### METHODOLOGICAL NOTES

# Atomic physics: computer calculations and theoretical analysis

E G Drukarev

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<u>Abstract.</u> It is demonstrated how a theoretical analysis preceding numerical calculations helps to determine the ground-state energy of the helium atom and enables one to avoid qualitative errors when calculating the characteristics of double photoionization.

### 1. Introduction

Many papers published over the years that deal with the interaction between photons and atoms or molecules have the same structure. First, the most general formula known from quantum mechanics is written down. Then a wave function that is as exact as possible and describes the bound system is substituted into the formula. Such a wave function is either derived in the same paper or is taken from previous publications. Since the binding energies of bound systems are measured to a high accuracy, the wave functions are tested for the reproducibility of this quantity. The most exact is considered the wave function that reproduces the value of the binding energy to the highest accuracy. The computer calculations follow afterwards. Sometimes attempts are made to account for the interaction in the final state, to which end combinations of Coulomb functions are usually utilized.

Two decades ago such an approach could be justified. Usually, the characteristics that can be measured are those that are calculated. In experiments, the energies transferred to the targets were usually of the order of the binding energies. Thus, no small parameter emerged in such a problem and the

E G Drukarev B P Konstantinov Petersburg Nuclear Physics Institute,

Russian Academy of Sciences,

Orlova Roshcha, 188300 Gatchina, Leningrad region, Russian Federation Tel. (7-813) 7146096. E-mail: drukarev@thd.pnpi.spb.ru

Received 16 March 2007 Uspekhi Fizicheskikh Nauk **177** (8) 877–887 (2007) Translated by E Yankovsky; edited by A Radzig general formulas provided by quantum mechanics did not allow for any further transformation. The only distance scale was the size of the bound system. Further investigations in this area of research amounted to battling for higher accuracy. The physics of processes in the immediate vicinity of a threshold, where a small parameter can be singled out, amounted to one of the exceptions.

The situation changed in the late 1980s, when new synchrotron sources of photons became available. Experiments in which atoms interacted with photons having energies up to 10 keV were begun. For light atoms, such energies are much higher than the binding energy of even the 1s-electrons. As a result, a small parameter emerged in theoretical problems.

A general approach to high-energy atomic physics can be based on Bethe's ideas [1] whose modern interpretation can be found in Refs [2, 3]. Bethe's approach [1] formulated for electron-atom scattering can be extended to any process of interaction between high-energy particles and bound systems. The term 'high energies' means that the energies considered in the specific problem are much higher than the binding energy. The cross sections of such processes can be expressed in terms of certain parameters of the bound system. The interactions between the fast and slow components of the compound system can be taken into account by applying the perturbation theory. Each act of transfer of momentum much larger than the characteristic momentum of the bound system leads to the emergence of a parametrically small factor. In the region in which a process involving a free electron is kinematically allowed, known as *Bethe's surface*, a momentum q on the order of bound-electron momentum  $\eta$  is transferred to the nucleus. Processes outside Bethe's surface require highmomentum transfers to the nucleus  $(q \ge \eta)$ . Therefore, processes outside Bethe's surface are highly suppressed.

Thus, the amplitudes of processes in high-energy atomic physics depend on the parameter

$$\kappa = \frac{\eta}{q} \,. \tag{1}$$

On the Bethe surface, one has  $\kappa \sim 1$ , while outside it  $\kappa \ll 1$ . The characteristic binding momentum may be defined as  $\eta = (2mI)^{1/2}$ , where I > 0 is the binding energy. Using the relativistic system of units in which  $\hbar = c = 1$ , for the ground state of a hydrogenlike atom we obtain

$$\eta = m\alpha Z \,, \tag{2}$$

where *m* is the electron rest mass,  $\alpha = 1/137$ , and *Z* is the charge of the nucleus.

Sometimes, the description of a fast electron by the perturbation theory, which is another item in Bethe's theory, leads to confusion. In the chapters devoted to perturbation theory in most textbooks on quantum mechanics, only shortrange forces are considered. In the case of the Coulomb field each term that emerges as a result of iteration of the Lippmann-Schwinger equation contains infrared-diverging contributions. In this sense, the perturbation series diverges, so that the possibility of describing fast electrons by plane waves appears unjustified. Nevertheless, a solution to this problem was found fairly early. In 1951, Dalitz [4] assumed that the divergent contributions to the electron-nucleus interaction amplitudes form a factor  $\exp(i\Phi)$ , where  $\Phi$ is real. This factor and the complex-conjugate factor cancel out when the cross section is calculated. Gorshkov [5] provided a rigorous proof of this assertion. Thus, representing the electrostatic electron-nucleus interaction in the form  $V(r) = -\alpha Z \exp(-\lambda r)/r$  with  $\lambda \to 0$ , we are justified in writing the Lippmann - Schwinger equation and solving it by perturbation theory technique. The terms that depend on  $\lambda$ will cancel out when the cross section is calculated.

The parameter of the perturbation theory for a continuous-spectrum nonrelativistic electron with an asymptotic momentum p moving in the field of the nucleus of electric charge Z can be written as follows (see Ref. [6]):

$$\xi_Z = \frac{m\alpha Z}{p} \,. \tag{3}$$

The condition  $\xi_Z \ll 1$  means that the relative contribution of the interaction with the nucleus to the electron wave function is much smaller than unity. Since for different terms in the wave function expansion in powers of  $\xi_Z$  different distances may be important, one must be careful to see that all terms contributing to a particular order in the series expansion of the *amplitude* are accounted for.

Nevertheless, large discrepancies between the results of calculations that use plane waves and Coulomb-field functions of the nucleus often show up even at very high energies. Sometimes this leads to statements like 'the plane-wave approximation never works'. Actually, the reason for all this lies in the simple fact (see Ref. [7]) that the electron – nucleus interaction contains two parameters that depend on the electron momentum p. In addition to the parameter  $\xi_Z^2$ , which is used as the small parameter in the expansion of the wave function at distances from the nucleus of order  $\eta^{-1}$ , there is the parameter  $\pi\xi_Z$  which comes into play in the interactions at small distances of order  $\sim p^{-1}$ . In any case, the dependence on the parameter  $\pi\xi_Z$  emerges in the normalization factor of the nonrelativistic Coulomb function. Additional contributions of order  $\pi \xi_Z$  appear in processes that require the transfer of large momenta to the nucleus, say, in the photoeffect. Luckily, all contributions that depend on  $\pi \xi_Z$  are factorable and appropriate factor can be calculated.

Thus, the perturbation theory has a broader range of applicability for the ratio of cross sections than for the cross sections proper [8]. Assuming that

$$\pi \xi_Z \sim 1 \,, \qquad \xi_Z^2 \ll 1 \,, \tag{4}$$

we can make expansion in powers of  $\xi_Z^2$ .

Attempts to account for the interaction of continuousspectrum particles in the final state with bound electrons were also fraught with difficulties caused by long-range interaction. In Ref. [9], we proposed an approach that takes into account the interaction in the lowest order in the parameter

$$\xi^2 = \frac{(m\alpha)^2}{p_{\rm r}^2} \,, \tag{5}$$

where  $p_r$  is the momentum of relative motion of the final-state electron and the bound electron [formula (5) is given for the cases of electron–electron interaction]. Calculations require accounting for the first- and second-order amplitudes. Infrared divergences emerge in the intermediate stages of the calculations, the same as in the case of electron–nucleus interaction, and in the final expression for the cross section these divergences cancel out.

Since for a long time experiments involving high-energy photons were unachievable, these ideas were not often used in theoretical works. As far as I know, only V G Gorshkov and his collaborators [10] used this approach, and only for hydrogenlike atoms.

