Chapter 2
Radiative Characteristics of Polarized Atoms and Ions

Abstract The chapter is devoted to an introduction of the main radiative characteristics of atoms and ions to describe the light-matter interaction. The presentation is based on the correspondence principle between classical and quantum physics in order to derive the basic radiative properties, including the Einstein coefficients and the dynamic polarizability of the atom. Attention is also paid to the description of the dynamic polarizability of atoms and ions including the static, high-frequency and resonance case. The innovative concept of local plasma frequency is introduced for the atom that allows describing the polarizability of many-electron systems at a semi-quantitative level. Finally, the prospective interesting polarizability of metal nanoparticles placed in a solid-state matrix is considered within the framework of the Mie theory and the dipole approximation.

2.1 Oscillator Strengths

The Bohr theory is not only a theory applicable to the hydrogen atom, but also a theory of interaction of electromagnetic radiation with an atom since important features of this interaction are described by the second and third Bohr postulates. Moreover, the theory of interaction of radiation with atoms can be studied without recourse to the consistent quantum-electrodynamic formalism, but with the help of the so-called *correspondence principle* in the spirit of the semiclassical Bohr approach. A starting point of such a consideration is the expression for dipole radiation power known from classical electrodynamics (Amusia 1990):

$$Q(t) = \frac{2}{3c^3}\left|\ddot{\boldsymbol{d}}(t)\right|^2, \tag{2.1}$$

where

$$\boldsymbol{d}(t) = e\boldsymbol{r}(t) \tag{2.2}$$

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is the dipole moment of a particle with charge e (understood hereafter to be an electron). The dots above the dipole moment symbol in the formula (2.1) denote the second time derivative. The criterion of applicability of the dipole approximation [framework of formula (2.1)] can be formulated as

$$\lambda \gg a, \tag{2.3}$$

where a is the size of the spatial region for radiation, λ is the radiation wavelength. In case of an atom, when $a \approx 10^{-8}$ cm, the condition (2.3) covers a wide range of wavelengths down to X-rays.

The second time derivative of the dipole moment appearing in the right-hand side of (2.1) can be expressed in terms of the electron acceleration $\boldsymbol{w} : \ddot{\boldsymbol{d}} = e\boldsymbol{w}$ and formula (2.1) can be rewritten as

$$Q = \frac{2e^2w^2}{3c^3}. \tag{2.4}$$

Thus within the framework of classical physics, an accelerated charged particle will lose its energy by dipole radiation with a rate determined by the formula (2.4). It should be noted that energy loss by a charge in the Coulomb field results not in a decrease, but in an increase of its kinetic energy. Increased kinetic energy of a charge is accompanied by a twofold decrease in its potential energy, which is connected with decreasing distance to the center of the Coulomb field. As a result, the total electron energy decreases.

In case of periodic motion of a charge with a circular frequency ω_0, as it occurs with an atomic electron, the radiation power of interest is those averaged over the period of motion $T = 2\pi/\omega_0$. To perform this averaging in the formula (2.1), we will use the following equation that is valid for a real periodic function $f(t)$:

$$\left\langle f(t)^2 \right\rangle_{\mathrm{T}} \equiv \frac{1}{T} \int_{-\mathrm{T}/2}^{T/2} f(t)^2 \mathrm{d}t = 2\sum_{\mathrm{n}=1}^{\infty} |f_{\mathrm{n}}|^2, \tag{2.5}$$

where

$$f_{\mathrm{n}} = \frac{1}{T} \int_{-\mathrm{T}/2}^{T/2} f(t) \exp(-n\,\omega_0 t)\mathrm{d}t \tag{2.6}$$

is the nth harmonic of the Fourier expansion of the function $f(t)$. In derivation of the formula (2.5), it was assumed that the average over the period of the function under consideration is equal to zero, that is, $f_0 = 0$. It should be noted that the factor 2 in the right-hand side of the (2.5) is connected with taking into account the contribution of negative harmonics of the Fourier series $(n < 0)$.

Using (2.5), in which it is assumed that $f(t) = \ddot{\boldsymbol{d}}(t)$, we obtain from (2.1) the following expression for dipole radiation power averaged over the period:

$$\langle Q(t)\rangle_{\mathrm{T}} = \sum_{\mathrm{n}=1}^{\infty} Q_{\mathrm{n}}, \tag{2.7}$$

where

$$Q_{\mathrm{n}} = \frac{4}{3c^3}\left|\left(\ddot{\boldsymbol{d}}\right)_{\mathrm{n}}\right|^2. \tag{2.8}$$

In view of

$$\left(\ddot{\boldsymbol{d}}\right)_{\mathrm{n}} = -(n\,\omega_0)^2(\boldsymbol{d})_{\mathrm{n}}, \tag{2.9}$$

we find with the help of (2.8)

$$Q_{\mathrm{n}} = \frac{4(n\,\omega_0)^4}{3c^3}\left|(\boldsymbol{d})_{\mathrm{n}}\right|^2. \tag{2.10}$$

The formula (2.10) describes the dipole radiation power at the nth harmonic frequency $\omega_{\mathrm{n}} = n\,\omega_0$. In particular, the radiation power at the frequency of periodic motion of an electron ω_0 ($n = 1$) is

$$Q(\omega_0) = \frac{4\omega_0^4}{3c^3}\left|\boldsymbol{d}(\omega_0)\right|^2. \tag{2.11}$$

Here, we re-designated the first Fourier harmonic of the dipole moment: $\boldsymbol{d}_1 = \boldsymbol{d}(\omega_0)$.

Now let us replace in the formula (2.11) the Fourier harmonic of the dipole moment with its matrix element calculated between the states $|m\rangle$ and $|n\rangle$ ($\Psi_{\mathrm{m,n}}(\boldsymbol{r})$ are the corresponding state wave functions):

$$\boldsymbol{d}(\omega_0) \to \boldsymbol{d}_{\mathrm{mn}} \equiv \langle m|\boldsymbol{d}|n\rangle = \int \mathrm{d}\boldsymbol{r}\,\Psi_{\mathrm{m}}^*(\boldsymbol{r})\cdot\boldsymbol{d}\cdot\Psi_{\mathrm{n}}(\boldsymbol{r}), \tag{2.12}$$

where the frequency of the periodic motion ω_0 will be replaced by the frequency of the transition $|n\rangle \to |m\rangle$:

$$\omega_0 \to \omega_{\mathrm{mn}} = \frac{E_{\mathrm{n}} - E_{\mathrm{m}}}{\hbar}. \tag{2.13}$$

As a result, instead of the formula (2.11), we will obtain

$$Q_{\mathrm{mn}} = \frac{4\,\omega_{\mathrm{mn}}^4}{3\,c^3}\,|\boldsymbol{d}_{\mathrm{mn}}|^2. \tag{2.14}$$

The quantity (2.14) can be called electromagnetic radiation power in transition of an atomic electron from the stationary state $|n\rangle$ to the stationary state $|m\rangle$. It describes the intensity of radiation of different spectral series of a hydrogen atom: the Lyman series ($m = 1$), the Balmer series ($m = 2$), the Paschen series ($m = 3$), etc. However, it should be remembered that, in contrast to the classical radiation power (2.1), the quantity (2.14) should be understood statistically, that is, as a result of averaging over an ensemble of atoms.

If now the radiation power (2.14) is divided by the energy of the transition under consideration $\Delta E_{\mathrm{mn}} = \hbar\,\omega_{\mathrm{mn}}$, we obtain a quantity with dimension of reciprocal time coinciding with the Einstein coefficient for spontaneous radiation A_{mn}:

$$\frac{Q_{\mathrm{mn}}}{\Delta E_{\mathrm{mn}}} = \frac{4\,\omega_{\mathrm{mn}}^3}{3\,\hbar\,c^3}\,|\boldsymbol{d}_{\mathrm{mn}}|^2 = A_{\mathrm{mn}} = \frac{1}{\tau_{\mathrm{mn}}}. \tag{2.15}$$

In the last equality of the formula (2.15), there is introduced the lifetime τ_{mn} of the state $|n\rangle$ with respect to its spontaneous decay to the lower state $|m\rangle$. This time for the transition $|2\rangle \to |1\rangle$ in a hydrogen atom is $\tau_{12} \approx 1.6 \times 10^{-9}$ s.

Thus the use of the formula of classical electrodynamics (2.1) and replacements in (2.12)–(2.13) allowed to obtain a quantum result for the power of radiation of spectral lines (2.14) and the probability of spontaneous radiation (2.15). This reflects the *principle of correspondence* between classical and quantum physics. This principle can be formulated as follows: Quantum-mechanical expressions are obtained from classical expressions if in the latter the Fourier components of physical quantities are replaced by the corresponding matrix elements. In this case, the quantum transition frequency should coincide with the Fourier component frequency (Brandt and Lundqvist 1965).

Curiously, the existence of a finite lifetime of the excited state $|n\rangle$ can be interpreted in the spirit of the correspondence principle as “falling” of an electron into the nucleus due to photon radiation—which is just the process, against which the second Bohr postulate “struggles”. This “falling” goes on until the electron reaches the ground state $m = 1$ with the lowest possible (from the point of view of quantum physics) energy.

