Multielectron processes in photoionization of endohedral atoms at high photon energies

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We calculate the probability of inelastic processes in the fullerene shell of an endohedral atom which follow the ionization of the caged atom by a high-energy photon. We demonstrate that the probability is close to unity in a large interval of the photoelectron energies. The inelastic processes are determined mainly by the final-state interactions, which have to be included beyond the perturbative approach. At photoelectron energies E of the order of several keV the probability drops as $1/E$. It is determined by the final-state interactions, which can be treated perturbatively. At still larger energies the probability is determined by the shake-off mechanism and does not depend on energy E. A model for calculating the shake-off contribution is also suggested. The actual calculations are carried out for the endohedral atoms $A@C_{60}$ and $A@C_{20}$.

I. INTRODUCTION

Until now, to the best of our knowledge, the papers on the multiple photoionization (mainly the double photoionization) of the endohedral atoms, i.e., of the systems consisting of an atom A caged inside the fullerene shell C_N, have focused on the case when all photoelectrons were ejected from the caged atom [1,2]. Here we consider another channel in which ejection of one electron from the caged atom is accompanied by inelastic multielectron processes in the fullerene shell (FS). These may be a single-electron excitation or ionization, double ionization, etc. We focus on the case when the energies of the photoelectrons ejected from the internal atom $E = \omega - I_a$ are large enough,

$$E \gg 1 \text{ Ry}. \tag{1}$$

Here ω and I_a are the energies of the photon and of the ionized state of the caged atom. We assume that the radius R of the FS is much larger than the size of the ionized state of the internal atom r_a,

$$R \gg r_a. \tag{2}$$

We consider, in agreement with what is known about fullerenes, that the thickness of the FS

$$\Delta \ll R. \tag{3}$$

We admit that the caged atom can be shifted from the center of the sphere.

In another channel the photon knocks out a FS electron, and the latter ionizes the internal atom. This mechanism requires a special direction for the momentum of the electron ejected from the FS. The probability is quenched by a small factor of the order of r_a^2/R^2. Thus we neglect the contribution of this mechanism.

As well as in the high-energy double photoionization of atoms [3], we can separate three mechanisms of the process in endohedrals $A@C_N$ (N is the number of the carbon atoms which constitute the fullerene). In the shake-off (SO) mechanism an atomic electron is moved to the continuum due to its direct interaction with the incoming photon. The second electron is ejected from the FS to the continuum because of the

sudden change of the effective field of the atom caged inside the FS of the endohedral. In the final-state-interaction (FSI) mechanism the second electron is knocked to the continuum due to the direct interaction of the ionized atomic electron with an electron belonging to the FS. In the quasifree mechanism (QFM), which was predicted long ago [3] and discovered recently in the experiments [4], absorption of the photon by the two-electron system takes place almost without participation of the nucleus.

In the double photoionization of atoms both cross section σ^{2+} and its spectrum are the result of interplay between SO, FSI, and QFM. If the photon energy ω is large enough, the SO mechanism dominates, and the double-to-single cross-section ratio $R(\omega) = \sigma^{2+}(\omega)/\sigma^+(\omega) = \text{const}$. At higher energies the contribution of the QFM to this ratio becomes important. At $\omega \geq c^2$ (c is the speed of light, and the atomic system of units is used) the contributions of SO and QFM to $R(\omega)$ are of the same order of magnitude.

We shall analyze the interplay of these mechanisms in the photoionization of the caged atom followed by excitations of the FS. Since the QFM requires the coalescence of the two bound electrons [5], it does not contribute to the considered channel. Thus we consider only the interplay between the SO and the FSI.

Because of the lack of detailed information about the FS wave functions, we calculate only the sum of the cross sections of inelastic processes, also called the cross section of absorption. Ionization of the internal atom can be followed by ionization of the FS or its transitions to excited states, double ionization of the FS, etc. We shall see that this sum is not sensitive to the details of the structure of the FS functions.