Thus, in high-energy processes involving bound electrons, distances of order  $\eta^{-1}$  and of order  $p^{-1} \ll \eta^{-1}$  may be important. Therefore, it is not enough to require (and is not really important) that the wave function correctly reproduce the binding energy. If the process is forbidden kinematically for free electrons, what is more important is the behavior of the wave function at small distances between an electron and the nucleus or between electrons. Here, the perturbation theory relying on the parameter  $\kappa^2$  can be used. In describing the final state one can employ the perturbation theory in the parameters  $\kappa^2$ ,  $\xi_Z^2$ , and  $\xi^2$ , making sure that all contributions of a given order are taken into account.

I believe that the history of studies of the helium double photoionization is a good illustration of how employing these principles helps to obtain results and also of the fact that ignoring them leads to qualitative mistakes. We begin with the static problem of calculating the binding energy of the helium atom.

# 2. Calculating the ground-state energy of the helium atom

The ground-state energy of the helium atom has been measured very accurately. In the late 1950s, the error amounted to one part in a million [6], and today it is  $2 \times 10^{-7}$  [11]. All this has stimulated a search for more exact solutions of the wave equation for helium, with the focus on solving the nonrelativistic equation (the Schrödinger equation) in the field of a force center.

The Hartree–Fock (HF) method developed at the beginning of the 1930s makes it possible to find the ground-state energy with an accuracy of 1.5%, whereas the accuracy achieved in experiments is incomparably higher. The reason for this failure is understandable. The wave function in the Hartree–Fock method constitutes a combination of single-

particle functions and does not depend on the relative distance  $r_{12}$  between the electrons, with the result that it does not reproduce the pattern of their motion in relation to each other.

Another approach was being advanced at the time when the Hartree–Fock method was being developed. What was postulated in this approach was the analytical dependence of the approximate wave function  $\psi_a(r_1, r_2, r_{12})$  on the distances  $r_1$  and  $r_2$  between the electrons and the nucleus and on the electron–electron separation  $r_{12}$ . Such functions  $\psi_a$  depend on several parameters determined by the condition of minimization of the mean value of the helium atom Hamiltonian, namely

$$E = \left\langle \psi_{\mathbf{a}} | H | \psi_{\mathbf{a}} \right\rangle. \tag{6}$$

The simplest example is the product of hydrogenlike functions with a certain 'effective charge of the nucleus',  $Z_{eff}$ , which acts as a variational parameter. In this case, one has

$$\psi_{\rm a}(r_1, r_2) = \psi_{\rm H}(r_1) \,\psi_{\rm H}(r_2) \,, \tag{7}$$

with the well-known expressions  $\psi_{\rm H}(r) = \exp(-ar)$ ,  $a = m\alpha Z_{\rm eff}$  for the ground-state hydrogenlike functions  $\psi_{\rm H}$ . (Here we used the normalization condition  $\psi(0) = 1$ .) The well-known solution  $Z_{\rm eff} = 27/16$  [6] reproduces the energy value with an error of 2%.

The approximate functions in the from

$$\psi_{a}(r_{1}, r_{2}, r_{12}) = \exp\left[-a(r_{1} + r_{2})\right] P(r_{1}, r_{2}, r_{12}),$$
(8)

were applied from the early days of quantum mechanics, where the parameter *a* and coefficients in the polynomial

$$P(r_1, r_2, r_{12}) = \sum c_{ijk} r_1^i r_2^j r_{12}^k$$
(9)

are variational parameters. In the first calculations, dating back to the late 1920s, wave functions (8) comprised three parameters. After three decades, the functions that were used could contain more than 200 parameters. Moreover, in addition to polynomial contributions (9), a dependence on the ratios

$$\frac{r_{12}}{r_1 + r_2}$$
 and  $\frac{(r_1 - r_2)^2}{r_{12}^2}$ 

was introduced into the functions  $P(r_1, r_2, r_{12})$ . This approach allowed achieving a continually refined quantity interpreted as the binding energy (the accuracy with which this quantity is determined may be as high as several parts in  $10^{-10}$ ), which also reproduces the experimental value. Calculations with an accuracy exceeding  $10^{-4}$  require taking into account relativistic corrections, the finite mass and size of the nucleus, and some other factors.

However, as early as 1935, Barlett et al. [12] pointed out that functions (8), in which *P* are polynomials, cannot satisfy the Schrödinger equation. Such solutions cannot exist because they do not reproduce the limiting case of triple coalescence,  $r_1 = r_2 = r_{12} = 0$ . Later on, Fock showed [13] that the inclusion of logarithmic terms in the polynomial

$$P(r_1, r_2, r_{12}) = \sum c_{ijkn} r_1^i r_2^i r_{12}^k \left[ \ln \left( r_1^2 + r_2^2 \right) \right]^n \tag{10}$$

yields correct behavior at this point and found the algorithm for building the appropriate expansion. Usually, such functions are specified in hyperspherical variables. The inclusion of logarithmic terms has little effect on the accuracy of energy calculations, but it does speed up the convergence of variational calculations. Here, allowance for logarithms makes possible a reduction in the number of parameters needed for acquiring the necessary accuracy. For instance, calculations with an accuracy of one part in a billion with the aid of functions (9) require introducing 1078 parameters, while the same accuracy can be achieved by functions of type (10) containing 52 parameters [15]. Furthermore, as noted by Myers et al. [16], the variational procedure for some functions of type (9) selects the values of the parameters in such a way that the function P can be represented in the form of expression (10) with a smaller number of parameters.

The behavior of the solution  $\Psi(r_1, r_2, r_{12})$  of the Schrödinger equation at the points  $r_1 = 0$ ,  $r_2 = 0$ , and  $r_{12} = 0$  of coalescence of two particles is determined by the Kato conditions [17]. For the point of coalescence of an electron and a nucleus we have

$$r_0 \, \frac{\partial \Psi(r_1, r_2, r_2)}{\partial r_1} = -Z\Psi(0, r_2, r_2)\,, \tag{11}$$

and the same relation emerges at  $r_2 = 0$ . At the point of coalescence of two electrons, one finds

$$r_0 \frac{\partial \Psi(r_1, r_1, r_{12})}{\partial r_{12}} = \frac{1}{2} \Psi(r_1, r_1, 0), \qquad (12)$$

where  $r_0 = 1/m\alpha$  is the Bohr radius. Equations (11) and (12) constitute the condition for the cancelling out of singular terms in the Schrödinger equation.

To illustrate, let us examine the single-electron wave function of the ground state in an effective field U(r) that approximates the electron's interaction with the nucleus and the electron cloud. The Schrödinger equation for this case is given by

$$-\frac{1}{2m}\left[\psi''(r) + \frac{2}{r}\psi'(r)\right] + U(r)\psi(r) = E\psi(r).$$
(13)

As  $r \to 0$ , the field U(r) begins to be determined by the interaction with the nucleus, viz.  $U(r \to 0) = -\alpha Z/r$ . Hence, as  $r \to 0$ , we can write

$$-\frac{1}{2m}\psi''(r) + \lim_{r \to 0} \left( -\frac{1}{m} \frac{\psi'(r)}{r} - \frac{\alpha Z \psi(r)}{r} \right) = E\psi(r) .$$
(14)

Since both sides of this equation must be regular, the expression in the parentheses on the left-hand side must have a finite value. Hence, we arrive at

$$r_0 \ \frac{\partial \psi(r)}{\partial r} = -Z\psi(0) \tag{15}$$

\ss as  $r \rightarrow 0$ . Analyzing the Schrödinger equation for the helium atom in a similar manner leads to Eqns (11) and (12). What is interesting is that these relations, which could have been derived immediately after the Schrödinger equation was written in 1926, were discovered only 30 years later.

