1 Elements of Atoms, Molecules, and Wave Propagation

1.1 One-Electron Atoms

1.1.1 Hydrogenic Atoms and Wavefunctions

This book begins with the simplest hydrogenic atom. Within the spectral resolution of its interaction with ultrafast light pulses, this atom can be considered as a nonrelativistic electron in the field of a Coulomb potential $V(r) = -Z/r$ from the nucleus of infinite mass with positive charge $Z(= 1)$. In spherical coordinates, the eigenstate can be expressed as

$$\psi_{Elm}(\mathbf{r}) = R_{El}(r)Y_{lm}(\theta, \phi), \tag{1.1}$$

where Y_{lm} is the familiar spherical harmonic. In this book, atomic units, where $m = |e| = \hbar = 1$ will be used unless otherwise noted. Here, m and e are the mass and charge of the electron, respectively. The inside back cover of the book gives fundamental constants and conversion factors that are useful for attosecond and strong-field physics.

Introducing $u_{El}(r) = rR_{El}(r)$, the radial equation for u_{El} reads

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right] u_{El}(r) = Eu_{El}(r). \tag{1.2}$$

For the bound states, the eigenvalues are

$$E_n = -\frac{Z^2}{2n^2}, \tag{1.3}$$

with the principal quantum number n.

The radial wavefunctions are given by

$$R_{nl}(r) = \frac{u_{nl}(r)}{r} = N_{nl}e^{-\frac{Z}{n}r}\left(\frac{2Z}{n}r\right)^l {}_1F_1\left(l+1-n, 2l+2, \frac{2Z}{n}r\right), \tag{1.4}$$

where ${}_1F_1$ is the confluent hypergeometric function. The normalization factor N_{nl} is

$$N_{nl} = \frac{1}{(2l+1)!}\sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n+l)!}{2n(n-l-1)!}}. \tag{1.5}$$

For the wavefunction of a continuum state, let $E = k^2/2$, the radial equation of a hydrogenic atom, where

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} + k^2 \right] u_{El}(r) = 0 \tag{1.6}$$

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has two linearly independent solutions: the regular Coulomb function $F_l(\gamma, kr)$ and the irregular Coulomb function $G_l(\gamma, kr)$. The former vanishes at $r = 0$ while the latter diverges. Therefore the allowed solution takes the form

$$u_{El}(r) = CF_l(\gamma, kr), \tag{1.7}$$

where the Sommerfeld parameter $\gamma = -\frac{Z}{k}$.

The asymptotic behaviors of F_l and G_l are

$$F_l(\gamma, kr) \overset{r \to \infty}{\sim} \sin(kr - \gamma \ln(2kr) - l\pi/2 + \sigma_{El}), \tag{1.8}$$

$$G_l(\gamma, kr) \overset{r \to \infty}{\sim} \cos(kr - \gamma \ln(2kr) - l\pi/2 + \sigma_{El}), \tag{1.9}$$

where the real quantity $\sigma_{El} = \arg[\Gamma(l + 1 + i\gamma)]$ is the Coulomb phase shift.

The radial wavefunctions $u_{El}(r)$ are not square integrable. They are usually momentum or energy normalized, which means

$$\int_0^\infty u_{El}(r)u_{E'l}(r)dr = \delta(k - k') \quad \text{momentum normalized}, \tag{1.10}$$

$$\int_0^\infty u_{El}(r)u_{E'l}(r)dr = \delta(E - E') \quad \text{energy normalized}. \tag{1.11}$$

For momentum normalization, the normalization constant $C = \sqrt{\frac{2}{\pi}}$ and for energy normalization $C = \sqrt{\frac{2}{\pi k}}$.

The hydrogenic wavefunction is also separable in parabolic coordinates defined by

$$\xi = r + z = r(1 + \cos\theta) \tag{1.12}$$

$$\eta = r - z = r(1 - \cos\theta) \tag{1.13}$$

$$\phi = \arctan\frac{y}{x} \tag{1.14}$$

with $0 \le \xi \le \infty$, $0 \le \eta \le \infty$, $0 \le \phi \le 2\pi$. The surfaces $\xi = const$ and $\eta = const$ are paraboloids of revolution about the z-axis.