From Eqs.(1) and (2) the cross section of the process with a transition of the FS to a particular final state n contains the cross section of the photoionization of the isolated atom σ_γ as a factor. The factorization is violated by terms of the order of V/E, with V being the potential of the FS "felt" by the photoelectron. Since $|V| \leq 1$ Ry, such terms can be neglected in our approach. Thus we write

$$\sigma_n = \sigma_\gamma S_n. \tag{4}$$

We investigate the behavior of the ratio

$$r(E) = \frac{\sigma_A(E)}{\sigma_\gamma(E)}, \tag{5}$$

where σ_γ and σ_A are the cross section of photoionization of the encapsulated atom and the absorption cross section, respectively. The energy of the photoelectron is $E = \omega - I_a$. We calculate the absorption cross section σ_A as the difference between the total cross section

$$\sigma_t = \sigma_\gamma S_t, \quad S_t = \sum_n S_n, \tag{6}$$

and the elastic cross section $\sigma_0 = \sigma_\gamma S_0$, which describes the process in which the FS state does not change, i.e.,

$$r(E) = S_t(E) - S_0(E). \tag{7}$$

We employ the model in which we assume that the electrons of the caged atom and those of the FS move in an independent way; that is, their wave functions do not mix. Thus we assume that the cross section of photoionization of the encapsulated atom σ_γ is equal to that of the isolated atom. It was shown [6–8], however, that in some cases this approach may not be true for the outer electrons since their mixing, called "hybridization," with those of the FS becomes important. In this case our analysis, which does not include the hybridization effects, is valid for inner subshells of the caged atom.

Since the FS electrons are separated from the caged atom by distances of the order of $R \gg 1$, all their interactions and their changes after the photoionization are quenched by a factor of the order of $1/R$, and the probability of the SO is of the order of $1/R^2$. Note that the FS reacts to the change of the field as a whole and the probability of the SO does not depend explicitly on the number of the electrons in the FS.

The FSI between the photoelectron moving with momentum **p** and *each* of the FS electrons is determined by the Sommerfeld parameter [9]

$$\xi = \frac{1}{pc} \ll 1, \tag{8}$$

with $p = |\mathbf{p}|$. Here we neglected the momenta of the FS electrons. One can write

$$\xi^2 \approx \frac{1}{2E} \ll 1. \tag{9}$$

However, due to the large number $N \gg 1$ of the FS electrons the actual parameter of the FSI between the photoelectron and the FS is $N\xi^2$. In the broad interval of energies $N\xi^2 \geqslant 1$. At these energies (we call them *intermediate energies*) the FSI provides the leading contribution to the absorption cross section. Due to conditions expressed by Eqs. (2) and (3) it appeared to be possible to find the contribution beyond the perturbative approach in a model-independent way [10]. The ratio $r(E)$ was shown to be close to unity for energies which are large enough ($E \gg 50$ eV) and for which $N\xi^2 \geqslant 1$. This is $E \leqslant 1.5$ keV for the fullerene C_{20} and $E \leqslant 5$ keV for the fullerene C_{60}.

In this paper we extend the analysis to the high-energy region where $N\xi^2 \ll 1$ and both FSI and SO mechanisms are important. Here the perturbative treatment of the FSI is possible. Calculating the contribution of the SO mechanism

requires knowledge of the ground-state wave functions of the FS. We suggest a simple model which assumes that the FS electrons have a uniform distribution. This enables us to trace the energy dependence of the function $r(E)$ determined by Eq. (5).

In the next section we calculate the FSI in the perturbative approach, following [11], and sum up all the perturbative series [10]. In Sec. III we suggest a model for the SO. In Secs. IV and V we present the partial-wave analysis and the results for the ratio $r(E)$. We summarize in Sec. VI.