The correct behavior of the approximate wave function near the two-particle coalescence point proves to be more important than near the three-particle coalescence point, since the latter manifests itself in a smaller phase volume. Myers et al. [16] analyzed the simplest approximate wave function

$$\psi_{a}(r_{1}, r_{2}, r_{12}) = \exp\left[-a(r_{1} + r_{2}) + br_{12}\right]$$
 (16)

satisfying both Kato conditions, with  $a = m\alpha Z$  and  $b = m\alpha/2$ . This function, which contains no adjustable parameters, reproduces the binding energy to the same accuracy as function (7), which contains the variational parameter  $Z_{\text{eff}}$ . Nevertheless, function (16) does not properly behave at the three-particle coalescence point  $r_1 = r_2 = r_{12} = 0$ . The simplest function with the correct behavior at this point was also given in Ref. [16].

If a meaningful form of the approximate function is selected, the variational procedure selects the values of the parameters at which the Kato conditions are met to a high accuracy as, for example, is true of the function

$$\psi_{a}(r_{1}, r_{2}, r_{12}) = \exp\left[-a(r_{1} + r_{2}) + br_{12}\right] \sum c_{ijk} r_{1}^{i} r_{2}^{j} r_{12}^{k}$$
(17)

 $(i + j + k \le N)$ , analyzed by Teng and Shakeshaft [18]. Even in the case of four parameters (N = 1), the relative errors in equalities (11) and (12) for function (17) amounted to 6 and 25%, respectively. When there are more parameters, the Kato conditions are met to a higher accuracy. Achieving the sought accuracy for functions of type (17) requires the use of a significantly smaller number of parameters than for functions (8), (9). For instance, function (17) with 14 parameters reproduces the binding energy with an error of  $3 \times 10^{-5}$ . Achieving such accuracy with a function from the (8), (9) class requires the use of 210 parameters.

In addition to determining the mean value of Hamiltonian (6), modern computations embrace the local energy

$$E(\mathbf{r}_1, \mathbf{r}_2) = \frac{H\psi_a}{\psi_a}, \qquad (18)$$

which provides detailed information on the relation between the approximate function  $\psi_a$  and the exact solution  $\Psi$  of the Schrödinger equation. Another approach consists in solving the Schrödinger equation directly. In one method belonging to this approach (see Ref. [19], where other methods are also discussed), the approximate wave function is the product of a correlation factor, which determines the behavior at the singular coalescence points, and a smooth function expanded in terms of the hyperspherical harmonics. A detailed description of these methods is beyond the scope of the present article.

Thus, we have shown that allowing for the correct analytical structure in approximate wave functions improves the results of binding-energy calculations, which is even more important when we are dealing with dynamical problems discussed in the sections that follow.

# 3. Asymptotics of double photoionization: $\omega^{-7/2}$ or $\omega^{-5/2}$ ?

Since the late 1950s, double photoionization of helium atoms has been studied as the simplest dynamical three-body problem with electromagnetic interaction. Large experimental data on this subject allows theoreticians to evaluate their approaches.

The mechanism that determines the high-energy nonrelativistic asymptotic behavior of the double-photoionization cross section  $\sigma^{2+}(\omega)$  (here,  $\omega$  is the photon energy) has been established by Kabir and Salpeter [20]. At energies  $\omega$  much higher than the electron binding energy *I*, the process can be considered single ionization accompanied by a change in the state of the second electron due to changes in the system's Hamiltonian. Here, the secondary electron acquires, basically, an amount of energy  $\varepsilon_2 \sim I$ . Thus, the amplitude and cross section of the process depend on  $\omega$  in the same way as they do in single ionization, and the asymptotic behavior of the cross-section ratio  $\sigma^{2+}(\omega)/\sigma^+(\omega)$  is energy-independent.

This resembles the ionization of atoms in beta-decay. The latter, as shown by Feinberg [21], basically occurs (at sufficiently high energies) due to change in the charge of the nucleus and the resulting redistribution over the final states of the atom (*shaking*). However, this analogy is not perfect. A change in the nuclear charge alters the effective *field*, which the atomic electrons 'feel'. As shown by Byron and Joachain [22], attempts to explain the knockout of the second electron into the continuum by a sudden change in the self-consistent *field* underestimate the asymptotic value by a factor of three. Thus, correlations that are not accounted for by the effective field play an important role in double ionization. Hence, approximate functions of the type (8) or (17), in which such correlations are effectively accounted for, are used in computations.

Despite the fact that the mechanism proposed by Kabir and Salpeter [20] is simple, calculations of the cross-section asymptotics have led to a paradox, and it took several years to resolve it. First, let us recall how the asymptotics of singleand double-ionization amplitudes are calculated.

#### 3.1 Single-ionization asymptotics

We will describe the electrons by single-particle wave functions. The general expression for the ionization amplitude can be represented in the form [23]

$$F^{+} = (4\pi\alpha)^{1/2} \int d^{3}r \psi_{p_{1}}^{*}(r) \gamma \exp\left[i(kr)\right] \psi(r), \qquad (19)$$

where  $\psi_{p_1}$  is the continuous-spectrum wave function with the asymptotic momentum  $p_1$ ,  $\psi$  describes the bound electron (we limit ourselves to the case of a 1s-electron), and  $\gamma$  is the electron–photon interaction operator. We begin with the case where this operator is given in its 'gradient form'

$$\gamma = -\mathbf{i} \ \frac{(\mathbf{e}\boldsymbol{\nabla}_{\mathbf{r}})}{m} \,, \tag{20}$$

where **e** is the photon polarization vector. The right-hand side of formula (19) is expressed in terms of the Fourier transforms  $\psi_{\rm F}$  of the wave function as follows:

$$F^{+} = (4\pi\alpha)^{1/2} \int \frac{\mathrm{d}^{3}q}{(2\pi)^{3}} \psi_{\mathrm{F}p_{1}}^{*}(\mathbf{q}) \,\frac{(\mathbf{e}\mathbf{q})}{m} \,\psi_{\mathrm{F}}(\mathbf{q}-\mathbf{k})\,. \tag{21}$$

Momentum transfer to the recoil ion accompanies the process. Note that the electron energy  $\varepsilon = p_1^2/2m$ , while the binding energy can be written as  $I = \eta^2/2m$ . Hence, the condition  $\omega \ge I$  leads to the inequality  $p_1 \ge \eta$ , i.e., the momentum of the outgoing electron is much higher than the binding momentum. Moreover,  $k = \omega$ , and at nonrelativistic energies of the outgoing electron we have  $p_1 \ge k$ . Thus, at asymptotic energies  $\omega \ge I$  the recoil ion acquires the momentum  $Q \ge \eta$ .

To begin with, we describe the electron belonging to the continuous spectrum by a plane wave:

$$\psi_{Fp_1}(\mathbf{q}) = \psi_{Fp_1}^{(0)}(\mathbf{q}) = (2\pi)^3 \,\delta(\mathbf{p}_1 - \mathbf{q}) \,. \tag{22}$$

In this case, the entire momentum Q is transferred to the ion by the initial-state electron. The respective contribution to the amplitude amounts to

$$F_0^+ = (4\pi\alpha)^{1/2} \ \frac{(\mathbf{e}\mathbf{p}_1)}{m} \psi_{\mathrm{F}}(p_1) \,. \tag{23}$$

For hydrogenlike functions, the asymptotics is given by

$$\psi_{\rm HF}(p_1) = \frac{8\pi^{1/2}\eta^{5/2}}{p_1^4} + O(p_1^{-6}).$$

One can expect the asymptotic function  $\psi_{\rm F}(p_1) \sim p_1^{-4}$  to retain its form if the electron–electron interaction is taken into account, since the condition  $p_1 \ge \eta$  corresponds to distances  $p_1^{-1}$  from the nucleus much smaller than the size  $\eta^{-1}$  of the atom, with the result that the interaction with the nucleus is predominant. The asymptotics of the wave function can be calculated without resorting to additional approximations. Since the s-state function is independent of the direction of vector **r**, we can perform the following transformations:

$$\psi_{\rm F}(p) = \int d^3 r \psi(r) \exp\left[-i\left(\mathbf{pr}\right)\right]$$
$$= -\frac{4\pi}{p^2} \int dr \, r \psi(r) \cos pr$$
$$= \dots -\frac{8\pi \psi'(0)}{p^4} + O(p^{-6}) \,. \tag{24}$$

The last equality is obtained as a result of two integrations by parts.