In parabolic coordinates, the eigensolutions can be written as

$$\psi(\xi, \eta, \phi) = f(\xi)g(\eta)\Phi(\phi), \tag{1.15}$$

where the ϕ dependence is $\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ with $m = 0, \pm 1, \pm 2, \ldots$ being the magnetic quantum number.

For bound states these are called Stark states. For unbound states that exhibit azimuthal symmetry ($m = 0$), the continuum wavefunction is

$$\psi(\mathbf{r}) = Ce^{ik\frac{\xi - \eta}{2}}{}_1F_1(-i\gamma, 1, ik\eta) = Ce^{ikz}{}_1F_1(-i\gamma, 1, ik(r - z)), \tag{1.16}$$

where C depends on the normalization convention.

1.1.2 Single Active Electron Model for Atoms

In principle, when an atom (or ion) consists of N electrons, one needs to solve the complicated N-electron Schrödinger equation. However, for measurements where the interaction involves only one electron, treating such an electron alone is desirable. In this single "active" electron model, all of the other electrons are assumed to provide only an effective potential to this active one. In this way, the whole atom may be analyzed in the framework of a one-electron system in a central model potential $V(r)$. This potential can be written as a pure Coulomb potential plus a short-range potential

$$V(r) = -\frac{Z_c}{r} + V_{sr}(r). \tag{1.17}$$

The short-range potential $V_{sr}(r)$ must satisfy

$$\lim_{r\to\infty} r^2 V_{sr}(r) = 0. \tag{1.18}$$

Note that the parameter Z_c in Equation 1.17 is the asymptotic charge felt by the active electron. In a neutral atom, $Z_c = 1$.

The radial equation for the bound state with energy $E = -\beta^2/2$ for such a model one-electron system is

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z_c}{r} - 2V_{sr}(r) - \beta^2\right] u_{El}(r) = 0. \tag{1.19}$$

This equation can be solved numerically. The energy level E_{nl} can be expressed by

$$E_{nl} = -\frac{Z_c^2}{2(n - \Delta_{nl})^2}, \tag{1.20}$$

where Δ_{nl} is called the quantum defect as a result of the short-range potential $V_{sr}(r)$. For large n, the quantum defect is independent of n.

For the unbound state with energy $E = k^2/2$, the radial equation for this system is

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z_c}{r} - 2V_{sr}(r) + k^2\right] u_{El}(r) = 0. \tag{1.21}$$

This equation can also be solved numerically. In the asymptotic region in which V_{sr} vanishes,

$$u_{El}(r) \overset{r\to\infty}{\sim} A F_l(\gamma, kr) + B G_l(\gamma, kr)$$
$$\overset{r\to\infty}{\sim} C \sin[kr - \gamma \ln(2kr) - l\pi/2 + \sigma_{El} + \delta_{El}]. \tag{1.22}$$

Here, $\gamma = -Z_c/k$ and $\sigma_{El} = \arg[\Gamma(l+1+i\gamma)]$ is the Coulomb phase shift. $C = \sqrt{A^2 + B^2}$ is the normalization constant mentioned previously. $\delta_{El} = \arctan\frac{B}{A}$ is the additional phase shift caused by the short-range potential.

1.1.3 Scattering of an Electron by a Central Field Potential

Scattering by a Short-Range Potential

Consider an electron scattered by a target where the interaction can be modeled by a short-range potential $V_{sr}(r)$. In the asymptotic region where $V_{sr}(r)$ vanishes, the wavefunction should take the form:

$$\psi \overset{r \to \infty}{\sim} e^{ikz} + f(\theta)\frac{e^{ikr}}{r}. \tag{1.23}$$