To clear up the physical justification of the second Bohr postulate, we will introduce a classical period of electron revolution for the orbit with principal quantum number n, radius r_{n} and velocity υ_{n}:

$$T_{\mathrm{n}} = \frac{2\pi r_{\mathrm{n}}}{\upsilon_{\mathrm{n}}} = n^3\,2\pi\tau_{\mathrm{a}}. \tag{2.16}$$

Table 2.1 Oscillator strengths for a hydrogen atom

Initial state	1*s*	2*s*	2*p*		3*s*	3*p*		3*d*	
Final state	*np*	*np*	*ns*	*nd*	*np*	*ns*	*nd*	*np*	*nf*
$n = 1$	–	–	−0.139	–	–	−0.026	–	–	–
2	0.4162	–	–	–	−0.141	0.145	–	−0.417	–
3	0.0791	0.4349	0.014	0.696	–	–	–	–	–
4	0.0290	0.1028	0.0031	0.122	0.484	0.032	0.619	0.011	1.016
5	0.0139	0.0419	0.0012	0.044	0.121	0.007	0.139	0.0022	0.156
6	0.0078	0.0216	0.0006	0.022	0.052	0.003	0.056	0.0009	0.053
7	0.0048	0.0127	0.0003	0.012	0.027	0.002	0.028	0.0004	0.025
8	0.0032	0.0081	0.0002	0.008	0.016	0.001	0.017	0.0002	0.015
$\sum_{n=9}^{\infty} f_{n0}$	0.0109	0.0268	0.0007	0.023	0.048	0.002	0.045	0.0007	0.037
Asymptotic formula	$1.6n^{-3}$	$3.7n^{-3}$	$0.1n^{-3}$	$3.3n^{-3}$	$6.2n^{-3}$	$0.3n^{-3}$	$6.1n^{-3}$	$0.07n^{-3}$	$4.4n^{-3}$
Discrete spectrum	0.5650	0.6489	−0.119	0.928	0.707	−0.121	0.904	−0.402	1.302
Continuous spectrum	0.4350	0.3511	0.008	0.183	0.293	0.010	0.207	0.002	0.098
Total sum	1.000	1.000	−0.111	1.111	1.000	−0.111	1.111	−0.400	1.400

Now let us estimate the ratio of the period (2.16) to the lifetime τ_{mn}. Using (2.15), (2.16) and assuming that $r_{\mathrm{mn}} \approx a_{\mathrm{B}} R(m, n)$, where $R(m, n)$ is a function of the order of unity, we have approximately

$$\frac{T_{\mathrm{n}}}{\tau_{\mathrm{mn}}} \approx \frac{T_{\mathrm{n}}}{\tau_{1\mathrm{n}}} \approx (\alpha n)^3 R^2(1, n) \approx 4 \times 10^{-7} n^3 R^2(1, n), \tag{2.17}$$

where $n^3 R^2(1, n) \to 1$ for large numbers n (see the asymptotic formula in Table 2.1). The second approximate equality in (2.17) reflects the fact that the lifetime of the excited state of a hydrogen atom is dominated by its transition to the ground state.

From the obtained relation (2.17), it follows that the period of electron revolution in the classical orbit is several orders of magnitude less than the lifetime in this state $|n\rangle$. Thus these states may be considered to a good degree of accuracy to be stationary according to the first two Bohr postulates. This stationary is a consequence of the small value of the fine structure constant α that is responsible for the electromagnetic interaction.

The principle of correspondence between classical and quantum physics concretized for radiative transitions in an atom is called the *spectroscopic principle of correspondence*. It can be formulated as follows: an atom in interaction with an electromagnetic field behaves as a set of classical oscillators with eigenfrequencies equal to frequencies of transitions between atomic energy levels. This means that to each transition between atomic states $|j\rangle$ and $|n\rangle$ is assigned an oscillator with an eigenfrequency ω_{nj}. Let us call these oscillators transition oscillators. The contribution of transition oscillators to the response of atoms to electromagnetic interaction is proportional to a dimensionless quantity called *oscillator strength*. The higher the value of the oscillator strength, the stronger is the corresponding transition. The oscillator strength for the transition between the discrete spectrum states

$|j\rangle \rightarrow |n\rangle, f_{\mathrm{nj}}$ (in quantum mechanics, it is the practice to write the state indices from right to left—corresponding to absorption), is determined by the formula

$$f_{\mathrm{nj}} = \frac{2\,m_{\mathrm{e}}\,\omega_{\mathrm{nj}}|\langle n|\boldsymbol{d}|j\rangle|^2}{3\,e^2\,\hbar\,g_{\mathrm{j}}}, \tag{2.18}$$

where g_{j} is the statistical weight of the state j. From the formula (2.18), it follows the relation $g_{\mathrm{j}} f_{\mathrm{nj}} = -g_{\mathrm{n}} f_{\mathrm{jn}}$ since the oscillator strength for a transition with decreasing energy is negative. According to its physical meaning, the oscillator strength of a one-electron atom is always less than one.

The formulation of the correspondence principle via the oscillator strength in the form of (2.18) corresponds to the dipole approximation if the criterion of (2.3) is fulfilled. Otherwise, the definition (2.18) should be generalized to include also the non-dipole part of the interaction of electromagnetic radiation with atomic electrons. The non-dipole nature of interaction is found to be essential if the matrix element of the dipole moment in the formula (2.18) is equal to zero. Such transitions are called *dipole-forbidden* transitions in contrast to *dipole-allowed* transitions, when $\langle n|\boldsymbol{d}|j\rangle \neq 0$. Equality or inequality with respect to zero of the dipole moment of a transition can be predicted from an analysis of the symmetry of states involved in the transition. The relations between characteristics of atomic states allow predictions of a nonzero value of $\langle n|\boldsymbol{d}|j\rangle$ are called *selection rules for dipole radiation*. These rules have the simplest form for the hydrogen-like ion where the systematics of its electronic states (neglecting the spin–orbit interaction) is rather simple. An energy level with a principal quantum number n has a $2\,n^2$-fold degeneracy that occurs as follows. First, there is a degeneracy with respect to the orbital quantum number l that is specific for a hydrogen-like ion: states of an atomic electron with $l = 0,\ 1, \ldots n-1$ designated as $|n,\ l\rangle$ have energy E_{n}. We note that to numerical designations $l = 0,\ 1,\ 2,\ 3,\ 4,\ 5,\ 6\ldots$ there correspond letter designations: $s, p, d, f, g, h, i\ldots$ Then, each state $|n,\ l\rangle$ is degenerated with respect to the value of the projection of an electron orbital moment on a dedicated axis. This degeneracy is of general character and is connected with the spherical symmetry of the atomic potential. The quantum number of the projection of a moment of momentum m_{l} runs over $2\,l+1$ values: $m_{\mathrm{l}} = -l, -l+1, \ldots, l-1, l$, to which the states $|n,\ l,\ m_{\mathrm{l}}\rangle$ correspond. Finally, the electronic states $|n,\ l,\ m_{\mathrm{l}}\rangle$ are doubly degenerated with respect to the electron spin projection, which results in a $2\,n^2$-fold degeneracy of an energy level of a hydrogen-like ion with a principal quantum number n. It should be noted that this classification is valid for discrete spectrum states. In the case of a continuous spectrum, there is an additional degeneracy of states resulting from different directions of electron momentum.

In terms of the given state classification, selection rules for dipole radiation of a hydrogen-like ion come into play as follows. Allowed transitions are transitions, for which an orbital quantum number changes by one: $l \rightarrow l \pm 1$. In this case, the magnetic quantum number changes by no more than one: $m_{\mathrm{l}} \rightarrow m_{\mathrm{l}}, m_{\mathrm{l}} \pm 1$. In particular, if the magnetic quantum number does not change, linearly polarized radiation is emitted (absorbed), whereas in the opposite case circularly polarized radiation is emitted (absorbed). A particular case of the selection rules is the average dipole moment of an atom in the absence of external fields. It is equal to zero, i.e., $\langle \boldsymbol{d} \rangle = 0$ as a consequence of the spherical symmetry of an atom.

Besides electron transitions in a discrete spectrum (bound–bound transitions), there are also transitions from bound states to continuous ones (bound-free transitions), for which the concept of oscillator strength by a formula similar to (2.18) can also be introduced. Physically, to a bound-free transition, there corresponds atomic ionization. In contrast to the case of a bound–bound transition, the oscillator strength $f_{\varepsilon \mathrm{j}}$ for a bound–free transition to a state with an energy ε is no longer a dimensionless quantity. The dimensionality of $f_{\varepsilon \mathrm{j}}$ is equal to a reciprocal energy, which corresponds to the normalization of the wave function of the continuous spectrum to the energy delta function. Therefore, for a bound–free transition, instead of oscillator strength, the concept of oscillator strength density is used: $f_{\varepsilon \mathrm{j}} \to \mathrm{d}f_{\mathrm{j}}/\mathrm{d}\varepsilon$.

The oscillator strengths for bound–bound and bound–free transitions in an atom satisfy the so-called *golden sum rule*. For transitions from the ground state it is expressed by the equation

$$\sum_{\mathrm{n}} f_{\mathrm{n}0} + \int\limits_{I_{\mathrm{P}}}^{\infty} \frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon}\,\mathrm{d}\varepsilon = N_{\mathrm{e}}, \tag{2.19}$$

where I_{p} is the atomic ionization potential, N_{e} is the number of electrons of the atom.

