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Two-electron photoionization of endohedral atoms

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Using He@C_{60} as an example, we demonstrate that the static potential of the fullerene core essentially alters the cross section of the two-electron ionization differential in one-electron energy $d\sigma^{++}(\omega)/d\varepsilon$. We found that at high photon energy prominent oscillations appear in it due to reflection of the second slow electron wave on the C_{60} shell, which "dies out" at relatively high ε values, of about 2–3 two-electron ionization potentials. The results were presented for ratios $R_{C_{60}}(\omega,\varepsilon)\equiv d\sigma^{++}(\omega,\varepsilon)/d\sigma^{a++}(\omega,\varepsilon)$, where $d\sigma^{a++}(\omega,\varepsilon)/d\varepsilon$ is the two-electron differential photoionization cross section. We have calculated the ratio $R_{i,\text{ful}}=\sigma_i^{++}(\omega)/\sigma_i^{a++}(\omega)$, that accounts for reflection of both photoelectrons by the C_{60} shell. We have also calculated the value of two-electron photoionization cross section $\sigma^{++}(\omega)$ and found that this value is close to that of an isolated He atom. Results similar to He@C_{60} are presented for He@C_{70} and He@C_{76}.

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I. INTRODUCTION

Elimination of two electrons by a single photon from an atom or multiatomic formation, such as cluster or fullerene, can take place only if the interelectron interaction is taken into account. The desire to study the manifestation of this interaction stimulates extensive experimental and theoretical investigation of the process that has particularly intensified over the last ten to fifteen years (see, e.g., Refs. [1,2]). Although a number of atoms were studied, primary attention was given to helium. At this moment theoretical and experimental investigations cover the frequency region from the near threshold region up to photon energy ω much higher than the two-electron ionization potential I^{++}.

Very close to threshold the two-electron photoionization cross section is determined by so-called Wannier regime [3] with both electrons strongly repulsing each other that results in acquiring almost the same energy and moving in opposite directions.

With the increase of ω for ω considerably more than I^{++}, the so-called shake-off (SO) mechanism [4] became dominant, in which one electron leaves the atom carrying away almost all energy ω, while the second is removed due to the alteration of the field acting upon it after the first electron emission. With energy growth the so-called quasifree (QF) mechanism [5] becomes increasingly important. This mechanism accounts for almost equal sharing of photon energy between photoelectrons, where their interaction on the way out of the ionized atom is inessential.

Obviously, the cross section of two-electron photoionization $\sigma^{++}(\omega)$ is determined by initial and final state wave function of the considered object-target atom at the beginning and ion with two continuous spectrum electrons at the end. The situation is simplified considerably at high enough ω, where cross sections and other characteristics of the two-electron ionization are expressed via the initial state wave function only.

In fact, one has to have in mind that two-electron ionization is a pure three-body problem only for two-electron atom and ions. This process for any other, more complicated objects is determined by more sophisticated wave functions. This is why most of the attention is given usually to studies of two-electron photoionization of H^-, He, and heliumlike atoms. At high ω the σ^{++} and σ^{+} have similar ω dependence [6]. Therefore it is convenient to characterize the process by the ratio $R(\omega)=\sigma^{++}(\omega)/\sigma^{+}(\omega)$.

The SO leads for $\omega \gg I^{++}$ to $R(\omega)=R_{SO}$ (see Ref. [7], and references therein). Inclusion of QF increases $R(\omega)$ considerably but at high enough ω the ratio again reaches its ω-independent value $R_{QF}>R_{SO}$ [8].

A lot of attention was given to photoionization of not isolated atoms, but atoms encapsulated into the fullerene, mainly C_{60} shell (see, e.g. Refs. [9,10]). The research in this area up to now has been purely theoretical. But we are positive that it will become an object of experimental studies in the not too distant future. It is well known that C_{60} radius R is much bigger than that of the atoms staffed inside the so-called endohedral atom A@C_{60}.

The inclusion of the C_{60} shell can affect the photoionization atom in four directions. At first, and this is usually taken into account, the photoelectron emitted by A is reflected by the C_{60} shell that "works" as a static potential. Then, the C_{60} shell has its internal degrees of freedom [11] that can be excited thus modifying the photoionization of the atomic shells in A@C_{60} in a similar way that one shell affects the photoionization of the other in isolated atoms [12]. Among the C_{60} degrees of freedom the most prominent is the giant resonance that persists not only in C_{60} [11], but in its ions as well [13]. Real or virtual excitations of the giant resonance can modify the A atom photoionization cross section from almost complete screening at $\omega \to 0$ to prominent enhancement at ω in the vicinity of the giant resonance maxima [14,15]. Note that at high ω this screening becomes mainly inessential, but has to be taken into account at low ω.

The other two directions of C_{60} influence upon the A atom photoionization is the direct knock out of C_{60} electrons by the photoelectron from A and the participation of C_{60} electrons in the decay, both radiative and nonradiative, of the vacancy, created in A after photon absorption. Note that this mechanism is similar to one of the frequently discussed channels of the molecular vacancy decay. The corresponding two possibilities in the application to C_{60} have not yet been studied at all.