In order to verify that formula (24) does indeed describe the asymptotic behavior of the amplitude (19), let us see what we get by taking into account the interaction of the outgoing atomic electron and the ion. The first correction of the perturbation theory for the interaction  $V^{\rm C}(r) = -\alpha Z/r$  with the nucleus can be written in the form

$$\psi_n^{(1)} = \sum \frac{V_{nm}^{\mathbf{C}} \psi_m^{(0)}}{\epsilon_n - \epsilon_m} \,, \tag{25}$$

where the sum is extended over the states *m* that differ from the state *n*,  $\epsilon_{m,n}$  are unperturbed energy values, and  $\psi_m^{(0)}$  are given by formula (22). Direct calculations produce the correction to wave function (22):

$$\psi_{\mathrm{F}p_{1}}^{(1)}(\mathbf{q}) = -\frac{8\pi\alpha Zm}{\left(\mathbf{p}_{1}-\mathbf{q}\right)^{2}\left(p_{1}^{2}-q^{2}\right)}$$
(26)

and to the amplitude:

$$F_{1}^{+} = -(4\pi\alpha)^{1/2} \int \frac{\mathrm{d}^{3}q}{(2\pi)^{3}} \frac{(\mathbf{e}\,\mathbf{q})}{m} \frac{8\pi\alpha Zm}{(\mathbf{p}_{1}-\mathbf{q})^{2}(p_{1}^{2}-q^{2})} \,\psi_{\mathrm{F}}(q)\,.$$
(27)

In the amplitude  $F_1^+$ , the large momentum can be transferred to the nucleus by the electron in the initial or final state. Here, in the former case  $q \ge \eta$ , and the integral is determined by the region where  $|p_1 - q| \sim \eta \ll p_1, q$ . In the latter case, the main contribution is provided by the region where  $q \sim \eta$ , i.e., the electron interacts with the photon over distances on the order of the size of the atomic shell, but then it moves closer to the nucleus to small distances of order  $p_1^{-1}$  and transfers a lot of momentum  $(Q \gg \eta)$ . Direct calculations of the integral on the right-hand side of Eqn (27) with the use of formula (24) show that the amplitude  $F_1^+$  does indeed contain a factor  $\xi_Z$  not present in  $F_0^+$ . The same approach is utilized to show that the interaction of the outgoing electron with the electron shell weakens (at least as much as  $p_1^{-1}$ ) and that, basically, a large momentum Q is transferred to the nucleus by the electron that is in the initial state. Thus, the asymptotic behavior of the amplitude is, indeed, described by the contribution  $F_0^+$  (23) in which  $\psi_F(p_1)$  is given by formula (24).

The large numerical factor in the leading contribution of order  $p_1^{-1}$  emerges, in particular, from the normalization factor of the wave function  $\psi_{p_1}(r) = \psi_{p_1}^{(0)}(r) + \psi_{p_1}^{(1)}(r)$ . Taking the integral

$$\psi_{p_1}(0) = \int \! rac{\mathrm{d}^3 q}{(2\pi)^3} \left[ \psi^{(0)}_{\mathrm{F} p_1}(q) + \psi^{(1)}_{\mathrm{F} p_1}(q) 
ight],$$

we get

$$\psi_{p_1}(0) = 1 + \xi_Z J, \tag{28}$$

where

$$J = \frac{1}{\pi} \int_0^\infty \frac{\mathrm{d}x}{x} \ln \frac{1+x}{|1-x|} = \frac{\pi}{2} \,. \tag{29}$$

Hence,  $\psi_{p_1}^{(0)}(0) = 1 + \pi \xi_Z/2$ . The factor  $\pi$  can be considered the result of integration in formula (29) in the complex plane with the discontinuity  $-i \ln (-1) = \pi$ . The normalization factor is not the only source of contributions of order  $\pi \xi_Z$ . In the case of photoionization, all contributions that depend on  $\pi \xi_Z$  are factorizable [7, 8]. In some processes, all such contributions cancel out and the dependence on  $\pi \xi_Z$ disappears [24].

Thus, the nonrelativistic asymptotics of the photoeffect cross section can be expressed by the following function

$$\sigma^{+}(\omega) = C_1(\pi\xi_Z)\,\omega^{-7/2}\,.$$
(30)

Here, the true asymptotics, in which we can put  $C_1(\pi\xi_Z) = C_1(0)$ , is achieved only for the lightest atoms. In other cases, relativistic effects begin to play a significant role before the expansion in powers of  $\pi\xi_Z$  becomes possible.

## **3.2 Double-photoionization asymptotics.**

#### An apparent contradiction

Let us write out the general expression for the doublephotoionization amplitude as follows:

$$F^{2+} = \left\langle \Psi_f | \gamma | \Psi_i \right\rangle, \tag{31}$$

where  $\Psi_i$  and  $\Psi_f$  are the exact wave functions of the initial and final states, and

$$\gamma = \gamma_1 + \gamma_2, \qquad \gamma_j = -i \, \frac{(\mathbf{e} \, \nabla_j)}{m}$$
(32)

describe the interaction between a photon and a two-electron system. The asymptotic behavior of the amplitude, as shown

by Kabir and Salpeter [20], is determined by the interaction in the initial state accompanied by the transfer of a small amount of energy to the secondary electron, and the momentum

$$\mathbf{Q} = \mathbf{k} - \mathbf{p}_1 - \mathbf{p}_2 \tag{33}$$

to the nucleus.

To calculate the cross-section asymptotics, it is sufficient to describe the final state by a product of single-electron functions and disregarding all interactions of the fast electron, i.e.,  $\psi_f(r_1, r_2) = \psi_{p_1}^{(0)}(r_1) \psi_{p_2}^C(r_2)$ , where the plane wave  $\psi_{p_1}^{(0)}$  is given by formula (22), and  $\psi_{p_2}^C$  is the continuous-spectrum wave function of an electron in the Coulomb field of the nucleus. Since  $p_1 \ge p_2$ , we can assume that  $\gamma = \gamma_1$ .

Analysis similar to that conducted in Section 3.1 yields

$$F^{2+} = (4\pi\alpha)^{1/2} \ \frac{(\mathbf{e}\mathbf{p}_1)}{m} \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \psi_{p_2}^{C*}(\mathbf{q}) \ \Psi_{\mathrm{F}}(\mathbf{p}_1, \mathbf{q}) \,. \tag{34}$$

