

# Chapter 1

## Main Points of the Theory of Photoabsorption

### 1.1 Most Important on Photoionization

As photoabsorption or photoionization in this book we consider a process, in which a photon of energy  $\omega$  and momentum  $\kappa$ ,  $\kappa = \omega/c$  ( $c$  is the speed of light) is absorbed by a target—an atom or an ion. As a result, the target object can be either *excited* or *ionized*. Excitation means a transition of an atom or ion to one or several discrete energy levels.

Ionization is a process in which as a result of photon absorption one or several electrons can leave the target atom or ion while the residual ion is left in its lowest possible energy state. The absorption of a photon can result also in *ionization with excitation*. This is a process in which one or several electrons are eliminated from the target object and the latter is left in an excited state, on one of the discrete excited levels of the residual ion.

If the atom is treated in the frame of a one-electron picture, i.e., all electrons are considered as noninteracting and moving independently in common potential field, atom or ion can be either ionized or excited, because a single photon can interact only with a single electron. In spite of limited accuracy of the one-electron approximation, we will perform and present results of calculations in its frame. In many cases they can serve as a good initial step and serve mainly for orientation. As one-electron the Hartree–Fock approximation (HF) will be used, which is the best method compatible with the idea of independent motion of all atomic electrons in a common, so-called *self-consistent* field. We will describe the main features of HF in the next section.

However, in almost all processes considered in this book, the role of interelectron interaction is essential, and in many instances is decisively important. The account of interelectron interaction that leads to *correlations* in the atomic electron motion essentially modifies the atomic (or ionic) response to the incoming photon. Considerably altered become the photon absorption probabilities and even probabilities of eliminating of one electron. Apart from it, a whole variety of atomic processes became possible that cannot take place in the frame of one-electron approximation.

Among them are the following: ionization of two and even more electrons by a single photon, ionization with excitation, and multielectron excitation.

To take into account the interelectron interaction, or as it is often called, the *multielectron correlations*, we will use in this book the random phase approximation with exchange (RPAE) or the many-body perturbation theory (MBPT). In essence, RPAE takes into account nonperturbatively, as a large correction, the dynamical variation of the self-consistent field acting upon each electron, which is caused by the incoming photon absorption [AM]. In a number of cases, however, MBPT can be used to consider atomic processes, because the interelectron interaction some times can be treated as a relatively small perturbation.

In this book, when considering photo processes we will limit ourselves by the so-called *dipole* approximation, which is valid, roughly speaking, if the wave length corresponding to the incoming photon,  $\lambda = 2\pi/\kappa = 2\pi c/\omega$  is much bigger than the atomic or ionic characteristic radius  $r_A$ ,  $\omega \ll 2\pi c/r_A$ .

The operator describing the interaction between a photon and an electron can be presented in the following form [BLP]:

$$\hat{M}(\vec{k}) = \sum_{i=1}^N \hat{\mu}_i(\vec{k}) \equiv \sum_{i=1}^N \exp(i\vec{k}\vec{r}_i)(\vec{e}\vec{\nabla}_i), \quad (1.1)$$

where  $\vec{e}$  is the polarization vector of the photon,  $r_i$  is the coordinate of the electron,  $\vec{\nabla}_i \equiv -i\partial/\partial\vec{r}_i$ , and  $N$  is the total number of atomic (ionic) electrons. In the dipole approximation, the photon momentum  $k$  can be neglected, so that instead of (1.1) the interaction of an atom with a photon reduces to

$$\hat{M}_d^V = \sum_{i=1}^N \hat{d}^V \equiv \sum_{i=1}^N (\vec{e}\vec{\nabla}_i). \quad (1.2)$$

The upper index  $V$  in  $M^V$  denotes that the interaction operator is in the so-called *velocity form*. Along with this form another one, so-called *length form* exists:

$$\hat{M}^R(\omega) = \sum_{i=1}^N \hat{d}^R(\omega) \equiv \sum_{i=1}^N \omega(\vec{e}\vec{r}_i). \quad (1.3)$$

The amplitude of the process, or the matrix element  $M_{i \rightarrow f}^{V,R}(\omega)$ , which is determined by the following integral, describes the interaction of an atom with a photon:

$$M_{i \rightarrow f}^{V,R}(\omega) = \int \Psi_i^*(x_1, \dots, x_N) \hat{M}^{V,R}(\omega) \Psi_f(x_1, \dots, x_N) \prod_{i=1}^N dx_i, \quad (1.4)$$

where  $\Psi_i(x_1, \dots, x_N)$  and  $\Psi_f(x_1, \dots, x_N)$  are the wave functions of the atom (ion) interacting with the photon, in the initial and final states, respectively. In case of

ionization,  $\Psi_f(x_1, \dots, x_N)$  includes states of continuous spectrum of one or several electrons. In (1.4) the variable  $x_i \equiv r_i, s_i$ , where  $r_i$  is the coordinate and  $s_i$  is the spin projection of an atomic electron. The integration over  $dx_i$  in (1.4) includes integration over all the infinite space  $\mathbf{r}$  and also summation over spin projection  $s$ .

The photoionization process is characterized by the *total*  $\sigma(\omega)$ , *partial*  $\sigma_q(\omega)$ , and *differential in angle*  $d\sigma_q(\omega)/d\Omega$  photoionization cross-sections, with  $\Omega$  being the solid angle of the outgoing electron. The total cross-section  $\sigma^{V,R}(\omega)$  is given by expression:

$$\sigma^{V,R}(\omega) = \frac{4\pi^2}{\omega c} \sum_f \int \left| M_{if}^{V,R}(\omega) \right|^2 \delta(E_f - E_i + \omega) dE_f, \quad (1.5)$$

here  $E_i$  is the energy of the atom in its initial state, while  $E_f$  is the final state energy of the system formed by target atom after photon absorption. The summation over  $f$  goes over all state  $s$  that have the same energy  $E_f$ .

If the state  $f$  belongs to discrete spectrum of atomic excitations, the photon–atom interaction is characterized by the so-called *oscillator strength*:

$$f_{if}^{V,R} = \frac{2}{\omega_{if}} |M_{if}|^2, \quad (1.6)$$

where  $\omega_{if} \equiv E_f - E_i$ . Note that for precise atomic wave function the cross-sections and oscillator strengths in the length  $R$  and velocity  $V$  forms coincide, but for approximate wave functions they may be different.

The total cross-section and oscillator strength, calculated with precise initial and final state wave functions obey the so-called *golden sum rule*:

$$\sum_f f_{if}^{V,R} + \frac{c}{2\pi^2} \int_I^\infty \sigma^{V,R}(\omega) d\omega = N, \quad (1.7)$$

where  $I$  is the ionization potential of an atom or the minimal energy that is necessary to remove an electron off the atom.

The partial cross-section  $\sigma_q^{V,R}(\omega)$  characterizes removal of an atomic electron from a given state or energy level. The differential in angle cross-section  $d\sigma_q^{V,R}(\omega)/d\Omega$  characterizes a process of photoionization, in which the outgoing electron, called *photoelectron*, leaves the atom at a given direction relative to that of incoming photon momentum or photon beam in the element of solid angle  $d\Omega$ .