In principle, the interelectron interaction in atom A that causes its two-electron ionization as well as ionization with excitation is modified due to its dynamical screening by virtual excitations of the C_{60} shell. As we will estimate, this contribution is very small, less than 1%, due to the smallness of atom A as compared to the fullerene radius.

In this paper we consider a more complex process, namely, the two-electron photoionization of $He@C_{60}$. We will concentrate on the high ω region. Of course, to investigate this process experimentally is more complicated than one-electron photoionization. However, there are no indications whatsoever that such an investigation is either impossible (or even extra-ordinarily difficult) or uninteresting.

The role of C_{60} shell in two-electron photoionization is more complex than in the single electron, since outgoing electrons can be either both from the inner atom A, or both from the C_{60}, or one from A and the other from C_{60}. However, by measuring two outgoing electrons in coincidence we can distinguish all the different processes. It is particularly important, since the cross section of the two-electron photoionization of C_{60} itself is much bigger than that of $He@C_{60}$.

While, as far as we know, the two-electron photoionization of endohedral atoms, e.g., $He@C_{60}$, was not discussed in the literature at all, two-electron photoionization was studied to some extent both experimentally [16] and theoretically [17].

In this paper we consider $He@C_{60}$ two-electron photoionization, mainly, at high ω. Having in mind that our aim is to study the C_{60} influence upon double ionization, we have to consider the SO mechanism only. Indeed, the QF leads to two fast electrons, which are not affected by C_{60}, while in SO one of the electrons is slow. Its probability to leave $He@C_{60}$ can therefore be strongly affected.

Our attention in this paper will be given to the differential in energy cross sections $d\sigma^{++}(\omega)/d\varepsilon_s$, where ε_s is the "slow" photoelectrons energy. It is implied that the "fast" electron energy ε_f is given by the conservation law $\varepsilon_f=\omega-\varepsilon_s-I^{++}$. The atomic system of units is accepted in this paper $e=m_e=\hbar=1$, where e and m are electron charge and mass, respectively.

We will assume that both electrons are removed from the He atom, thus intensionally neglecting a process that one can call "$A@C_{60}$ shake off," in which after "fast" electron leaves A, the "slow" electron is emitted by the C_{60} shell instead of located inside atom A. The $A@C_{60}$ shake off is potentially very important due to large number of C_{60} electrons, that can be easily removed. . Therefore, it is possible that $He@C_{60}$ shake off is much more probable than the ordinary one. It is possible, that an important role can be played by multiple $A@C_{60}$ shake off, in which not one but several electrons can be removed from C_{60} after instant creation of a vacancy in A. One has to have in mind that for an isolated atom A the photoionization with excitation cross section $\sigma^{+*}(\omega)$ can be of the order or even bigger than $\sigma^{++}(\omega)$. It is essential to have in mind that the $\sigma^{+*}(\omega)$ for $A@C_{60}$ can be converted into $\sigma^{++}(\omega)$, since the excitation energy of A^{+}, particularly in the case of He, is bigger than the ionization potential of C_{60}. We plan, however, to concentrate on $A@C_{60}$ shake off in another paper.

Let us note that the approach developed in this paper permits one to make the problem of two-electron ionization of $He@C_{60}$ much simpler than the two-electron ionization of C_{60} itself. In fact, the only assumptions that are made is that the fullerene radius R is much bigger than the atomic radius r_a and that the thickness of the C_{60} shell ΔR is much smaller than R, $R \gg r_a$ and $R \gg \Delta R$. In the frame of this approximations it is possible to reduce the influence of C_{60} upon two-electron photoionization of $A@C_{60}$ to easily calculative factors that depend only upon the fullerene radii R and their electron affinities.

It is of interest to see how the size of the fullerene affects all the picture of two-electron photoionization of endohedral atoms. This is why we performed calculations not only for $He@C_{60}$ but for $He@C_{70}$ and $He@C_{76}$ also. Since C_{70} and C_{76} are nonspherical, the approach presented below works for them, perhaps worse, than for C_{60}. However, in order to obtain qualitative trends, we perform calculations for C_{70} and C_{76} as for spherical objects with radii of an equiareal sphere [27]. All three fullerens mentioned above we will denote as C_N.

II. MAIN FORMULAS

The two-electron photoionization cross section of an atom A in initial state i, $\sigma_i^{a++}(\omega)$, can be presented by the following expressions:

$$\sigma_i^{a++}(\omega)=\int_0^{\omega-I^{++}}\frac{d\sigma_i^{a++}(\omega,\varepsilon)}{d\varepsilon}d\varepsilon, \qquad (1)$$

where at high ω, $\omega \gg I^{++}$, the differential in energy cross section $d\sigma_i^{a++}(\omega,\varepsilon)/d\varepsilon$ is given by the expression [18]

$$\frac{d\sigma_i^{a++}(\omega,\varepsilon)}{d\varepsilon}=\frac{32\sqrt{2}Z^2\pi}{3c\omega^{7/2}}\left|\int\Psi_i(0,\mathbf{r})\varphi_{\varepsilon 0}(\mathbf{r})d\mathbf{r}\right|^2. \qquad (2)$$

Here $\Psi_i(0,\mathbf{r})$ is the $\mathbf{r}_1=0$ value of $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)$, which is in our case the initial state wave function of atomic He. The "slow" outgoing electron is described by a pure Coulomb wave function, that describes an s-wave electron, that moves in the field of a nucleus with charge Z.