Here, the energy of the incident electron $E = k^2/2$. The first term is an incident plane wave traveling along the z direction; the second term is an outgoing scattered spherical wave. The scattering amplitude $f(\theta)$ is a complex quantity depending on scattering angle θ and energy E. Due to cylindrical symmetry, f is independent of ϕ. The differential cross-section is

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2, \tag{1.24}$$

and the total cross-section is

$$\sigma = \int |f(\theta)|^2 d\Omega = 2\pi \int_0^\pi |f(\theta)|^2 \sin\theta d\theta. \tag{1.25}$$

The total wavefunction ψ can be expanded in a series of partial waves as

$$\psi = \sum_{l=0}^\infty A_l \frac{u_{El}(r)}{r} P_l(\cos\theta), \tag{1.26}$$

where $u_{El}(r)$ is the solution of the radial equation

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - 2V_{sr}(r) + k^2 \right] u_{El}(r) = 0. \tag{1.27}$$

In the asymptotic region as r goes to infinity

$$
\begin{aligned}
u_{El}(r) &\overset{r \to \infty}{\sim} Akrj_l(kr) + Bkrn_l(kr) \\
&\overset{r \to \infty}{\sim} A\sin(kr - l\pi/2) - B\cos(kr - l\pi/2) \\
&= C\sin(kr - l\pi/2 + \delta_{El}),
\end{aligned}
\tag{1.28}
$$

where j_l and n_l are spherical Bessel and Neumann functions, $C = \sqrt{A^2 + B^2}$ and $\delta_{El} = -\arctan(B/A)$. The phase shift δ_{El} is an important quantity because it carries information about the short-range potential near the nucleus to physical effect in the asymptotic region. Note that δ_{El} depends on both the energy E and the angular momentum quantum number l.

With the help of

$$e^{ikz} = \sum_{l=0}^\infty (2l+1) i^l j_l(kr) P_l(\cos\theta) \overset{r \to \infty}{\sim} \sum_{l=0}^\infty (2l+1) e^{il\pi/2} \frac{\sin(kr - l\pi/2)}{kr} P_l(\cos\theta), \tag{1.29}$$

and comparison to Equation 1.26 in the asymptotic region (here, choose $C = 1$), one can obtain

$$A_l e^{-i\delta_{El}} = \frac{1}{k}(2l + 1)e^{il\pi/2}. \tag{1.30}$$

By comparing Equations 1.23 and 1.26 in the asymptotic region, one can easily obtain

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l + 1)e^{i\delta_{El}}\sin\delta_{El}P_l(\cos\theta). \tag{1.31}$$

The differential cross-section is $|f(\theta)|^2$. The total cross-section is

$$\sigma = 2\pi\int_0^{\pi}|f(\theta)|^2\sin\theta d\theta = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l + 1)\sin^2\delta_{El}. \tag{1.32}$$

Each partial wave contributes

$$\sigma_l = \frac{4\pi}{k^2}(2l + 1)\sin^2\delta_{El} \tag{1.33}$$

to the total cross-section. When evaluating the cross-section, it is not practical to include all partial waves. If the short-range potential has a range a, it is reasonable to cut off the partial-wave expansion at $l_{max} \approx ka$. Thus, in low-energy scattering, only a few partial waves are needed.

Scattering by a Pure Coulomb Potential

If the incident direction of the electron is chosen as the z direction, for a pure Coulomb potential $V(r) = -Z/r$, the total wavefunction can be expressed in parabolic coordinates as

$$\psi = Ce^{ikz}{}_1F_1(-i\gamma, 1, ik(r - z)), \tag{1.34}$$

where $\gamma = -Z/k$. By choosing $C = e^{-\pi\gamma/2}\Gamma(1 + i\gamma)$, at large $|r - z|$ the wavefunction has the asymptotic form

$$\psi \overset{|r-z|\to\infty}{\sim} e^{ikz+i\gamma\,\ln[k(r-z)]}\left(1 + \frac{\gamma^2}{ik(r - z)} + \cdots\right)$$
$$+ f_c(\theta)\frac{e^{ikr-i\gamma\,\ln(2kr)}}{r}\left(1 + \frac{(1 + i\gamma)^2}{ik(r - z)} + \cdots\right). \tag{1.35}$$

The Coulomb scattering amplitude is given by

$$f_c(\theta) = -\frac{\gamma}{2k\sin^2(\theta/2)}e^{-i\gamma\,\ln[\sin^2(\theta/2)]+2i\sigma_{E0}}, \tag{1.36}$$

in which $\sigma_{E0} = \arg[\Gamma(1 + i\gamma)]$.

