\hbar\begin{pmatrix}\dot{c}_1\\ \dot{c}_2\\ \dot{c}_3\\ \vdots\end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}\exp\left(i\omega_{12}t\right) & & \cdots \\ V_{21}\exp\left(i\omega_{21}t\right) & V_{22} & & \cdots \\ & & V_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix}c_1\\ c_2\\ c_3\\ \vdots\end{pmatrix}. \tag{6.157}$$

6.4.2 Two-State Problems: Nuclear Magnetic Resonance

The two-state problem with a sinusoidal oscillating potential is defined by

$$\begin{aligned} H_0 &= E_1\left|1\right\rangle\left\langle 1\right| + E_2\left|2\right\rangle\left\langle 2\right|, \quad E_2 > E_1 \\ V(t) &= \gamma\exp\left(i\omega t\right)\left|1\right\rangle\left\langle 2\right| + \gamma\exp\left(-i\omega t\right)\left|2\right\rangle\left\langle 1\right|, \end{aligned} \tag{6.158}$$

where γ and ω are real and positive. Here

$$\begin{aligned} V_{12} &= V_{21}^* = \gamma \exp(i\omega t) \\ V_{11} &= V_{22} = 0 \end{aligned} . \tag{6.159}$$

If initially

$$c_1(0) = 1, \quad c_2(0) = 0, \tag{6.160}$$

then the probability for being found in each of the two states is given by **Rabi's formula**:

$$\begin{aligned} |c_2(t)|^2 &= \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega-\omega_{21})^2/4} \sin^2\left(\left(\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}\right)^{1/2} t\right), \\ |c_1(t)|^2 &= 1 - |c_2(t)|^2 \end{aligned} \tag{6.161}$$

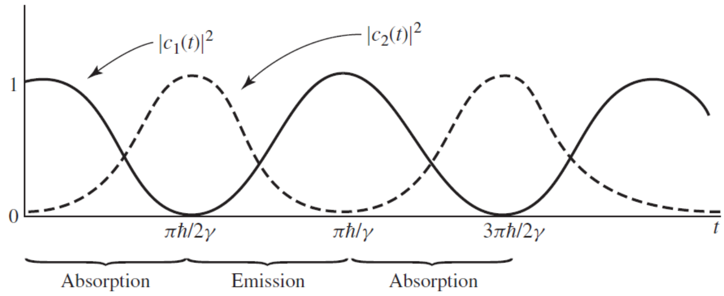
where

$$\omega_{21} \equiv \frac{E_2 - E_1}{\hbar}. \tag{6.162}$$

The amplitude of the oscillation for $|c_2(t)|^2$ is very large when

$$\omega \simeq \omega_{21} = \frac{E_2 - E_1}{\hbar}, \tag{6.163}$$

which is known as the **resonance condition**.



Plot of $|c_1(t)|^2$ and $|c_2(t)|^2$ against time t exactly at resonance $\omega = \omega_{21}$ and $\Omega = \gamma/\hbar$. The graph also illustrates the back-and-forth behavior between $|1\rangle$ and $|2\rangle$.

6.4.3 Spin-Magnetic Resonance

A bound electron with spin 1/2 is subjected to a t-independent uniform magnetic field in the z-direction along with a t-dependent magnetic field rotating in the xy-plane:

$$\mathbf{B} = B_0\hat{\mathbf{z}} + B_1(\hat{\mathbf{x}}\cos\omega t + \hat{\mathbf{y}}\sin\omega t) \tag{6.164}$$

with B_0 and B_1 constant. We can treat the effect of B_0 as H_0 and B_1 as V. For

$$\boldsymbol{\mu} = \frac{e}{m_e c}\mathbf{S}, \tag{6.165}$$

we have

$$H_0 = \left(\frac{e\hbar B_0}{2m_e c}\right)\left(|+\rangle\langle+| - |-\rangle\langle-|\right)$$
$$V(t) = -\left(\frac{e\hbar B_1}{2m_e c}\right)\left[\cos\omega t\left(|+\rangle\langle-| + |-\rangle\langle+|\right) + \sin\omega t\left(-i|+\rangle\langle-| + i|-\rangle\langle+|\right)\right] \quad . \tag{6.166}$$

Corresponding to Eq. (6.158), with $e < 0$, we identify

$$\begin{aligned} &E_+ \to E_2, \quad E_- \to E_1 \\ &|+\rangle \to |2\rangle, \quad |-\rangle \to |1\rangle . \\ &\frac{-e\hbar B_1}{2m_e c} \to \gamma, \quad \omega \to \omega \end{aligned} \tag{6.167}$$

The angular-frequency characteristic is

$$\omega_{21} = \frac{E_+ - E_-}{\hbar} = \frac{|e| B_0}{m_e c} . \tag{6.168}$$

The changes of $|c_+(t)|^2$ and $|c_-(t)|^2$ with time implies that the spin 1/2 system undergoes a succession of spin-flips in addition to spin precession. *The resonance condition is satisfied whenever the frequency of the rotating magnetic field coincides with the frequency of precession determined by the uniform magnetic field.*

6.4.4 Sudden Approximation

The "sudden approximation" applies to the case when the Hamiltonian changes so quickly that the system leaves in the same state before the change.