II. FINAL-STATE INTERACTIONS

A. Perturbative approach

The amplitude of a process which includes the final-state interaction between the fast electron and the electronic shell up to terms of the order of ξ^2 is [11]

$$F_x = F_x^{(0)} + F_x^{(1)} + F_x^{(2)}, \tag{10}$$

where the upper index denotes the number of interactions between the fast electron and the FS and index x labels the final state of the FS. The amplitudes $F_x^{(i)}$ contain the amplitude of ionization of the isolated atom F_γ as a factor [11]:

$$F_x^{(i)} = F_\gamma T_x^{(i)}, \quad i = 0,1,2. \tag{11}$$

Here $T_x^{(0)} = \langle \Phi_x | \Psi_i \rangle$, Ψ_i is the initial-state wave function of the FS with the encapsulated atom, and Φ_x is the final-state wave function of the FS with the encapsulated ion. The amplitude $T_x^{(0)}$ describes the SO, where the FSI are neglected (the "zero-order" FSI term). The accuracy of this equation is $V_a/E \ll 1$, with V_a being the potential energy of the photoelectron in the field of the caged atom.

One can write for the cross section of the process with a transition of the FS to a particular final state x [11] [see Eq. (4)]

$$S_x = \left|T_x^{(0)}\right|^2 + 2T_x^{(0)}\mathrm{Re}T_x^{(1)} + \left|\mathrm{Im}T_x^{(1)}\right|^2 + 2T_x^{(0)}\mathrm{Re}T_x^{(2)}. \tag{12}$$

Now we calculate the FSI amplitudes. One can write

$$T_x^{(1)} = \langle \Phi_x | U_1 | \Psi_0 \rangle, \tag{13}$$

where $U_1 = \sum_k U_1(\mathbf{r}^{(k)})$, with k labeling the FS electron, and $U_1(\mathbf{r}^{(k)})$ is its interaction with the photoelectron in the lowest order of the FSI. One can write

$$U_1(\mathbf{r}^{(k)}) = \frac{1}{c} \int \frac{d^3 f}{(2\pi)^3} G(\mathbf{f}) g(f) e^{i(\mathbf{f} \cdot \mathbf{r}^{(k)})}, \tag{14}$$

where $G(f) = 2[\mu^2 - (\mathbf{p} + \mathbf{f})^2 + i\nu]$, with $\mu^2 = p^2 + 2\varepsilon_{fi}$, is the free-electron propagator. The energy ε_{fi} is transferred by the FSI, $g(f) = 4\pi/(f^2 + \lambda^2)$, $\lambda \to 0$. Keeping only the term proportional to the large momentum p in the denominator of the electron propagator, we can put

$$G(\mathbf{f}) = \frac{-2}{2(\mathbf{p} \cdot \mathbf{f}) - i\nu}. \tag{15}$$

Using the well-known formula

$$\frac{1}{a}\frac{1}{c} = \int_0^1 \frac{dx}{[ax + c(1-x)]^2}, \tag{16}$$

we obtain

$$-\frac{1}{2(\mathbf{p} \cdot \mathbf{f}) - i\nu} \frac{1}{f^2 + \lambda^2}$$

$$= -\int_0^1 \frac{dx}{[2(\mathbf{p} \cdot \mathbf{f})(1 - x) + f^2 x + \lambda^2 x - i\nu]^2}. \quad (17)$$

Introducing $y = (1 - x)/x$ and $\mathbf{f}' = \mathbf{f} + \mathbf{p}y$ and integrating over $\mathbf{f}'$ by using the relation

$$\int \frac{d^3 f}{(2\pi)^3} \frac{4\pi e^{i(\mathbf{f} \cdot \mathbf{r})}}{(f^2 - b^2 - i\nu)^2} = \frac{1}{2b} \frac{\partial}{\partial b} \frac{e^{ibr}}{r} = i\frac{e^{ibr}}{2b},$$
$$b^2 = p^2 y^2 - \lambda^2, \quad (18)$$

we find

$$U_1(\mathbf{r}^{(k)}) = -i\frac{1}{c} \int_0^\infty \frac{dy}{b(y)} e^{ib(y)r^{(k)} - i(\mathbf{p} \cdot \mathbf{r}^{(k)})y}. \quad (19)$$

