Harmonic Perturbation

We now consider a sinusoidally varying time-dependent potential, commonly referred to as **harmonic perturbation**:

$$V(t) = \mathcal{V} e^{i\omega t} + \mathcal{V}^{\dagger} e^{-i\omega t}$$

where $\mathcal{V}$ may still depend on **x**, **p**, **s**, and so on. Actually, we have already encountered a time-dependent potential of this kind in Section 5.5 in discussing t-dependent two-level problems.

Again assume that only one of the eigenstates of H_0 is populated initially. Perturbation (5.6.39) is assumed to be turned on at $t = 0$, so

$$c_n^{(1)} = \frac{-i}{\hbar} \int_0^t \left(\mathcal{V}_{nl} e^{i\omega t'} + \mathcal{V}_{nl}^{\dagger} e^{-i\omega t'} \right) e^{i\omega_{nl} t'} \, dt'$$

$$= \frac{1}{\hbar} \left[\frac{1 - e^{i(\omega + \omega_{nl})t}}{\omega + \omega_{nl}} \mathcal{V}_{nl} + \frac{1 - e^{i(\omega_{nl} - \omega)t}}{-\omega + \omega_{nl}} \mathcal{V}_{nl}^{\dagger} \right]$$

We see that this formula is similar to the constant perturbation case.

Harmonic Perturbation

$$c_n^{(1)} = \frac{-i}{\hbar}\int_0^t \left(\mathcal{V}_{nl}e^{i\omega t'} + \mathcal{V}_{nl}^{\dagger}e^{-i\omega t'}\right)e^{i\omega_{nl}t'}\,dt'$$

$$= \frac{1}{\hbar}\left[\frac{1-e^{i(\omega+\omega_{nl})t}}{\omega+\omega_{nl}}\mathcal{V}_{nl} + \frac{1-e^{i(\omega_{nl}-\omega)t}}{-\omega+\omega_{nl}}\mathcal{V}_{nl}^{\dagger}\right]$$

Constant Perturbation

$$c_n^{(1)} = \frac{-i}{\hbar}V_{nl}\int_0^t e^{i\omega_{nl}t'}\,dt'$$

$$= \frac{V_{nl}}{E_n - E_l}\left(1-e^{i\omega_{nl}t}\right)$$

The only change needed is

$$\omega_{nl} = \frac{E_n - E_l}{\hbar} \rightarrow \omega_{nl} \pm \omega$$

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

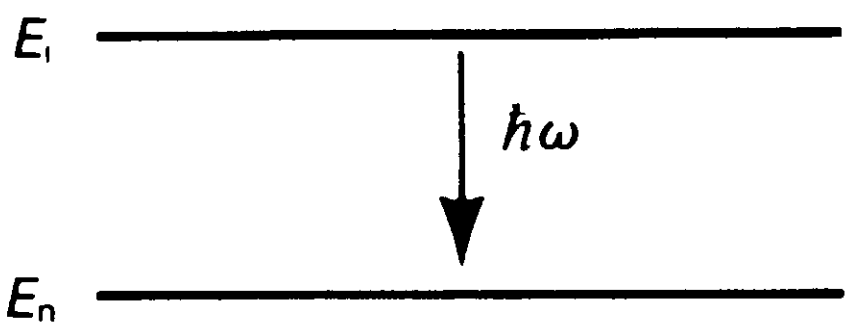
$$\omega_{nl} + \omega \simeq 0 \quad \text{or} \quad E_n \simeq E_l - \hbar\omega$$

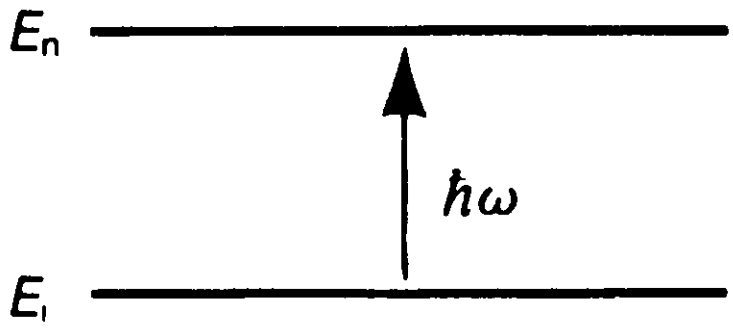
$$\omega_{nl} - \omega \simeq 0 \quad \text{or} \quad E_n \simeq E_l + \hbar\omega$$

$$c_n^{(1)} = \frac{-i}{\hbar}\int_0^t \left(\mathscr{V}_{nI}e^{i\omega t'} + \mathscr{V}_{nI}^{\dagger}e^{-i\omega t'}\right)e^{i\omega_{nI}t'}\,dt' \qquad \omega_{nI} + \omega \simeq 0 \quad \text{or} \quad E_n \simeq E_I - \hbar\omega$$

$$= \frac{1}{\hbar}\left[\frac{1 - e^{i(\omega+\omega_{nI})t}}{\omega + \omega_{nI}}\mathscr{V}_{nI} + \frac{1 - e^{i(\omega_{nI}-\omega)t}}{-\omega + \omega_{nI}}\mathscr{V}_{nI}^{\dagger}\right] \qquad \omega_{nI} - \omega \simeq 0 \quad \text{or} \quad E_n \simeq E_I + \hbar\omega$$

Clearly, whenever the first term is important because of (5.6.42a), the second term is unimportant, and vice versa. We see that we have no energy-conservation condition satisfied by the quantum-mechanical system alone; rather the apparent lack of energy conservation is compensated by the energy given out to—or energy taken away from—the "external" potential $V(t)$. Pictorially, we have Figure 5.9. In the first case (*stimulated emission*), the quantum-mechanical system gives up energy $\hbar\omega$ to V; this is clearly possible only if the initial state is excited. In the second case (*absorption*), the quantum-mechanical system receives energy $\hbar\omega$ from V and ends up as an excited state. Thus a time-dependent perturbation can be regarded as an inexhaustible source or sink of energy.