Rewrite the Schrödinger equation for the time-evolution operator as

$$i\frac{\partial}{\partial s}\mathscr{U}(t,t_0) = \frac{H}{\hbar / T}\mathscr{U}(t,t_0) = \frac{H}{\hbar\Omega}\mathscr{U}(t,t_0), \tag{6.169}$$

where $t = sT$ and $\Omega \equiv 1/T$. In the sudden approximation, $T \to 0$, so $\hbar\Omega \gg H$ and $\mathscr{U}(t,t_0) \to 1$ despite the arbitrary energy constant and phase factor.

6.4.5 Adiabatic Approximation

If the parameters for energy eigenvalues vary "slowly" with time, then the energy eigenvalues should follow the change of the parameters. "Slowly" means the time scale *T* for the change of the parameters is much larger than $2\pi / \omega_{ab} = 2\pi\hbar / E_{ab}$, where E_{ab} is some difference in energy eigenvalues.

Begin with the eigenvalue equation

$$H(t)|n;t\rangle = E_n(t)|n;t\rangle . \tag{6.170}$$

The Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\alpha;t\rangle = H(t)|\alpha;t\rangle \tag{6.171}$$

has the general solutions

$$|\alpha;t\rangle = \sum_n c_n(t)\exp\left(i\theta_n(t)\right)|n;t\rangle , \tag{6.172}$$

where

$$\theta_n(t) \equiv -\frac{1}{\hbar}\int_0^t E_n(t')\,\mathrm{d}t' . \tag{6.173}$$

Substituting Eq. (6.172) into Eq. (6.171) and using Eq. (6.170), we find

$$\sum_n \exp\left(i\theta_n(t)\right)\left[\dot{c}_n(t)|n;t\rangle + c_n(t)\frac{\partial}{\partial t}|n;t\rangle\right] = 0 . \tag{6.174}$$

Multiplying $\langle m;t|$ from the left to the above equation, we have

$$\dot{c}_m(t) = -\sum_n c_n(t)\exp\left[i\left(\theta_n(t) - \theta_m(t)\right)\right]\langle m;t|\left(\frac{\partial}{\partial t}|n;t\rangle\right). \tag{6.175}$$

Since for the case $m \neq n$, Eq. (6.170) leads to

$$\langle m;t|\dot{H}|n;t\rangle = \left[E_n(t) - E_m(t)\right]\langle m;t|\left[\frac{\partial}{\partial t}|n;t\rangle\right], \tag{6.176}$$

Eq. (6.175) becomes

$$\dot{c}_m(t) = -c_m(t)\langle m;t|\left[\frac{\partial}{\partial t}|m;t\rangle\right] - \sum_{n\neq m} c_n(t)\exp\left[i\left(\theta_n - \theta_m\right)\right]\frac{\langle m;t|\dot{H}|n;t\rangle}{E_n - E_m}. \tag{6.177}$$

This is a **formal solution** to the general time-dependent problem, demonstrating that states with $n \neq m$ will mix with $|m;t\rangle$.

The **adiabatic approximation** gives

$$\frac{\langle m;t|\dot{H}|n;t\rangle}{E_n - E_m} \equiv \frac{1}{\tau} \ll \langle m;t|\left[\frac{\partial}{\partial t}|m;t\rangle\right] \sim \frac{E_m}{\hbar}, \tag{6.178}$$

so the second term in Eq. (6.177) can be neglected to have the approximate equation:

$$\dot{c}_m(t) = -c_m(t)\langle m;t|\left[\frac{\partial}{\partial t}|m;t\rangle\right], \tag{6.179}$$

whose solution leads to

$$c_n(t) = \exp\left(i\gamma_n(t)\right)c_n(0), \tag{6.180}$$

where the **geometric phase**

$$\gamma_n(t) \equiv i\int_0^t \langle n;t'|\left[\frac{\partial}{\partial t'}|n;t'\rangle\right]\mathrm{d}t' . \tag{6.181}$$

Note that $\gamma_n(t)$ is real since

$$0 = \frac{\partial}{\partial t}\langle n;t|n;t\rangle = \left[\frac{\partial}{\partial t}\langle n;t|\right]|n;t\rangle + \langle n;t|\left[\frac{\partial}{\partial t}|n;t\rangle\right], \tag{6.182}$$

that is,

$$\left(\langle n;t|\left[\frac{\partial}{\partial t}|n;t\rangle\right]\right)^* = -\langle n;t|\left[\frac{\partial}{\partial t}|n;t\rangle\right]. \tag{6.183}$$

Using Eq. (6.172) with Eq. (6.180), we have

$$|\alpha;t\rangle = \sum_n \exp\left(i\gamma_n(t)\right)\exp\left(i\theta_n(t)\right)|n;t\rangle . \tag{6.184}$$

6.4.6 Berry's Phase

Berry's phase is the accumulated phase for systems that travel in a closed loop.