The region of small  $q \sim \eta \ll p_1$  determines the integral. A transformation similar to Eqn (24) yields  $\Psi_F(p_1, q) \sim p_1^{-4}$  for  $p_1 \gg \eta$ . Thus, at  $\varepsilon_2 \sim I$  and  $p_2 \sim \eta$ , the dependence of the amplitude  $F_2^+$  on  $p_1$  is the same as that of  $F_0^+$  (23). The energy distribution drops off very rapidly with increasing  $\varepsilon_2$ , and the integral with respect to  $\varepsilon_2$ , which converges on  $\varepsilon_2 \sim I$ , is independence of the photon energy. Hence, the asymptotic dependence of the cross sections  $\sigma^{2+}$  and  $\sigma^+$  is the same. It can be shown that their dependence on the parameter  $\pi\xi_Z$  is also similar. What is important here, however, is that

$$\sigma^{2+}(\omega) = C_2 \omega^{-7/2} \,. \tag{35}$$

Byron and Joachain [22] calculated the double-ionization cross section by using a variational wave function of type (8) to describe the ground state, while the cross-section asymptotics was the leading term in the expansion in powers of  $\xi_Z$ . Here, for the  $\gamma$  operators the researchers used both the 'gradient form' (20) and the 'length form'

$$\gamma = \gamma_1 + \gamma_2, \quad \gamma_j = \omega_{fi}(\mathbf{er}_j), \quad (36)$$

where  $\omega_{fi}$  is the difference between the energies of the final and initial states of the atomic system (in our case  $\omega_{fi} = \omega$ ). The matrix elements of the operators (32) and (36) sandwiched between the *exact* solutions of the Schrödinger equation are the same. Discrepancies caused by the use of approximate functions have been repeatedly discussed in the literature. This time, however, the results were qualitatively different. Calculations with the use of Eqn (36) yielded

$$\sigma^{2+}(\omega) = C_2^{\rm L} \omega^{-5/2} \,. \tag{37}$$

Such a result can be explained as follows. When  $p_2 \ll p_1$ , the important range of distances is  $r_1 \ll r_2$ , and we can put  $\gamma = \gamma_2$ . In contrast to the case of single photoionization, the fast electron acquires no orbital momentum. The electron that directly interacts with the photon carries away only a small fraction of the energy,  $\varepsilon_2 \sim I$ , so that almost all energy  $\varepsilon_1 \sim \omega$  is carried away by the secondary electron. From the standpoint of physics, this picture appears to be unrealistic. Nevertheless, by using a plane wave to describe the fast electron in the formula for the amplitude in the 'length

form'

$$F^{2+} = (4\pi\alpha)^{1/2} \omega \int \frac{d^3 q_1 d^3 q_2}{(2\pi)^6} \times \psi_{p_1}^{C*}(\mathbf{q}_1) \psi_{p_2}^{C*}(\mathbf{q}_2)(\mathbf{e}\mathbf{q}_2) \Psi_{\mathrm{F}}(\mathbf{q}_1, \mathbf{q}_2)$$
(38)

we find that the amplitude's dependence on the fast electron's momentum  $p_1 \sim (2m\omega)^{1/2}$  is determined by the factor

$$\omega \Psi_{\rm F}(\mathbf{p}_1, \mathbf{q}_2) \sim \frac{\omega}{p_1^4} \tag{39}$$

which contains the additional [compared to the right-hand side of formula (23)] factor  $\omega^{1/2}$ . This leads to a behavior of the cross section described by formula (37). In Ref. [22], the given result remains valid if one allows for interaction between the fast electron and the nucleus.

Byron and Joachain [22] assumed that the contradiction appeared because the approximate functions were used for the ground state and that the contribution  $\omega^{-5/2}$  to the cross section vanishes when exact functions are used. Several years later, this guess was confirmed by Åberg [25].

#### **3.3 Resolving the contradiction**

Åberg's results in Ref. [25] can be presented as follows. The large momentum  $Q \approx p_1 \ge \eta$  can be transferred to the nucleus by the electron in the initial or final state. In contrast to the 'gradient form', when employing the 'length form', both cases yield parametrically similar contributions. Thus, the wave function of the fast electron can be written as the sum of a plane wave and the first Coulomb correction, whereas the amplitude can be written as  $F_{\rm L}^{2+} = F_{\rm L0}^{2+} + F_{\rm L1}^{2+}$ , namely

$$F_{Lk}^{2+} = (4\pi\alpha)^{1/2} \int \frac{d^3q_2}{(2\pi)^3} \psi_{Fp_2}^*(\mathbf{q}_2)(\mathbf{eq}_2) A_k(\mathbf{q}_2) , \qquad (40)$$

where

$$A_k(\mathbf{q}_2) = \omega \int \frac{\mathrm{d}^3 q_1}{(2\pi)^3} \psi_{Fp_1}^{(k)*}(\mathbf{q}_1) \,\Psi_{\mathrm{F}}(\mathbf{q}_1, \mathbf{q}_2) \,, \quad k = 0, 1 \,. \tag{41}$$

For the contribution provided by the plane wave we immediately have

$$A_0(q_2) = \omega \Psi_{\mathrm{F}}(p_1, q_2) \tag{42}$$

with the large momentum  $p_1 \ge \eta$  transferred to the nucleus by the electron in the initial state. While  $A_0$  is determined by large  $q_1 = p_1 \ge \eta$ , the respective integral for  $A_1$  is saturated by small momenta  $q_1 \sim \eta$ . This is obvious if we look at formula (26) which directly expresses a correction to the wave function. We can ignore the momentum  $q_1$  everywhere except in the wave function  $\Psi_F(\mathbf{q}_1, \mathbf{q}_2)$ . As a result, we arrive at

$$\begin{aligned} \mathbf{A}_{1}(\mathbf{q}_{2}) &= -\omega \; \frac{8\pi\eta}{p_{1}^{4}} \int \frac{d^{3}q_{1}}{(2\pi)^{3}} \; \boldsymbol{\Psi}_{\mathrm{F}}(\mathbf{q}_{1}, \mathbf{q}_{2}) \\ &= -\omega \frac{8\pi\eta}{p_{1}^{4}} \; \boldsymbol{\Psi}_{\mathrm{PF}}(0, q_{2}) \,. \end{aligned}$$
(43)

Here, we have introduced the partial Fourier transform

$$\Psi_{\rm PF}(\mathbf{r}, \mathbf{q}_2) = \int d^3 r_2 \Psi(\mathbf{r}, \mathbf{r}_2) \exp\left[-i\left(\mathbf{q}_2 \mathbf{r}_2\right)\right]. \tag{44}$$

A transformation similar to formula (26) yields

$$A_0(\mathbf{q}_2) = -\frac{8\pi\omega}{p_1^4} \,\Psi_{\rm PF}'(0,\mathbf{q}_2)\,. \tag{45}$$

Thus, the amplitudes  $F_{L0}^{2+}$  and  $F_{L1}^{2+}$  are, indeed, of the same order. This does not contradict the fact that at any point *r* the function  $\psi^{(1)}(r)$  is  $\xi_Z$  times smaller than  $\psi^{(0)}(r)$ . The amplitudes  $A_0(q_2)$  and  $A_1(q_2)$ , which can be written as

$$A_k(\mathbf{q}_2) = \omega \int \mathrm{d}^3 r_1 \psi_{p_1}^{(k)*}(\mathbf{r}_1) \, \Psi_{\mathrm{PF}}(\mathbf{r}_1, \mathbf{q}_2) \,, \tag{46}$$

are formed by different ranges of distances  $r_1$ . While  $A_0$  is determined by the range  $r_1 \sim p_1^{-1}$  of distances, much larger distances  $r \sim \eta^{-1}$  contribute the most to  $A_1$ .

Each  $A_{0,1}$  examined separately provides contribution to the cross section that decreases as  $\omega^{-5/2}$ . However, using formulas (43) and (45), we have  $A_0(q_2) + A_1(q_2) = 0$  for any  $q_2$ , with the result that

$$F_{\rm L0}^{2+} + F_{\rm L1}^{2+} = 0.$$
<sup>(47)</sup>

Therefore, the contributions of order  $\omega^{-5/2}$  cancelled out because of the Kato condition (11). In the calculations done in Ref. [22], the researchers used an approximate wave function that does not meet condition (11), and this led to incorrect asymptotic behavior in calculations using the 'length form'.

#### 3.4 The Lippmann-Schwinger equation

In this section we will show that the Lippmann–Schwinger equation is a convenient instrument for asymptotic analysis. The general form of this equation for a two-electron system in the field of the nucleus is given by

$$\Psi = \Psi^{(0)} + G^{\epsilon} V \Psi.$$
(48)

Here, V denotes the interactions in the system,  $\epsilon$  is the energy eigenvalue of the respective Schrödinger equation, and  $\psi^{(0)}$  and  $G^{\epsilon}$  are the solution of the Schrödinger equation and Green's function at V = 0 (free motion), respectively. In the nonrelativistic case, the Feynman diagram technique can be considered a graphic illustration of the Lippmann–Schwinger equation.