## 1.2 Single Electron Hartree–Fock (HF) Approximation

In HF approximation, the initial and final atomic wave functions are presented as antisymmetrized product of one-electron wave functions  $\varphi_i(\vec{r}, s)$ . In this approach, it is assumed that all electrons are moving in a self-consistent potential  $\hat{U}_{\text{HF}}(r)$ ,

so that the following equation should be solved to obtain the atomic wave function:

$$\begin{aligned}\hat{H}^{\text{HF}}\Psi_E(x_1, \dots, x_N) &= \sum_{j=1}^N \left[ -\frac{\Delta_j}{2} - \frac{Z}{r_j} + \hat{U}_{\text{HF}}(r_j) \right] \Psi_E(x_1, \dots, x_N) \\ &= E\Psi_E(x_1, \dots, x_N).\end{aligned}\quad (1.8)$$

In HF approximation, the solution of (1.8) is presented as

$$\Psi_E(x_1, \dots, x_N) \equiv \Psi_E^{\text{HF}} = \frac{1}{\sqrt{N!}} \hat{A} \prod_{j=1}^N \varphi_j(x_j), \quad (1.9)$$

where  $\hat{A}$  is the operator of permutation of coordinates and spins, which is equal to  $+1$  in the case of even number of permutations and  $-1$  in the case of the odd number of permutations. Determining the one-electron wave functions  $\varphi_i(\vec{r}, s)$  and the self-consistent potential  $\hat{U}_{\text{HF}}(r)$  from the requirement of minimal total energy of an atom on the bases of functions (1.9), the following equation is obtained:

$$\begin{aligned}-\frac{\Delta}{2}\varphi_j(x) - \frac{Z}{r}\varphi_j(x) + \sum_{k=1}^N \int dx' \varphi_k^*(x') \frac{1}{|\vec{r}' - \vec{r}|} \\ \times [\varphi_k(x')\varphi_j(x) - \varphi_j(x')\varphi_k(x)] = \varepsilon_j \varphi_j(x),\end{aligned}\quad (1.10)$$

here  $\varepsilon_j$  stands for the individual electron energy. In the ground state of the atom, all lowest levels are successively filled. Let us introduce the *Fermi level*  $F$  as a filled level with the highest possible energy. Then the limitation in the sum over  $k$  may be denoted as  $k \leq F$ .

The electron energy  $\varepsilon_j$  is determined by the *principal quantum number*  $n_j$  and angular momentum  $l_j$ , which determines the radial part of the wave function. The electron levels of the same energy form a *subshell*, while all levels with the same principal quantum number form a *shell*. The one-electron wave functions are orthogonal and normalized:

$$\int \varphi_j^*(x) \varphi_k(x) dx = \delta_{ik}, \quad (1.11)$$

where  $\delta_{ii} = 1$  and  $\delta_{j \neq k} = 0$ .

The solutions of (1.10) for  $j > F$  are the wave functions of an additional, i.e.,  $(N + 1)^{\text{th}}$  electron. They can correspond to the *discrete* ( $\varepsilon_j < 0$ ) and *continuous* ( $\varepsilon_j > 0$ ) spectrum. At  $\varepsilon_j > 0$  the solutions of (1.10) exist for any value of  $\varepsilon$ . At large distance from the atom these solutions oscillate and they are normalized by the following condition:

$$\int \varphi_{\varepsilon}^*(x) \varphi_{\varepsilon'}(x) dx = \delta(\varepsilon - \varepsilon') \delta_{ll'} \delta_{mm'} \delta_{ss'}, \quad (1.12)$$

where  $\delta(\varepsilon - \varepsilon')$  is the Dirac delta function,  $l(l')$  is an electron angular momentum,  $m(m')$  is its projection on an arbitrary chosen axis, and  $s(s')$  is its spin.

In HF approximation (1.10), the dipole amplitude of photoabsorption is determined as matrix elements of the operators

$$\hat{d}^V = (\vec{e} \vec{\nabla}) \text{ or } \hat{d}^R = \omega(\vec{e} \vec{r}) \quad (1.13)$$

[see (1.2) and (1.3)]:

$$d_{if}^{V,R}(\omega) = \int dx \varphi_i^*(x) \hat{d}^{V,R} \varphi_f(x). \quad (1.14)$$

The HF photoionization cross-section is determined by the equation similar to (1.5), with  $\hat{M}^{V,R}(\omega)$  substituted by  $\hat{d}^{V,R}$ . The same is the situation for oscillator strengths.

### 1.3 Diagrammatical Technique

An important element of the theoretical description of the processes that are considered in this book is their schematic sketch: a diagram, in which the notations and method of construction presented below are used. These diagrams were introduced half a century ago in quantum electrodynamics and then successfully applied to solid state, condensed matter, and nuclear physics.

The following notations on diagrams are used:

- (a) A dashed line stands for the nonstationary external field, namely a photon.

$$- - - - \quad (1.15)$$

- (b) A line with an arrow to the right denotes an electron in  $v_1$  state described by the HF wave function  $\varphi_{v_1}(\vec{r}, s)$ , which is determined by (1.10).

$$\longrightarrow_{v_1} \quad (1.16)$$

- (c) A line with a double arrow represents an electron in discrete excited state  $v_1$  described by the HF wave function given by (1.10).

$$\longrightarrow\!\!\!\longrightarrow_{v_1} \quad (1.17)$$

- (d) A line with an arrow to the left denotes a vacancy (hole) in the state  $v_2$  described by the HF wave function determined by (1.10).


(1.18)

- (e) A wavy line represents the Coulomb interaction between atomic electrons or that between atomic electrons and the incoming electron or positron in the process of scattering.


(1.19)

- (f) A full circle-dot stands for an event of interaction between a field and an electron.


(1.20)

Using these notations, just as “words” of a very simple “vocabulary,” we can build up the elementary diagrams describing the interaction between atomic electrons or between atomic electrons and the field. The following diagram accounts for the interaction of a photon with atomic electrons, which leads to creation of an electron-hole pair  $\nu_1 \nu_2$  and absorption of a photon with energy  $\omega$ :


(1.21)

*Annihilation* (disappearance) of an electron-hole pair  $\nu_1 \nu_2$  with emission of a photon  $\omega$  is presented like that:


(1.22)

The following elementary processes can be only virtual (temporary): “creation” of an electron-hole pair  $\nu_1 \nu_2$  and a photon  $\omega$  from vacuum:


(1.23)

and annihilation of an electron-hole pair and a photon  $\omega$  into vacuum.


(1.24)

The interaction between two electrons  $\nu_1$  and  $\nu_3$  is depicted as an electron  $\nu_1$  scattered by another electron  $\nu_3$  leading to electrons  $\nu_2$  and  $\nu_4$ :

$$(1.25)$$

or as a hole  $v_1$  scattered by another hole  $v_3$ :

$$(1.26)$$

and a hole  $v_4$  scattered by an electron  $v_1$  or vice versa.

$$(1.27)$$

The second diagram in (1.27) represents the annihilation of a pair  $v_1 v_4$  followed by creation of the pair in different state  $v_2 v_3$ .

The propagation of an electron  $v_1$  (or a hole  $v_2$ ) may be accompanied by its transition to  $v_2(v_1)$  and creation of the pair  $v_3 v_4$ . This is described as follows:

$$(1.28)$$

The propagation of an electron  $v_1$  or a hole  $v_2$  may be accompanied as well by pair annihilation, which is represented by the diagrams that are mirror reflections of (1.28) relative to the Coulomb interelectron interaction wavy line.