The oscillator strengths for a number of electron transitions in a hydrogen atom are given in Table 2.1 taken from Bethe and Salpeter (1977).

From this table, we observe the following. First, for transitions with increasing energy, the oscillator strength is larger in the case of increasing orbital quantum number, i.e., the transition $n, l \to n', l+1$ is stronger than the transition $n,\ l \to n', l-1$ if $n < n'$. Secondly, the sum of oscillator strengths for transitions to the continuous spectrum decreases with increasing orbital quantum number of the initial state, that is, states with higher orbital moments are more difficult to ionize. Third, transitions to a state with a nearest principal quantum number have the highest oscillator strength. Fourthly, oscillator strengths for transitions from lower levels to states with large quantum numbers $n \geq 10$ decrease as n^{-3}. These regularities define the probabilities of corresponding radiative transitions in a hydrogen atom.

An important property of the oscillator strength for a hydrogen-like ion is its independence of the nucleus charge Z. This is easily seen from the definition (2.18). Here two values appear that depend on the nuclear charge: the transition frequency ω_{jn} and the matrix element of the dipole moment of a transition $\boldsymbol{d}_{\mathrm{nj}}$. If it is remembered that $\omega_{\mathrm{jn}} \propto Z^2$ and $\boldsymbol{d}_{\mathrm{nj}} \propto Z^{-1}$, we immediately obtain $f_{\mathrm{nj}} \propto Z^0$.

It is instructive to calculate oscillator strengths for transitions between energy levels of a quantum harmonic oscillator. In this case, the formula (2.18) can be rewritten as

$$f_{\mathrm{N'N}} = \frac{2\,m\,\omega_0 |\langle N'|\hat{z}|N\rangle|^2}{\hbar}, \tag{2.20}$$

where $\langle N'|\hat{z}|N\rangle$ is the matrix element to be determined of the harmonic oscillator with an eigenfrequency ω_0 and mass m. The oscillator coordinate operator is expressed in terms of the annihilation operator $\hat{a}$ and the creation operator $\hat{a}^+$ as follows: $\hat{z} = \sqrt{\hbar/2m\,\omega_0}(\hat{a} + \hat{a}^+)$. Using the definitions and the property of orthogonality of the state vectors $|N\rangle$, we obtain for the required matrix element:

$$\langle N'|\hat{z}|N\rangle = \sqrt{\frac{\hbar}{2m\,\omega_0}}\left[\sqrt{N+1}\,\delta(N', N+1) + \sqrt{N}\,\delta(N', N-1)\right], \tag{2.21}$$

where $\delta(m, n)$ is the Kronecker symbol. Substituting (2.21) into the definition (2.20), we find the simple relation

$$f_{\mathrm{N'N}} = (N+1)\cdot\,\delta(N', N+1) - N\cdot\,\delta(N', N-1). \tag{2.22}$$

Hence, it follows in particular that oscillator strengths are nonzero only for transitions to nearest energy states (the selection rule for a linear harmonic oscillator). From formula (2.22), it is likewise shown how the sum rule (2.19) is fulfilled (with $N_{\mathrm{e}} = 1$). Finally, the considered case is an example of the situation when an oscillator strength can be an arbitrarily large quantity.

2.2 Classical and Quantum Expressions for Einstein Coefficients

Einstein coefficients were introduced phenomenologically for the description of the probability per unit time for three fundamental photoprocesses (photoabsorption, spontaneous radiation, and induced radiation) in interaction of thermal radiation with a two-level system. The consistent derivation of expressions for these coefficients is possible only within the framework of quantum electrodynamics, a complex physical discipline considering radiation and a substance on the quantum basis. Nevertheless, if the correspondence principle and the oscillator strength concept are used, corresponding formulas can be also obtained in a classical manner.

The spectroscopic principle of correspondence makes it possible to represent an atom and its interaction with radiation as a set of charged harmonic oscillators corresponding to transitions between atomic energy levels $n \rightarrow j$ ($E_{\mathrm{j}} > E_{\mathrm{n}}$). These oscillators describing the system response to electromagnetic disturbance are called transition oscillators. Their coordinate x_{nj} satisfies a damped oscillator equation with external force, in the right-hand side of which the oscillator strength $f_{\mathrm{jn}} \neq 0$ (a dipole-allowed transition) is substituted as a factor:

$$\ddot{x}_{\mathrm{jn}} + 2\,\delta_{\mathrm{jn}}\dot{x}_{\mathrm{jn}} + \omega_{\mathrm{jn}}^2\, x_{\mathrm{jn}} = f_{\mathrm{jn}}\frac{e}{m}\,E(t). \tag{2.23}$$

Here $\omega_{\mathrm{jn}} = (E_{\mathrm{j}} - E_{\mathrm{n}})/\hbar$ is the transition frequency, δ_{nj} is the damping constant, e is the oscillator charge, dots above the coordinate symbol denote differentiation with respect to time, the electric field strength $E(t)$ is assumed to be independent of the coordinate [the dipole approximation (2.3)].

In the absence of a radiation field, the transition oscillator is at rest: $x_{\mathrm{jn}} = 0$ and $\dot{x}_{\mathrm{jn}} = 0$. An external field begins to "swing" the oscillator, imparting energy; forced oscillations of the transition oscillator occur, the time dependence of which, $x_{\mathrm{jn}}(t)$, can be found from the (2.23).

We obtain the following expression for forced oscillations of an oscillator for the transition $j \to n$:

$$x_{\mathrm{jn}}(t) = f_{\mathrm{jn}}\frac{e}{m}\int\limits_{-\infty}^{\infty}\frac{E(\omega')\exp(-i\omega' t)}{\omega_{\mathrm{jn}}^2 - \omega'^2 - 2i\omega'\delta_{\mathrm{jn}}}\frac{\mathrm{d}\omega'}{2\pi}, \tag{2.24}$$

where $E(\omega')$ is the Fourier transform of the electric field strength $E(t)$.

An oscillating charged oscillator radiates electromagnetic waves according to the formula for the radiation power of a dipole (2.1). In case of oscillations under the action of an external field, this radiation is induced radiation. If the pulse of the external field ceases, and the charged oscillator still oscillates, corresponding radiation is spontaneous. The probability per unit time for spontaneous radiation at the transition between atomic energy levels $j \to n$ is given by the Einstein coefficient A_{nj}. The explicit form of this coefficient can be obtained on the basis of classical consideration with the use of the spectroscopic principle of correspondence:

$$A_{\mathrm{nj}} = \frac{2 f_{\mathrm{jn}}\, e^2 \omega_{\mathrm{jn}}^2}{3\, m\, c^3}. \tag{2.25}$$

The formula (2.25) gives the expression for the Einstein coefficient for spontaneous radiation in terms of the oscillator strength for a corresponding transition. It should be noted that the oscillator strength can be calculated theoretically or determined experimentally.

If now in the right-hand side of the (2.25) the expression for the oscillator strength (2.18) is substituted, we come to the following formula for the Einstein coefficient for spontaneous radiation:

$$A_{\mathrm{nj}} = \frac{4\omega_{\mathrm{jn}}^3 \left|\boldsymbol{d}_{\mathrm{nj}}\right|^2}{3g_{\mathrm{j}}\hbar c^3}, \tag{2.26}$$

where $\boldsymbol{d}_{\mathrm{nj}}$ is the matrix element of the electric dipole moment (see also Chap. 7).

To derive the formula for the Einstein coefficient for absorption B_{jn} while remaining within the framework of classical physics, we proceed from the (2.24), from which the expressions for the transition oscillator rate can be obtained:

$$\dot{x}_{\mathrm{jn}}(t) = -if_{\mathrm{jn}}\frac{e}{m}\int\limits_{-\infty}^{\infty}\frac{\omega' E(\omega')\exp(-i\omega' t)}{\omega_{\mathrm{jn}}^2 - \omega'^2 - 2i\omega'\delta_{\mathrm{jn}}}\frac{\mathrm{d}\omega'}{2\pi}. \tag{2.27}$$

From (2.27), we find for the period-averaged power absorbed by the transition under the action of radiation with a spectral energy density $\rho(\omega)$:

$$P_{\mathrm{jn}} = f_{\mathrm{jn}}\frac{2\,\pi^2\,e^2}{3\,m}\,\rho\left(\omega_{\mathrm{jn}}\right). \tag{2.28}$$

It will be remembered that in obtaining this relation it was assumed that the radiation spectrum width is much larger than the spectrum width for a transition in an atom which is true, for example, for thermal radiation.