To simplify notation, we write out this equation for the single-particle wave function  $\psi$  in a certain effective field U(r):

$$\psi = \psi^{(0)} + G^{\epsilon} U \psi \,. \tag{49}$$

Now,  $G^{\epsilon}$  is a free single-particle Green function. In the momentum representation, one finds

$$\langle \mathbf{p} | G^{\epsilon} | \mathbf{f} \rangle = \frac{\delta(\mathbf{p} - \mathbf{f})}{\epsilon - p^2/2m + \mathrm{i}v}, \quad v \to 0.$$
 (50)

For bound electrons  $\psi^{(0)} = 0$  and

$$\psi_{\mathrm{F}}(\mathbf{p}) = \frac{2m}{2m\epsilon - p^2} \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \left\langle \mathbf{p} \mid U \mid \mathbf{q} \right\rangle \psi_{\mathrm{F}}(\mathbf{q}) \,, \tag{51}$$

where  $\epsilon$  is the single-particle binding energy. Asymptotically,  $p^2 \gg 2m|\epsilon|$ . The integral on the right-hand side of formula (51) converges at momenta  $q \sim \eta$ . Thus, Eqn (51) expresses

the bound-state wave function for large momenta in terms of the same wave function as for momenta of order of the binding momentum.

For s-states we can put  $\langle \mathbf{p} | U | \mathbf{q} \rangle = \langle \mathbf{p} | U | 0 \rangle$ . Since large momenta *p* correspond to small distances *r*, only interactions with the nucleus are important in the asymptotic region. Hence, one obtains

$$\langle p|U|0\rangle = -\frac{4\pi\alpha Z}{p^2}$$

and

$$\psi_{\rm F}(p) = \frac{8\pi\alpha Z\psi(0)}{p^4} + O(p^{-6}).$$
(52)

Using the Kato condition (15), we find that expression (52) coincides with formula (24). The same approach can be applied to find the asymptotic behavior of the wave function of the helium atom:

$$\Psi_{\rm F}(p,q_2) = \frac{8\pi\alpha Z \Psi_{\rm PF}(0,q_2)}{p^4} + O(p^{-6}), \qquad (53)$$

where the function  $\Psi_{\rm PF}$  is defined in formula (44).

Calculations of the double – photoionization amplitude in the 'length form' with the use of expression (53) yield

$$A_0(\mathbf{q}_2) = \frac{8\pi\omega\eta}{p_1^4} \, \Psi_{\rm PF}(0,\mathbf{q}_2)$$

instead of formula (45). Both formulas are equivalent in view of the Kato condition (11). However, in the approach based on the Lippmann–Schwinger equation, contributions of order  $\omega^{-5/2}$  automatically cancel out, even without using the Kato relation.

# 4. Shape of the double-photoionization spectrum: U or W?

#### 4.1 Mechanisms of the process

Late in the 1980s, progress in experimental techniques made it possible to measure the energy distributions of doublephotoionization electrons for helium. Measurements at low photon energies have already been conducted, and results for high energies are expected soon.

The evolution of the shape of the double-photoionization spectrum was analyzed even earlier, in the mid-1970s [26]. The distribution  $d\sigma^{2+}/d\epsilon_2$  reaches its maximum values at  $\epsilon_2 \sim I$ ,  $\varepsilon \sim \omega$  (it is assumed that  $\varepsilon_2 \leq \varepsilon_1$ ), i.e., at the spectrum's edges. We discussed this mechanism [20] in Section 3. As we move away from the edges to the center, i.e., at  $\varepsilon_{1,2} \sim \omega$ , photoionization with subsequent scattering of the knocked-out electron by the remaining bound electron becomes the main mechanism of the process [27, 28]. This mechanism of finalstate scattering (FSS) is predominant for all  $\omega \ge I$ , but up to a certain distance from the center of the spectrum. For close energy values  $|\varepsilon_1 - \varepsilon_2| \ll \omega$ , the FSS mechanism competes with the quasifree (QF) mechanism, in which the electrons leave the nucleus by transferring only a small amount of momentum,  $Q \sim \eta$ , to it. At sufficiently high photon energies  $\omega$ , the QF mechanism is predominant near the center of the spectrum.

To clarify the nature of the QF mechanism, we note that each act of exchange of a large momentum leads to suppression of the scattering amplitude. In the FSS mechanism, large momentum is transferred twice: in single ionization (between a bound electron and the nucleus), and in electron – electron scattering (between the electrons). However, a single transfer is also possible. An electron that directly interacts with the photon can transfer a large momentum to a second electron even without the nucleus participation in the process. In contrast to single photoionization, the process may involve free electrons as well. The Bethe surface is determined by the condition Q = 0, namely

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{k} \,, \tag{54}$$

which requires that

$$\delta = \frac{\varepsilon_1 - \varepsilon_2}{\omega} \leqslant \sqrt{\frac{\omega}{\omega + m}} \leqslant 1.$$
(55)

In this review we do not examine the case of very high energies  $\omega \sim m$  (the reader will recall that  $m \approx 511$  keV), which requires a relativistic description of the electrons. Such a problem was solved in Ref. [29]. Hence, in formula (55) we set  $\omega \ll m$ , and  $\delta \ll 1$ .

Following the analysis carried out in Section 1, we find that small  $Q \sim \eta$  play an important role in the QF mechanism. Ignoring the momentum  $Q \ll p_i$  in the final-state electron wave functions, we can express the QF amplitude  $F_{\rm QF}$  in terms of the amplitude  $F_{\rm fr}$  of the process involving free electrons:

$$F_{\rm QF}(\mathbf{p}, \mathbf{Q}) = D(Q^2) F_{\rm fr}(\omega, \delta), \qquad (56)$$

where  $p = (p_1 - p_2)/2 \approx p_1 \approx -p_2$ . The factor  $D(Q^2)$  contains the parameters of the initial state. Its explicit form is given below, in formula (70), while here we focus on the second factor on the right-hand side of formula (56), i.e., on the scattering amplitude of the free process. The amplitude of photon absorption by a system of two free electrons can be written down as follows:

$$F_{\rm fr}(\omega,\delta) = (\mathbf{e}\mathbf{p}_1)f(\omega,\delta) + (\mathbf{e}\mathbf{p}_2)f(\omega,-\delta).$$
(57)

For the time being, the explicit form of the function  $f(\omega, \delta)$  is unimportant. We immediately note that the process cannot be described correctly if we limit ourselves to the lowest-order approximation in powers of  $k/p_i$ . Indeed, in this case  $p_1 = -p_2$ , and the electrons cannot carry away a unit angular momentum transferred by the photon. This follows from formula (57) if we limit ourselves to the lowest term in the expansion in powers of  $\delta$ :

$$F_{\rm fr}(\omega, 0) = (\mathbf{e}, \mathbf{p}_1 + \mathbf{p}_2) f(\omega, 0) = (\mathbf{e}\mathbf{k}) f(\omega, 0) = 0, \quad (58)$$

and the leading nonvanishing contribution is given by

$$F_{\rm fr}(\omega,\delta) = 2(\mathbf{ep})\,\delta f'(\omega,0)\,. \tag{59}$$

Here, f' is the derivative with respect to  $\delta$ . For a free process, one finds

$$\delta = \frac{(\mathbf{p}\,\mathbf{k})}{m\omega} \,. \tag{60}$$

Hence, the QF mechanism requires stepping beyond the limits of the dipole approximation, which approximation would correspond to the zeroth term in the expansion in powers of  $k/p_i$ . Unfortunately, this fact was not pointed out by Amusia et al. [26] and by the author in the more detailed paper [28].