There are two following virtual elementary processes: creation of two electron–hole pairs  $v_2 v_1$  and  $v_3 v_4$  from vacuum and annihilation of them:

$$(1.29)$$

One or a combination of these elementary diagrams will present any physical process that will be considered in this and the following chapters of this book.

To build up a diagram of an atomic process, first of all the initial and the final states should be presented by means of elementary diagrams. For example, for photoionization with elimination of a single electron off the target atom, a photon (1.15) and an electron–hole pair account for the initial and final states, respectively. For the elastic scattering of an electron, both initial and final states are represented

by lines with right arrows (1.16). For vacancy “decay,” when the state of a vacancy changes, the transition energy being released as the creation of an electron–hole pair, the initial state is a vacancy (1.18), while the final state is a vacancy and an electron–hole pair.

Building up a diagram starts from the lowest possible order in interelectron interaction. The goal is to present the process under investigation as developing from its initial to the final state as the shortest possible series of interparticle interaction elements. For instance, the simplest diagram of photoionization is (1.21), while (1.28, left) is the simplest diagram of the inelastic scattering of an electron with creation of an electron–hole pair.

The initial and the final states may be as well joined together with a bigger series of elementary events. For example, the following diagram presents the contribution to the amplitude of one-electron photoionization with creation of an electron  $\nu_4$  and a vacancy  $\nu_3$  that involves interaction with electron–hole pair  $\nu_1 \nu_2$ :

The diagrams present the process evolving in time. The normal course of time runs from left to the right. The following so-called correspondence rules allow us to relate an analytical expression to the diagram:

- Assign  $\nu_1, \nu_2, \dots, \nu_n$  to all electron and hole states.
- Introduce the “sections” of diagrams, i.e., draw in reality or imagination vertical lines separating each event of interaction between atomic electrons, or that of an atomic electron and a photon.
- To relate to every section the energy denominator:

$$\left( \sum \varepsilon_h - \sum \varepsilon_p + E_{in} + i\eta \right)^{-1}, \quad (1.31)$$

where  $\sum \varepsilon_h$  and  $\sum \varepsilon_p$  are, respectively, the total energies of all holes and electrons involved in the section, while  $E_{in}$  is the incoming energy,  $\eta \rightarrow 0$ .

- To each event of the interaction of a photon with an electron or a hole (1.21)–(1.24), with  $\mu(\vec{k})$  given by (1.1) the following matrix element is related:

$$\langle \nu_1 | \hat{\mu}(\vec{k}) | \nu_2 \rangle \equiv \int dx \varphi_{\nu_1}^*(x) \hat{\mu}(\vec{k}) \varphi_{\nu_2}(x). \quad (1.32)$$

- To interelectron interaction  $V$  the following matrix element appearing in diagrams (1.25)–(1.29) is related:



$$\langle v_1 v_3 | V | v_2 v_4 \rangle \equiv \int dx dx' \varphi_{v_1}^*(x) \varphi_{v_3}^* \frac{1}{|\vec{r} - \vec{r}'|} \varphi_{v_2}(x) \varphi_{v_4}(x'). \quad (1.33)$$

- To sum (and integrate) over all internal electron and hole states  $v$ , while  $\eta \rightarrow 0$  in (1.31) shows the direction of tracing the singularities.
- Multiply the obtained expression by  $(-1)^Q$ , where  $Q$  is the number of hole lines in the diagram added to the number of closed electron–hole loops.

The result is the contribution of the diagram to the amplitude of the process under investigation.

For instance, the contribution of diagram (1.30) is equal to

$$\Delta\mu_{v_3 v_4}(\omega) = \sum_{v_1 > F, v_2 < F} \frac{\langle v_1 | \hat{\mu}(\vec{k}) | v_2 \rangle \langle v_2 v_3 | V | v_1 v_4 \rangle}{\varepsilon_{v_2} - \varepsilon_{v_1} + \omega + i\eta} \times (-1)^3, \quad (1.34)$$

here  $Q = 3$  since there is an electron–hole loop and two hole lines ( $v_2$  and  $v_3$ ) in the diagram. More complex diagrams can be built up similarly, and analytical expressions are related to them in the same way.

In principle, infinite variety of diagrams corresponds to any physical process with given initial and final states. Having restricted the consideration to some selected diagrams, one can relate them to respective analytical expressions and thus obtain the amplitude of the investigated process, whose probability is proportional to the square of the amplitude's modulus. The total probability of the process per unit time is the sum of amplitudes' modulus squares over all possible final states averaged over the initial states with the account taken of energy conservation. Total energies of the system in its initial and final states must be equal in accordance with the energy conservation law.

## 1.4 Many-Body Perturbation Theory

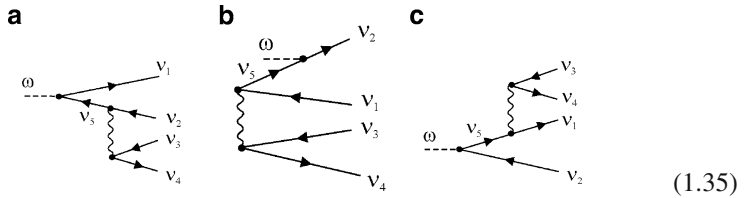
Till now, in spite of rapid development of the computation technique, it is impossible to describe an  $N$ -electron atom, with  $N > 2$ , precisely, by solving the Schrödinger equation of  $N$  electrons interacting with each other via the Coulomb potential and moving in the field of a nucleus. Thus, one has to use simplifying models to study and describe atoms.

Essential simplifications become possible and justified when the interaction is weak. Then it can be considered using *perturbation theory*. In this book, we will investigate the interaction of atoms with only low intensity photon field. Therefore, the photon–electron interaction is sufficient to take into account only in the lowest order of the perturbation theory. For photoabsorption, it means that the corresponding amplitudes will be calculated in first order in  $\hat{\mu}(\vec{k})$  [see (1.1)].

The situation with electron–electron and electron–nucleus interaction is much more complicated. Indeed, these interactions can be treated as perturbation in general only when the relative velocity of the interacting particles is big. Inside an atom this is not the case. Without any doubt, the HF field differs from pure nucleus field strong enough. Therefore, as one-electron or one-hole states those calculated in HF approximation (1.10) will be used.

The interaction between fast incident particle and target electrons will be limited to the first order in  $V$ . However, there exist a number of processes, e.g., vacancy decay with emission of fast electrons or high-energy photons where perturbation theory in interelectron interaction can be also applied. Perturbation theory, even in its lowest order, can be used in any case while studying a complicated process, which otherwise is too difficult or impossible to consider. In the latter case, the data obtained can be used with reasonable precaution admitting that it cannot be accurate enough.

The advantage of the perturbative approach is that the rough approximation is relatively easy to obtain, and the mechanism under consideration becomes clear and obvious. As an example of the latter situation, let us consider two-electron photoionization, i.e., a process in which two electrons are eliminated from an atom after absorbing a single photon. The simplest diagrams describing creation of two electron–vacancy pairs by one photon look as follows:



where diagrams (1.35a) and (1.35c) are describing the knockout of an electron and the creation of the state  $v_3v_4$  due to the scattering of an electron (or a hole)  $v_5$  followed by the transition of the latter into the state  $v_2$  or  $v_1$ . Note that in the first order along with diagram (1.35b) a similar one exists, in which the incoming photon interacts not with an electron but a hole. This diagram together with (1.35b) corresponds to the interaction between the electrons in the ground state. As a result of action of the mechanisms presented by (1.35), two electrons are removed from the atom or occupy an excited state.