By definition, the Einstein coefficient for absorption (in case of transition of an atom from the state $|n\rangle$ to the state $|j\rangle$) is

$$B_{\mathrm{jn}} = \frac{w_{\mathrm{jn}}}{\rho\left(\omega_{\mathrm{jn}}\right)}. \tag{2.29}$$

According to the physical picture of the process, the photoabsorption probability per unit time, w_{jn}, is equal to the ratio of absorbed power to the transition energy:

$$w_{\mathrm{nj}} = \frac{P_{\mathrm{nj}}}{\hbar\,\omega_{\mathrm{nj}}}. \tag{2.30}$$

Gathering the formulas (2.28)–(2.30), we obtain:

$$B_{\mathrm{jn}} = \frac{2\pi^2 e^2 f_{\mathrm{jn}}}{m\,\hbar\omega_{\mathrm{jn}}}. \tag{2.31}$$

In view of the explicit form of the oscillator strength (2.18), we find from (2.31) the expressions for the Einstein coefficient in terms of the matrix element of the transition dipole moment:

$$B_{\mathrm{jn}} = \frac{4\,\pi^2 \left|\boldsymbol{d}_{\mathrm{jn}}\right|^2}{3\,g_{\mathrm{n}}\hbar^2}. \tag{2.32}$$

The formula for the Einstein coefficient describing induced radiation follows from (2.32):

$$B_{\mathrm{nj}} = \frac{4\,\pi^2 \left|\boldsymbol{d}_{\mathrm{nj}}\right|^2}{3\,g_{\mathrm{j}}\,\hbar^2}. \tag{2.33}$$

It should be noted that the matrix element of the dipole moment can be considered to be symmetric with respect to its indices: $\boldsymbol{d}_{\mathrm{nj}} = \boldsymbol{d}_{\mathrm{jn}}$ (see also Chap. 7).

It is worth noting that the presented approach is valid if the external field is not too strong, i.e., when the amplitude of oscillations of a transition oscillator is linear with respect to the strength of the electric field in an electromagnetic wave. Otherwise, it is necessary to take into account nonlinear effects, and more complex considerations are required. It should be noted that the Einstein coefficient for spontaneous radiation can be represented as

$$A_{\mathrm{nj}} = B_{\mathrm{nj}}\,\rho_{\mathrm{vac}}\left(\omega_{\mathrm{nj}}\right), \tag{2.34}$$

where

$$\rho_{\mathrm{vac}}(\omega) = \frac{\hbar\omega^3}{\pi^2\,c^3} \tag{2.35}$$

is a quantity that can be interpreted as the spectral density of energy of vacuum fluctuations of an electromagnetic field. Equations (2.34), (2.35) correspond to an interpretation of spontaneous radiation as radiation induced by vacuum fluctuations.

2.3 Dynamic Polarizability of Atoms

The expression for dynamic polarizability of an atom can likewise be obtained without recourse to quantum mechanics with the use of the spectroscopic principle of correspondence. Let us calculate the dipole moment of an atom $\boldsymbol{d}$ in the monochromatic field $\boldsymbol{E}(t) = 2Re\{\boldsymbol{E}_{\omega}\,\exp(-i\,\omega\,t)\}$ that is by definition equal to

$$\boldsymbol{d}(t) = 2Re\{\beta(\omega)\,\boldsymbol{E}_{\omega}\,\exp(-i\,\omega\,t)\}. \tag{2.36}$$

The Fourier component of the dipole moment is given by the expression

$$\boldsymbol{d}_{\omega} = \beta(\omega)\boldsymbol{E}_{\omega}. \tag{2.37}$$

In the formulas (2.36)–(2.37), $\boldsymbol{E}_{\omega}$ is the complex electric field vector for monochromatic radiation that is a Fourier component of $\boldsymbol{E}(t)$.

It will be remembered that the dipole moment of an atom in the absence of external fields is equal to zero due to spherical symmetry, so the value of an induced dipole moment can really be a measure of perturbation of an atom by external action. The linear dependence of $\boldsymbol{d}(t)$ on the electric field strength (2.36) is valid for small values of E (smallness of perturbation of an atomic electron state as a result of interaction with an electromagnetic field). Thus for sufficiently weak fields, the response of an atom to electromagnetic disturbance can be characterized by its polarizability $\beta(\omega)$.

According to the spectroscopic principle of correspondence, the change of an atomic state is made up of changes of motion of oscillators that correspond to transitions between atomic states (transition oscillators). Thus the deviations of transition oscillators from the equilibrium position under the action of the field $\boldsymbol{E}(t)$ can be considered to be small. For the nth oscillator, the equation of motion in the harmonic approximation is given by:

$$\ddot{\boldsymbol{r}}_{\mathrm{n}} + \delta_{0\mathrm{n}}\dot{\boldsymbol{r}}_{\mathrm{n}} + \omega_{0\mathrm{n}}^{2}\boldsymbol{r}_{\mathrm{n}} = \frac{e}{m} f_{0\mathrm{n}}\boldsymbol{E}(t), \tag{2.38}$$

where $\boldsymbol{r}_{\mathrm{n}}$ is the radius vector corresponding to the deviation of a transition oscillator from the equilibrium position, $\delta_{0\mathrm{n}}$, $\omega_{0\mathrm{n}}$, $f_{0\mathrm{n}}$ are the damping constant, the eigenfrequency, and the oscillator strength. For simplicity, we consider a one-electron atom in the ground state and its dipole moment $\boldsymbol{d} = e\boldsymbol{r}$. In case of a multielectron atom, the dipole moment is equal to the sum of dipole moments of atomic electrons. In view of the correspondence principle, an induced dipole moment of an atom is made up of the induced dipole moments $\boldsymbol{d}_{\mathrm{n}}$ of oscillators of transitions to the nth state: $\boldsymbol{d} = \sum\limits_{\mathrm{n}} \boldsymbol{d}_{\mathrm{n}} = e\sum\limits_{\mathrm{n}} \boldsymbol{r}_{\mathrm{n}}$. Going to Fourier components in this equation, we have

$$\boldsymbol{d}_{\omega} = e\sum_{\mathrm{n}} \boldsymbol{r}_{\mathrm{n}\omega}, \tag{2.39}$$

where $\boldsymbol{r}_{\mathrm{n}\omega}$ is the Fourier transform of the radius vector deviation (from the equilibrium position) of the transition oscillator. From the equation of motion (2.38), it follows:

$$\boldsymbol{r}_{\mathrm{n}\omega} = \frac{e}{m}\frac{f_{0\mathrm{n}}}{\omega_{0\mathrm{n}}^{2} - \omega^{2} - i\,\omega\,\delta_{0\mathrm{n}}}\boldsymbol{E}_{\omega}. \tag{2.40}$$

Substituting formula (2.40) into the (2.39) and using the definition of polarizability (2.37), we find

$$\beta(\omega) = \frac{e^2}{m} \sum_{\mathrm{n}} \frac{f_{0\mathrm{n}}}{\omega_{0\mathrm{n}}^2 - \omega^2 - i\,\omega\,\delta_{0\mathrm{n}}}. \tag{2.41}$$

Hence it follows that the dynamic polarizability of an atom, generally speaking, is a complex value with the dimensionality of a volume. The imaginary part of the polarizability is proportional to the damping constants of the transition oscillators. The sum in the right-hand side of the (2.41) includes both summations over the discrete energy spectrum and integration over the continuous energy spectrum. The imaginary part of the polarizability is responsible for absorption of radiation, and the real part defines the refraction of an electromagnetic wave in a medium. The expression (2.41) describes not only a one-electron atom, but also a multielectron atom. The multielectron nature of an atom is taken into account by the fact that in the definition of the oscillator strength (2.18) the dipole moment of an atom is equal to the sum of dipole moments of each of its electrons.

From the (2.41), several important limiting cases can be obtained. For example, if the frequency of an external field is equal to zero, the formula (2.41) gives the expression for the static polarizability of an atom:

$$\beta_0 \equiv \beta(\omega = 0) = \frac{e^2}{m} \sum_{\mathrm{n}} \frac{f_{0\mathrm{n}}}{\omega_{0\mathrm{n}}^2}. \tag{2.42}$$

Hence it is seen that static polarizability is a real and positive value. It has large numerical values if in the spectrum transitions high oscillator strengths and low eigenfrequencies are encountered.

In the opposite (high-frequency) limit, when $\hbar\,\omega \gg I_{\mathrm{P}}$, ($I_{\mathrm{P}}$ is the atomic ionization potential) and the eigenfrequencies in the denominators of (2.41) can be neglected, in view of the golden sum rule (2.19), we obtain from the formula (2.41):

$$\beta_{\infty}(\omega) = -\frac{e^2\,N_{\mathrm{e}}}{m\,\omega^2}. \tag{2.43}$$

The high-frequency polarizability of an atom (2.43) is a real and negative value.

If the frequency of an external field is close to one of the eigenfrequencies of the transition oscillators, so that the resonance condition

$$|\omega - \omega_{0\mathrm{n}}| \le \delta_{0\mathrm{n}} \tag{2.44}$$

is fulfilled, and only one resonance term can be left in the sum (2.41), we obtain the following expression for the resonance polarizability:

$$\beta_{\mathrm{res}}(\omega) = \left(\frac{e^2}{2\,m\,\omega_{0\mathrm{n}}}\right) \cdot \frac{f_{0\mathrm{n}}}{\omega_{0\mathrm{n}} - \omega - i\,\delta_{0\mathrm{n}}/2}. \tag{2.45}$$

In derivation of (2.45) from (2.41), in non-resonance combinations, the distinction of the external field frequency from the transition eigenfrequency was neglected. Resonance polarizability is a complex value, and the real part of which can be both positive and negative.