Thus, near the spectrum's center, two factors contribute to the energy distribution: scattering in the final state with a minimum at the very center, and the QF mechanism which has a peak at the center (the contribution of 'shaking' is sure to be smaller). The relative role of the QF mechanism increases with photon energy, and for  $\omega > 1.2$  keV [30] the peak at the center becomes noticeable, with the result that the U-shaped spectrum is replaced by a W-shaped one. The reader will recall that the corresponding calculations require stepping beyond the limits of the dipole approximation.

#### 4.2 Calculations in the dipole approximation

Meanwhile, some results of computations of double-photoionization spectra at high energies have been published. The results are based on direct computations of the scattering amplitudes. According to the above analysis, these spectra must have a dip at the center. However, Kornberg and Miraglia [31] obtained a U-shaped spectrum only by ignoring the final-state interaction (FSI) between the outgoing electrons. Allowance for this interaction led to a W-shaped spectrum. The result from Teng and Shakeshaft [32] was just the opposite: at  $\omega = 2.8$  keV, a low peak without allowing for the final-state interaction was replaced by a U-shaped spectrum when this interaction was taken into account. Later on, Kornberg and Miraglia [33, 34] did calculations without allowing for the final-state interaction and arrived at a peak in the spectrum's center.

# 4.3 An explanation of the results obtained in the dipole approximation

It was Surić et al. [35] who explained these results (see also Ref. [36]). By introducing the variables  $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$  and  $\mathbf{\rho} = \mathbf{r}_1 - \mathbf{r}_2$  and the notation  $\tilde{\Psi}(\mathbf{R}, \mathbf{\rho}) = \Psi(\mathbf{r}_1, \mathbf{r}_2)$ , we can write down the amplitude with all final-state interactions ignored:

$$F^{(0)} = (4\pi\alpha)^{1/2} \int d^3 R \, d^3 \rho \exp\left[i\left(\mathbf{Q}\mathbf{R}\right) - i\left(\mathbf{p} - \mathbf{k}, \boldsymbol{\rho}\right)\right]$$
$$\times \gamma \tilde{\Psi}(\mathbf{R}, \boldsymbol{\rho}) \,. \tag{61}$$

According to the analysis in Section 3, the asymptotics  $F^{(0)}(p_i, Q) \sim 1/p^4 Q^4$  for  $p, Q \ge \eta$ . However, with the QF mechanism we need to know the asymptotic behavior for  $p \ge \eta$  and  $Q \sim \eta$ , since such values of Q determine the energy distribution near the spectrum's center. Calculations similar to those with formula (24) yield the following result in the dipole approximation:

$$F^{(0)} = -(4\pi\alpha)^{1/2} \frac{(\mathbf{e}\mathbf{Q})}{m} \frac{8\pi\alpha}{p^4} \times \int d^3 R \exp\left[i\left(\mathbf{Q}\mathbf{R}\right)\right] r_0 \frac{\partial\tilde{\Psi}(R,\rho=0)}{\partial\rho}.$$
 (62)

For  $p \ge \eta$  and  $Q \sim \eta$ , the partial derivative of  $\Psi$  is evaluated at the point  $\rho = 0$ . The energy dependence is determined by the factor  $p^{-4}$ , and near the spectrum's center  $p \approx (m\omega)^{1/2}$ .

Electrons may exchange by large momentum in the final state as well. To account for this mechanism, we must build a wave function of the final state that allows for electron–

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electron interaction. This can be done by using formula (25) with  $V^{\rm C}$  replaced with the electron–electron interaction. Direct calculations yield the following expression for the appropriate amplitude:

$$F^{(1)} = (4\pi\alpha)^{1/2} \frac{(\mathbf{e}\mathbf{Q})}{m} \frac{4\pi\alpha}{p^4} \int d^3 R \exp\left[i\left(\mathbf{Q}\mathbf{R}\right)\right] \tilde{\Psi}(R,\rho=0)$$
(63)

for  $p \ge \eta$  and  $Q \sim \eta$ . Each amplitude  $F^{(0,1)}$  taken separately is much larger than the FSS amplitude which requires large momenta  $Q \ge \eta$ . Thus, each contribution defined by Eqns (62) and (63) should result in a peak at the center, but their sum

$$F^{(0)} + F^{(1)} = (4\pi\alpha)^{1/2} \frac{(\mathbf{e}\mathbf{Q})}{m} \frac{4\pi\alpha}{p^4} \int d^3 R \exp\left[i\left(\mathbf{Q}\mathbf{R}\right)\right] \\ \times \left(\tilde{\Psi}(R,\rho=0) - 2r_0 \frac{\partial\tilde{\Psi}(R,\rho=0)}{\partial\rho}\right) = 0, \quad (64)$$

since the expression in parentheses vanishes in view of the Kato condition (12). Hence, the contribution from small momenta  $Q \sim \eta$  is suppressed in the dipole approximation and for all  $\varepsilon_{1,2} \sim \omega$  the spectrum is determined by the region where  $Q \ge \eta$ , in which the FSS mechanism is predominant. The spectrum should have had a minimum at its center.

Now, the results of Kornberg and Miraglia [31, 33, 34] and Teng and Shakeshaft [32] are understandable. Kornberg and Miraglia [31] used an initial-state wave function that depended only weakly on  $\rho$ . Therefore, amplitude (62) proved to be too small to lead to a peak at the spectrum's center. Inclusion of a final-state interaction produced a false uncompensated maximum. On the other hand, Teng and Shakeshaft [32] used an approximate wave function that satisfied condition (12). Hence, they obtained a peak in the absence of a final-state interaction, which was cancelled out when such interaction was taken into account. The spurious peak at the center obtained later by Kornberg and Miraglia [33, 34] without allowing for final-state interaction is of the same origin. The main drawback of all these calculations in Refs [31-34] is that the researchers did not go beyond the limits of the dipole approximation, which provides a very simplified approach in the case at hand.

This result may be obtained much more simply if we rely on the Lippmann–Schwinger equation (48). The amplitude  $F^{(0)}$  can be expressed in terms of the asymptotic form of the Fourier transform of the wave function:

$$F^{(0)} = -(4\pi\alpha)^{1/2} \frac{(\mathbf{e}\mathbf{Q})}{m} \ \tilde{\Psi}_{\mathrm{F}}(-\mathbf{Q},\mathbf{p}), \qquad (65)$$

which in turn satisfies the Lippmann-Schwinger equation

$$\tilde{\Psi}_{\rm F}(-\mathbf{Q},\mathbf{p}) = -\frac{4\pi m\alpha}{p^4} \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \; \tilde{\Psi}_{\rm F}(-\mathbf{Q},\mathbf{q}) \tag{66}$$

at  $Q \sim \eta$  and for  $p \ge \eta$ . The integral on the right-hand side of Eqn (66) converges on the region where  $q \sim \eta$ . Thus, the Lippmann–Schwinger equation expresses the function  $\tilde{\Psi}_{\rm F}(Q \sim \eta, p \ge \eta)$  in terms of the function  $\tilde{\Psi}_{\rm F}(Q \sim \eta, q \sim \eta)$ . Using formula (63) and (65), we immediately find that  $F^{(0)} + F^{(1)} = 0$ , in accordance with Eqn (64).

Note that in our case the electron – electron interaction turned out to be more important than the electron – nucleus interaction. The latter produces only a small correction, while the former determines the mechanism of the process. Of course, all these results may also be obtained by starting with a description of the electrons from the continuum by Coulomb function, which was done in Ref. [35].