In complete analogy with (5.6.34), we have

Constant Perturbation

$$w_{i\to[n]}=\frac{2\pi}{\hbar}\overline{|V_{ni}|^2}\rho(E_n)\,{}_{E_n\simeq E_i}$$

$$w_{i\to[n]}=\left.\frac{2\pi}{\hbar}\overline{|\mathscr{V}_{ni}|^2}\rho(E_n)\right|_{E_n\cong E_i-\hbar\omega}$$

$$w_{i\to[n]}=\left.\frac{2\pi}{\hbar}\overline{|\mathscr{V}_{ni}^{\dagger}|^2}\rho(E_n)\right|_{E_n\cong E_i+\hbar\omega}$$

or, more commonly,

$$w_{i\to n}=\frac{2\pi}{\hbar}\left\{\begin{matrix}|\mathscr{V}_{ni}|^2\\ |\mathscr{V}_{ni}^{\dagger}|^2\end{matrix}\right\}\delta(E_n-E_i\pm\hbar\omega).$$

Note also that

$$|\mathscr{V}_{ni}|^2=|\mathscr{V}_{in}^{\dagger}|^2,$$

which is a consequence of

$$\langle i|\mathscr{V}^{\dagger}|n\rangle=\langle n|\mathscr{V}|i\rangle^*$$

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|\mathscr{V}_{ni}|^2}\rho(E_n)\Big|_{E_n\cong E_i-\hbar\omega}$$

$$|\mathscr{V}_{ni}|^2 = |\mathscr{V}_{in}^{\dagger}|^2$$

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|\mathscr{V}_{ni}^{\dagger}|^2}\rho(E_n)\Big|_{E_n\cong E_i+\hbar\omega}$$

$$\frac{\text{emission rate for } i\to[n]}{\text{density of final states for } [n]} = \frac{\text{absorption rate for } n\to[i]}{\text{density of final states for } [i]}$$

where in the absorption case we let i stand for final states. Equation (5.6.47), which expresses symmetry between emission and absorption, is known as **detailed balancing**.

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

APPLICATIONS TO INTERACTIONS WITH THE CLASSICAL RADIATION FIELD

Absorption and Stimulated Emission

We apply the formalism of time-dependent perturbation theory to the interactions of atomic electron with the classical radiation field. By a **classical radiation field** we mean the electric or magnetic field derivable from a classical (as opposed to quantized) radiation field.

The basic Hamiltonian, with $|\mathbf{A}|^2$ omitted, is

$$H = \frac{\mathbf{p}^2}{2m_e} + e\phi(\mathbf{x}) - \frac{e}{m_e c}\mathbf{A}\cdot\mathbf{p},$$

which is justified if

$$\nabla\cdot\mathbf{A} = 0;$$

specifically, we work with a monochromatic field of the plane wave for

$$\mathbf{A} = 2A_0\hat{\boldsymbol{\varepsilon}}\cos\left(\frac{\omega}{c}\hat{\mathbf{n}}\cdot\mathbf{x} - \omega t\right) \qquad \nabla\cdot\mathbf{A} = 0$$

where $\hat{\boldsymbol{\varepsilon}}$ and $\hat{\mathbf{n}}$ are the (linear) polarization and propagation direction.

$$\cos\left(\frac{\omega}{c}\hat{\mathbf{n}}\cdot\mathbf{x}-\omega t\right)=\frac{1}{2}\left[e^{i(\omega/c)\hat{\mathbf{n}}\cdot\mathbf{x}-i\omega t}+e^{-i(\omega/c)\hat{\mathbf{n}}\cdot\mathbf{x}+i\omega t}\right]$$

and treat $-(e/m_e c)\mathbf{A}\cdot\mathbf{p}$ as time-dependent potential, where we express $\mathbf{A}$

$$\mathbf{A}=A_0\hat{\boldsymbol{\varepsilon}}\left[e^{i(\omega/c)\hat{\mathbf{n}}\cdot\mathbf{x}-i\omega t}+e^{-i(\omega/c)\hat{\mathbf{n}}\cdot\mathbf{x}+i\omega t}\right]$$

If we compare it with: $V(t)=\mathscr{V}e^{i\omega t}+\mathscr{V}^{\dagger}e^{-i\omega t}$

we see that the $e^{-i\omega t}$-term in

$$-\left(\frac{e}{m_e c}\right)\mathbf{A}\cdot\mathbf{p}=-\left(\frac{e}{m_e c}\right)A_0\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p}\left[e^{i(\omega/c)\hat{\mathbf{n}}\cdot\mathbf{x}-i\omega t}+e^{-i(\omega/c)\hat{\mathbf{n}}\cdot\mathbf{x}+i\omega t}\right]$$

is responsible for absorption, while the $e^{+i\omega t}$-term is responsible for stimulated emission.