To obtain accurate enough results for the two-electron photoionization at not very high  $\omega$ , one should take into account nonperturbatively at least the interaction between two atomic electrons  $v_1v_4$ . In the initial state, the interaction between two ionizing electrons must be taken into account nonperturbatively even for high  $\omega$ . However, calculations using the amplitude depicted in (1.35) give a very good first approximation to the reality.

It is rather difficult to take into account next orders corrections in  $V$  to (1.35). In fact, already inclusion of all third-order terms is a very complicated task. Therefore, calculations in MBPT are limited to not more than all third-order diagrams. Of course, some even infinite order terms are taken into account by the choice of HF functions as the one electron. But in general, with the number of interelectron interactions exceeding three, even to draw all diagrams became a rather time-consuming task. As to the calculations of corresponding matrix elements, they simply became almost impossible. Indeed, with a number of interaction events  $N_{\text{int}}$ , the number of diagrams amounts to  $N_{\text{int}}!$ . As to the calculation of a contribution of a given diagram, they became more and more complicated with increasing  $N_{\text{int}}$  since the number of intermediate state increases, and so the number of required integrations and summations.

However, another approach is often used. Terms of all powers of  $V$  are accounted for, but in each order  $q$  (with the product of  $q$  matrix elements of  $V$ ) only a limited number of terms of the expansion are retained. Evidently, even the part of the terms of all powers in  $V$  cannot be summed up sequentially, one order after the other. However, in some cases such summation may be performed by means of establishing and solving an equation (or a set of the equations) called the closed equation wherein all functions to be found are expressed in terms of the functions already known. A version of this approach is called the random-phase approximation with exchange (RPAE).

## 1.5 Random Phase Approximation with Exchange

The RPAE is a generalization of HF approximation for the atom in a weak electromagnetic external field or in an excited state populated, for instance, in the collision of the atom with an electron, etc. The method is based on the assumption that both in the presence and absence of the nonstationary applied field the wave function of an atom at every moment is a Slater determinant composed from one-electron wave functions  $\varphi_v(x, t)$ . It is assumed in RPAE that the variation of the one-electron wave functions under the action of external electromagnetic field is small.

The RPAE equations account not only for the action of the external field with particular atomic electron, but also for the interaction of the external field with all other electrons. The virtual transitions induced by this interaction change the mean atomic field and therefore lead to removal or excitation of the atomic electron. In terms of the diagrams, RPAE corresponds to the account of an event of interaction between a hole and an electron. Diagrammatically, the RPAE equation is presented in the following way:

$$(1.36)$$

Here the shaded circle denotes the electron–photon interaction operator in RPAE. The diagram equation (1.36) can be iterated. The first step of this iteration is to substitute the shaded circle by a dot. Then the diagram (1.36c) transforms into (1.30).

The diagrams (1.36) present photo ionization process as developing in time, from left to right, starting with a photon and ending up with an electron–hole pair. This is why diagrams (1.36b)–(1.36d) are called “time-forward,” whereas (1.36e) and (1.36f) are called “time-reverse” diagrams.

The diagram equation (1.36) may be analytically presented as an integral equation. In dipole approximation, which will be used in all but one section of this book, one has (see [AC]):

$$\begin{aligned} \langle v_1 | D(\omega) | v_2 \rangle &= \langle v_1 | \hat{d} | v_2 \rangle + \sum_{v_3, v_4} \frac{\langle v_3 | D(\omega) | v_4 \rangle (n_{v_4} - n_{v_3}) \langle v_4 v_1 | U | v_3 v_2 \rangle}{\varepsilon_{v_4} - \varepsilon_{v_3} + \omega + i\eta(1 - 2n_{v_3})}, \\ \langle v_4 v_1 | U | v_3 v_2 \rangle &\equiv \langle v_4 v_1 | V | v_3 v_2 \rangle - \langle v_4 v_1 | V | v_2 v_3 \rangle \end{aligned} \quad (1.37)$$

here  $\langle v_1 | \hat{d} | v_2 \rangle$  is determined as (1.32) with  $\mu(\vec{k})$  substituted by  $\hat{d}^{V,R}$  from (1.13) and  $n_v$  is the so-called *Fermi step function*:

$$n_v = \begin{cases} 1 & v \leq F \\ 0 & v > F \end{cases}. \quad (1.38)$$

Summation over continuous states in (1.37) includes also integration over their energies and therefore (1.37) is an integral equation. Important features of RPAE are that the results of “length” and “velocity” forms have to coincide and the sum rule (1.6) must be fulfilled, contrary to the HF and, in general, MBPT, approximation cases. These features will be used to check the numerical accuracy of our calculations. The RPAE photoionization cross-section is determined by equation similar to (1.4), with  $\hat{M}^{V,R}(\omega)$  substituted by  $\hat{D}(\omega)$ . The same is the situation for oscillator strengths.

An important element of RPAE is the *effective interaction*  $\Gamma(\omega)$ . It differs from the pure Coulomb interaction  $V$  by the corrections caused by the virtual excitation of other atomic electrons in the course of interaction of the pair of electrons under investigation. We can express in terms of effective interaction  $\Gamma(\omega)$  the RPAE corrections to the physical features of atoms and atomic processes obtained in HF approximation. Those are called *correlation corrections*.

The following considerations enable us to write an RPAE equation for  $\Gamma(\omega)$ . The effect of one atomic electron upon the other may be regarded as the external field:

$$B_{v_3 v_4}(\vec{r}) = \int dx \varphi_{v_3}(x) \frac{1}{|\vec{r} - \vec{r}'|} \varphi_{v_4}^*(x). \quad (1.39)$$

Substituting (1.39) for  $\hat{d}$  in (1.37) we obtain the expression for the effective interelectron interaction in RPAE:

$$\begin{aligned} \langle v_1 v_3 | \Gamma(\omega) | v_2 v_4 \rangle &= \langle v_1 v_3 | U | v_2 v_4 \rangle \\ &+ \sum_{v_5, v_6} \frac{\langle v_3 v_5 | \Gamma(\omega) | v_4 v_6 \rangle (n_{v_6} - n_{v_5}) \langle v_6 v_1 | U | v_5 v_2 \rangle}{\varepsilon_{v_6} - \varepsilon_{v_5} + \omega + i\eta(1 - 2n_{v_5})}. \end{aligned} \quad (1.40)$$

In terms of diagrams, the effective interaction  $\Gamma(\omega)$  is presented by an equation constructed similarly to (1.36) where the first term in the right-hand side is (1.27) instead of (1.21).

It is essential to note that some uncertainty exists in the definition of HF approximation for the excited states. It was shown (see [AM]) that as a result of this some parts of RPAE diagrams contributions can be taken into account by a corresponding choice of one-electron wave functions in HF approximation. This technique will be widely used in the following parts of this book.