Assume that the components of a vector $\mathbf{R}(t)$ specify the Hamiltonian, then we have

$$E_n(t) = E_n(\mathbf{R}(t)), \quad |n;t\rangle = |n(\mathbf{R}(t))\rangle, \tag{6.185}$$

and also

$$\langle n;t|\left[\frac{\partial}{\partial t}|n;t\rangle\right] = \langle n;t|\left[\nabla_{\mathbf{R}}|n;t\rangle\right]\cdot\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t}. \tag{6.186}$$

The geometric phase Eq. (6.181) then becomes

$$\gamma_n(T) = i\int_0^T \langle n;t|\left[\nabla_{\mathbf{R}}|n;t\rangle\right]\cdot\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t}\mathrm{d}t = i\int_{\mathbf{R}(0)}^{\mathbf{R}(T)}\langle n;t|\left[\nabla_{\mathbf{R}}|n;t\rangle\right]\cdot\mathrm{d}\mathbf{R}. \tag{6.187}$$

In the case $\mathbf{R}(T) = \mathbf{R}(0)$, where the vector **R** traces a curve *C*, we have

$$\gamma_n(C) = i\oint\langle n;t|\left[\nabla_{\mathrm{R}}|n;t\rangle\right]\cdot\mathrm{d}\mathbf{R}. \tag{6.188}$$

Define

$$\mathbf{A}_n(\mathbf{R}) \equiv i\langle n;t|\left[\nabla_{\mathbf{R}}|n;t\rangle\right], \tag{6.189}$$

then

$$\gamma_n(C) = \oint_C \mathbf{A}_n(\mathbf{R})\cdot\mathrm{d}\mathbf{R} = \int\left[\nabla_{\mathbf{R}}\times\mathbf{A}_n(\mathbf{R})\right]\cdot\mathrm{d}\mathbf{a}, \tag{6.190}$$

where $\mathrm{d}\mathbf{a}$ is a small area element on some surface bounded by the closed path. Thus, Berry's phase is determined by the "flux" of a generalized field

$$\mathbf{B}_n(\mathbf{R}) \equiv \nabla_{\mathbf{R}}\times\mathbf{A}_n(\mathbf{R}) \tag{6.191}$$

through a surface **S** bounded by the circuit followed by $\mathbf{R}(t)$ over one complete cycle. Both $\mathbf{A}_n(\mathbf{R})$ and $\mathbf{B}_n(\mathbf{R})$ are purely real quantities.

By combining Eq. (6.189) and Eq. (6.191), we get

$$\mathbf{B}_n(\mathbf{R}) = i\left[\nabla_{\mathbf{R}}\langle n;t|\right]\times\left[\nabla_{\mathbf{R}}|n;t\rangle\right]. \tag{6.192}$$

Insert a complete set of states $|m;t\rangle$ to find

$$\mathbf{B}_n(\mathbf{R}) = i\sum_{m\neq n}\left[\nabla_{\mathbf{R}}\langle n;t|\right]|m;t\rangle\times\langle m;t|\left[\nabla_{\mathbf{R}}|n;t\rangle\right], \tag{6.193}$$

where the explicitly discarded term with $m = n$ is actually zero. Taking the **R**-gradient of Eq. (6.170) and the inner product with $\langle m;t|$, we determine

$$\langle m;t|\left[\nabla_{\mathbf{R}}|n;t\rangle\right] = \frac{\langle m;t|\left[\nabla_{\mathbf{R}}H\right]|n;t\rangle}{E_n - E_m}, \quad m\neq n. \tag{6.194}$$

This enables us to finally write

$$\gamma_n(C) = \int \mathbf{B}_n(\mathbf{R}) \cdot d\mathbf{a}, \tag{6.195}$$

where

$$\mathbf{B}_n(\mathbf{R}) = i \sum_{m \neq n} \frac{\langle n;t|[\nabla_{\mathbf{R}} H]|m;t\rangle \times \langle m;t|[\nabla_{\mathbf{R}} H]|n;t\rangle}{(E_m - E_n)^2}. \tag{6.196}$$

Example: Berry's phase for spin 1/2: the phase motion for a spin 1/2 particle manipulated slowly through a time-varying magnetic field.

For a magnetic moment μ, the Hamiltonian is

$$H(t) = H(\mathbf{R}(t)) = -\frac{2\mu}{\hbar} \mathbf{S} \cdot \mathbf{R}(t), \tag{6.197}$$

where $\mathbf{S}$ is the spin 1/2 angular-momentum operator, $\mathbf{R}(t)$ is the external magnetic field (to avoid the confliction with $\mathbf{B}$ in Eq. (6.196)), and the expectation value for the magnetic moment in the spin-up state is simply μ.