Equation (2.37) defines the dynamic polarizability. Taking the inverse Fourier transform, we obtain

$$\boldsymbol{d}(t) = \int\limits_{-\infty}^{\infty} \beta(\tau)\,\boldsymbol{E}(t-\tau)\,\mathrm{d}\tau, \tag{2.46}$$

where $\beta(\tau)$ is a real function of time where its Fourier transform is equal to the dynamic polarizability $\beta(\omega)$. The simplest expression for $\beta(\tau)$ follows from the formula (2.45):

$$\beta_{\mathrm{res}}(\tau) = -i\frac{e^2 f_{0\mathrm{n}}}{2\,m\,\omega_{0\mathrm{n}}} \cdot \theta(\tau) \cdot \exp(-i\,\omega_{0\mathrm{n}}\,\tau - \delta_{0\mathrm{n}}\,\tau/2), \tag{2.47}$$

where $\theta(\tau)$ is the Heaviside step function. The time dependence of the induced dipole moment $\boldsymbol{d}(t)$ coincides with the time dependence of the right-hand side of (2.47) for a delta pulse of the field: $\boldsymbol{E}(t) = \boldsymbol{E}_0\,\delta(t)$, where $\delta(t)$ is the Dirac delta function. In the general case, the expression for $\beta(\tau)$ can be obtained by replacement of the frequency $\omega_{0\mathrm{n}} \to \sqrt{\omega_{0\mathrm{n}}^2 - (\delta_{0\mathrm{n}}/2)^2}$ and summation over all transition oscillators. It should be noted that a decrease in the oscillation eigenfrequency in view of damping that follows from this replacement is quite natural since friction (the analog of damping) decreases the rate of motion.

2.4 General Relations of Atomic Polarizability

From the formula (2.47), it follows in particular that the function $\beta(\tau)$ is zero for times $\tau < 0$, which is a reflection of the *causality* principle. Really, as seen from (2.46), in order for the effect to appear after its cause, the fulfillment of the condition $\beta(\tau < 0) = 0$ is necessary. The causality principle imposes certain restrictions on the form of the function $\beta(\omega)$, from which the *Kramers–Kronig* relations follow that connect the real and imaginary parts of dynamic polarizability:

$$Re\{\beta(\omega)\} = \frac{1}{\pi}\,V.P.\int\limits_{-\infty}^{\infty} \frac{Im\{\beta(\omega')\}}{\omega' - \omega}\,\mathrm{d}\omega', \tag{2.48}$$

$$Im\{\beta(\omega)\} = \frac{1}{\pi}\, V.P. \int\limits_{-\infty}^{\infty} \frac{Re\{\beta(\omega')\}}{\omega - \omega'}\, \mathrm{d}\omega', \tag{2.49}$$

where the principal-value integral is given by:

$$V.P. \int\limits_{-\infty}^{+\infty} \frac{f(x)}{x-a}\mathrm{d}x = \lim_{\Delta\to 0}\left\{ \int\limits_{-\infty}^{a-\Delta} \frac{f(x)}{x-a}\mathrm{d}x + \int\limits_{\mathrm{a}+\Delta}^{+\infty} \frac{f(x)}{x-a}\mathrm{d}x \right\}. \tag{2.50}$$

With the use of (2.48), (2.49), it is possible to obtain the real part of the polarizability via the imaginary part and vice versa. For practical purposes, it is convenient to integrate (2.48) over positive frequencies and to represent the principal value of the integral as a "punctured" integral:

$$Re(\beta(\omega)) = \frac{2}{\pi}\int\limits_{0}^{\infty} \frac{\omega' Im(\beta(\omega')) - \omega\, Im(\beta(\omega))}{\omega'^2 - \omega^2}\mathrm{d}\omega'. \tag{2.51}$$

In derivation of (2.51), it was assumed that the imaginary part of the polarizability is an odd function of frequency.

There is an important relation connecting the imaginary part of the dynamic polarizability and the photoabsorption cross section $\sigma_{\mathrm{ph}}(\omega)$. This relation is called the *optical theorem* and looks like

$$Im(\beta(\omega)) = \frac{c}{4\,\pi\,\omega}\,\sigma_{\mathrm{ph}}(\omega). \tag{2.52}$$

With the use of the optical theorem we find with (2.51)

$$Re(\beta(\omega)) = \frac{c}{2\pi^2}\int\limits_{0}^{\infty} \frac{\sigma_{\mathrm{ph}}(\omega') - \sigma_{\mathrm{ph}}(\omega)}{\omega'^2 - \omega^2}\mathrm{d}\omega'. \tag{2.53}$$

Equation (2.53) expresses the real part of polarizability in terms of the photoabsorption cross section. In particular, for static polarizability, we have:

$$\beta(0) = \frac{c}{2\,\pi^2}\int\limits_{0}^{\infty} \frac{\sigma_{\mathrm{ph}}(\omega)}{\omega^2}\,\mathrm{d}\omega. \tag{2.54}$$

From (2.53), it is possible to obtain the sum rule for the photoabsorption cross section when going to the limit $\omega \to \infty$ and using the expression (2.43) for the high-frequency polarizability:

$$\frac{mc}{2\,\pi^2\,e^2}\int\limits_0^\infty \sigma_{\mathrm{ph}}(\omega)\,\mathrm{d}\omega = N;\quad \frac{2m}{\pi\,e^2}\int\limits_0^\infty \omega\,Im\{\beta(\omega)\}\,\mathrm{d}\omega = N. \tag{2.55}$$

The second equality in (2.55) follows from the first equality in view of the optical theorem (2.52).

As it was noted, the above formulas for the polarizability are valid for a spherically symmetric atomic state. In the general case, the polarizability β_{ij} is a tensor. For an atom being in the state $|n\,l\,m\rangle$, where *n, l, m* are the principal, orbital, and magnetic quantum numbers, the tensor can be represented as (Amusia 1990)

$$\beta_{\mathrm{ij}} = \begin{bmatrix} \beta^s_{\mathrm{nl}} - \frac{1}{2}\,P_2\,\beta^a_{\mathrm{nl}} & \frac{i}{2}\,P_1\,\beta^a_{\mathrm{nl}} & 0 \\ -\frac{i}{2}\,P_1\,\beta^a_{\mathrm{nl}} & \beta^s_{\mathrm{nl}} - \frac{1}{2}\,P_2\,\beta^a_{\mathrm{nl}} & 0 \\ 0 & 0 & \beta^s_{\mathrm{nl}} + P_2\,\beta^t_{\mathrm{nl}} \end{bmatrix}. \tag{2.56}$$

Here β^s_{nl}, β^a_{nl}, β^t_{nl} are the scalar, antisymmetric, and tensor components of the polarizability. The functions of magnetic and orbital quantum numbers $P_{1,\,2}(m)$ for $l \neq 0$ are

$$P_1(m) = \frac{m}{l};\quad P_2(m) = \frac{3\,m^2 - l(l+1)}{l(2l-1)}. \tag{2.57}$$

For a spherically symmetric state, when $l = m = 0$, $P_1 = P_2 = 0$, formula (2.56) shows that the atomic polarizability becomes a scalar.

With the use of (2.56), it is possible to write the shift and splitting of magnetic sublevels of the state $|n\,l\,m\rangle$ in the ac field $\boldsymbol{E}(t) = E\,Re\{\boldsymbol{e}\,\exp(-i\,\omega\,t)\}$ (in the general case, $\boldsymbol{e}$ is a complex vector, and $|\boldsymbol{e}| = 1$) far from the resonance as

$$\Delta E_{\mathrm{nlm}} = -\frac{1}{4}\,E^2\,\left[\beta^s_{\mathrm{nl}}(\omega) + P_2(m)\,\beta^t_{\mathrm{nl}}(\omega)\right] \tag{2.58}$$

for linear polarization of the electric field and

$$\Delta E_{\mathrm{nlm}} = -\frac{1}{4}\,E^2\left[\beta^s_{\mathrm{nl}}(\omega) \pm P_1(m)\,\beta^a_{\mathrm{nl}}(\omega) - \frac{1}{2}P_2(m)\,\beta^t_{\mathrm{nl}}(\omega)\right] \tag{2.59}$$

for right-hand (+) and left-hand (−) circular polarizations of the unit vector $\boldsymbol{e}$. The components of the polarizability tensor $\beta^s_{\mathrm{nl}}, \beta^a_{\mathrm{nl}}, \beta^t_{\mathrm{nl}}$ are

$$\beta^s_{\mathrm{nl}}(\omega) = \frac{1}{3\,(2l+1)}\,[l\,\sigma_{\mathrm{l-1}}(\omega) + (l+1)\,\sigma_{\mathrm{l+1}}(\omega)], \tag{2.60}$$

$$\beta^a_{\mathrm{nl}}(\omega) = \frac{1}{2\,l+1}\,\left[\sigma^-_{\mathrm{l-1}}(\omega) - \sigma^-_{\mathrm{l+1}}(\omega)\right], \tag{2.61}$$

$$\beta^{t}_{\mathrm{nl}}(\omega) = -\frac{1}{3\,(2\,l+1)} \cdot \left[\sigma_{\mathrm{l-1}}(\omega) + \frac{2\,l-1}{2\,l+3}\,\sigma_{\mathrm{l+1}}(\omega)\right], \tag{2.62}$$

where

$$\sigma_{\mathrm{l'}}(\omega) = \sum_{\mathrm{n'}} \frac{f^{n'l'}_{\mathrm{nl}}}{\omega^2_{\mathrm{n'n}} - \omega^2 - i\omega\delta_{\mathrm{n'n}}}, \tag{2.63}$$

$$\sigma^{-}_{\mathrm{l'}}(\omega) = \omega \sum_{\mathrm{n'}} \frac{f^{n'l'}_{\mathrm{nl}}}{\omega_{\mathrm{n'n}}\left(\omega^2_{\mathrm{n'n}} - \omega^2 - i\omega\delta_{\mathrm{n'n}}\right)} \tag{2.64}$$

are the corresponding spectral sums. Thus the formulas (2.56)–(2.64) generalize the concept of dynamic (dipole) polarizability of an atom to the general non-spherical case of the state $|n\,l\,m\rangle$ $(l \neq 0)$ when polarizability is a tensor.