The HF and RPAE equations will be solved, just as MBPT calculations will be performed numerically. But to foresee what are the qualitative features that could be expected as a result of taking into account the many-electron correlations, the following approach can be used. Let us present (1.37) and (1.40) in a symbolic operator form:

$$\hat{D}(\omega) = \hat{d} + \hat{D}(\omega) \times \hat{\chi}(\omega) \times \hat{U} \quad (1.41a)$$

and

$$\hat{\Gamma}(\omega) = \hat{U} + \hat{\Gamma}(\omega) \times \hat{\chi}(\omega) \times \hat{U}, \quad (1.41b)$$

respectively. Notations are evident from comparison with (1.37) and (1.40). Using (1.41b), (1.41a) can be presented in the following form:

$$\hat{D}(\omega) = \hat{d} + \hat{d}(\omega) \times \hat{\chi}(\omega) \times \hat{\Gamma}(\omega). \quad (1.42)$$

Equations (1.41a) and (1.41b) can be easily solved in the operator form, which leads to

$$\hat{D}(\omega) = \frac{\hat{d}}{[1 - \hat{\chi}(\omega) \times \hat{U}]} \quad (1.43a)$$

and

$$\hat{\Gamma}(\omega) = \frac{\hat{U}}{[1 - \hat{\chi}(\omega) \times \hat{U}]} \quad (1.43b)$$

Equation (1.41b) has an important feature that is of importance in solving it. Let us present  $\chi(\omega)$  as a sum of two terms  $\chi(\omega) = \chi_1(\omega) + \chi_2(\omega)$ . Then, defining  $\Gamma_1(\omega)$  by:

$$\hat{\Gamma}_1(\omega) = \hat{U} + \hat{\Gamma}_1(\omega) \times \hat{\chi}_1(\omega) \hat{U}, \quad (1.44)$$

one has from (1.41b) an expression for  $\Gamma(\omega)$ :

$$\hat{\Gamma}(\omega) = \hat{\Gamma}_1(\omega) + \hat{\Gamma}(\omega) \times \hat{\chi}_2(\omega) \times \hat{\Gamma}_1(\omega). \quad (1.45)$$

Expressions (1.43a) and (1.43b) permit to perform qualitative analysis of the RPAE solutions. Indeed, the amplitude  $\hat{D}(\omega)$  is strongly enhanced in the  $\omega$  region where the denominator in (1.43) is small. If the interelectron interaction  $U$  is strong enough, the denominator at some  $\omega = \Omega_{\text{GR}}$ , can reach zero value:

$$1 - \chi(\Omega_{\text{GR}}) \times \hat{U} = 0. \quad (1.46)$$

The corresponding frequency  $\Omega_{\text{GR}}$  is complex,  $\Omega_{\text{GR}} = \text{Re}\Omega_{\text{GR}} + i \text{Im}\Omega_{\text{GR}}$ , where  $\text{Re}\Omega_{\text{GR}}$  and  $\Gamma_{\text{GR}} = \text{Im}\Omega_{\text{GR}}$  are the energy and width, respectively, of the so-called *Giant resonance* (GR). They manifest themselves as powerful, broad and high, maxima in the photoionization cross-sections.

Another kind of maxima, named *Interference Resonances* (IR) and corresponding *Interference Minima* (IM) appear under the action of a subshell  $b$ , with big photoionization cross-section, upon any other,  $a$ , if the inter-subshell interaction  $U_{ab}$  is strong enough. Indeed, according to (1.41a), the amplitude of the  $a$ -subshell photoionization is given by the following equation:

$$\begin{aligned} \hat{D}_a(\omega_{\text{IR}}) &= d_a + \hat{D}_b(\omega_{\text{IR}}) \times \hat{\chi}_b(\omega_{\text{IR}}) \times \hat{U}_{ba} \\ &\approx \hat{D}_b(\omega_{\text{IR}}) \times \hat{\chi}_b(\omega_{\text{IR}}) \times \hat{U}_{ba} \gg d_a. \end{aligned} \quad (1.47)$$

The photoionization cross-section of an outer subshell, i.e., that with smaller ionization potential  $I_o$  is strongly modified in the vicinity of discrete excitation of the inner subshell, i.e., that with bigger ionization potential  $I_i$ ,  $I_i > I_o$ . In this case, in the vicinity of the discrete level with energy  $\omega_d$  the continuous spectrum photoionization amplitude  $D_c(\omega)$  can be presented, in accordance to (1.41a) in a rather simple form.

Indeed, approximating  $\chi(\omega)$  as  $\chi(\omega) \approx (\omega - \omega_d)^{-1}$ , it is easy to obtain an expression for the continuous spectrum amplitude having in mind that close to the singularity in  $\chi(\omega)$  it is represented as  $\chi(\omega) \approx \tilde{\chi}_1(\omega_d) + (\omega - \omega_d + i\delta)^{-1} = \tilde{\chi}_1(\omega_d) + (\omega - \omega_d)^{-1} - i\pi\delta(\omega - \omega_d)$ . Discarding for simplicity the term  $\tilde{\chi}_1(\omega_d)$ ,

one obtains

$$\hat{D}_c(\omega) \approx \frac{d_c}{(\omega - \omega_d - U_{dc} - i\Gamma_d)}, \quad (1.48)$$

here the *width*  $\Gamma_d$  is a result of the decay of the discrete level  $d$  due to its interaction with the continuous spectrum  $c$ . The symbolic relation determines  $\Gamma_d$

$$\Gamma_d = 2\pi|U_{cd}|^2. \quad (1.49)$$

In principle, if there are several continuous spectra interacting with the isolated discrete level  $d$ , the relation (1.49) must be modified by adding summation over all  $d$ . Using (1.48) and (1.49), the following expression for the photoionization cross-section near discrete excitation–resonance,  $\sigma_R(\omega)$  can be obtained

$$\sigma_R(\omega) = \sigma_0 \left[ (1 - \rho^2) + \rho^2 \frac{(q + \zeta)^2}{1 + \zeta^2} \right]. \quad (1.50)$$

Fano derived this formula for the first time in 1961 [1.1].<sup>1</sup> We present here simplified expressions and explanations for the parameters in (1.50). Detailed expressions can be found in [AM]. In (1.50)  $\rho$  describes the contribution due to admixture of several continuous spectra interacting with the same discrete level  $d$ . If only one continuous spectrum interacts with the level  $d$ , then  $\rho = 1$ . The parameter  $\zeta$  in (1.50) is defined as  $\zeta = (\omega - \omega_d - U_{cd})/\Gamma_d$ ,  $\sigma_0$  is the cross-section *without* resonance and  $q$  is the *asymmetry* parameter, determined by the relation  $q = U_{cd}/\Gamma_d$ .

If there are two instead of one discrete interacting level, the formulas for the cross-sections become more complicated because in this case (1.41a) reduces instead of one to a system of two coupled algebraic equations.