Similar to Eq. (1) the cross section of ionization with excitation $\sigma^{+*}(\omega)$ is given by the following expression:

$$\frac{d\sigma_i^{a++}(\omega,\varepsilon)}{d\varepsilon}=\frac{32\sqrt{2}Z^2\pi}{3c\omega^{7/2}}\sum_{n>0}\left|\int\Psi_i(0,\mathbf{r})\varphi_{n0}(\mathbf{r})d\mathbf{r}\right|^2. \qquad (3)$$

Here n is the principal quantum number of the second electron excitation level.

Now let us consider $He@C_N$ two-electron photoionization and take into account the C_{60} shell. It is clear that C_N

potential does not affect the “fast” electron, which remains to be described by a plane wave. The C_N shell generates potential field, that is almost uniform at atomic distances r_a, where the initial state of He is located. Therefore, for the initial state the embedding of an atom A into C_N can lead only to the shift of the energy scale, i.e., to modification of the ionization threshold. This feature is inessential for us, since $\omega \gg I^{++}$.

Thus, we have to take into account the action of C_N upon the slow outgoing electron. The fullerene is a very complex structure. Therefore, to take into account its action upon photoelectron essential simplifications are necessary. We will follow here the approach developed in a number of papers (see Refs. [19,20], and references therein), that substitutes the complicated C_N multiatomic structure by a very simple so-called bubble potential $V(r)=V_0\delta(r-R)$, where V_0 is chosen to reproduce the affinity energy of the negative ion C_N, and $\delta(r-R)$ is the Dirac delta function.

As it was demonstrated in Refs. [20,21] in connection to the one-electron photoionization, the influence of the bubble potential can be taken into account analytically, by constructing the outgoing wave function as a superposition of regular $\varphi_{\varepsilon l}(\mathbf{r})$ and irregular $\chi_{\varepsilon l}(\mathbf{r})$ (singular at $\mathbf{r}\to 0$) solutions of the Schrödinger equation for an electron with energy ε. Inside the potential bubble the photoelectron wave function $\psi_{\varepsilon l}(\mathbf{r})$ differs from $\varphi \varepsilon l(\mathbf{r})$ only by a normalization factor $D_l(\varepsilon): \psi_{\varepsilon l}(\mathbf{r})=D_l(\varepsilon)\varphi_{\varepsilon l}(\mathbf{r})$. The factor $D_l(\varepsilon)$ depends upon the photoelectron energy ε, with l being its electron angular momentum. Outside the δ sphere the function $\psi_{\varepsilon l}(\mathbf{r})$ is a linear combination of $\varphi_{\varepsilon l}(\mathbf{r})$ and $\chi_{\varepsilon l}(\mathbf{r})$. The coefficients of the linear combination are defined by the matching conditions of the wave functions on the spherical shell, i.e., at $r=R$.

In the δ-potential approximation the differential two-electron photoionization of He@C_N is thus given by formula similar to Eq. (1), that includes, however, the factor $D_l(\varepsilon)$

$$\frac{d\sigma_i^{++}(\omega,\varepsilon)}{d\varepsilon} = \frac{32\sqrt{2}Z^2\pi}{3c\omega^{7/2}}|D_0(\varepsilon)|^2\left|\int \Psi_i(0,\mathbf{r})\varphi_{\varepsilon 0}(\mathbf{r})d\mathbf{r}\right|^2. \tag{4}$$

The expression for $|D_l(\varepsilon)|^2$ is derived in Refs. [21,22] and is presented as

$$|D_l(\varepsilon)|^2 \equiv \frac{(k/\Delta L)^2}{[u_{kl}(R)v_{kl}(R)-k/\Delta L]^2+u_{kl}^4(R)}. \tag{5}$$

Here $u_{kl}(R)$ and $v_{kl}(R)$ are functions connected to the radial parts of regular $\varphi_{\varepsilon l}(\mathbf{r})$ and irregular $\chi_{\varepsilon l}(\mathbf{r})$ functions by relations $u_{kl}(r)=r\varphi_{\varepsilon l}(r)$ and $\nu_{kl}(r)=r\chi_{\varepsilon l}(r)$; $k=\sqrt{2\varepsilon}$, ΔL is the discontinuity of the logarithmic derivative of the wave function at $r=R$, connected to the fullerene radius R and the electron affinity I_f of the empty C_N through the expression

$$\Delta L = -\beta(1+\coth \beta R), \tag{6}$$

where $\beta=\sqrt{2I_f}$. The formula obtained are valid for low enough energies of the slow photoelectron. Namely, its wave length should be much bigger than the thickness of the fullerene shell. The factor $D_l(\varepsilon)$, as it is seen from its definition, takes into account the reflection and refraction of the photoelectron’s l wave by the C_N shell potential.