Clearly, the asymptotic expansion does not hold for $\theta = 0$ ($r = z$). For large $|r - z|$ the incident wave and the outgoing wave have each acquired a logarithmic phase. The differential cross-section is

$$\frac{d\sigma_c}{d\Omega} = |f_c(\theta)|^2 = \frac{\gamma^2}{4k^2\sin^4(\theta/2)} = \frac{Z^2}{16E^2\sin^4(\theta/2)}. \tag{1.37}$$

This result is identical to the Rutherford formula derived from classical mechanics. The Rutherford differential cross-section diverges strongly in the forward direction $\theta = 0$, and the total cross-section is not defined since the integral also diverges. This is the consequence of the long-range Coulomb potential. However, in actual situations, the Coulomb potential at large distance is screened by the environment, and thus the cross-section is finite.

Scattering by a Modified Coulomb Potential

For an electron scattered by a model potential, which consists of a Coulomb part and a short-range part $V(r) = -Z_c/r + V_{sr}(r)$, the scattering amplitude can be written as

$$f(\theta) = f_c(\theta) + f_s(\theta), \tag{1.38}$$

where f_c is the Coulomb scattering amplitude given by Equation 1.36 with $\gamma = -Z_c/k$, and f_s denotes the modification due to the short-range potential. Using partial-wave expansion, f_s is given by

$$f_s(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1)e^{2i\sigma_{El}}e^{i\delta_{El}} \sin \delta_{El} P_l(\cos \theta), \tag{1.39}$$

where $\sigma_{El} = \arg[\Gamma(l+1+i\gamma)]$ is the Coulomb phase shift. δ_{El} is the additional phase shift due to the short-range potential (see Equation 1.22). The differential cross-section is

$$\frac{d\sigma}{d\Omega} = |f_c(\theta) + f_s(\theta)|^2. \tag{1.40}$$

Scattering Cross-Section across a Resonance

In general, the phase shift δ_{El} varies smoothly with the incident energy E as does the partial cross-section σ_l. However, δ_{El} may vary rapidly near a resonance. As a result, the corresponding partial cross-section σ_l may also change dramatically in this energy interval. Resonance usually happens for a certain partial wave. Near the resonance, the total cross-section is dominated by this partial wave, that is, $\sigma \approx \sigma_l$. For example, the effective potential for the lth partial wave

$$V_{eff}(r) = V(r) + \frac{l(l+1)}{2r^2} \tag{1.41}$$

may have a potential barrier at large r that can support a metastable state with a positive energy E_r that is below the top of the barrier. An incoming particle with an energy close to E_r will be trapped for a long time before it tunnels out of the barrier. This metastable state has a finite lifetime or a resonance width Γ. In this example, the resonance is called a shape resonance because it is an effect of the shape of the effective potential.

Near the resonance energy, the phase shift δ_{El} can be expressed by

$$\delta_{El} = \xi + \arctan \frac{\Gamma/2}{E_r - E}, \tag{1.42}$$

where ξ is a background phase shift and the second term changes rapidly by π as the energy goes through the resonance from below to above.

If ξ is negligible, the cross-section has the Breit–Wigner form

$$
\begin{aligned}
\sigma_l &= \frac{4\pi}{k^2}(2l+1)\sin^2\left(\arctan\frac{\Gamma/2}{E_r-E}\right) \\
&= \frac{4\pi}{k^2}(2l+1)\frac{\Gamma^2/4}{(E-E_r)^2+\Gamma^2/4}.
\end{aligned}
\tag{1.43}
$$

Near the resonance energy, k can be taken to be constant and so σ_l has a Lorentzian shape characterized by the width Γ and the resonance energy E_r.