This leads to

$$U_1 = i\xi \sum_k \ln\left(r^{(k)} - r_z^{(k)}\right)\lambda. \quad (20)$$

Thus the amplitude $T_x^{(1)}$ is mostly imaginary,

$$T_x^{(1)} = i\xi \langle \Phi_x | \sum_k \ln\left(r^{(k)} - r_z^{(k)}\right)\lambda |\Psi_0\rangle. \quad (21)$$

The imaginary part dominates since the pole of the electron propagator provides the leading contribution. This means that the photoelectron passes the distances of the order of the FS radius $R \gg 1$ and interacts with the FS electrons at the region of their location. The divergence at $\lambda = 0$ is just the Coulomb phase of the interaction between the photoelectron and the electronic shell [11]. The divergent contributions will cancel after the second-order terms are taken into account.

Since the leading contribution to $T_x^{(1)}$ is imaginary, while $T_x^{(0)}$ is real, the leading nonvanishing contribution of the FSI is of the order of ξ^2. In order to find it one has to include the second-order amplitude $T_x^{(2)}$ and the terms of the order of f/p in the first-order amplitude $T_x^{(1)}$.

The second-order amplitude can be written as

$$T_x^{(2)} = \langle \Phi_x | U_2 | \Psi_0 \rangle, \quad (22)$$

with

$$U_2 = \frac{1}{c^2} \sum_{k_1 k_2} \int \frac{d^3 f_1}{(2\pi)^3} \frac{d^3 f_2}{(2\pi)^3} G(\mathbf{f_1}) g(f_1)$$
$$\times G(\mathbf{f_1} + \mathbf{f_2}) g(f_2) e^{i(\mathbf{f_1} \cdot \mathbf{r}^{(k_1)})} e^{i(\mathbf{f_2} \cdot \mathbf{r}^{(k_2)})}. \quad (23)$$

Using Eq. (15) for the Green's function G and putting in the integrand

$$\frac{1}{(\mathbf{p} \cdot \mathbf{f_1})} \frac{1}{[\mathbf{p}(\mathbf{f_1} + \mathbf{f_2})]}$$
$$= \frac{1}{2}\left(\frac{1}{(\mathbf{p} \cdot \mathbf{f_1})} \frac{1}{[\mathbf{p}(\mathbf{f_1} + \mathbf{f_2})]} + \frac{1}{(\mathbf{p} \cdot \mathbf{f_2})} \frac{1}{[\mathbf{p}(\mathbf{f_1} + \mathbf{f_2})]}\right) \quad (24)$$
$$= \frac{1}{2} \frac{1}{(\mathbf{p} \cdot \mathbf{f_1})} \frac{1}{(\mathbf{p} \cdot \mathbf{f_2})},$$

we find that

$$U_2 = U_1^2/2. \quad (25)$$

Here again the FSI takes place in the region of the FS. As for the terms of the order of f/p in the amplitude $T_x^{(1)}$, they determine its real part $\text{Re}\,T_x^{(1)}$. They describe the interactions between the photoelectron while it is close to the caged atom. Thus they have additional factor $1/R \ll 1$. Hence, the second term on the right-hand side (RHS) of Eq. (12) is

$$T_x^{(0)}\text{Re}\,T_x^{(1)} \approx \frac{\xi^2 N}{R} |\langle \Phi_x | \Psi_0 \rangle|^2 \approx \frac{\xi^2 N}{R^3}. \quad (26)$$

Thus neglecting terms of the order of $1/R^2$ in the FSI terms, we find

$$S_t = 1, \quad S_0 = \left|T_0^{(0)}\right|^2 + |\langle \Psi_0 | U_1 | \Psi_0 \rangle|^2 - \langle \Psi_0 | U_1^2 | \Psi_0 \rangle. \quad (27)$$