We now evaluate $\mathbf{B}(\mathbf{R})$ using Eq. (6.196). The two energy eigenvalues for Eq. (6.197) are

$$E_{\pm}(t) = \mp \mu R(t), \tag{6.198}$$

where $R(t)$ is the magnitude of the magnetic-field vector, and the spin-up (down) eigenstates are $|\pm, t\rangle$. The summation in Eq. (6.196) consists of only one term, with denominator

$$(E_{\pm} - E_{\mp})^2 = 4\mu^2 R^2. \tag{6.199}$$

It is also clear that

$$\nabla_{\mathbf{R}} H = -\frac{2\mu}{\hbar} \mathbf{S}. \tag{6.200}$$

We need further evaluate

$$\langle \pm;t|\mathbf{S}|\mp;t\rangle \times \langle \mp;t|\mathbf{S}|\pm;t\rangle = \langle \pm;t|\mathbf{S}|\mp;t\rangle \times \langle \pm;t|\mathbf{S}|\mp;t\rangle^*. \tag{6.201}$$

Since

$$\mathbf{S} = \frac{1}{2}(S_+ + S_-)\hat{\mathbf{x}} + \frac{1}{2i}(S_+ - S_-)\hat{\mathbf{y}} + S_z \hat{\mathbf{z}}, \tag{6.202}$$

we have

$$\langle \pm;t|\mathbf{S}|\mp;t\rangle = \frac{\hbar}{2}(\hat{\mathbf{x}} \mp i\hat{\mathbf{y}}). \tag{6.203}$$

Combining Eq. (6.199), Eq. (6.201), and Eq. (6.203), we have

$$\mathbf{B}_{\pm}(\mathbf{R}) = \mp \frac{1}{2R^2(t)} \hat{\mathbf{z}} = \mp \frac{1}{2R^2(t)} \hat{\mathbf{R}}. \tag{6.204}$$

Finally, Berry's Phase in Eq. (6.195) is calculated as

$$r_{\pm}(C) = \mp \frac{1}{2} \int \frac{\hat{\mathbf{R}} \cdot d\mathbf{a}}{R^2} = \mp \frac{1}{2} \Omega, \tag{6.205}$$

where Ω is the "solid angle" subtended by the path through which the parameter vector $\mathbf{R}(t)$ travels, relative to an origin $\mathbf{R}=0$ that is the source point for the field **B**.

6.5 Time-Dependent Perturbation Theory

6.5.1 Dyson Series

The approximate solutions to Eq. (6.157) can be obtained by perturbation expansion:

$$c_n(t)=c_n^{(0)}+c_n^{(1)}+c_n^{(2)}+\cdots, \tag{6.206}$$

where $c_n^{(1)},c_n^{(2)},\cdots$ signify amplitudes of different orders in the strength parameter of the time-dependent potential. The iteration method is similar to time-independent perturbation theory.

Define the time-evolution operator in the interaction picture

$$|\alpha,t_0;t\rangle_I=U_I(t,t_0)|\alpha,t_0;t_0\rangle_I, \tag{6.207}$$

then the differential equation in Eq. (6.151) can be written as

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}U_I(t,t_0)=V_I(t)U_I(t,t_0), \tag{6.208}$$

which together with the initial condition

$$U_I(t,t_0)\Big|_{t=t_0}=1 \tag{6.209}$$

is equivalent to

$$U_I(t,t_0)=1-\frac{i}{\hbar}\int_{t_0}^{t}V_I(t')U_I(t',t_0)\mathrm{d}t'. \tag{6.210}$$

The approximate solution of this equation can be obtained by iteration:

$$\begin{aligned}U_I(t,t_0)&=1-\frac{i}{\hbar}\int_{t_0}^{t}V_I(t')\left[1-\frac{i}{\hbar}\int_{0}^{t'}V_I(t'')U_I(t'',t_0)\mathrm{d}t''\right]\mathrm{d}t'\\&=1-\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}t'V_I(t')+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}\mathrm{d}t'\int_{t_0}^{t'}\mathrm{d}t''V_I(t')V_I(t'')+\cdots\\&+\left(\frac{-i}{\hbar}\right)^n\int_{t_0}^{t}\mathrm{d}t'\int_{t_0}^{t'}\mathrm{d}t''\cdots\int_{t_0}^{t^{(n-1)}}\mathrm{d}t^{(n)}V_I(t')V_I(t'')\cdots V_I\left(t^{(n)}\right)+\cdots\end{aligned}, \tag{6.211}$$

which is known as the **Dyson series** which can be used to compute $U_I(t,t_0)$ to any finite order.