Let us now treat the absorption case in detail. We have

$$\mathscr{V}_{ni}^{\dagger} = -\frac{eA_0}{m_e c}\left(e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})}\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p}\right)_{ni}$$

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|\mathscr{V}_{ni}|^2}\rho(E_n)\Big|_{E_n\cong E_i-\hbar\omega}$$

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|\mathscr{V}_{ni}^{\dagger}|^2}\rho(E_n)\Big|_{E_n\cong E_i+\hbar\omega}$$

$$w_{i\to n} = \frac{2\pi}{\hbar}\frac{e^2}{m_e^2c^2}|A_0|^2|\langle n|e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})}\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p}|i\rangle|^2\delta(E_n - E_i - \hbar\omega)$$

The meaning of the δ-function is clear. If $|n\rangle$ forms a continuum, we simply integrate with $\rho(E_n)$. But even if $|n\rangle$ is discrete, because $|n\rangle$ cannot be a ground state (albeit a bound-state energy level), its energy is not infinitely sharp; there may be a natural broadening due to a finite lifetime (see Section 5.8); there can also be a mechanism for broadening due to collisions. In such cases, we regard $\delta(\omega-\omega_{ni})$ as

$$\delta(\omega-\omega_{ni}) = \lim_{\gamma\to 0}\left(\frac{\gamma}{2\pi}\right)\frac{1}{\left[(\omega-\omega_{ni})^2+\gamma^2/4\right]}$$

Finally, the incident electromagnetic wave itself is not perfectly monochromatic; in fact, there is always a finite frequency width.

We derive an absorption cross section as

$$\frac{\text{(Energy/unit time) absorbed by the atom } (i \to n)}{\text{Energy flux of the radiation field}}$$

For the energy flux (energy per area per unit time), classical electromagnetic theory gives us

$$c\mathscr{U} = \frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2,$$

where we have used

$$\mathscr{U} = \frac{1}{2}\left(\frac{E_{\max}^2}{8\pi} + \frac{B_{\max}^2}{8\pi}\right)$$

for energy density (energy per unit volume) with

$$\mathbf{E} = -\frac{1}{c}\frac{\partial}{\partial t}\mathbf{A}, \qquad \mathbf{B} = \nabla \times \mathbf{A}.$$

Putting everything together, we get (remembering that $\hbar\omega =$ energy absorbed by atom for each absorption process)

$$\sigma_{abs} = \frac{\hbar\omega(2\pi/\hbar)\left(e^2/m_e^2c^2\right)|A_0|^2|\langle n|e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})}\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p}|i\rangle|^2\delta(E_n - E_i - \hbar\omega)}{(1/2\pi)(\omega^2/c)|A_0|^2}$$

$$= \frac{4\pi^2\hbar}{m_e^2\omega}\left(\frac{e^2}{\hbar c}\right)|\langle n|e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})}\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p}|i\rangle|^2\delta(E_n - E_i - \hbar\omega). \qquad (5.7.14)$$

Equation (5.7.14) has the correct dimension $[1/(M^2/T)](M^2L^2/T^2)T = L^2$ if we recognize that $\alpha = e^2/\hbar c \simeq 1/137$ (dimensionless) and $\delta(E_n - E_i - \hbar\omega) = (1/\hbar)\delta(\omega_{ni} - \omega)$, where $\delta(\omega_{ni} - \omega)$ has time dimension T.

Electric Dipole Approximation

The *electric dipole approximation* (E1 approximation) is based on the fact that the wavelength of the radiation field is far longer than the atomic dimension, so that the series (remember $\omega/c = 1/\lambda\!\!\!^{-}$)

$$e^{i(\omega/c)\hat{\mathbf{n}}\cdot\mathbf{x}} = 1 + i\frac{\omega}{c}\hat{\mathbf{n}}\cdot\mathbf{x} + \cdots \tag{5.7.15}$$

can be approximated by its leading term, 1. The validity of this for a light atom is as follows: First, the $\hbar\omega$ of the radiation field must be of order of atomic level spacing, so

$$\hbar\omega \sim \frac{Ze^2}{(a_0/Z)} \approx \frac{Ze^2}{R_{\text{atom}}}. \tag{5.7.16}$$

This leads to

$$\frac{c}{\omega} = \lambda\!\!\!^{-} \sim \frac{c\hbar R_{\text{atom}}}{Ze^2} \approx \frac{137R_{\text{atom}}}{Z}. \tag{5.7.17}$$

In other words,

$$\frac{1}{\lambda\!\!\!^{-}} R_{\text{atom}} \sim \frac{Z}{137} \ll 1 \tag{5.7.18}$$

for light atoms (small Z). Because the matrix element of x is of order R_{atom}, that of x^2, of order R_{atom}^2, and so on, we see that the approximation of replacing (5.7.15) by its leading term is an excellent one.

Now we have

$$\langle n | e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})} \hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} | i \rangle \to \hat{\boldsymbol{\varepsilon}} \cdot \langle n | \mathbf{p} | i \rangle . \tag{5.7.19}$$

In particular, we take $\hat{\boldsymbol{\varepsilon}}$ along the x-axis (and $\hat{\mathbf{n}}$ along the z-axis). We must calculate $\langle n | p_x | i \rangle$. Using

$$[x, H_0] = \frac{i\hbar p_x}{m}, \tag{5.7.20}$$

we have

$$\begin{aligned} \langle n | p_x | i \rangle &= \frac{m}{i\hbar} \langle n | [x, H_0] | i \rangle \\ &= im\omega_{ni} \langle n | x | i \rangle . \end{aligned} \tag{5.7.21}$$

Because of the approximation of the dipole operator, this approximation scheme is called the **electric dipole approximation**. We may here recall [see (3.10.39)] the selection rule for the dipole matrix element. Since **x** is a spherical tensor of rank 1 with $q = \pm 1$, we must have $m' - m = \pm 1$, $|j' - j| = 0,1$ (no $0 \rightarrow 0$ transition). If $\hat{\boldsymbol{\varepsilon}}$ is along the y-axis, the same selection rule applies. On the other hand, if $\hat{\boldsymbol{\varepsilon}}$ is in the z-direction, $q = 0$; hence, $m' = m$.