In the foregoing, we were dealing with dipole polarizability that describes the response of the atom to a spatially homogeneous electric field. If the characteristic dimension of the spatial homogeneity of a field is less than the size of the atom, the dipole polarizability should be replaced by the generalized polarizability of an atom $\beta(\omega,\, q)$ that depends also on the impulse $\hbar\boldsymbol{q}$ transmitted to the atom as a result of the atom–field interaction. With the use of $\beta(\omega,\ q)$, the dipole polarizability of the atomic core due to an external electric field is given by

$$\boldsymbol{D}(\omega) = \int \beta(\omega,\, q)\,\boldsymbol{E}(\omega,\boldsymbol{q})\,\frac{\mathrm{d}\boldsymbol{q}}{(2\,\pi)^3}, \tag{2.65}$$

where $\boldsymbol{E}(\omega,\, \boldsymbol{q})$ is the space-time Fourier transform of the electric field. For the spatially homogeneous field $\boldsymbol{E}(\omega,\, \boldsymbol{q}) = \boldsymbol{E}(\omega)\,\delta(\boldsymbol{q})$ and $\beta(\omega) = \beta(\omega,\, \boldsymbol{q} = 0)$ (2.65) turns (in case of a spherically symmetric atomic state) into an entirely local approximation $D(\omega) = \boldsymbol{E}(\omega) \cdot \beta(\omega)$.

2.5 Static Polarizability of Atoms and Ions

The static polarizability β_0 of a hydrogen-like ion in the ground 1s-state is

$$\beta_0 = \frac{9}{2}\,\frac{a^3_{\mathrm{B}}}{Z^4}, \tag{2.66}$$

where a_{B} is the Bohr radius. The value of the static polarizability β_0 rapidly decreases with increasing nuclear charge and increases sharply with principal quantum number n. These regularities are easily understood at the qualitative level if it is remembered that static polarizability is proportional to the volume of an atom that decreases with increasing Z and increases strongly with n.

Table 2.2 Static dipole polarizability: The value of static polarizability is given in atomic units

Ion	Ca^{+10}	Ti^{+12}	Fe^{+16}	Co^{+17}	Ni^{+18}
I_n, eV	558.2	737.8	1168	1293	1419
Z_{eff}	12.8	14.73	18.54	19.5	20.43
β_0^{exp}	1.74×10^{-2}	1.04×10^{-2}	4.44×10^{-3}	3.69×10^{-3}	3.08×10^{-3}
β_0	1.89×10^{-2}	1.09×10^{-2}	4.33×10^{-3}	3.53×10^{-3}	2.94×10^{-3}

An atomic unit of polarizability is equal to 0.149 Å^3 (1 Å = 10^{-8} cm)

For multiply charged ions ($N \ll Z$, N is the number of electrons in the ion core, Z is the nuclear charge), the following approximate expression for the static polarizability can be obtained:

$$\beta_0 = \frac{63}{16}\frac{N^3}{Z^4}a_B^3. \tag{2.67}$$

The dependence of the static polarizability of a multiply charged ion on the nuclear charge is the same as for a hydrogen-like ion (2.66). This follows from quantum considerations for ions with filled shells. In this case, if $Z \gg N$, the minimum frequency of a virtual transition is proportional to the squared nuclear charge. Then from the general quantum-mechanical expression for the polarizability (2.41), it follows the above Z-dependence.

For ions with partially filled electron shells, the main contribution to static polarizability is made by a virtual transition with no change in principal quantum number $\Delta n = 0$. In this case, $\beta_0 \propto Z^{-3}$.

For ions with a filled outer shell, rather good agreement with experimental data is provided by the simple empirical formula for the static dipole polarizability of an outer shell with principal quantum number n:

$$\beta_0 = N_n \frac{n^6}{Z_{eff}^4}a_B^3, \tag{2.68}$$

where N_n and Z_{eff} are, respectively the number of electrons in the outer electron shell and the effective nuclear charge. The latter value can be determined from $Z_{eff} = n\sqrt{I_n/Ry}$, where I_n is the ionization potential of the outer shell. The formula (2.68) provides particular good results for neon-like ions $(n = 2,\ N_n = 8)$. This can be seen from Table 2.2.

2.6 Local Plasma Frequency Model of Polarizability of Many Electron Systems

The local plasma model was proposed by Brandt and Lundqvist in the mid-1960s (Brandt and Lundqvist 1965) for the description of the photoabsorption by multi-electron atoms in the spectral range $\omega \sim Z$ a.u. (here 1 a.u. = 27.2 eV is the atomic unit of energy). In this case, in contrast to ranges of high ($\omega \sim Z^2$ a.u.) and low ($\omega \sim 1$ a.u.) frequencies, photon absorption is defined more by collective effects rather than by one-particle interaction. Based on these qualitative considerations, the electron core of an atom is approximated by the inhomogeneous distribution of the charge and the interaction which an electromagnetic field is defined by the plasma resonance condition:

$$\omega = \omega_{\mathrm{p}}(r) = \sqrt{\frac{4\,\pi\,n(r)\,e^2}{m}}, \tag{2.69}$$

where $n(r)$ is the local electron density and $\omega_{\mathrm{p}}(r)$ is its associated local plasma frequency. It can be shown that to the condition (2.69) there corresponds the following expression for the dipole dynamic polarizability that satisfies the Kramers–Kronig relations (2.48), (2.49) and the sum rule (2.55):

$$\beta^{\mathrm{BL}}(\omega) = \int\limits_0^{R_0} \frac{\omega_{\mathrm{p}}^2(r) r^2\, \mathrm{d}r}{\omega_{\mathrm{p}}^2(r) - \omega^2 - i \cdot 0} = \int \beta^{\mathrm{BL}}(r, \omega)\, \mathrm{d}\boldsymbol{r}. \tag{2.70}$$

Here, the value $\beta^{\mathrm{BL}}(r, \omega)$ is introduced that corresponds to a so-called spatial polarizability density in the Brandt–Lundqvist approximation, R_0 is the size of the atom (ion). In the denominator of the integrand of (2.70) an infinitesimal imaginary additive (designated as "$i \cdot 0$") is introduced that indicates the rule of pole bypass in calculation of the integral.

The expression (2.70) has correct high-frequency asymptotics (2.43). In the low-frequency limit, it gives

$$\beta^{\mathrm{BL}}(\omega \to 0) \to R_0^3/3, \tag{2.71}$$

that is, static polarizability is found to be proportional to the volume of an atom.

Despite of its apparent simplicity, the formula (2.71) well describes available experimental data. First of all, this concerns multielectron atoms with filled shells since in this case the main contribution to polarizability is made by the continuous energy spectrum of an atom, and the local plasma frequency approximation (2.70) is the most adequate. This fact is demonstrated by Table 2.3, where the values

Table 2.3 Static polarizability

Atom (ion)	Kr I	Xe I	KI I	Rb II	Cs II	Sr III	Ba III
β_0^{exp}	17	27	7.5	12	16.3	6.6	11.4
β_0^{var}	26.8	30.9	9.1	14.3	17.8	8.7	11.4
β_0^{USh}	21.1	25.5	6.6	11.9	15.3	7.5	9.7
β_0^{StZ}	17.2	27.3	5.25	8.5	14.6		
β_0^{BL}	24	27	8.6	11.6	13.5	7	8.4

(in atomic units) of the static polarizability of atoms and ions with filled electron shells are calculated within the framework of different models as well as experimental data. For the calculations of the static polarizability in the framework of the Brandt–Lundqvist model, the used atomic/ionic radius was calculated from the Thomas–Fermi–Dirac model including correlation allowance.

β_0^{var} is the calculation from the variational method, β_0^{USh} is the calculation of Shevelko and Ulanzev (1994), β_0^{StZ} is the calculation of Stott and Zaremba (1980) within the framework of the electron density formalism, $\beta_0^{\mathrm{BL}} = R^3/3$ is the calculation in the framework of the Brandt-Lundqvist model.