Oscillator strengths are also affected by the RPAE correlations. As a result they are presented by an expression that differs from (1.5) by a factor  $F_d$ :

$$f_d = \frac{2}{\tilde{\omega}_d} F_d \left| \tilde{D}_d(\tilde{\omega}_d) \right|^2, \quad (1.51)$$

here the discrete level  $d$  and excitation energy  $\omega_d$ , modified due to RPAE corrections is given by the equation  $\tilde{\omega}_d = \omega_d + \tilde{\Gamma}_{dd}(\tilde{\omega}_d)$ . The amplitude  $\tilde{D}_d(\tilde{\omega}_d)$  and the matrix element  $\tilde{\Gamma}_{dd}(\tilde{\omega}_d)$  are solutions of corresponding RPAE equations, but where the terms with denominator  $1/(\omega - \omega_d)$  in (1.41a) and (1.41b) are eliminated from  $\chi(\omega)$ . The factor  $F_d$  is connected to the derivative of  $\tilde{\Gamma}_{dd}(\omega)$  in  $\omega$ :

$$F_d = \left[ 1 - \frac{\partial \tilde{\Gamma}_{dd}(\omega)}{\partial \omega} \Big|_{\omega=\tilde{\omega}_d} \right]^{-1}. \quad (1.52)$$

---

<sup>1</sup>In other chapters, this and the subsequent references will be given mentioning also its number. For example, [1.1] will be presented in other chapters as [1.1].

Again, details of the derivation of (1.51) can be found in [AM]. The factor  $F_d$  determines the admixture of other electron–hole excitations to the discrete excitation  $d$ . Quite naturally,  $F_d < 1$ . Most transparently the meaning of  $F_d$  is seen when the quantity  $\partial \tilde{\Gamma}_{dd}(\omega)/\partial \omega$  is small and only second-order correction is enough to include in  $\tilde{\Gamma}_{dd}(\omega)$ . Considering only the important “time-forward” contribution into  $\tilde{\Gamma}_{dd}(\omega)$ , one has:

$$F_d \approx 1 + \left. \frac{\partial \tilde{\Gamma}_{dd}(\omega)}{\partial \omega} \right|_{\omega=\tilde{\omega}_d} \approx 1 - \sum_c \frac{|U_{dc}|^2}{(\omega_d - \omega_c)^2} < 1. \quad (1.53)$$

The sum over  $c$  in (1.53) presents the usual quantum-mechanical probability for the lowest order interaction between  $d$  and  $c$  to mix  $d$  with other states  $c$ .

## 1.6 Generalizations of RPAE

In the RPAE frame, the wave functions of all vacancies are considered as solutions of (1.10) where summation is performed over all  $i$ , from 1 to  $N$  where  $N$  is the total number of electrons in a considered atom. As it was mentioned in Sect. 1.2, for an excited electron or that in continuous spectrum the solutions of (1.10) are the wave functions of an additional,  $(N + 1)^{\text{th}}$  electron. However, even pure intuitively it is natural to take into account the presence of the vacancy  $i$  created after photon absorption. At first, the creation of this vacancy modifies the equation that determines the wave function of the entire excited or outgoing ionized electron. Instead of (1.10), it had to be determined by an equation, in which from the sum over all atomic electrons one term representing the ionized electron is eliminated. As a result, one has for  $\varphi_k(x)$  ( $k > F$ ) instead of (1.10)

$$\begin{aligned} -\frac{\Delta}{2}\varphi_k(x) - \frac{Z}{r}\varphi_k(x) + \sum_{j \neq i=1}^N \int dx' \varphi_j^*(x') \frac{1}{|\vec{r}' - \vec{r}|} \\ \times [\varphi_j(x')\varphi_k(x) - \varphi_k(x')\varphi_j(x)] = \varepsilon_k \varphi_k(x). \end{aligned} \quad (1.54)$$

Similarly, the equation for the wave functions of other occupied states  $i'$  can be modified by eliminating in the sum over  $j$  the term with  $j = i$ .

Then, correspondingly, the RPAE equations can be altered: instead of (1.37), one has the following:

$$\langle i | D(\omega) | v_2 \rangle = \langle i | \hat{d} | v_2 \rangle + \sum_{v_3, v_4 \neq i} \frac{\langle v_3 | D(\omega) | v_4 \rangle (n_{v_4} - n_{v_3}) \langle v_4 i | U | v_3 v_2 \rangle}{\varepsilon_{v_4} - \varepsilon_{v_3} + \omega + i\eta(1 - 2n_{v_3})}. \quad (1.55)$$



This equation represents the *generalized* version of RPAE or GRPAE. It goes beyond the theoretically consistent approach of RPAE by taking into account that while the outgoing or photoelectron leaves the atom, all states of atomic electrons are modified due to creation of this vacancy. As a result of this rearrangement or relaxation, the field of the ion acting upon the photoelectron became modified. This affects the photoionization cross-section. The alteration increases with decrease of the photoelectron energy.

The relaxation of atomic electron states due to creation of a hole leads to modification of the electron ionization potentials as compared to their HF values. Therefore, in GRPAE calculations as vacancy energies instead of HF values, the experimental ionization potentials are used.

For inner vacancies, it is essential to take into account that while the photoelectron leaves the atom, the vacancy can decay via the Auger process. As a result of this, the photoelectron moves in the field of at least double instead of a single charged ion

$$-\frac{\Delta}{2}\varphi_k(x) - \frac{Z}{r}\varphi_k(x) + \sum_{j \neq p, q=1}^N \int dx' \varphi_j^*(x') \frac{1}{|\vec{r}' - \vec{r}|} \times [\varphi_j(x')\varphi_k(x) - \varphi_k(x')\varphi_j(x)] = \varepsilon_k \varphi_k(x), \quad (1.56)$$

here  $i \rightarrow p, q$ ,  $\varepsilon_A$  is the dominating channel of the Auger decay of the hole  $i$ . Correspondingly, the system of equations (1.55) has to be modified by eliminating two terms from the sum  $\nu$  in the right-hand side:  $\nu_3, \nu_4 \neq p, q$ . This approximation is called GRPAEII.

## 1.7 Calculation Procedures

To obtain cross-sections, oscillator strength, and other characteristics of atomic processes, calculations, both numeric and analytic, must be performed.

As a first step, the one-electron wave functions  $\varphi_k(x) \equiv \varphi_{\varepsilon(n)lm\sigma}(\vec{r}, s)$ —solutions of HF equations (1.10)—must be presented as a product of radial  $R_{\varepsilon(n)l}(r) \equiv r^{-1}P_{\varepsilon(n)l}(r)$ , angular  $Y_{lm}(\vartheta, \varphi)$ , and spin functions  $\chi_\sigma$ :

$$\varphi_{\varepsilon(n)lm\sigma}(\vec{r}, s) = r^{-1}P_{\varepsilon(n)l}(r)Y_{lm}(\vartheta, \varphi)\chi_\sigma, \quad (1.57)$$

here  $Y_{lm}(\vartheta, \varphi)$  is the spherical function,  $\chi_\sigma$  is the spin function,  $\varepsilon(n)$  is the one-electron energy (principal quantum number),  $l$  is the angular momentum quantum number,  $m$  is its projection upon a selected axis,  $\sigma$  is the electron spin projection,  $\vartheta$  and  $\varphi$  are polar and azimuthal angles of the electron coordinate  $\mathbf{r}$ . Using expression (1.57), one can perform analytically the integration over angular variables and summation over spin variables, since the analytic expressions for  $Y_{lm}(\vartheta, \varphi)$  and  $\chi_\sigma$  are well known.