With the electric dipole approximation, the absorption cross section (5.7.14) now takes a simpler form upon using (5.7.19) and (5.7.21) as

$$\sigma_{abs} = 4\pi^2 \alpha \omega_{ni} |\langle n|x|i\rangle|^2 \delta(\omega - \omega_{ni}). \tag{5.7.22}$$

In other words, σ_{abs} treated as a function of ω exhibits a sharp δ-function-like peak whenever $\hbar\omega$ corresponds to the energy-level spacing at $\omega \simeq (E_n - E_i)/\hbar$. Suppose $|i\rangle$ is the ground state, then ω_{ni} is necessarily positive; integrating (5.7.22), we get

$$\int \sigma_{abs}(\omega)\, d\omega = \sum_n 4\pi^2 \alpha \omega_{ni} |\langle n|x|i\rangle|^2. \tag{5.7.23}$$

The Wigner-Eckart Theorem. The matrix elements of tensor operators with respect to angular-momentum eigenstates satisfy

$$\langle \alpha', j'm'|T_q^{(k)}|\alpha, jm\rangle = \langle jk; mq|jk; j'm'\rangle \frac{\langle \alpha' j'||T^{(k)}||\alpha j\rangle}{\sqrt{2j+1}}, \tag{3.10.31}$$

where the **double-bar matrix element** *is independent of m and m', and q.*

$$T_q^{(k)} = Y_{l=k}^{m=q}(\mathbf{V})$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \to T_0^{(1)} = \sqrt{\frac{3}{4\pi}}V_z,$$

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{4\pi}}\frac{x \pm iy}{\sqrt{2}r} \to T_{\pm 1}^{(1)} = \sqrt{\frac{3}{4\pi}}\left(\mp\frac{V_x \pm iV_y}{\sqrt{2}}\right)$$

Example 1. Tensor of rank 0, that is, scalar $T_0^{(0)} = S$. The matrix element of a scalar operator satisfies

$$\langle \alpha', j'm'|S|\alpha, jm\rangle = \delta_{jj'}\delta_{mm'}\frac{\langle \alpha' j'||S||\alpha j\rangle}{\sqrt{2j+1}} \tag{3.10.38}$$

because S acting on $|\alpha, jm\rangle$ is like adding an angular momentum of zero. Thus the scalar operator cannot change j, m values.

Example 2. Vector operator which in the spherical tensor language is a rank 1 tensor. The spherical component of $\mathbf{V}$ can be written as $V_{q=\pm 1,0}$, so we have the selection rule

$$\Delta m \equiv m' - m = \pm 1, 0 \qquad \Delta j \equiv j' - j = \begin{cases} \pm 1 \\ 0. \end{cases} \tag{3.10.39}$$

In atomic physics we define **oscillator strength**, f_{ni}, as

$$f_{ni} \equiv \frac{2m\omega_{ni}}{\hbar}|\langle n|x|i\rangle|^2. \tag{5.7.24}$$

It is then straightforward (consider $[x,[x, H_0]]$) to establish the **Thomas-Reiche-Kuhn sum rule**,

$$\sum_n f_{ni} = 1. \tag{5.7.25}$$

In terms of the integration over the absorption cross section, we have

$$\int \sigma_{abs}(\omega)\, d\omega = \sum_n 4\pi^2 \alpha \omega_{ni} |\langle n|x|i\rangle|^2 \qquad \alpha = e^2/\hbar c \simeq 1/137$$

$$\int \sigma_{abs}(\omega)\, d\omega = \frac{4\pi^2 \alpha \hbar}{2m_e} = 2\pi^2 c \left(\frac{e^2}{m_e c^2}\right). \tag{5.7.26}$$

Notice how $\hbar$ has disappeared. Indeed, this is just the oscillation sum rule already known in classical electrodynamics (Jackson 1975, for instance). Historically, this was one of the first examples of how "new quantum mechanics" led to the correct classical result. This sum rule is quite remarkable because we did not specify in detail the form of the Hamiltonian.

$$\exp[\mathrm{i}\,(\omega/c)\,\mathbf{n}\cdot\mathbf{r}] = 1 + \mathrm{i}\,\frac{\omega}{c}\,\mathbf{n}\cdot\mathbf{r} + \cdots,$$

$$\langle n|\exp[\mathrm{i}\,(\omega/c)\,\mathbf{n}\cdot\mathbf{r}]\,\boldsymbol{\epsilon}\cdot\mathbf{p}\,|i\rangle \simeq \boldsymbol{\epsilon}\cdot\langle n|\mathbf{p}|i\rangle.$$

$$[\mathbf{r}, H_0] = \frac{\mathrm{i}\,\hbar\,\mathbf{p}}{m_e},$$

$$\langle n|\mathbf{p}|i\rangle = -\mathrm{i}\,\frac{m_e}{\hbar}\langle n|[\mathbf{r}, H_0]|i\rangle = \mathrm{i}\,m_e\,\omega_{ni}\,\langle n|\mathbf{r}|i\rangle.$$

$$\sigma_{\mathrm{abs}} = 4\pi^2\,\alpha\,\omega_{ni}\,|\langle n|\boldsymbol{\epsilon}\cdot\mathbf{r}|i\rangle|^2\,\delta(\omega-\omega_{ni}),$$