With the use of the formula (2.70) and the statistical model of an atom, the following expression for the dynamic polarizability can be obtained:

$$\begin{aligned} \beta(\omega, Z) &= r_{\mathrm{TF}}^3 \tilde{\beta}\left(\frac{\omega}{Z}\right) = \frac{b^3 a_{\mathrm{B}}^3}{Z} \tilde{\beta}\left(\frac{\omega}{Z v_{\mathrm{a}}}\right), \\ \tilde{\beta}(v) &= \int_0^{x_0} \frac{4\pi f(x) x^2 \, \mathrm{d}x}{4\pi f(x) - v^2 - i \cdot 0}, \end{aligned} \tag{2.72}$$

where $r_{\mathrm{TF}} = b\, a_{\mathrm{B}}/Z^{1/3}$ is the Thomas–Fermi radius, Z is the atomic nucleus charge, a_{B} is the Bohr radius, $b \cong 0.8853$, $\tilde{\beta}(v)$ is the dimensionless polarizability as a function of the reduced frequency $v = \omega/Z\, v_{\mathrm{a}}$, $x_0 = R_0/r_{\mathrm{TF}}$ is the reduced atomic radius, $f(x)$ is the universal function describing the distribution of the electron density $n(r)$ in an atom according to the formula $n(r) = Z^2 f(r/r_{\mathrm{TF}})$, $v_{\mathrm{a}} \cong 4.13 \times 10^{16}\,\mathrm{s}^{-1}$ is the atomic unit of frequency.

It should be emphasized that the dimensionless polarizability $\tilde{\beta}(v)$ does not depend on the atomic nuclear charge. Thus, the representation of the dynamic polarizability of a statistical atom (2.72) reveals a scaling law with respect to the parameter $v = \omega/Z\, v_{\mathrm{a}}$.

The results of calculation of the real and imaginary parts of the dipole dynamic polarizability of a krypton atom within the framework of the local plasma frequency method by the formula (2.70) using the Slater and Lenz–Jensen electron densities are presented in Fig. 2.1. Given in the same figure (curve 3) are the results of calculation for the corresponding values in the random phase exchange approximation that is today the most consistent quantum-mechanical method of description of the electronic structure of atoms. It is seen that the dynamic polarizability of a krypton atom calculated in the local plasma frequency model for the Lenz–Jensen electron density renders in a smoothed manner the quantum-mechanical features of the frequency behavior of dynamic polarizability. These are most pronounced in the vicinity of potentials of ionization of electron subshells. The use of Slater wave functions allows to some extent to resolve the spectral fluctuations of the polarizability in the vicinity of the ionization potentials of the electron subshells. However, in this case, we loose the universality of the description like in the statistical model.

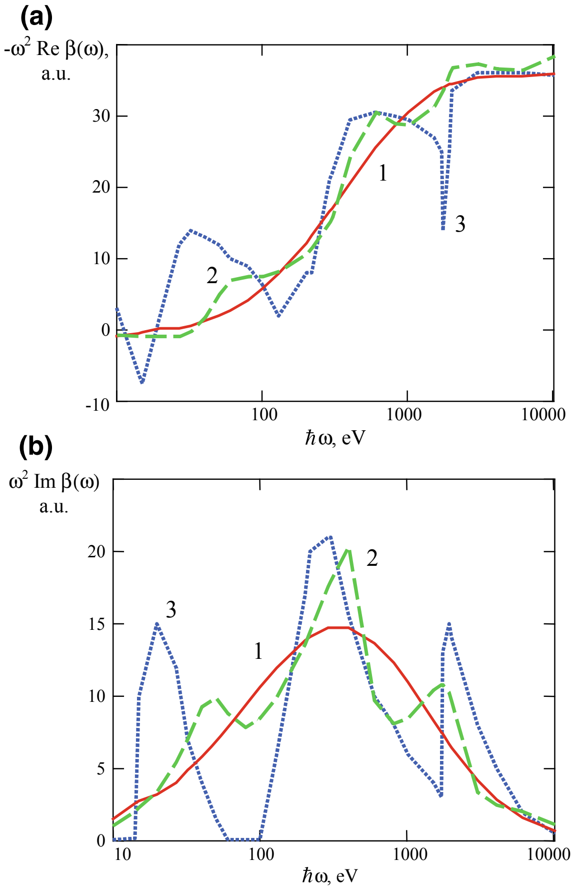

Fig. 2.1 Frequency dependences of the real (**a**) and imaginary (**b**) parts of the polarizability of a krypton atom calculated in different approximations: in the local plasma frequency approximation for the Lenz–Jensen electron density (1), in the local plasma frequency approximation for the Slater electron density (2), in the random phase exchange approximation (3) (Korol et al. 1998)

Let us present the high-frequency asymptotics of dimensionless polarizability that follows from the formula (2.72) in view of the explicit form of the function $f(x)$ for distribution of the Thomas–Fermi and Lenz–Jensen electron densities. For the imaginary part $\tilde{\beta}(\nu)$, we have

$$Im\left\{\tilde{\beta}^{T-F}(\nu \to \infty)\right\} \to \frac{4.35}{\nu^4}, \tag{2.73a}$$

$$Im\left\{\tilde{\beta}^{L-J}(\nu \to \infty)\right\} \to \frac{4.615}{\nu^4}. \tag{2.73b}$$

From the formulas (2.73), it is seen that the above statistical models give a similar result for the imaginary part of polarizability. It should be noted that in the hydrogen-like approximation (for a spherically symmetric atomic state) the imaginary part of polarizability decreases as $\nu^{-4.5}$. The high-frequency asymptotics of the real part of the dimensionless polarizability $\tilde{\beta}(\nu)$ in both models of atomic core electron density looks like

$$Re\left\{\tilde{\beta}(\nu \to \infty)\right\} \to -\frac{b^{-3}}{\nu^2}, \tag{2.74}$$

which is in qualitative agreement with the general formula (2.43). From comparison of the expressions (2.73) and (2.74), it follows in particular that at high frequencies the imaginary part of polarizability decreases much more rapidly than its real part.

2.7 Dynamic Polarizability of Nanoparticles

Let us calculate the dynamic polarizability of a sphere placed in a dielectric medium. We assume that the sphere radius is much larger than the distance between atoms in the substance. In this case, for the description of the interaction of the sphere with an electromagnetic field the concept of the dielectric permittivity can be used.

Using the Mie theory for calculation of the cross section of radiation scattering by a spherical particle of radius r_s, it is possible to obtain the following expression for the polarizability of a spherical particle in terms of the Mie coefficients:

$$\beta_s = \frac{3}{2}\,\varepsilon_m \left(\frac{r_s}{x}\right)^3 \cdot \left[-i\,a_1(x, mx, m) + b_1(x, mx, m)\right], \tag{2.75}$$

where

$$x = k\,r_s = \sqrt{\varepsilon_m}\,\frac{\omega}{c}\,r_s, \tag{2.76}$$

$$m = \sqrt{\frac{\varepsilon_s(\omega)}{\varepsilon_m}}. \tag{2.77}$$

m is the relative refractive index; ε_m, $\varepsilon_s(\omega)$ are the dielectric permittivities of the matrix and the material of the sphere; a_n and b_n are the Mie coefficients in the Legendre polynomial and spherical Hankel function expansions of a scattered wave outside the sphere.

Hereafter, we assume that the dependence of the value ε_m on the radiation frequency ω can be neglected. With the use of boundary conditions (for a more detailed description, see Sect. 4.5.1), the following formulas for the Mie coefficients can be obtained (Van der Hulst 1981):

$$a_{\mathrm{n}}(x,y,m)=\frac{\psi'_{\mathrm{n}}(y)\,\psi_{\mathrm{n}}(x)-m\,\psi'_{\mathrm{n}}(x)\,\psi_{\mathrm{n}}(y)}{\psi'_{\mathrm{n}}(y)\,\zeta_{\mathrm{n}}(x)-m\,\zeta'_{\mathrm{n}}(x)\,\psi_{\mathrm{n}}(y)}, \tag{2.78}$$

$$b_{\mathrm{n}}(x,y,m)=\frac{m\,\psi'_{\mathrm{n}}(y)\,\psi_{\mathrm{n}}(x)-\psi'_{\mathrm{n}}(y)\,\psi'_{\mathrm{n}}(x)}{m\psi'_{\mathrm{n}}(y)\,\zeta_{\mathrm{n}}(x)-\zeta'_{\mathrm{n}}(x)\,\psi_{\mathrm{n}}(y)}, \tag{2.79}$$

where

$$\psi_{\mathrm{n}}(z)=z j_{\mathrm{n}}(z)=\sqrt{\frac{\pi z}{2}}J_{\mathrm{n}+1/2}(z), \tag{2.80}$$

$$\zeta_{\mathrm{n}}(z)=z\,h^{(1)}_{\mathrm{n}}(z)=\sqrt{\frac{\pi z}{2}}H^{(1)}_{\mathrm{n}+1/2}(z) \tag{2.81}$$

are the functions introduced by Debye in 1909; $j_{\mathrm{n}}(z)$ is the spherical Bessel function, $J_{\mathrm{n}+1/2}(z)$ and $H^{(1)}_{\mathrm{n}+1/2}(z)$ are the Bessel and Hankel functions of half-integer order. For $n=1$, we have

$$j_1(z)=\frac{\sin(z)}{z^2}-\frac{\cos(z)}{z}, \tag{2.82}$$

$$h^{(1)}_1(z)=\frac{\sin(z)}{z^2}-\frac{\cos(z)}{z}-i\left[\frac{\sin(z)}{z}+\frac{\cos(z)}{z^2}\right]. \tag{2.83}$$