6.5.2 Transition Probability

According to Eq. (6.147), we have

$$\begin{aligned}|\alpha,t_0;t\rangle_I&=\exp(iH_0t/\hbar)|\alpha,t_0;t\rangle_S\\&=\exp(iH_0t/\hbar)U(t,t_0)|\alpha,t_0;t_0\rangle_S\\&=\exp(iH_0t/\hbar)U(t,t_0)\exp(-iH_0t_0/\hbar)|\alpha,t_0;t_0\rangle_I\end{aligned}, \tag{6.212}$$

so the time-evolution operators in the interaction and Schrödinger pictures are connected by

$$U_I(t,t_0) = \exp(iH_0 t/\hbar)U(t,t_0)\exp(-iH_0 t_0/\hbar). \qquad (6.213)$$

The matrix element of $U_I(t,t_0)$ between energy eigenstates of H_0 is

$$\langle n|U_I(t,t_0)|i\rangle = \exp\left[i(E_n t - E_i t_0)/\hbar\right]\langle n|U(t,t_0)|i\rangle. \qquad (6.214)$$

The *transition probabilities* in the two pictures are the same:

$$\left|\langle n|U_I(t,t_0)|i\rangle\right|^2 = \left|\langle n|U(t,t_0)|i\rangle\right|^2. \qquad (6.215)$$

Choosing the phase factor at $t = t_0$ in the Schrödinger picture so that

$$|i,t_0;t_0\rangle_S = \exp(-iE_i t_0/\hbar)|i\rangle, \qquad (6.216)$$

which in the interaction picture is

$$|i,t_0;t_0\rangle_I = |i\rangle. \qquad (6.217)$$

At a later time, we have

$$|i,t_0;t\rangle_I = U_I(t,t_0)|i\rangle. \qquad (6.218)$$

Compared with the expansion

$$|i,t_0;t\rangle_I = \sum_n c_n(t)|n\rangle, \qquad (6.219)$$

we see that

$$c_n(t) = \langle n|U_I(t,t_0)|i\rangle. \qquad (6.220)$$

Using Eq. (6.211) and expanding $c_n(t)$ as in Eq. (6.206), we obtain by comparing both sides of the above equation:

$$\begin{aligned} c_n^{(0)}(t) &= \delta_{ni} \\ c_n^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^{t}\langle n|V_I(t')|i\rangle \mathrm{d}t' = -\frac{i}{\hbar}\int_{t_0}^{t}\exp(i\omega_{ni}t')V_{ni}(t')\mathrm{d}t' \\ c_n^{(2)}(t) &= \left(\frac{-i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t}\mathrm{d}t'\int_{t_0}^{t'}\mathrm{d}t''\exp(i\omega_{nm}t')V_{nm}(t')\exp(i\omega_{nm}t'')V_{mi}(t'') \end{aligned}, \qquad (6.221)$$

where $\omega_{nm} = \frac{E_n - E_m}{\hbar}$. The transition probability for $|i\rangle \to |n\rangle$ with $n \neq i$ is obtained by

$$P(i \to n) = \left|c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots\right|^2. \qquad (6.222)$$

6.5.3 Case 1: Constant Perturbation

Consider a constant perturbation

$$V(t) = \begin{cases} 0, & t < 0 \\ V, & t \geq 0 \end{cases}. \qquad (6.223)$$

If the system is only at $|i\rangle$ at $t=0$, according to Eq. (6.221), we obtain

$$\begin{aligned} c_n^{(0)} &= c_n^{(0)}(0) = \delta_{ni} \\ c_n^{(1)} &= -\frac{i}{\hbar} V_{ni} \int_0^t \exp(i\omega_{ni} t')\mathrm{d}t' = \frac{V_{ni}}{E_n - E_i}\left(1 - \exp(i\omega_{ni} t)\right) \end{aligned}. \tag{6.224}$$

So by defining $\omega_{ni} \equiv \dfrac{E_n - E_i}{\hbar}$, we have

$$\left|c_n^{(1)}\right|^2 = \frac{|V_{ni}|^2}{|E_n - E_i|^2}\left(2 - 2\cos\omega_{ni} t\right) = \frac{4|V_{ni}|^2}{|E_n - E_i|^2}\sin^2\left(\frac{\omega t}{2}\right). \tag{6.225}$$

Assume there are so many states with $E \sim E_n$ that there are almost a continuum of final states with nearly the same energy, we can thus define $\omega \simeq \omega_{ni}$. As t becomes large, $\left|c_n^{(1)}(t)\right|^2$ is appreciable only for those final states $|n\rangle$ satisfying

$$t \sim \frac{2\pi}{\omega} = \frac{2\pi\hbar}{|E_n - E_i|}, \tag{6.226}$$

which verifies the uncertainty relation

$$\Delta t \Delta E \sim \hbar. \tag{6.227}$$

For those transitions with exact energy conservation $E_n = E_i$, we have

$$\left|c_n^{(1)}(t)\right|^2 = \frac{1}{\hbar^2}|V_{ni}|^2 t^2, \tag{6.228}$$

which indicates that the probability of finding $|n\rangle$ after a time interval t is quadratic rather than linear. This can be understood by that a group of final states all with nearly the same energy as the initial state $|i\rangle$.