$$\int \sigma_{\mathrm{abs}}(\omega)\,d\omega = \sum_n 4\pi^2\,\alpha\,\omega_{ni}\,|\langle n|\boldsymbol{\epsilon}\cdot\mathbf{r}|i\rangle|^2.$$

$$[x, [x, H_0]\,] = -\frac{\hbar^2}{m_e}.$$

$$\langle i|[x, [x, H_0]\,]|i\rangle = \langle i|x^2\,H_0 + H_0\,x^2 - 2\,x\,H_0\,x|i\rangle = -\frac{\hbar^2}{m_e},$$

$$2\sum_n\left(\langle i|x|n\rangle\,E_i\langle n|x|i\rangle - \langle i|x|n\rangle\,E_n\langle n|x|i\rangle\right) = -\frac{\hbar^2}{m_e}.$$

$$\frac{2\,m_e}{\hbar}\sum_n \omega_{ni}\,|\langle n|x|i\rangle|^2 = 1.$$

$$\int \sigma_{\mathrm{abs}}(\omega)\,d\omega = \frac{2\pi^2\alpha\,\hbar}{m_e} = \frac{\pi\,e^2}{2\,\epsilon_0\,m_e\,c}.$$

Z:

$$\Delta l = \pm 1,$$
$$\Delta m = 0.$$

X, y:

$$\Delta l = \pm 1,$$
$$\Delta m = \pm 1.$$

general:

$$\Delta l = \pm 1,$$
$$\Delta m = 0, \pm 1.$$

These are termed the *selection rules* for electric dipole transitions. It is clear, for instance, that the electric dipole approximation allows a transition from a $2p$ state to a $1s$ state, but disallows a transition from a $2s$ to a $1s$ state. The latter transition is called a *forbidden transition*.

Forbidden transitions are not strictly forbidden. Instead, they take place at a far lower rate than transitions which are allowed according to the electric dipole approximation. After electric dipole transitions, the next most likely type of transition is a *magnetic dipole transition*, which is due to the interaction between the electron spin and the oscillating magnetic field of the incident electromagnetic radiation. Magnetic dipole transitions are typically about 10^5 times more unlikely than similar electric dipole transitions. The first-order term in Eq. (845) yields so-called *electric quadrupole transitions*. These are typically about 10^8 times more unlikely than electric dipole transitions. Magnetic dipole and electric quadrupole transitions satisfy different selection rules than electric dipole transitions: for instance, the selection rules for electric quadrupole transitions are $\Delta l = 0, \pm 2$. Thus, transitions which are forbidden as electric dipole transitions may well be allowed as magnetic dipole or electric quadrupole transitions.

Photoelectric Effect

We now consider the **photoelectric effect**—that is, the ejection of an electron when an atom is placed in the radiation field. The basic process is considered to be the transition from an atomic (bound) state to a continuum state $E > 0$. Therefore, $|i\rangle$ is the ket for an atomic state, while $|n\rangle$ is the ket for a continuum state, which can be taken to be a plane-wave state $|\mathbf{k}_f\rangle$, an approximation that is valid if the final electron is not too slow. Our earlier formula for $\sigma_{abs}(\omega)$ can still be used, except that we must now integrate $\delta(\omega_{ni} - \omega)$ together with the density of final states $\rho(E_n)$.

Our basic task is to calculate the number of final states per unit energy interval. As we will see in a moment, this is an example where the matrix element depends not only on the final state energy but also on the momentum *direction*. We must therefore consider a group of final states with both similar momentum directions and similar energies.

To count the number of states it is convenient to use the box normalization convention for plane-wave states. We consider a plane-wave state normalized if when we integrate the square modulus of its wave function for a cubic box of side L, we obtain unity. Furthermore, the state is assumed to satisfy the periodic boundary condition with periodicity of the side of the box. The wave function must then be of form

$$\langle \mathbf{x}|\mathbf{k}_f\rangle = \frac{e^{i\mathbf{k}_f\cdot\mathbf{x}}}{L^{3/2}}, \tag{5.7.27}$$

where the allowed values of k_x must satisfy

$$k_x = \frac{2\pi n_x}{L}, \ldots, \tag{5.7.28}$$

with n_x a positive or negative integer. Similar restrictions hold for k_y and k_z. Notice that as $L \to \infty$, k_x, k_y, and k_z become continuous variables.

The problem of counting the number of states is reduced to that of counting the number of dots in three-dimensional lattice space. We define n such that

$$n^2 = n_x^2 + n_y^2 + n_z^2. \tag{5.7.29}$$

As $L \to \infty$, it is a good approximation to treat n as a continuous variable; in fact it is just the magnitude of the radial vector in the lattice space. Let us consider a small-volume element such that the radial vector falls within n and $n + dn$ and the solid angle element $d\Omega$; clearly, it is of volume $n^2\, dn\, d\Omega$. The energy of the final-state plane wave is related to k_f and hence to n; we have

$$E = \frac{\hbar^2 k_f^2}{2m_e} = \frac{\hbar^2}{2m_e} \frac{n^2(2\pi)^2}{L^2}. \tag{5.7.30}$$

Furthermore, the direction of the radial vector in the lattice space is just the momentum direction of the final state, so the number of states in the interval between E and $E + dE$ with direction into $d\Omega$ being $\mathbf{k}_f$ is (remember $dE = (\hbar^2 k_f / m_e)\, dk_f$) given by*

$$n^2\, d\Omega \frac{dn}{dE}\, dE = \left(\frac{L}{2\pi}\right)^3 \left(\mathbf{k}_f^2\right) \frac{dk_f}{dE}\, d\Omega\, dE$$