For a nonzero ξ, by introducing the reduced energy $\epsilon = \frac{E-E_r}{\Gamma/2}$ and the shape parameter $q = -\cot\xi$, the cross-section can be reduced to

$$
\begin{aligned}
\sigma_l &= \frac{4\pi}{k^2}(2l+1)\sin^2\left(\xi+\arctan\frac{\Gamma/2}{E_r-E}\right) \\
&= \frac{4\pi}{k^2}(2l+1)\frac{1}{1+q^2}\frac{(q+\epsilon)^2}{1+\epsilon^2}.
\end{aligned}
\tag{1.44}
$$

This cross-section Equation 1.44 has the form of the Fano profile. When $q \to \pm\infty$ it reduces to the Lorentzian profile. For small q values, σ_l is smaller at the center of the resonance than at the wings. Such resonances are called window resonances.

The First Born Approximation

For collisions at high energies, partial-wave expansion is not practical. One can use the plane wave or first Born approximation. Let the incident wave be given by $\psi_i = e^{i\mathbf{k}_i\cdot\mathbf{r}}$ and the scattered wave by $\psi_f = e^{i\mathbf{k}_f\cdot\mathbf{r}}$ where the momentum $\mathbf{k}_i$ and $\mathbf{k}_f$ only differ in direction but not in magnitude. Then, a momentum transfer can be defined as

$$
\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i,
\tag{1.45}
$$

with its magnitude given by

$$
q = 2k\sin\frac{\theta}{2}.
\tag{1.46}
$$

The scattering amplitude given by the first Born approximation reads

$$
f^{B1} = -\frac{1}{2\pi}\langle\psi_f|V|\psi_i\rangle = -\frac{1}{2\pi}\int V(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}.
\tag{1.47}
$$

If the potential $V(\mathbf{r})$ is central symmetric, the scattering amplitude is

$$
f^{B1} = -\frac{2}{q}\int_0^\infty rV(r)\sin(qr)dr.
\tag{1.48}
$$

Consider the incident electron scattered by N-independent atoms. Each atom is modeled by a local potential $V_i(\mathbf{r}')$ and located at $\mathbf{r} = \mathbf{R}_i$. By making the first Born approximation, the total scattering amplitude has a simple form:

$$f^{B1} = -\frac{1}{2\pi} \int \left[\sum_{i=1}^{N} V_i(\mathbf{r} - \mathbf{R}_i) \right] e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$= \sum_{i=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{R}_i} \left[-\frac{1}{2\pi} \int V_i(\mathbf{r} - \mathbf{R}_i) e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_i)} d\mathbf{r} \right]$$

$$= \sum_{i=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{R}_i} \left[-\frac{1}{2\pi} \int V_i(\mathbf{r}') e^{-i\mathbf{q}\cdot\mathbf{r}'} d\mathbf{r}' \right]$$

$$= \sum_{i=1}^{N} f_i^{B1} e^{-i\mathbf{q}\cdot\mathbf{R}_i} \tag{1.49}$$

in which f_i^{B1} is the individual scattering amplitude for the ith atom. The phase factor $e^{-i\mathbf{q}\cdot\mathbf{R}_i}$ accounts for the interference between different scattering centers. This interference depends on the momentum transfer $\mathbf{q}$ and the geometric configuration determined by $\mathbf{R}_i$.