At first one should calculate the ratio of differential cross sections (4), (3), and (2) $R_C(\varepsilon)$ that according to Eqs. (3) and (4) is independent upon ω

$$R_C(\varepsilon) \equiv d\sigma_i^{++}(\omega,\varepsilon)/d\sigma_i^{a++}(\omega,\varepsilon)=|D_0(\varepsilon)|^2, \tag{7}$$

and then turn to the ratio $R_{i,\text{ful}}$ of cross sections $\sigma^{++}(\omega)$ and $\sigma^{a++}(\omega)$, that are determined using Eq. (1) with $d\sigma_i^{++}(\omega,\varepsilon)/d\varepsilon$ given by Eqs. (4) and (2), respectively,

$$R_{i,\text{ful}} = \sigma_i^{++}(\omega)/\sigma_i^{a++}(\omega). \tag{8}$$

In the formulas we replace C_N by C, for simplicity.

It is evident from Eq. (7), that determined in this way $R_{i,\text{ful}}$ is ω independent at high ω. Since $\varphi_{\varepsilon 0}(\mathbf{r})$ and $\chi_{\varepsilon l}(\mathbf{r})$ are pure Coulomb functions, the functions u_{kl} and v_{kl} [from Eqs. (6) and (7)] are expressed via the regular $F_l(\eta,\rho)$ and irregular $G_l(\eta,\rho)$ Coulomb wave function, respectively. Namely, one has $u_{kl}(r)=F_l\left(-\frac{Z}{k},kr\right)$ and $v_{kl}(r)=G_l\left(-\frac{Z}{k},kr\right)$, i.e., regular and irregular Coulomb wave functions that can be found in Ref. [22].

Let us note that the formula (7) can be extended to lower ω. Indeed, the interaction between two ionized electrons is particularly essential near ionization threshold $\omega \geqslant I^{++}$, where the Wannier regime prevails. It is known that already several eV above threshold the Wannier expressions are no more valid. Therefore, it is reasonable to assume that at about 10 eV the interaction between outgoing electrons is inessential. One of them is represented by an s wave, while the other by a p wave, in order to preserve the total initial state angular momentum that is zero for He@C_N and $l=1$ for the photon. Due to action of the C_N shell the second electrons wave function is modified in the same way as $\varphi_{\varepsilon 0}(\mathbf{r})$ in Eq. (2). Thus, it is reasonable to expect that to take this action into account one has to introduce the factor $|D_1(\bar{\varepsilon})|^2$ into Eq. (7). As a result, one obtains instead of Eq. (7) the following expression:

$$\begin{aligned} R_C(\omega,\varepsilon) &\equiv d\sigma_i^{++}(\omega,\varepsilon)/d\sigma_i^{a++}(\omega,\varepsilon) \\ &= |D_0(\varepsilon)|^2|D_1(\omega-I^{++}-\varepsilon)|^2. \end{aligned} \tag{9}$$

Since for low and medium energies the cross section $d\sigma_i^{a++}(\omega,\varepsilon)/d\varepsilon$ cannot be calculated using Eq. (2), we have to use other sources of absolute values of it in order to obtain $R_C(\omega)$.

As such, either experimental data or results of existing calculations of differential in energy ε cross section can be used to substitute into

$$\begin{aligned} R_C(\omega) \equiv \int_0^{\omega-I^{++}} &|D_0(\varepsilon)|^2|D_1(\omega-I^{++}-\varepsilon)|^2 \\ &\times d\sigma_i^{a++}(\omega,\varepsilon)/\int_0^{\omega-I^{++}} d\sigma_i^{a++}(\omega,\varepsilon). \end{aligned} \tag{10}$$

In order to have a crude estimation of the role of both factors in Eq. (9), we have calculated in Eq. (10) the factor $R_C(\omega)$ using Eq. (1) well outside its range of validity $\omega \gg I^{++}$, which gives us $R_C^{(h)}(\omega)$.

Since at ω close to I^{++}, $d\sigma_i^{a++}(\omega,\varepsilon)/d\varepsilon$ is almost ω independent, as an estimation for $R_C(\omega)$ at $\omega \geqslant I^{++}$ can serve an approximate relation

$$R_C^{(l)}(\omega) \equiv \int_0^{\omega-I^{++}} |D_0(\varepsilon)|^2 |D_1(\omega - I^{++} - \varepsilon)|^2 d\varepsilon/(\omega - I^{++}). \tag{11}$$

Note, that in the approximation presented above for single-electron photoionization cross section $\sigma_i^{+}(\omega)$ of He@C_N one has

$$\sigma_i^{+}(\omega) = |D_1(\omega)|^2 \sigma_i^{a+}(\omega), \tag{12}$$

since for He the outgoing electron is a p wave. Using Eqs. (10) and (1), one can obtain a relation for the ratio $R_{++/+}(\omega) \equiv \sigma_i^{++}(\omega)/\sigma_i^{+}(\omega)$

$$R_{++/+}(\omega) = R_C(\omega) R_{++/+}^{a}(\omega)/|D_1(\omega - I^{++})|^2, \tag{13}$$

where $R_{++/+}^{a}(\omega) \equiv \sigma_i^{a++}(\omega)/\sigma_i^{a+}(\omega)$.