The technique of integrating different products of  $Y_{lm}(\vartheta, \varphi)$  over  $\vartheta$ ,  $\varphi$  and summation of products  $\chi_\sigma$  over  $\sigma$  is well developed and discussed at length in a number of books, e.g., in [LL, IS]. Applying this technique, at first the system of HF equations (1.10) is reduced to that for radial wave functions  $R_{\varepsilon(n)l}(r) \equiv r^{-1}P_{\varepsilon(n)l}(r)$ . This system is solved numerically.

After performing integration over  $\vartheta$  and  $\varphi$ , one can present the dipole matrix elements (1.14) in the following form:

$$d_{i \rightarrow f}^{V,R} = (-1)^{l_i - m_i} \begin{pmatrix} l_i & 1 & l_f \\ -m_i & \mu & m_f \end{pmatrix} \langle n_i l_i \| d^{V,R} \| \varepsilon_f(n_f), l_f \rangle, \quad (1.58)$$

here  $\begin{pmatrix} l_i & 1 & l_f \\ -m_i & \mu & m_f \end{pmatrix}$  is a  $3j$ -symbol (see [IS]),  $l_f = l_i \pm 1$ ,  $\langle n_i l_i \| d^{V,R} \| \varepsilon_f(n_f), l_f \rangle$  is the dipole reduced matrix element. The latter are determined by the expressions [AC] that become particularly simple for closed shell atoms:

$$d_{nl,n'l'}^R \equiv \langle nl \| d^R \| n'l' \rangle = (-1)^{(l+l'+1)/2} \times \sqrt{\frac{(l+l'+1)}{2}} \omega \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr, \quad l' = l \pm 1, \quad (1.59a)$$

$$d_{nl,n'l'}^V \equiv \langle nl \| d^V \| n'l' \rangle = (-1)^{(l+l'+1)/2} \sqrt{\frac{(l+l'+1)}{2}} \times \int_0^\infty P_{nl}(r) \left( \frac{d}{dr} \pm \frac{l+l'+1}{2r} \right) P_{n'l'}(r) dr, \quad (1.59b)$$

here sign  $+$  corresponds to  $l' = l + 1$  and  $-$  to  $l' = l - 1$ .

The following notations are used for the radial integrals in (1.59):

$$d_l^R \equiv \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \quad \text{and} \\ d_{l'}^V \equiv \int_0^\infty P_{nl}(r) \left( \frac{d}{dr} \pm \frac{l+l'+1}{2r} \right) P_{n'l'}(r) dr. \quad (1.60)$$

Similarly to (1.58), in Coulomb matrix elements (1.33) integration over angular parts of one-electron wave functions lead to the following expression:

$$\langle \alpha | V | \beta \rangle = \sum_{\lambda=0}^\infty \sum_{m=-\lambda}^\lambda (-1)^{m_1+m_3+m} \begin{pmatrix} l_1 & \lambda & l_2 \\ -m_1 & m & m_2 \end{pmatrix} \begin{pmatrix} l_3 & \lambda & l_4 \\ -m_3 & m & m_4 \end{pmatrix} V_{\alpha\beta}^\lambda, \quad (1.61)$$

here the matrix element  $V_{\alpha\beta}^\lambda$  is determined as:

$$\begin{aligned}
V_{\alpha\beta}^{\lambda} &\equiv \langle v_1 v_4 \| V_{\lambda} \| v_2 v_3 \rangle \\
&= \sqrt{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)} \begin{pmatrix} l_1 & \lambda & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_3 & \lambda & l_4 \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad \times R_{\lambda}(v_1 v_2 v_3 v_4), \tag{1.62}
\end{aligned}$$

with  $v \equiv nl(v \leq F)$  or  $v \equiv n(\varepsilon)l(v > F)$ , i.e., the state labels  $v_j$  include two quantum numbers instead of four in (1.33). In (1.61),  $R_{\lambda}(v_1 v_2 v_3 v_4)$  is a pure radial matrix element given by the following two-dimensional integral:

$$R_{\lambda}(v_1 v_2 v_3 v_4) = \int_0^{\infty} P_{v_1}(r) P_{v_2}(r) dr \int_0^r \frac{r'^{\lambda}}{r'^{\lambda+1}} P_{v_3}(r') P_{v_4}(r') dr'. \tag{1.63}$$

The radial integrals in (1.59) and (1.63) are calculated numerically, substituting integrals with infinite upper limits by finite sums which cover distances up to  $r \leq R$ . In concrete calculations, we chose  $R$  as big as  $R \approx 50$  atomic units, i.e., considerably bigger than the atomic size  $r \approx 1$ . This is possible because usually the integrands are decreasing faster than  $1/r^2$ . If this is not the case, the contribution of  $r$  region,  $r > R$ , is found analytically because far from the atom all electron wave functions and expressions that include Coulomb interelectron interaction simplify considerably.

The specific of atomic problem, i.e., the presence of the nuclear Coulomb field, dictates that it is desirable to have more points of integration in the vicinity of the nucleus, i.e., at small  $r$ . This is achieved by introducing a new variable,  $\rho = \alpha r + \beta \ln r$ , which permits to place integration points in  $\rho$  equidistantly. The number of integration points in  $\rho$  is about 1,000.

After the radial integrals are calculated, the contribution of isolated diagrams or the solution of RPAE (or in principle any other similar equations) may be obtained. This requires integration over one-electron energy variables  $\varepsilon$  and summation over discrete excitations  $n$ . Usually the integrals in  $\varepsilon$  are substituted by a finite sum with points located equidistantly in  $k = \sqrt{2\varepsilon}$ . As a result, more points are placed at small  $\varepsilon$  where the integrands as functions of  $\varepsilon$  are rapidly changing while fewer points are in the high  $\varepsilon$  area.

Usually the integrands are decreasing fast enough and it is sufficient to have about 50 points in  $p$  with the upper limit of about 5–6 ionization potentials of the considered subshell which is excited or ionized. By increasing the number of points in  $\rho$ , we can go to higher energies  $\varepsilon$ . Using modern PC, one can reach in consideration of photo ionization energies of outgoing electrons as big values as 150–200 Ry. To study higher  $\varepsilon$  considerably large computer memory is required.

An essential difficulty in numerical calculations in the frames of MBPT or RPAE originates from the fact that they include energy denominators that as it is seen from (1.31), (1.34), (1.37), and (1.40), can become equal to zero, thus leading to poles in the integrands. To calculate these singular expressions, the following idea is used: to separate the singular part and to calculate it analytically, while to calculate the

rest numerically. Indeed, let us present the integral in the vicinity of singularity as

$$\int_{\varepsilon_n}^{\varepsilon_{n+1}} d\varepsilon \frac{Q(\varepsilon)}{(\omega + \varepsilon_v - \varepsilon + i\eta)} \approx -Q(\omega + \varepsilon_v) \ln \left| \frac{\omega + \varepsilon_v - \varepsilon_n}{\omega + \varepsilon_v - \varepsilon_{n+1}} \right| - i\pi Q(\omega + \varepsilon_v), \quad (1.64)$$

here  $\varepsilon_n \rightarrow \varepsilon_{n+1}$  is the energy interval that includes the singularity of the integrand in (1.64). Outside this interval calculations are performed pure numerically, while the right-hand side of (1.64) presents the contribution of this interval. The accuracy of (1.64) is increasing with decrease of the interval  $\varepsilon_n \rightarrow \varepsilon_{n+1}$ .