Defining the density of final states within $(E, E + \mathrm{d}E)$:

$$\rho(E)\mathrm{d}E, \tag{6.229}$$

the total transition probability summed over final states with $E_n \simeq E_i$ is

$$\sum_{n, E_n \simeq E_i}\left|c_n^{(1)}\right|^2 \Rightarrow \int \mathrm{d}E_n \rho(E_n)\left|c_n^{(1)}\right|^2 = 4\int \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right]\frac{|V_{ni}|^2}{|E_n - E_i|^2}\rho(E_n)\mathrm{d}E_n. \tag{6.230}$$

As $t \to \infty$, because

$$\lim_{\alpha\to\infty}\frac{1}{\pi}\frac{\sin^2 \alpha x}{\alpha x^2} = \delta(x), \tag{6.231}$$

we have

$$\lim_{t\to\infty}\frac{1}{\left|E_n-E_i\right|^2}\sin^2\left[\frac{\left(E_n-E_i\right)t}{2\hbar}\right]=\frac{\pi t}{2\hbar}\delta\left(E_n-E_i\right). \quad (6.232)$$

Therefore, from Eq. (6.230), we obtain

$$\lim_{t\to\infty}\int \mathrm{d}E_n\rho\left(E_n\right)\left|c_n^{(1)}(t)\right|^2=\left(\frac{2\pi}{\hbar}\right)\overline{\left|V_{ni}\right|^2}\rho\left(E_n\right)t\Big|_{E_n\simeq E_i}, \quad (6.233)$$

which indicates that the *total* transition probability *is* proportional to *t* for large values of *t*. This equation shows that the **total transition rate**—the transition probability per unit time following the **Fermi's golden rule**

$$w_{i\to[n]}\equiv\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_n\left|c_n^{(1)}\right|^2\right)=\frac{2\pi}{\hbar}\overline{\left|V_{ni}\right|^2}\rho\left(E_n\right)_{E_n\simeq E_i} \quad (6.234)$$

is constant for large *t*, where $[n]$ stands for a group of final state with energy similar to $|i\rangle$. It can be equivalently expressed in terms of a single final state $|n\rangle$ as

$$w_{i\to n}=\frac{2\pi}{\hbar}\left|V_{ni}\right|^2\delta\left(E_n-E_i\right). \quad (6.235)$$

From Eq. (6.221), the second-order term is

$$\begin{aligned}c_n^{(2)}&=\left(\frac{-i}{\hbar}\right)^2\sum_m V_{nm}V_{mi}\int_0^t \mathrm{d}t'\exp\left(i\omega_{nm}t'\right)\int_0^{t'}\mathrm{d}t''\exp\left(i\omega_{mi}t''\right)\\&=\frac{i}{\hbar}\sum_m\frac{V_{nm}V_{mi}}{E_m-E_i}\int_0^t\left[\exp\left(i\omega_{ni}t'\right)-\exp\left(i\omega_{mn}t'\right)\right]\mathrm{d}t'\end{aligned}. \quad (6.236)$$

When E_m differs from E_n and E_i, the second term on the RHS gives rise to a rapid oscillation that does not contribute to the growth of the transition probability with *t*, while the first term has the same *t* dependence as $c_n^{(1)}$.

With $c^{(1)}$ and $c^{(2)}$ together, we have

$$w_{i\to[n]}=\frac{2\pi}{\hbar}\overline{\left|V_{ni}+\sum_m\frac{V_{nm}V_{mi}}{E_i-E_m}\right|^2}\rho\left(E_n\right)\Bigg|_{E_n\simeq E_i}. \quad (6.237)$$

6.5.4 Case 2: Harmonic Perturbation

The harmonic perturbation

$$V(t)=v\exp\left(i\omega t\right)+v^\dagger\exp\left(-i\omega t\right) \quad (6.238)$$

is turned on at $t=0$, so according to Eq. (6.221), we have

$$c_n^{(1)} = \frac{-i}{\hbar}\int_0^t \left(v_{ni}\exp(i\omega t') + v_{ni}^{\dagger}\exp(-i\omega t')\right)\exp(i\omega_{ni}t')\mathrm{d}t'$$
$$= \frac{1}{\hbar}\left(\frac{1-\exp\left(i(\omega+\omega_{ni})t\right)}{\omega+\omega_{ni}}v_{ni} + \frac{1-\exp\left(i(\omega_{ni}-\omega)t\right)}{-\omega+\omega_{ni}}v_{ni}^{\dagger}\right). \tag{6.239}$$

The only difference from the constant-perturbation case can be eliminated by the change

$$\omega_{ni} = \frac{E_n - E_i}{\hbar} \to \omega_{ni} \pm \omega . \tag{6.240}$$

So as $t \to \infty$, $\left|c_n^{(1)}\right|^2$ is appreciable only if

$$\omega_{ni} + \omega \simeq 0, \quad \omega_{ni} - \omega \simeq 0 . \tag{6.241}$$

Obviously, the energy is not conserved, and the difference is compensated by the "external" potential $V(t)$.