In the limit of small parameters $x=k\,r_{\mathrm{s}}$, the following expansions for the Mie coefficients can be obtained from the formulas (2.78)–(2.83) (Van der Hulst 1981):

$$a_1\cong i\,s\,x^3\left(1+t\,x^2-i\,s\,x^3\right),\quad b_1=i\,s\,u\,x^5, \tag{2.84}$$

where

$$s=\frac{2}{3}\,\frac{m^2-1}{m^2+2},\quad t=\frac{3}{5}\,\frac{m^2-2}{m^2+2},\quad u=\frac{1}{30}\left(m^2+2\right) \tag{2.85}$$

are the auxiliary functions of the relative refractive index. In view of the formulas (2.84), (2.85), in the limit $x=k\,r_{\mathrm{s}}\ll 1$ we obtain

$$\beta_{\mathrm{s}}(\omega,\,r_{\mathrm{s}})=\,r_{\mathrm{s}}^3\,\varepsilon_{\mathrm{m}}\,\frac{\varepsilon_{\mathrm{s}}(\omega)-\varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{s}}(\omega)+2\,\varepsilon_{\mathrm{m}}}, \tag{2.86}$$

the so-called Lorentz formula for the polarizability of a small spherical particle of radius $r_{\mathrm{s}}\ll\lambda/2\,\pi\,\sqrt{\varepsilon_{\mathrm{m}}}$ and dielectric permittivity $\varepsilon_{\mathrm{s}}(\omega)$ that is placed in a matrix with a dielectric permittivity ε_{m}.

The expression (2.86) is valid for a sufficiently small nanosphere radius $r_s \ll 2\pi\sqrt{\varepsilon_m}\,\lambda$, where λ is the wavelength of a scattered photon. The analysis shows that for a metal sphere in glass the formula (2.86) for the optical spectral and adjacent spectral ranges works well for nanosphere radii less than 20 nm.

It should be noted that the expression (2.86) can be obtained to an accuracy of the factor ε_m with the use of the Clausius–Mossotti formula $\frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} = \frac{4}{3}\pi N_a \beta(\omega)$ if in the latter it is assumed that $\varepsilon(\omega) = \varepsilon_s(\omega)/\varepsilon_m$ and $N_a = 1/V_s$, where V_s is the sphere volume. From the formula (2.86), it follows that the dynamic polarizability of a sphere with small radius has a maximum for the frequency ω_r defined by setting the real part of the denominator in the right-hand side of the (2.86) to zero:

$$Re\{\varepsilon_s(\omega_r) + 2\,\varepsilon_m\} = 0. \tag{2.87}$$

The resonance (2.87) is connected with excitation of plasmons at the surface of the sphere.

The dielectric permittivity $\varepsilon_s(\omega)$ appearing in (2.86) can be expressed in terms of the real n_s and imaginary κ_s parts of the refractive index of the sphere material by the known formula:

$$\varepsilon_s(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega) = [n_s(\omega)]^2 - [\kappa_s(\omega)]^2 + 2\,i n_s(\omega)\,\kappa_s(\omega). \tag{2.88}$$

The spectral dependences of the refractive index components $n_s(\omega)$ and $\kappa_s(\omega)$ for a number of metals are determined experimentally in the work of Johnson and Christy (1972) in a range of photon energies $\hbar\,\omega$ from 0.64 to 6.6 eV. Experiments were carried with thin films with thickness' ranging from 18.5 to 50 nm. In doing so, it was found that the complex refractive index does not depend on the film thickness in the range from 25 to 50 nm. Corresponding plots for silver and gold are given in Fig. 2.2.

From the plots in Fig. 2.2, it follows that practically throughout the presented range of photon energies the condition $n_s(\omega) < \kappa_s(\omega)$ is fulfilled, which corresponds to a negative value of the real part of dielectric permittivity. Negative dielectric permittivity means the impossibility of propagation of an electromagnetic wave in a volumetric sample as well as reflection of radiation from such a medium.

The results of calculation from the formula (2.86) of the real and imaginary parts of the polarizability of a silver nanosphere placed in glass $\varepsilon_m = 2.25$ with the use of the data on the refractive index of silver of Fig. 2.2a are presented in Fig. 2.3. From the figure, there follows the presence of a polarizability resonance at a photon energy of about 3.1 eV. Within the framework of the simplest model, when the dielectric permittivity of a metal is described by the plasma formula $\varepsilon_s(\omega) = 1 - \omega_p^2/\omega^2$ (ω_p is the plasma frequency), the position of the maximum of the imaginary part of the metal sphere polarizability is given by the equation following from the resonance condition (2.87):

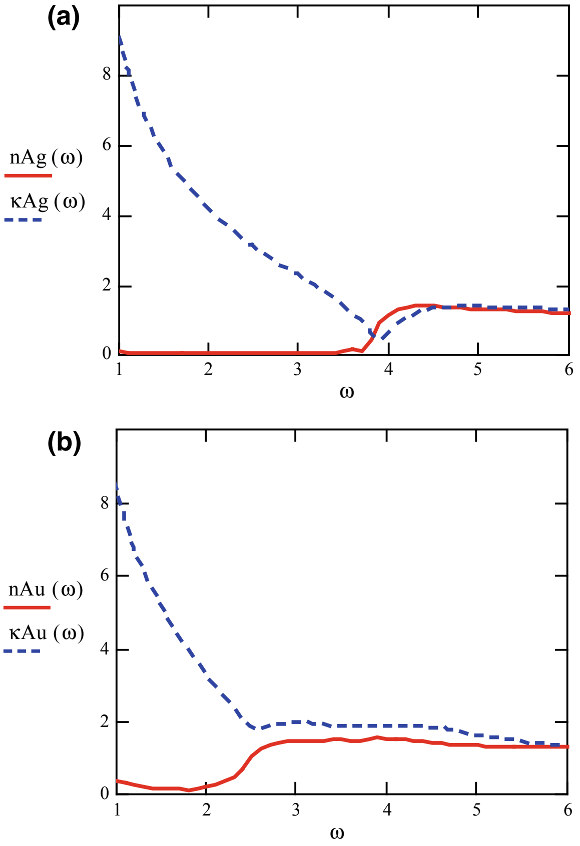

Fig. 2.2 Experimental dependences of the real (solid curve) and imaginary (dotted curve) parts of the refractive index of silver (**a**) and gold (**b**) films as functions of the photon energy (Johnson and Christy 1972); the photon energy in electron–volts is plotted on the abscissa

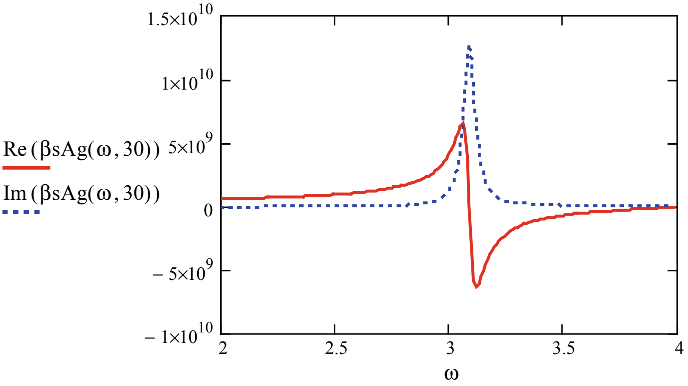

Fig. 2.3 The real and imaginary parts of the polarizability of a silver sphere with radius of 30 nm in a glass matrix; the abscissa is plotted in electron–volts, the ordinate is plotted in atomic units

$$\omega_{\mathrm{res}} = \frac{\omega_{\mathrm{p}}}{\sqrt{1 + 2\,\varepsilon_{\mathrm{m}}}}. \tag{2.89}$$

In derivation of (2.89), it was assumed that the dielectric permittivity of a matrix in the frequency range under consideration does not depend on frequency. It should be noted that in vacuum the resonance frequency of a plasmon at the sphere surface is $\omega_{\mathrm{res}} = \omega_{\mathrm{p}}/\sqrt{3}$.

For silver $\hbar\,\omega_{\mathrm{p}} \approx 9$ eV, so in case of a glass matrix, it follows from (2.89) that $\hbar\,\omega_{\mathrm{res}} \approx 3.8$ eV. The difference of this value from the data of Fig. 2.3 is connected with the fact that the plasma formula for the dielectric permittivity used in derivation of (2.89) has an appreciable error due to neglect of the contribution of bound electrons.

A resonance increase in the polarizability of a metal nanosphere results in a number of important optical effects caused by increasing the electric field strength of the electromagnetic wave near the nanosphere if the condition (2.87) is fulfilled. It should be noted that one of such effects is an increase (by more than 10 orders of magnitude) in the probability of spontaneous Raman scattering of light by molecules attached to metal nanoparticles. This effect was observed experimentally now several times, and it has great prospects for applications.

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