It is essential to note that considerable part of RPAE diagrams may be taken into account by a proper choice of excited states one-electron HF wave functions. The more many-body diagrams are taken by the choice of the one-electron wave function, the less is left for the many-body corrections. In our calculations, we choose those wave functions that, together with respective vacancy wave functions form a given term, i.e., a state with given total angular momentum  $L$  and spin  $S$ . Angular momentum and spin projections of the excited electron and vacancy states separately are not defined in this approach. The following “time-forward” diagrams are included by this choice of wave functions:

$$\begin{aligned} & \omega \text{---} \text{---} \text{---} v \text{---} i \text{---} = \omega \text{---} \text{---} v \text{---} i \text{---} + \omega \text{---} \text{---} v_1 \text{---} i' \text{---} v \text{---} i \text{---} \\ & + \omega \text{---} \text{---} v_1 \text{---} i' \text{---} v \text{---} i \text{---} \end{aligned} \quad (1.65)$$

Those states  $i'$  are taken into account in (1.65) that have the same energy, i.e.,  $\varepsilon_i = \varepsilon_{i'}$ . More details can be found in [AM] and [AC].

## 1.8 Angular Anisotropy Parameter

An important characteristic of the photoionization process is the angular distribution of photoelectrons. In dipole approximation, this is particularly simple and is presented for the unpolarized beam of photons by the following expression:

$$\frac{d\sigma_{nl}(\omega)}{d\Omega} = \frac{\sigma_{nl}(\omega)}{4\pi} [1 - \beta_{nl}(\omega) P_2(\cos \theta)], \quad (1.66)$$

here  $nl$  denotes the principal quantum number  $n$  and angular momentum  $l$  of the ionized subshell,  $\Omega$  is the solid angle of photoelectron emission,  $P_2(\cos \theta)$  is

the second-order Legendre polynomial,  $\theta$  is the angle between the photoelectron momentum and photon beam directions, and  $\beta_{nl}(\omega)$  is the angular anisotropy parameter. The angle, for which  $P_2(\cos \theta_M) = 0$ , is called the magic angle. This angle equals to  $\theta_M \approx 54.7^\circ$ . For this angle, the corrections to  $d\sigma_{nl}(\omega)/d\Omega$ , defined by  $\beta$ , do not appear.

For polarized light, the formula for angular distribution of photoelectrons is written as:

$$\frac{d\sigma_{nl}(\omega)}{d\Omega} = \frac{\sigma_{nl}(\omega)}{4\pi} [1 + (-2)^{-|\mu|} \beta_{nl}(\omega) P_2(\cos \vartheta)], \quad (1.67)$$

here  $\mu$  characterizes incoming light polarization. For linearly polarized light,  $\mu = 0$  and for circularly polarized light, left and right, respectively,  $\mu = \pm 1$ . The angle  $\vartheta$  is between the direction of polarization vector and photoelectron's momentum.

The partial photoionization cross-section  $\sigma_{nl}^{R,V}(\omega)$  of  $nl$ -subshell in HF approximation is determined by the dipole matrix elements (1.60) calculated by making use of radial parts  $P_{n(\varepsilon)l}(r)$  of HF wave functions (1.10) as follows [AM]:

$$\sigma_{nl}^{R,V}(\omega) = 2.689 \frac{\omega N_{nl}}{2l+1} [l|d_{\varepsilon,l-1}^{R,V}|^2 + (l+1)|d_{\varepsilon,l+1}^{R,V}|^2], \quad (10^{-18} \text{ cm}^2). \quad (1.68)$$

Expression for the photoionization cross-section  $\sigma_{nl}(\omega)$  of  $nl$ -subshell in RPAE is similar to (1.68) but the dipole matrix elements are calculated now in PRAE:

$$\sigma_{nl}(\omega) = 2.689 \frac{\omega N_{nl}}{2l+1} [l|D_{\varepsilon,l-1}|^2 + (l+1)|D_{\varepsilon,l+1}|^2], \quad (10^{-18} \text{ cm}^2), \quad (1.69)$$

here the matrix elements  $D_{\varepsilon l \pm 1} \equiv D_{nl, \varepsilon l \pm 1}^{V,R}(\omega)$  are solutions of RPAE equations for the radial matrix elements, obtained from (1.37) after integration over angular and summation over spin variables. The total photoionization cross-section  $\sigma(\omega)$  is expressed via  $\sigma_{nl}(\omega)$ :

$$\sigma(\omega) = \sum_{nl} \sigma_{nl}(\omega), \quad (1.70)$$

where summation is performed over all subshells  $nl$ , whose ionization potential  $I_{nl}$  is smaller than  $\omega$ .

In HF approximation, the angular anisotropy parameter  $\beta_{nl}(\varepsilon)$  is expressed via the dipole radial matrix elements (1.60):

$$\begin{aligned} \beta_{nl}(\omega) = & \frac{1}{(2l+1)[ld_{l-1}^2 + (l+1)d_{l+1}^2]} [l(l-1)d_{l-1}^2 + (l+1)(l+2)d_{l+1}^2 \\ & - 6l(l+1)d_{l-1}d_{l+1} \cos(\delta_{l-1} - \delta_{l+1})]. \end{aligned} \quad (1.71)$$

The scattering phases of the outgoing photoelectrons waves  $\delta_{l\pm 1} \equiv \delta_{l\pm 1}(\varepsilon)$  are usually defined from the wave functions asymptotic. The definition of scattering phases is given by (3.8) and (3.10) (see, e.g., [LL]).

The  $\beta_{nl}(\varepsilon)$  parameter in RPAE may be obtained from (1.71) by making use of the following replacement:

$$\begin{aligned}
 d_{l+1}d_{l-1} \cos(\delta_{l+1} - \delta_{l-1}) &\rightarrow [(\operatorname{Re} D_{l+1} \operatorname{Re} D_{l-1} \\
 &+ \operatorname{Im} D_{l+1} \operatorname{Im} D_{l-1}) \cos(\delta_{l+1} - \delta_{l-1}) \\
 &- (\operatorname{Re} D_{l+1} \operatorname{Im} D_{l-1} - \operatorname{Im} D_{l+1} \operatorname{Re} D_{l-1}) \sin(\delta_{l+1} - \delta_{l-1})] \\
 &\equiv \tilde{D}_{l+1} \tilde{D}_{l-1} \cos(\delta_{l+1} + \Delta_{l+1} - \delta_{l-1} - \Delta_{l-1}), \\
 d_{l\pm 1}^2 &\rightarrow \operatorname{Re} D_{l\pm 1}^2 + \operatorname{Im} D_{l\pm 1}^2 \equiv \tilde{D}_{l\pm 1}^2.
 \end{aligned} \tag{1.72}$$

The following notation for the dipole matrix elements with correlations is used in the above formula:

$$D_{l\pm 1}(\omega) \equiv \tilde{D}_{l\pm 1}(\omega) \exp[i\Delta_{l\pm 1}(\varepsilon)], \tag{1.73}$$

where  $\tilde{D}_{l\pm 1}(\omega)$  and  $\Delta_{l\pm 1}$  are the absolute values (modules) of the amplitudes of the corresponding transitions and the phases of photoelectrons with angular moments  $l \pm 1$ .

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