Analogous with (6.234), we have

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{\left|v_{ni}\right|^2}\rho(E_n)\Big|_{E_n \simeq E_i - \hbar\omega}$$
$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{\left|v_{ni}^{\dagger}\right|^2}\rho(E_n)\Big|_{E_n \simeq E_i + \hbar\omega} \tag{6.242}$$

Since

$$\langle i|v^{\dagger}|n\rangle = \langle n|v|i\rangle^{*}, \tag{6.243}$$

which leads to

$$\left|v_{ni}\right|^2 = \left|v_{in}^{\dagger}\right|^2, \tag{6.244}$$

combined with Eq. (6.242), we have

$$\frac{r_{\mathrm{e}}\left(i\to[n]\right)}{\rho([n])} = \frac{r_{\mathrm{a}}\left([n]\to i\right)}{\rho([i])}, \tag{6.245}$$

where r_{e} and r_{a} are emission and absorption rates, respectively, and ρ is density of final states. This symmetric relation between emission and absorption satisfies the **detailed-balancing** requirement.

To summarize, we obtain appreciable transition probability for $|i\rangle \to |n\rangle$ only if $E_n \simeq E_i$ for constant perturbation; only if $E_n \simeq E_i - \hbar\omega$ (stimulated emission) or $E_n \simeq E_i + \hbar\omega$ (absorption) for harmonic perturbation.

6.6 Energy Shift and Decay Width

We now want to see what happens to $c_i(t)$ itself? Assume the perturbation is adiabatic (slow-turn-on):

$$V(t) = \exp(\eta t)V \ , \tag{6.246}$$

where V is constant and η is small and positive. Using Eq. (6.221), we have

$$\begin{aligned} & c_n^{(0)}(t) = 0 \\ & c_n^{(1)}(t) = -\frac{i}{\hbar}V_{ni} \lim_{t_0 \to -\infty} \int_{t_0}^{t} \exp(\eta t')\exp(i\omega_{ni}t')\mathrm{d}t' = -\frac{i}{\hbar}V_{ni}\frac{\exp(\eta t + i\omega_{ni}t)}{\eta + i\omega_{ni}} \cdot \end{aligned} \tag{6.247}$$

Therefore, the transition probability is

$$\left|c_n(t)\right|^2 \simeq \frac{\left|V_{ni}\right|^2}{\hbar^2}\frac{\exp(2\eta t)}{\eta^2 + \omega_{ni}^2} \ , \tag{6.248}$$

and then

$$\frac{\mathrm{d}}{\mathrm{d}t}\left|c_n(t)\right|^2 \simeq \frac{2\left|V_{ni}\right|^2}{\hbar^2}\frac{\eta\exp(2\eta t)}{\eta^2 + \omega_{ni}^2} \ . \tag{6.249}$$

Now let $\eta \to 0$ so that $\exp(\eta t)$ can be replaced by unity. Because

$$\lim_{\eta \to 0}\frac{\eta}{\eta^2 + \omega_{ni}^2} = \pi\delta(\omega_{ni}) = \pi\hbar\delta(E_n - E_i) \ , \tag{6.250}$$

we recover the golden rule

$$\omega_{i\to n} \simeq \frac{2\pi}{\hbar}\left|V_{ni}\right|^2\delta(E_n - E_i) \ . \tag{6.251}$$

Again using Eq. (6.221), we have

$$\begin{aligned} & c_i^{(0)} = 1 \\ & c_i^{(1)} = -\frac{i}{\hbar}V_{ii} \lim_{t_0 \to -\infty}\int_{t_0}^{t}\exp(\eta t')\mathrm{d}t' = -\frac{i}{\hbar}\frac{V_{ii}}{\eta}\exp(\eta t) \\ & c_i^{(2)} = \left(-\frac{i}{\hbar}\right)^2 \sum_m \left|V_{mi}\right|^2 \lim_{t_0 \to -\infty}\int_{t_0}^{t}\exp(i\omega_{im}t' + \eta t')\frac{\exp(i\omega_{im}t' + \eta t')}{i(\omega_{mi} - i\eta)}\mathrm{d}t' \cdot \\ & = \left(-\frac{i}{\hbar}\right)^2 \left|V_{ii}\right|^2 \frac{\exp(2\eta t)}{2\eta^2} + \left(-\frac{i}{\hbar}\right)\sum_{m\neq i}\frac{\left|V_{mi}\right|^2\exp(2\eta t)}{2\eta(E_i - E_m + i\hbar\eta)} \end{aligned} \tag{6.252}$$