1.1.4 One-Electron Atoms in Weak Electromagnetic Fields

Basic Formulation

With the one-electron potential $V(r)$, the Hamiltonian of a one-electron system in an electromagnetic field reads

$$H = \frac{1}{2}(\mathbf{p} + \mathbf{A})^2 - \phi + V(r), \tag{1.50}$$

where $\mathbf{A}$ and ϕ are the vector and scalar potential of the electromagnetic field, respectively. There is no external source for the cases considered in this book. Thus, it is convenient to choose the Coulomb gauge

$$\nabla \cdot \mathbf{A} = 0, \tag{1.51}$$

$$\phi = 0. \tag{1.52}$$

The vector potential satisfies the wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} = 0. \tag{1.53}$$

In general, $\mathbf{A}$ can be represented as a superposition of plane-wave components with propagation direction $\hat{k}$ and polarization direction $\hat{\epsilon}$. Each component takes the form

$$\mathbf{A} = \hat{\epsilon} A_0(\omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \tag{1.54}$$

where ω is the angular frequency, $\mathbf{k} = \frac{\omega}{c}\hat{k}$ is the wave-number vector, and $A_0(\omega)$ describes the magnitude of this plane-wave component. Equation 1.51 requires the wave to be transverse, i.e., $\mathbf{k} \cdot \hat{\epsilon} = 0$. The intensity distribution (intensity per unit angular frequency range) is given by

$$I(\omega) = \frac{c}{8\pi}\omega^2 A_0^2(\omega). \tag{1.55}$$

Additionally, $I(\omega)$ is related to the number of photons $N(\omega)$ in a box with volume V by

$$I(\omega) = \frac{c\omega}{V}N(\omega). \tag{1.56}$$

In the Coulomb gauge, the Hamiltonian can be written as

$$H = -\frac{1}{2}\nabla^2 + V(r) - i\mathbf{A} \cdot \nabla + \frac{1}{2}A^2 = H_0 + H'(t), \tag{1.57}$$

where $H_0 = -\frac{1}{2}\nabla^2 + V(r)$ is the field-free Hamiltonian and $H'(t)$ is the time-dependent perturbation. Consider a weak field such that the A^2 term can be dropped. The perturbation becomes

$$H'(t) \approx -i\mathbf{A} \cdot \nabla. \tag{1.58}$$

According to first-order, time-dependent perturbation theory, transition probability from an initial state $|a\rangle$ to a final state $|b\rangle$ is given by

$$P_{ba}(t) = \left| \int_0^t \langle b|H'(t')|a\rangle e^{i\omega_{ba}t'} \, dt' \right|^2, \tag{1.59}$$

where $|a\rangle$ and $|b\rangle$ are eigenstates of the field-free Hamiltonian H_0 with energies E_a and E_b, respectively. $\omega_{ba} = E_b - E_a$ is the transition energy. For $E_b > E_a$, $\omega_{ba} > 0$, which is the case of photoabsorption, the transition probability due to a certain frequency component of the electromagnetic field can be calculated by rewriting Equation 1.54 into two exponential terms. After dropping the integral involving $e^{i(\omega + \omega_{ba})t'}$, the result is

$$P_{ba}(t) = A_0^2(\omega)|M_{ba}(\omega)|^2 \frac{\sin^2\left(\frac{\omega - \omega_{ba}}{2}t\right)}{(\omega - \omega_{ba})^2}. \tag{1.60}$$

The matrix element M_{ba} is given by

$$M_{ba}(\omega) = \langle b|e^{i\mathbf{k}\cdot\mathbf{r}}\hat{\epsilon} \cdot \nabla|a\rangle. \tag{1.61}$$

Assuming that the radiation is incoherent, the transition probability due to all of the frequency components is obtained by integrating Equation 1.60 over the frequency ω. When t is large,

$$\frac{\sin^2\left(\frac{\omega - \omega_{ba}}{2}t\right)}{(\omega - \omega_{ba})^2} \approx \frac{\pi t}{2}\delta(\omega - \omega_{ba}). \tag{1.62}$$

Then, the transition probability integrated over the frequency is

$$P_{ba}(t) = \frac{\pi}{2}A_0^2(\omega_{ba})|M_{ba}(\omega_{ba})|^2 t \tag{1.63}$$

and the transition rate for photoabsorption is

$$W_{ba} = \frac{\pi}{2}A_0^2(\omega_{ba})|M_{ba}(\omega_{ba})|^2 = \frac{4\pi^2}{c\omega_{ba}^2}I(\omega_{ba})|M_{ba}(\omega_{ba})|^2. \tag{1.64}$$