#### 4.4 Evolution of the shape of the spectrum

The evolution of the shape of the double-photoionization spectrum of the helium atom under variations in the photon energy  $\omega$  was first described in Refs [26, 28]. Without discussing the possible variations in shape at low photon energies  $\omega \sim I$ , we note that at energies of several hundred electron-volts the spectral curve is U-shaped, and the process at large  $\varepsilon_{1,2} \gg I$  is determined by the FSS mechanism [27]. As the photon energy grows, near the center of the spectrum the FSS mechanism competes with the QF mechanism whose role increases with a rise in  $\omega$ . This leads, at a certain photon energy  $\omega = \omega_1$ , to the emergence of a peak at the center, and the spectral curve becomes W-shaped. At an even higher energy  $\omega = \omega_2$ , the central peak splits into two peaks shifted symmetrically with respect to the center, while at the center there appears a local minimum. This last variation of shape is due to the quadrupole nature of the OF mechanism. What we have just discussed is illustrated by Fig. 1.

The characteristic energies  $\omega_{1,2}$  depend on the approximate functions used to describe the initial state. Liverts et al. [30] described the helium atom by approximate functions based on Haftel and Mandelzweig's approach [19], which we mentioned at the end of Section 2. This provided  $\omega_1 = 1.9 \text{ keV}$  and  $\omega_2 = 8.9 \text{ keV}$ . The dependence of the energies  $\omega_{1,2}$  on the nuclear charge Z for two-electron ions has been studied in Refs [28, 37].



**Figure 1.** Evolution of the shape of the double-photoionization spectrum of helium atom caused by variations in the photon energy  $\omega$ . The lowest diagram corresponds to energies  $\omega < \omega_1$ , where the knocking out of two fast electrons is due to FSS. In the next diagram corresponding to the energy  $\omega = \omega_1 = 1.9$  keV, the QF mechanism becomes noticeable near the center. Within the interval  $\omega_1 < \omega < \omega_2$  (the third diagram), there appears a peak at the spectrum's center, caused by the contribution from the QF mechanism. At  $\omega = \omega_2 = 8.9$  keV and within the interval  $\omega > \omega_2$  (the next two diagrams), the peak acquires an inner structure thanks to the quadrupole nature of the QF mechanism.

Most computations of the double-photoionization spectrum are based on the general formalism of quantum mechanics. This leads to the use of the formula for the cross section in the form

$$d\sigma^{2+} = \frac{\pi}{\omega} |\bar{F}|^2 \delta(\varepsilon_1 + \varepsilon_2 - \omega - I^{2+}) \frac{d^3 p_1}{(2\pi)^3} \frac{d^3 p_2}{(2\pi)^3}$$
(67)

with the amplitude of the process defined by

$$F = \int d^{3}r_{1} d^{3}r_{2} \psi_{fa}^{*}(\mathbf{r}_{1}, \mathbf{r}_{2})$$
$$\times \left(\gamma_{1} \exp\left[i\left(\mathbf{kr}_{1}\right)\right] + \gamma_{2} \exp\left[i\left(\mathbf{kr}_{2}\right)\right]\right) \psi_{a}(\mathbf{r}_{1}, \mathbf{r}_{2}) \qquad (68)$$

and a direct calculation of the integral. In order to describe the final and initial states, we are forced to use *approximate* wave functions,  $\psi_{fa}$  and  $\psi_{a}$ . To reproduce the main physical mechanisms of the process, the approximate wave functions must demonstrate certain properties of the exact solutions of the Schrödinger equation.

As shown in Section 3, near  $\varepsilon_2 \sim I$  and  $\varepsilon_1 \sim \omega$  the interaction of electrons in the final state does not play a significant role, and the final state can be approximated by the product of single-particle wave functions:  $\psi_{fa}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{ap_1}(r_1) \psi_{ap_2}(r_2)$ . Here, the slow electron must be described by the Coulomb function of the nucleus, while in the gradient form for the operator  $\gamma$  the fast electron can be described by a plane wave [20]. But the description of the initial state by the product of single-particle functions, namely

$$\psi_{\mathbf{a}}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{\mathbf{s}}(r_1) \psi_{\mathbf{s}}(r_2) \,, \tag{69}$$

will lead to quantitatively incorrect results [22]. Still, it is impossible to write out a formula that would allow us in this case to select a 'good' wave function. Here, one must be very careful in using the operator  $\gamma$  in the 'length form'. A plane wave is not suitable for the fast electron, and one should take into account the first Coulomb correction. Moreover, the initial-state function must satisfy the Kato condition (11).

In the region where  $\varepsilon_{1,2} \ge I$ , the interaction between finalstate electrons must be accounted for in the function  $\psi_a$ , since it is this interaction that determines the main mechanism of the process in the larger part of this region. Here, no special conditions are imposed on the initial-state function far from the center. However, to describe the central region of the spectrum we need an initial-state function  $\psi_a$  that satisfies the Kato condition (12), since otherwise the spectrum acquires a false peak in the dipole approximation, in which the exponential factors exp [i ( $\mathbf{k}r_j$ )] are replaced by the unities in formula (68).

Thus, the true W-peak appears when we step outside the limits of the dipole approximation. Technically, this means allowing for the second terms in the expansion  $\exp [i (\mathbf{kr}_j)] = 1 + i (\mathbf{kr}_j) + \dots$  Such an approach leads to formula (56) for the amplitude of the QF mechanism with the amplitudes  $F_{\rm fr}(\omega, \delta)$  defined in formula (59) and

$$D(Q^{2}) = 2r_{0} \int d^{3}R \exp\left[i\left(\mathbf{QR}\right)\right] \frac{\partial\psi_{a}(R,\rho=0)}{\partial\rho}.$$
 (70)

The derivative  $\partial \tilde{\psi}_a(R, \rho = 0)/\partial \rho$  is determined by the Kato relation [17]. Hence, even isolating the quadrupole contribu-

tions, we must use a function  $\psi_a$  that satisfies this condition [12]. Of course, any approximate function  $\psi_a$  with a nonzero value of  $\partial \tilde{\psi}_a(R, \rho = 0)/\partial \rho$  produces a central peak, but quantitative results are reliable only if condition (12) is met.

It should be emphasized that a combination of products of single-particle functions does not reproduce the contribution from the QF mechanism. For such functions, it follows that

$$\tilde{\psi}_{a}(\mathbf{R},\boldsymbol{\rho}) = \tilde{\psi}_{s}\left(\mathbf{R} + \frac{\boldsymbol{\rho}}{2}\right)\tilde{\psi}_{s}\left(\mathbf{R} - \frac{\boldsymbol{\rho}}{2}\right)$$
(71)

is an even function of  $\rho$ , with the result that  $D(q^2) = 0$ , and no trace of the QF mechanism is left. In particular, this is true of the wave functions in the Hartree–Fock approximation.

Note that the simplest functions describing electrons at two-particle coalescence points and satisfying the Kato conditions,  $\psi_a(0, r, r) = \exp\left[-(Z - 1/2)r\right]$  and  $\psi_a(r, r, 0) = \exp\left[-2Zr\right]$  [38], reproduce the values of  $\omega_1$  and  $\omega_2$  to within several percent. What is more, the first function yields good results in calculations of the single-photoionization asymptotics of the helium atom. This explains the old evidence that photoionization of the K-shells by high-energy photons is described well by hydrogenlike functions with an effective charge  $Z_{\text{eff}} = Z - a$ , where  $a \approx 0.5$  [39].

## 5. Conclusion

One can see from the above consideration that theoretical analysis preceding computer calculations proves very useful. In the static problem of determining the binding energy of the ground-state helium atom, such an analysis accelerates the convergence of the procedure and substantially reduces the number of phenomenological parameters introduced. Theoretical analysis makes it possible to avoid hidden obstacles in calculating the asymptotics of the double-photoionization cross sections and to find the true shape of the spectrum.

The Lippmann–Schwinger equation turns out to be very effective in studying asymptotic behavior. This equation, as well as its graphic illustration, Feynman diagrams, could become useful in studies dealing with high-energy atomic physics.

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