Up to now we have neglected the virtual excitation of C_N by the incoming photon with the frequency ω. It was demonstrated in Refs. [14,15] that this influence presents a factor $F(\omega) = |1 - \alpha(\omega)/R^3|^2$, where $\alpha(\omega)$ is the dynamic dipole polarizability of C_N. Using $\alpha(\omega)$ obtained in Ref. [15] and having in mind that $\omega \geqslant I^{++}$, one obtains for $F(\omega)$ an upper value of 1.4. Note that starting from about 60–70 eV the polarizability $\alpha(\omega)$ can be substituted accurately enough for its asymptotic high ω value $\alpha(\omega) \approx -\tilde{N}/\omega^2$, where $\tilde{N}$ is the number of collectivized electrons in C_N, namely, $\tilde{N} = 4N$. Here N is a number of carbon atoms in fullerene, as before. Thus, $F(\omega)$ can be presented as a monotonically decreasing with ω growth function $\eta_C(\omega) = [1 + 2\tilde{N}/(\omega^2 R^3)]$, that leads to the ratios $\tilde{R}_C(\omega,\varepsilon)$ and $\tilde{R}_C^{(l,h)}(\omega)$ for the endohedral and isolated atoms photoionization cross sections

$$\tilde{R}_C(\omega,\varepsilon) \simeq \eta_C(\omega) R_C(\omega,\varepsilon). \tag{14}$$

Instead of Eqs. (10) and (11) one has

$$\tilde{R}_C^{(l,h)}(\omega) \simeq \eta_C(\omega) R_C^{(l,h)}(\omega). \tag{15}$$

At $\omega = I^{++}$ the correcting factor η_C is close to 1.2 and decreases approaching unit, as it is seen from the definition of $\eta_C(\omega)$ with further growth of ω, at $\omega > I^{++}$.

Since we plan to extend the ratio $R_{i,\mathrm{ful}}$ as a function of ω up to values close to I^{++}, we plot upon the corresponding figure $\tilde{R}_{i,\mathrm{ful}} = \eta_C(\omega) R_{i,\mathrm{ful}}$. Note, that virtual excitation of C_N that are reduced to the factor $F(\omega)$ depending only upon ω are not altering the ratio $R_{++/+}(\omega)$.

Now let us estimate how the virtual excitation of C_N modifies the Coulomb interelectron V between two electrons in He by transforming it into V_{eff}. Taking into account that the He radius r_a is much smaller than R, one can estimate the ratio V_{eff}/V

$$\frac{V_{\mathrm{eff}}}{V} \approx \left| 1 - \left(\frac{r_a}{R}\right)^3 \frac{\tilde{N}}{\omega^2 R^3} \right|^2 \leqslant 1.007 \tag{16}$$

at $\omega \geqslant I^{++}$. Therefore, this correction can be neglected.

III. DETAILS OF CALCULATIONS

First of all, one should notice that the term $k/\Delta L$ in denominator of Eq. (5) was taken with the minus sign, whereas there was a plus sign in Refs. [20,21]. This is because the authors of the latter references used the irregular Coulomb functions $\bar{v}_{kl}(r) = -v_{kl}(r)$, while we used the Coulomb functions $v_{kl}(r)$ presented in the Ref. [22].

Equations (9)–(11) include the function $D_1(\bar{\varepsilon})$ at $\bar{\varepsilon} = 0$, for $\varepsilon = \omega - I^{++}$. It is clear that the Coulomb functions $F_l(-\frac{Z}{k}, kr)$ and $G_l(-\frac{Z}{k}, kr)$, presented in expression (5) for D_l^2, have singularities at zero energy, i.e., at $k = 0$ that corresponds to $\bar{\varepsilon} = 0$. However, the presentations of Coulomb functions given in Ref. [22] enable us to obtain the following limit relations:

$$\lim_{k\to 0} \frac{u_{kl}(r)}{\sqrt{k}} \equiv f_l(Z,r) = \sqrt{\pi r} J_{2l+1}(\sqrt{8Zr}), \tag{17}$$

$$\lim_{k\to 0} \frac{v_{k0}(r)}{\sqrt{k}} \equiv g_0(Z,r) = \frac{p(2Zr)}{\sqrt{2\pi Z}} - \sqrt{\frac{r}{\pi}}[2\gamma - 1 + \ln(2Zr)] J_1(\sqrt{8Zr}). \tag{18}$$

Here γ is Euler's constant $J_\mu(x)$ is a usual Bessel function of the first kind and $p(\alpha)$ is the following sum, which is infinite but rapidly convergent: $p(\alpha) = \sum_{j=0}^{\infty} P_j(\alpha)$, where $P_j(\alpha)$ could be obtained by the recurrence relations

$$P_j = -\frac{\alpha}{j(j-1)} \left[(-1)^j \frac{(2j-1) j \alpha^{j-1}}{(j!)^2} + P_{j-1} \right] \tag{19}$$

with the initial values $P_0 = 1$, $P_1 = 0$. Functions $g_l(Z,r)$ for $l > 0$ could be then obtained by using Eqs. (17)–(19) and the following recurrence relation:

$$g_l(Z,r) f_{l-1}(Z,r) = g_{l-1}(Z,r) f_l(Z,r) + \frac{l}{Z}. \tag{20}$$

The latter is a consequence of the Wronskian relation [see Eq. (14.2.5) in Ref. [22]] for the regular and irregular Coulomb functions. Note that Eq. (17) for the regular Coulomb functions could be found in numerous handbooks on nonrelativistic quantum mechanics (see, e.g., Ref. [23]), within the accuracy of a normalization factor. However, we did not find in scientific literature the corresponding relations (18)–(20) for irregular Coulomb functions.