Density of States (DOS)
We can see AS1.1 page 17 to 23

$$= \left(\frac{L}{2\pi}\right)^3 \frac{m_e}{\hbar^2} k_f\, dE\, d\Omega. \qquad (5.7.31)$$

We can now put everything together to obtain an expression for the differential cross section for the photoelectric effect:

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2 \alpha \hbar}{m_e^2 \omega} |\langle \mathbf{k}_f | e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})} \hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} | i \rangle|^2 \frac{m_e k_f L^3}{\hbar^2 (2\pi)^3}. \qquad (5.7.32)$$

To be specific, let us consider the ejection of a K shell (the innermost shell) electron caused by absorption of light. The initial-state wave function is essentially the same as the ground-state hydrogen atom wave function except that the Bohr radius a_0 is replaced by a_0/Z. Thus

$$\langle \mathbf{k}_f | e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})}\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p}|i\rangle = \hat{\boldsymbol{\varepsilon}}\cdot\int d^3x \frac{e^{-i\mathbf{k}_f\cdot\mathbf{x}}}{L^{3/2}} e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})} \times(-i\hbar\nabla)\left[e^{-Zr/a_0}\left(\frac{Z}{a_0}\right)^{3/2}\right]. \tag{5.7.33}$$

Integrating by parts, we can pass ∇ to the left side. Furthermore,

$$\hat{\boldsymbol{\varepsilon}}\cdot[\nabla e^{i(\omega/c)(\hat{\mathbf{n}}\cdot\mathbf{x})}] = 0 \tag{5.7.34}$$

because $\hat{\boldsymbol{\varepsilon}}$ is perpendicular to $\hat{\mathbf{n}}$. On the other hand, ∇ acting on $e^{-i\mathbf{k}_f\cdot\mathbf{x}}$ brings down $-i\mathbf{k}_f$, which can be taken outside the integral. Thus to evaluate (5.7.33), all we need to do is take the Fourier transform of the atomic wave function with respect to

$$\mathbf{q} \equiv \mathbf{k}_f - \left(\frac{\omega}{c}\right)\hat{\mathbf{n}}. \tag{5.7.35}$$

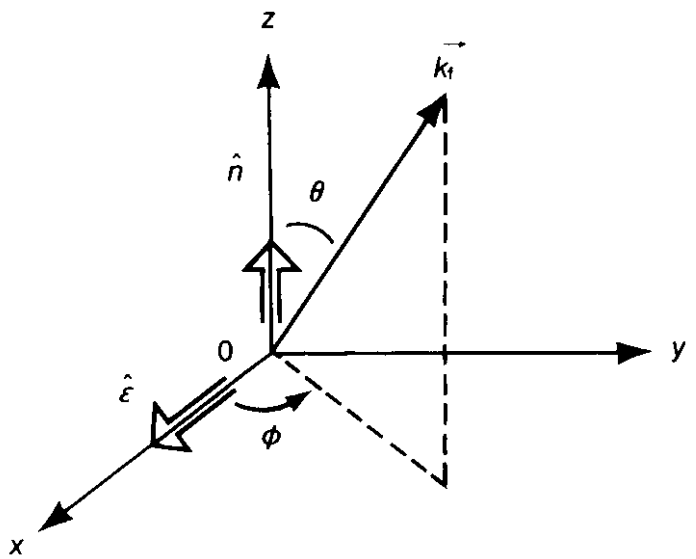
The final answer is (see Problem 39 of this chapter for the Fourier transform of the hydrogen atom wave function)

$$\frac{d\sigma}{d\Omega} = 32e^2k_f\frac{\left(\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{k}_f\right)^2}{mc\omega}\frac{Z^5}{a_0^5}\frac{1}{\left[\left(Z^2/a_0^2\right)+q^2\right]^4}. \tag{5.7.36}$$

If we introduce the coordinate system shown in Figure 5.10, we can write the differential cross section in terms of θ and ϕ using

$$\left(\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{k}_f\right)^2 = k_f^2\sin^2\theta\cos^2\phi$$

$$q^2 = k_f^2 - 2k_f\frac{\omega}{c}\cos\theta + \left(\frac{\omega}{c}\right)^2. \tag{5.7.37}$$



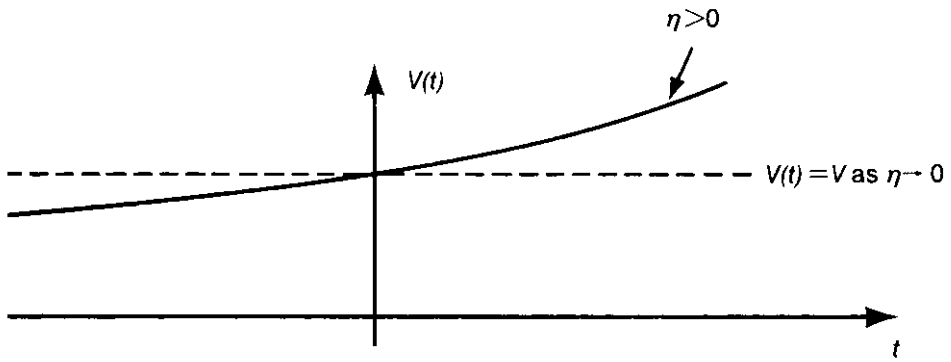
ENERGY SHIFT AND DECAY WIDTH

Our considerations so far have been restricted to the question of how states other than the initial state get populated. In other words, we have been concerned with the time development of the coefficient $c_n(t)$ with $n \neq i$. The question naturally arises, What happens to $c_i(t)$ itself?