Thus, to the second order, we have

$$\begin{aligned} & c_i(t) \simeq 1 - \frac{i}{\hbar\eta}V_{ii}\exp(\eta t) \\ & + \left(-\frac{i}{\hbar}\right)^2 \left|V_{ii}\right|^2 \frac{\exp(2\eta t)}{2\eta^2} + \left(-\frac{i}{\hbar}\right)\sum_{m\neq i}\frac{\left|V_{mi}\right|^2\exp(2\eta t)}{2\eta(E_i - E_m + i\hbar\eta)} \end{aligned} \ . \tag{6.253}$$

Letting $\eta \to 0$ and replacing $\exp(\eta t)$ and $\exp(2\eta t)$ by unity, we get

$$\frac{\dot{c}_i}{c_i} \simeq \frac{-\frac{i}{\hbar}V_{ii} + \left(-\frac{i}{\hbar}\right)^2 \frac{|V_{ii}|^2}{\eta} + \left(-\frac{i}{\hbar}\right)\sum_{m\neq i}\frac{|V_{mi}|^2}{(E_i - E_m + i\hbar\eta)}}{1 - \frac{i}{\hbar}\frac{V_{ii}}{\eta}}, \qquad (6.254)$$
$$\simeq -\frac{i}{\hbar}V_{ii} + \left(-\frac{i}{\hbar}\right)\sum_{m\neq i}\frac{|V_{mi}|^2}{(E_i - E_m + i\hbar\eta)} \equiv -\frac{i}{\hbar}\Delta_i$$

which is independent of *t*. So

$$c_i(t) = \exp(-i\Delta_i t/\hbar). \qquad (6.255)$$

Because $\exp(-i\Delta_i t/\hbar)|i\rangle$ in the interaction picture equals to $\exp(-i\Delta_i t/\hbar - iE_i\hbar)|i\rangle$ in the Schrödinger picture, the effect of perturbation is

$$E_i \to E_i + \Delta_i. \qquad (6.256)$$

That is, we have calculated the **level shift** using *time-dependent perturbation theory*.

Expanding

$$\Delta_i = \Delta_i^{(1)} + \Delta_i^{(2)} + \cdots, \qquad (6.257)$$

we know from (6.254) that

$$\Delta_i^{(1)} = V_{ii}, \qquad (6.258)$$

which is the result from *time-independent perturbation theory*. Since

$$\lim_{\varepsilon\to 0}\frac{1}{x+i\varepsilon} = \text{Pr.}\frac{1}{x} - i\pi\delta(x), \qquad (6.259)$$

where Pr. means taking the principle part (without singularities), we have

$$\text{Re}\left(\Delta_i^{(2)}\right) = \text{Pr.}\sum_{m\neq i}\frac{|V_{mi}|^2}{E_i - E_m}$$
$$\text{Im}\left(\Delta_i^{(2)}\right) = -\pi\sum_{m\neq i}|V_{mi}|^2\,\delta(E_i - E_m). \qquad (6.260)$$

Comparing with the golden rule Eq. (6.251), we identify

$$\sum_{m\neq i} w_{i\to m} = \frac{2\pi}{\hbar}\sum_{m\neq i}|V_{mi}|^2\,\delta(E_i - E_m) = -\frac{2}{\hbar}\text{Im}\left(\Delta_i^{(2)}\right). \qquad (6.261)$$

Eq. (6.255) can then be written as

$$c_i(t) = \exp\left\{-\frac{i}{\hbar}\left[\text{Re}(\Delta_i)t\right] + \frac{1}{\hbar}\left[\text{Im}(\Delta_i)t\right]\right\}. \qquad (6.262)$$

If we define

$$\frac{\Gamma_i}{\hbar} \equiv -\frac{2}{\hbar}\text{Im}(\Delta_i), \quad \tau_i \equiv \frac{\hbar}{\Gamma_i}, \qquad (6.263)$$

then

$$|c_i|^2 = \exp\left[2\,\text{Im}(\Delta_i)t/\hbar\right] = \exp(-\Gamma_i t/\hbar) = \exp(-t/\tau_i). \qquad (6.264)$$

Therefore, Γ_i characterizes the rate at which $|i\rangle$ disappears, and τ_i is the mean lifetime of state $|i\rangle$. The probability conservation up to second order in V for small t can be expressed as

$$|c_i|^2 + \sum_{m \neq i} |c_m|^2 = \left(1 - \Gamma_i t / \hbar\right) + \sum_{m \neq i} w_{i \to m} t = 1 \,. \tag{6.265}$$

To summarize, the real part of the energy shift is associated with the level shift, while the imaginary part (apart from -2) is the **decay width**.