Using the limit relations (17)–(20), one could present Eq. (5) for the zero energy in the form

$$D_l^2(0) = \frac{1}{[(\Delta L) g_l(Z,R) f_l(Z,R) - 1]^2 + (\Delta L)^2 f_l^4(Z,R)}. \tag{21}$$

In particular, the helium atom expression (21) yields $D_0^2(0) = 1.38590$ and $D_1^2(0) = 3.09129$.

The function Ψ_i can be obtained using the variational principle that minimizes the initial state energy. One has to have in mind that, generally speaking, this procedure is able to reproduce an absolutely accurate initial state energy, leading to a wave function that satisfies the precise Schrödinger equation for two electrons in the field of a nucleus with the

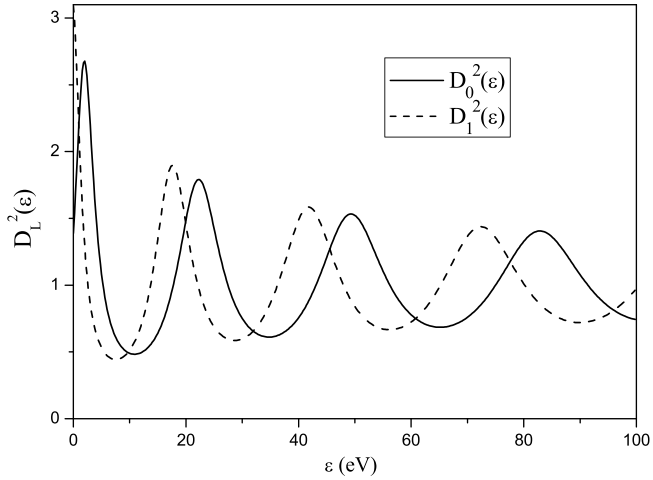

FIG. 1. The reflection and refraction factors D_L^2 $(L=0,1)$ as a function of photoelectron energy ε for He@C$_{60}$.

charge Z. In practical implementation, however, the variation wave functions reproduces the initial energy approximately and therefore is good on average.

As to photoionization, since one of the outgoing electrons is fast, its wave function is a plane wave with a short wavelength in the atomic scale. Therefore, the photoeffect is able to test the short range behavior of $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)$, namely, as is seen from Eq. (1), $\Psi_i(0,\mathbf{r})$.

This is why instead of a variational, we use a locally correct wave function [24–26], that describes with high accuracy the two-electron photoionization [18] and some average characteristics of the initial state.

IV. RESULTS OF CALCULATIONS

Here we present the results of our calculations for the two-electron photoionization of He@C$_{60}$, He@C$_{70}$, and He@C$_{76}$. For the C$_{60}$ fullerene, the radius R is equal to 6.64 a.u. and the electron affinity of the empty fullerene I_f $=2.65$ eV [20]. Although C$_{60}$ is already nonspherical, we simplify the real shape substituting it for an equiareal sphere [27]. The same was done for C$_{70}$ and C$_{76}$. Thus, we obtained $R=7.21$ a.u. and $R=7.53$ a.u. for C$_{70}$ and C$_{76}$, respectively. Corresponding values of electron affinity $I_f(\mathrm{C}_{70})=2.72$ eV and $I_f(\mathrm{C}_{76})=2.88$ eV could be found in Refs. [28,29]. The initial state of He considered in this paper is $i=1$ s, i.e., $l=0$. The two-electron ionization potential $I^{++}=2.9037$ a.u. is the ground state energy of the helium atom.

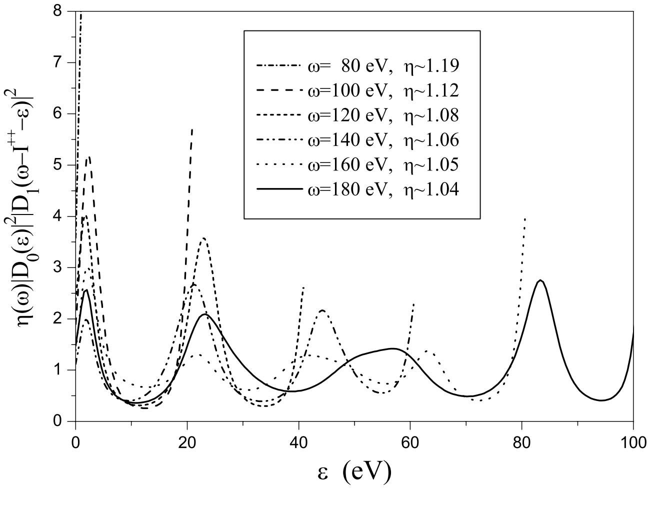

FIG. 2. The cross sections ratio $\widetilde{R}_{\mathrm{C}_{60}}(\omega,\varepsilon)$ as a function of photoelectron energy ε for different values of photon energy ω.