To avoid the effect of a sudden change in the Hamiltonian, we propose to increase the perturbation very slowly. In the remote past $(t \to -\infty)$ the time-dependent potential is assumed to be zero. We then *gradually* turn on the perturbation to its full value; specifically,

$$V(t) = e^{\eta t} V \tag{5.8.1}$$

where V is assumed to be constant and η is small and positive. At the end of the calculation, we let $\eta \to 0$ (see Figure 5.11), and the potential then becomes constant at all times.



In the remote past, we take this time to be $-\infty$, so the state ket in the interaction picture is assumed to be $|i\rangle$. Our basic aim is to evaluate $c_i(t)$. However, before we do that, let us make sure that the old formula of the golden rule (see Section 5.6) can be reproduced using this slow-turn-on method. For $c_n(t)$ with $n \neq i$, we have [using (5.6.17)]

$$c_n^{(0)}(t) = 0$$

$$c_n^{(1)}(t) = \frac{-i}{\hbar} V_{ni} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} e^{i\omega_{ni} t'} \, dt'$$

$$= \frac{-i}{\hbar} V_{ni} \frac{e^{\eta t + i\omega_{ni} t}}{\eta + i\omega_{ni}}. \tag{5.8.2}$$

To lowest nonvanishing order, the transition probability is therefore given by

$$|c_n(t)|^2 \simeq \frac{|V_{ni}|^2}{\hbar^2} \frac{e^{2\eta t}}{\eta^2 + \omega_{ni}^2}, \tag{5.8.3}$$

or

$$\frac{d}{dt}|c_n(t)|^2 \simeq \frac{2|V_{ni}|^2}{\hbar^2} \left(\frac{\eta e^{2\eta t}}{\eta^2 + \omega_{ni}^2} \right). \tag{5.8.4}$$

We now let $\eta \to 0$. Clearly, it is all right to replace $e^{\eta t}$ by unity, but note

$$\lim_{\eta \to 0} \frac{\eta}{\eta^2 + \omega_{ni}^2} = \pi \delta(\omega_{ni}) = \pi \hbar \delta(E_n - E_i). \tag{5.8.5}$$

This leads to the golden rule,

$$w_{i \to n} \simeq \left(\frac{2\pi}{\hbar} \right) |V_{ni}|^2 \delta(E_n - E_i). \tag{5.8.6}$$

Encouraged by this result, let us calculate $c_i^{(0)}$, $c_i^{(1)}$, and $c_i^{(2)}$, again using (5.6.17). We have

$$c_i^{(0)} = 1$$

$$c_i^{(1)} = \frac{-i}{\hbar} V_{ii} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} \, dt' = \frac{-i}{\hbar \eta} V_{ii} e^{\eta t}$$

$$c_i^{(2)} = \left(\frac{-i}{\hbar} \right)^2 \sum_m |V_{mi}|^2 \lim_{t_0 \to -\infty} \int_{t_0}^{t} dt' \, e^{i\omega_{im} t' + \eta t'} \frac{e^{i\omega_{mi} t' + \eta t'}}{i(\omega_{mi} - i\eta)}$$

$$= \left(\frac{-i}{\hbar} \right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} + \left(\frac{-i}{\hbar} \right) \sum_{m \neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta (E_i - E_m + i\hbar\eta)}. \tag{5.8.7}$$

Thus up to second order we have

$$c_i(t) \simeq 1 - \frac{i}{\hbar\eta} V_{ii} e^{\eta t} + \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} + \left(\frac{-i}{\hbar}\right) \sum_{m \neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta(E_i - E_m + i\hbar\eta)}. \tag{5.8.8}$$

Now consider the time derivative of c_i [$dc_i(t)/dt \equiv \dot{c}_i$], which we have from (5.8.8). Upon dividing by c_i and letting $\eta \to 0$ (thus replacing $e^{\eta t}$ and $e^{2\eta t}$ by unity), we get

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

$$\simeq \frac{-i}{\hbar} V_{ii} + \left(\frac{-i}{\hbar}\right) \sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta}. \tag{5.8.9}$$

$$\frac{\dot{c}_i}{c_i} = \left(\frac{-\mathrm{i}}{\hbar}\right) \Delta_i, \quad \Delta_i = H_{ii} + \lim_{\eta \to 0} \sum_{m \neq i} \frac{|H_{mi}|^2}{E_i - E_m + \mathrm{i}\hbar\eta}$$

$$\lim_{\epsilon \to 0} \frac{1}{x + \mathrm{i}\epsilon} = P\frac{1}{x} - \mathrm{i}\pi\delta(x),$$

$$\Delta_i = H_{ii} + P \sum_{m \neq i} \frac{|H_{mi}|^2}{E_i - E_m} - \mathrm{i}\pi \sum_{m \neq i} |H_{mi}|^2 \delta(E_i - E_m).$$