Here we employed the closure condition

$$\sum_x \Phi_x |\rangle\langle \Phi_x| = 1. \quad (28)$$

From Eq. (3) we can put $r^{(k)} = R$ in Eq. (20), resulting in

$$U_1 = i\xi\Lambda, \quad \Lambda = \sum_k \ln(1 - t^{(k)}), \quad (29)$$

with $t^{(k)} = r_z^{(k)}/r^{(k)}$. Thus Eq. (27) takes the form

$$S_0 = \left|T_0^{(0)}\right|^2 + \xi^2(|\langle \Psi_0 | \Lambda | \Psi_0 \rangle|^2 - \langle \Psi_0 | \Lambda^2 | \Psi_0 \rangle). \quad (30)$$

Here the three terms on the RHS describe the SO, FSI, and their interference. respectively. Direct calculation provides

$$r(E) = \zeta + \xi^2 N, \quad \zeta = 1 - \left|T_0^{(0)}\right|^2. \quad (31)$$

Here we neglected the higher-order term $\zeta\xi^2 N$.

Employing the closure condition requires that the energy E is large enough to include all important excited states

$$E \gg \bar{\varepsilon}, \quad (32)$$

with $\bar{\varepsilon}$ being the energy loss of the photoelectron. At large energies $\varepsilon \gg I_{\text{FS}}$ the energy distributions drop as $1/\varepsilon^2$, and thus $\bar{\varepsilon}$ is determined by $I_{\text{FS}} \ll \varepsilon \ll E$. It is [12]

$$\bar{\varepsilon} = \frac{\xi^2 N}{4R^2} \ln\frac{E}{I_{\text{FS}}}. \quad (33)$$

Thus we need $E \gg 50$ eV for both C_{60} and C_{20}.

B. Beyond the perturbative approach

One can see that Eq. (24) can be generalized for the case of an arbitrary number n of interactions between the photoelectron and the FS. Introducing $a_n = \mathbf{p} \cdot \mathbf{f_1} + \mathbf{p} \cdot \mathbf{f_2} + \cdots + \mathbf{p} \cdot \mathbf{f_n}$, we can write

$$\frac{1}{a_1} \cdot \frac{1}{a_2} \cdot \ldots \cdot \frac{1}{a_n} = \frac{1}{n!} \frac{1}{a_1^n}. \quad (34)$$

This equation, which can be proved by the induction method, was used to calculate the radiative corrections in the electromagnetic interactions [13]. Thus for the interaction of the nth order between the photoelectron and the FS,

$$U_n = \frac{U_1^n}{n!}. \quad (35)$$

We denote $U_0 = 1$ and find for the total amplitude, which also includes the SO (zero order in FSI) term,

$$T_x = \sum_n T_x^{(n)} = \langle \Phi_x | e^{i\xi\Lambda} | \Psi_0 \rangle, \tag{36}$$

with Λ defined by Eq. (26). Employing Eq. (3), we can put $r^{(k)} = R$ and find for any excited state

$$T_x = \langle \Phi_x | \Pi_k (1 - t^{(k)})^{i\xi} | \Psi_0 \rangle, \tag{37}$$

with $t^{(k)} = \mathbf{p}\mathbf{r}^{(k)}/p r^{(k)}$. Here we omitted the constant factor $(R\lambda)^{i\xi}$.

The absorption cross section can be defined as the difference between the total cross section and the elastic one. At large E the sum over the exited states of the FS can be calculated by employing the closure condition, as in the previous section. This provides

$$
\begin{aligned}
r(E) &= 1 - |\langle \Phi_0 | e^{i\xi\Lambda} | \Psi_0 \rangle|^2 \\
&= 1 - |\langle \Phi_0 | \Pi_k (1 - t^{(k)})^{i\xi} | \Psi_0 \rangle|^2,
\end{aligned}
\tag{38}
$$

and thus

$$r(E) = 1 - \frac{|T_0^{(0)}|^2}{(1+\xi^2)^{N_1}} = 1 - e^{-N_1 \ln(1+\xi^2)} |T_0^{(0)}|^2, \tag{39}$$

with N_1 being the number of electrons which can participate in the process. At $E \leqslant I_c$, with $I_c \approx 300$ eV being the binding energy of the core electrons in the FS, only the valence FS electrons can participate. Thus $N_1 = 4N$. At larger energies all electrons participate, and $N_1 = 6N$. Here we do not need the actual value of the SO amplitudes. It is sufficient to know that $1 - |T_0^{(0)}|^2 \ll 1$.