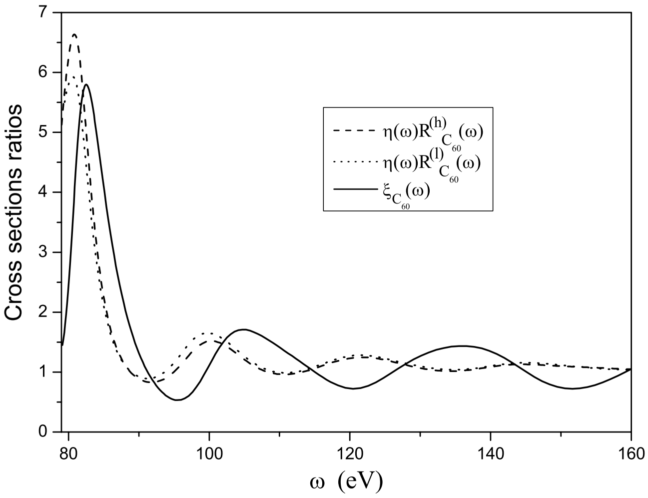

FIG. 3. The cross sections ratios $\widetilde{R}^{(h)}_{\mathrm{C}_{60}}$, $\widetilde{R}^{(l)}_{\mathrm{C}_{60}}$, and $\xi_{\mathrm{C}_{60}}(\omega)$ $=R_{\mathrm{C}_{60}}(\omega)/D_1^2(\omega-I^{++})$ as functions of ω for He@C$_{60}$.

The results for $R_{\mathrm{C}_{60}}(\varepsilon)$ from Eq. (7) are presented in Fig. 1 together with the function $D_1^2(\varepsilon)$ from Eqs. (17)–(21). As was expected and similar to the case of one-electron photoionization, the ratio $R_{\mathrm{C}_{60}}(\varepsilon)$ is a strongly oscillating function of ε.

Figure 2 depicts $\widetilde{R}_{\mathrm{C}_{60}}(\omega,\varepsilon)$, given by Eq. (14) for several ω as functions of ε. It is not incidental that the curves behavior at $\varepsilon=0$ and $\varepsilon=\omega-I^{++}$ are different. This is because one of the electrons is represented by an s wave, while the other by a p wave. Note that $\widetilde{R}_{\mathrm{C}_{60}}(\omega,\varepsilon)$ becomes a promi-

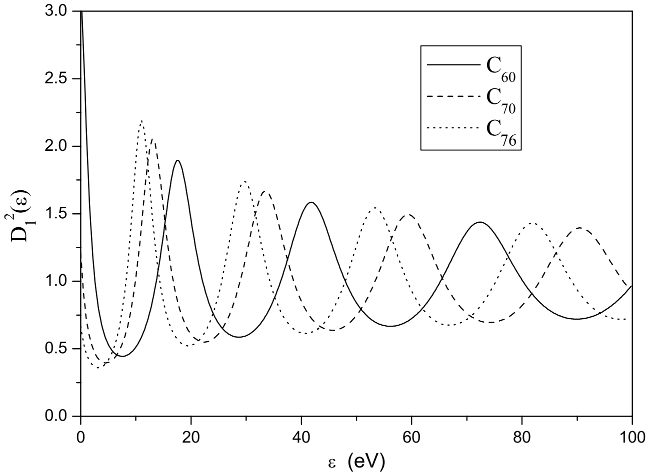

FIG. 4. The reflection and refraction factors D_1^2 as a function of photoelectron energy ε for He@C_N with $N=60,70,76$.

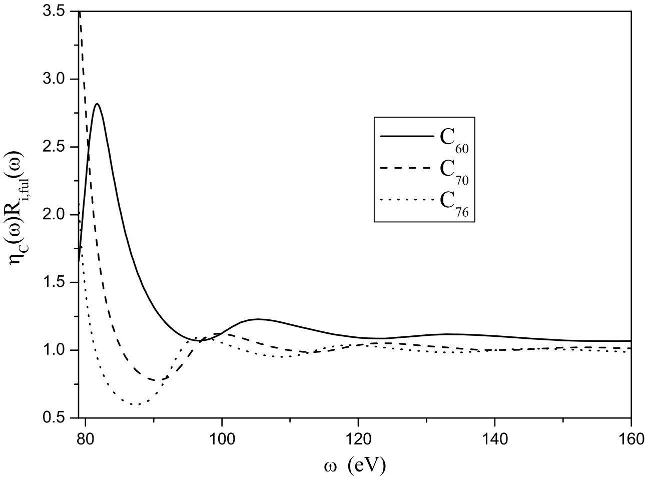

FIG. 5. The cross sections ratio $\tilde{R}_{i,\mathrm{ful}}$ as a function of photon energy ω for He@C_{60}, He@C_{70}, and He@C_{76}.

nently variating curve already for $\omega - I^{++} \geqslant 20$ eV. For $\omega - I^{++} \geqslant 60$ eV it has many oscillations.