Expansion (5.8.9) is formally correct up to second order in V. Note here that $\dot{c}_i(t)/c_i(t)$ is now independent of t. Equation (5.8.9) is a differential equation that is to hold *at all times*. Having obtained this, it is convenient to renormalize c_i so that $c_i(0)=1$. We now try the ansatz

$$c_i(t)=e^{-i\Delta_i t/\hbar}, \qquad \frac{\dot{c}_i(t)}{c_i(t)}=\frac{-i}{\hbar}\Delta_i \tag{5.8.10}$$

with Δ_i constant (in time) but not necessarily real. Clearly (5.8.10) is consistent with (5.8.9) because the right-hand side of (5.8.10) is constant. We can see the physical meaning of Δ_i by noting that $e^{-i\Delta_i t/\hbar}|i\rangle$ in the interaction picture implies $e^{-i\Delta_i t/\hbar - iE_i t/\hbar}|i\rangle$ in the Schrödinger picture. In other words,

$$E_i \to E_i + \Delta_i \tag{5.8.11}$$

as a result of perturbation. That is, we have calculated the *level shift* using time-*dependent* perturbation theory. Now expand, as usual,

$$\Delta_i = \Delta_i^{(1)} + \Delta_i^{(2)} + \cdots, \tag{5.8.12}$$

and compare (5.8.10) with (5.8.9); we get to first order

$$\Delta_i^{(1)} = V_{ii}. \tag{5.8.13}$$

But this is just what we expect from *t-independent perturbation theory*. Before we look at $\Delta_i^{(2)}$, recall

$$\lim_{\varepsilon \to 0} \frac{1}{x + i\varepsilon} = \mathrm{Pr}.\frac{1}{x} - i\pi\delta(x). \tag{5.8.14}$$

Thus

$$\mathrm{Re}\left(\Delta_i^{(2)}\right) = \mathrm{Pr}.\sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m} \tag{5.8.15a}$$

$$\mathrm{Im}\left(\Delta_i^{(2)}\right) = -\pi \sum_{m \neq i} |V_{mi}|^2 \delta(E_i - E_m). \tag{5.8.15b}$$

But the right-hand side of (5.8.15b) is familiar from the golden rule, so we can identify

$$\sum_{m \neq i} w_{i \to m} = \frac{2\pi}{\hbar} \sum_{m \neq i} |V_{mi}|^2 \delta(E_i - E_m) = -\frac{2}{\hbar}\mathrm{Im}\left[\Delta_i^{(2)}\right]. \tag{5.8.16}$$

Coming back to $c_i(t)$, we can write (5.8.10) as

$$c_i(t) = e^{-(i/\hbar)[\mathrm{Re}(\Delta_i)t] + (1/\hbar)[\mathrm{Im}(\Delta_i)t]}. \tag{5.8.17}$$

If we define

$$\frac{\Gamma_i}{\hbar} \equiv -\frac{2}{\hbar}\mathrm{Im}(\Delta_i), \tag{5.8.18}$$

then

$$|c_i|^2 = e^{2\,\mathrm{Im}(\Delta_i)t/\hbar} = e^{-\Gamma_i t/\hbar}. \tag{5.8.19}$$

Therefore, Γ_i characterizes the rate at which state $|i\rangle$ disappears.

It is worth checking the probability conservation up to second order in V for small t:

$$|c_i|^2 + \sum_{m \neq i} |c_m|^2 = (1 - \Gamma_i t/\hbar) + \sum_{m \neq i} w_{i \to m} t = 1, \tag{5.8.20}$$

where (5.8.16) has been used. Thus the probabilities for finding the initial state and all other states add up to 1. Put in another way, the depletion of state $|i\rangle$ is compensated by the growth of states other than $|i\rangle$.

To summarize, the real part of the energy shift is what we usually associate with the level shift. The imaginary part of the energy shift is, apart from -2 [see (5.8.18)], the **decay width**. Note also

$$\frac{\hbar}{\Gamma_i} = \tau_i \tag{5.8.21}$$

where τ_i is the mean lifetime of state $|i\rangle$ because

$$|c_i|^2 = e^{-t/\tau_i}. \tag{5.8.22}$$

To see why Γ_i is called *width*, we look at the Fourier decomposition

$$\int f(E) e^{-iEt/\hbar}\, dE = e^{-i[E_i + \mathrm{Re}(\Delta_i)]t/\hbar - \Gamma_i t/2\hbar}. \tag{5.8.23}$$

Using the Fourier inversion formula, we get

$$|f(E)|^2 \propto \frac{1}{\{E - [E_i + \mathrm{Re}(\Delta_i)]\}^2 + \Gamma_i^2/4} \tag{5.8.24}$$

Therefore, Γ_i has the usual meaning of full width at half maximum. Notice that we get the time-energy uncertainty relation from (5.8.21)

$$\Delta t \, \Delta E \sim \hbar, \tag{5.8.25}$$

where we identify the uncertainty in the energy with Γ_i and the mean lifetime with Δt.

Even though we discussed the subject of energy shift and decay width using the constant perturbation V obtained as the limit of (5.8.1) when $\eta \to 0$, we can easily generalize our considerations to the harmonic perturbation case discussed in Section 5.6. All we must do is to let

$$E_{n(m)} - E_i \to E_{n(m)} - E_i \pm \hbar\omega \tag{5.8.26}$$

in (5.8.2), (5.8.8), and (5.8.15), and so on. The quantum-mechanical description of unstable states we have developed here is originally due to Wigner and Weisskopf in 1930.

Energy-shifts and decay-widths

We have examined how a state $|n\rangle$, other than the initial state $|i\rangle$, becomes populated as a result of some time-dependent perturbation applied to the system. Let us now consider how the initial state becomes depopulated.

It is convenient to gradually turn on the perturbation from zero at $t = -\infty$. Thus,

$$H_1(t) = \exp(\eta\, t)\, H_1, \tag{862}$$

where η is small and positive, and H_1 is a constant.