An integrated absorption cross-section σ_{ba}, which is the rate of absorption of energy $\omega_{ba}W_{ba}$ divided by $I(\omega_{ba})$, can also be defined as

$$\sigma_{ba} = \frac{4\pi^2}{c\omega_{ba}}|M_{ba}(\omega_{ba})|^2. \tag{1.65}$$

When $E_b < E_a$, $\omega_{ba} < 0$, one can obtain the transition rate and cross-section integrated over frequency for stimulated emission in a similar way:

$$W_{ba} = \frac{4\pi^2}{c|\omega_{ba}|^2} I(|\omega_{ba}|)|\tilde{M}_{ba}(|\omega_{ba}|)|^2, \tag{1.66}$$

$$\sigma_{ba} = \frac{4\pi^2}{c|\omega_{ba}|}|\tilde{M}_{ba}(|\omega_{ba}|)|^2. \tag{1.67}$$

The transition-matrix elements between photoabsorption and photoemission are related by

$$\tilde{M}_{ba}(\omega) = \langle b|e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\epsilon}\cdot\nabla|a\rangle = -M^*_{ab}(\omega). \tag{1.68}$$

The stimulated emission and photoabsorption are in detailed balance, i.e., $W_{ba} = W_{ab}$ and $\sigma_{ba} = \sigma_{ab}$.

First-order perturbation theory can also be used for photoionization from an initial bound state $|i\rangle$ to continuum states $|E\rangle$. The ionization rate per unit energy is

$$\frac{dW_{ion}}{dE} = \frac{4\pi^2}{c\omega_{Ei}^2} I(\omega_{Ei})|M_{Ei}(\omega_{Ei})|^2\rho(E), \tag{1.69}$$

where $\omega_{Ei} = E - E_i$, $M_{Ei}(\omega) = \langle E|e^{i\mathbf{k}\cdot\mathbf{r}}\hat{\epsilon}\cdot\nabla|i\rangle$ and $\rho(E)$ is the number of states per unit energy. If $|E\rangle$ is energy normalized, $\rho(E) = 1$. The photoionization cross-section (per unit energy) is

$$\sigma_{ion} = \frac{4\pi^2}{c\omega_{Ei}}|M_{Ei}(\omega_{Ei})|^2\rho(E). \tag{1.70}$$

The semiclassical theory does not include spontaneous emission. According to quantum electrodynamics, when there is no external electromagnetic field, the transition from $|a\rangle$ to $|b\rangle$ ($E_a > E_b$) can still happen, and thus can emit a photon with momentum $\mathbf{k}$ and polarization $\hat{\epsilon}_\lambda$. Here, λ can be one or two to specify two independent polarizations perpendicular to $\mathbf{k}$. The spontaneous-emission rate for a single mode of photon is

$$W^s_{ba} = \frac{4\pi^2}{V\omega}|\tilde{M}^\lambda_{ba}(\omega)|^2\delta(\omega - |\omega_{ba}|). \tag{1.71}$$

The matrix element $\tilde{M}^\lambda_{ba}$ is given in Equation 1.68 with $\hat{\epsilon}$ replaced by $\hat{\epsilon}_\lambda$.

It is desirable to calculate the total rate for emitting photons with all possible energy ω, propagation direction $\hat{k}$, and polarization $\hat{\epsilon}$. Using box normalization, the number of photon modes is given by

$$dn = \frac{V}{(2\pi)^3}k^2dkd\Omega = \frac{V}{(2\pi c)^3}\omega^2d\omega d\Omega_k, \tag{1.72}$$

where Ω_k is the solid angle. Integrating over $d\omega$, $d\Omega_k$ and summing over two polarizations, the total spontaneous emission rate is

$$W^s_{ba} = \frac{|\omega_{ba}|}{2\pi c^3}\int d\Omega_k \sum_{\lambda=1,2}|\tilde{M}^\lambda_{ba}(|\omega_{ba}|)|^2. \tag{1.73}$$