Figure 3 presents the relations $\tilde{R}_{C_{60}}(\omega)$ given by Eqs. (10), (11), and (15) for the both ε distributions, that are valid, respectively, at high and low ω. It is seen that both curves $\tilde{R}^{(h)}_{C_{60}}(\omega)$ and $\tilde{R}^{(l)}_{C_{60}}(\omega)$ prominently oscillate up to $\omega \sim 150$ eV and are close to each other. This permits us to suggest that the curves $\tilde{R}^{(h,l)}_{C_{60}}(\omega)$ are almost valid for correct ε distribution instead of only their limiting cases for high and low ω. The strongest is the role of the fullerene shell at $\omega < 110$ eV.

The results of the calculations using Eq. (13) for He@C_{60}, namely, the ratio

$$\xi(\omega) \equiv R_{++/+}(\omega)/R^{a}_{++/+}(\omega) = R_C(\omega)/|D_1(\omega - I^{++})|^2 \quad (22)$$

are also presented in Fig. 3. It is seen that at low ω, i.e., near the I^{++} threshold, the ratio $\xi(\omega)$ reaches its biggest value. Note, however, that with ω growth it is still a prominently oscillating curve, while the ratios $\tilde{R}_{C_{60}}(\omega)$ very rapidly become almost ω independent. This signals that the ratio $R_{++/+}$ can be modified as compared to its pure He atom values up to high ω.

In Fig. 4 we present factors $|D_1(\varepsilon)|^2$, given by Eq. (5), for C_{60}, C_{70}, and C_{76}. The results for different fullerenes look like almost a single curve shifted in phase, although there are some differences in amplitudes, as well.

Figure 5 presents the results for the ratio $\tilde{R}_{i,\mathrm{ful}}(\omega) = \eta_C(\omega)R_{i,\mathrm{ful}}(\omega)$, where $R_{i,\mathrm{ful}}$ is determined by Eq. (8) for C_{60}, C_{70}, and C_{76}. As one could see, with ω growth these ratios rapidly approaches the asymptotic value $\tilde{R}_{i,\mathrm{ful}} \to 1$. Note, that in Eq. (8) we assumed that slow electron wave function is modified by the C_N shell. In fact, this is incorrect already for $\omega \geqslant 160$ eV. While at low ω the differences between $\tilde{R}_{i,\mathrm{ful}}$ for C_{60}, C_{70}, and C_{76} are large, it almost disappear for higher ω, with values for C_{60} slightly bigger, than for C_{70} and C_{76}.

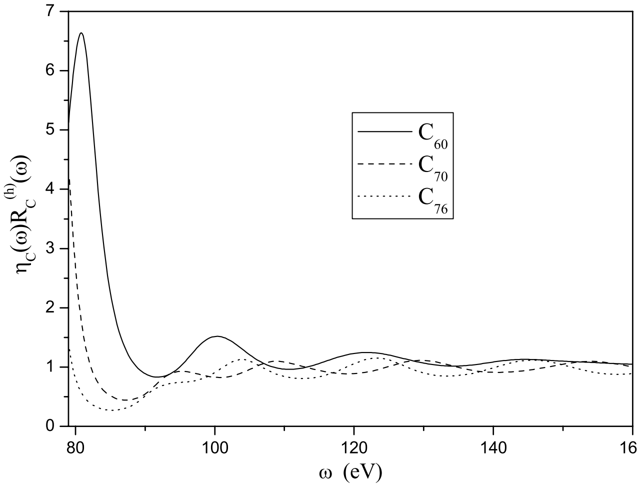

FIG. 6. The cross sections ratios $\tilde{R}^{(h)}_{C}$ as a function of ω for He@C_{60}, He@C_{70}, and He@C_{76}.

Figure 6 presents $\tilde{R}^{(h)}_{C}(\omega)$, given by Eqs. (15) for He@C_{60}, He@C_{70}, and He@C_{76}. Note, that according to our calculations for C_{70} and C_{76} the difference between high (h) and low (l) photon energy limits is inessential. These ratios are again different for C_{60}, C_{70}, and C_{76} only at low ω. With the ω increase all the ratios tend to one.

In Figs. 4–6 we compare the results for C_{70} and C_{76} with that of C_{60}. Therefore, we repeat on them the curves for C_{60} presented in Figs. 1–3.

Qualitatively, the picture of the fullerene shell effects are similar in all considered objects. Indeed, as is evident from pure qualitative physical considerations the shell results in prominent oscillatory effects. The zero-range potential model overestimates to some extent the sharpness of oscillations but without any doubt preserves their existence. It is seen that the fullerene radius and the value of electron affinity affects the considered ratios prominently but only in the two-electron photoionization threshold region. As is clear from qualitative consideration the effect of the fullerene shell dies out already at $\omega \geqslant 180$ eV.

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