Thus we can write

$$r(E) = 1 - e^{-N_1 \ln(1+\xi^2)}. \tag{40}$$

If the photon energy is so large that $N\xi^4 \ll 1$ (i.e., $E \gg 300$ eV for C_{60}, $E \gg 100$ eV for C_{20}), we find

$$r(E) = 1 - e^{-N\xi^2}. \tag{41}$$

At these energies all the FS electrons participate, and $N_1 = 360$ for C_{60}, while $N_1 = 120$ for C_{20}. At $N\xi^2 \ll 1$ the second equality of Eq. (39) provides the perturbative behavior (31).

In the broad energy region $r(E)$ is close to unity. At $E = 2$ keV we find that for C_{60} $1 - r(E) \approx 0.09$; that is, $r(E)$ is still very close to unity. At $E = 5$ keV, $r(E) \approx 0.62$, dropping as $1/E$ at larger energies, following Eq. (31). For C_{20} the ratio $r(E)$ reaches this value at $E \approx 1.7$ keV.

Now we focus on the region where $N\xi^2 \leqslant 1$. Here we need some model for the SO.

III. SHAKE-OFF

A. General equation

Let us totally neglect the FSI. The SO amplitude is

$$F_{SO} = F_\gamma \langle \Phi_x | \Psi_0 \rangle. \tag{42}$$

Recall that F_γ is the amplitude of photoionization of the caged atom, and Ψ_0 describes the ground state of the FS electrons moving in the superposition of its self-consistent field and that of the internal atom. In the final state Φ_x the electrons "feel" the self-consistent field of the FS and that of the ion with the

hole in its electronic shell. The matrix element on the RHS of Eq. (42) obtains nonzero values only if the initial and final states have the same angular momenta. Thus the SO can lead to only the monopole transitions.

The sum of the cross sections of inelastic processes can be written as

$$\sigma_{SO} = \sigma_\gamma (1 - \langle \Phi_0 | \Psi_0 \rangle^2), \tag{43}$$

where σ_γ is the cross section of the photoionization and $|\Phi_0\rangle$ is the ground state of the FS with a hole in the electronic shell of the caged atom created by the photon impact.

B. A model for the ground state

The wave function Ψ_0 is strongly quenched outside the region

$$R \leqslant r \leqslant R + \Delta, \tag{44}$$

with the radial part depending on

$$x = r - R, \quad 0 \leqslant x \leqslant \Delta. \tag{45}$$

The same is true for the function Φ_0. However, the values of parameters R and Δ in state $|\Phi_0\rangle$ differ from those in state $|\Psi_0\rangle$.

To estimate the matrix element $\langle \Phi_0 | \Psi_0 \rangle$ in Eq. (43) we assume that in the ground state the FS density does not depend on x. Under this assumption the wave function of the FS electrons with the angular momentum ℓ is

$$\Psi_i(\mathbf{r}) = \left(\frac{N_\ell}{V} \right)^{1/2} Y_{\ell m}(\Omega) \tag{46}$$

for r in the interval determined by Eq. (45), and it vanishes otherwise (Ω is the solid angle). In this equation $V = 4\pi R^2 \Delta$ is the volume of the FS.

The FS electrons can be viewed as moving in an effective self-consistent field U_i which also does not depend on x. The Thomas-Fermi equation

$$\rho_0 = (2U_0)^{3/2} \frac{1}{3\pi^2} \tag{47}$$

relates the electron density ρ_0 and the potential

$$U_0 = \frac{1}{2} \left(3\pi^2 \frac{N}{V} \right)^{2/3}. \tag{48}$$

Here N is the total number of active electrons.

After the ejection of the photoelectron the new value of the potential is

$$U_f = U_0 + U_h, \tag{49}$$

where U_h is the potential created by the hole in state n of the internal atom,

$$U_h(r) = \int d^3 r_a \frac{\rho_n(\mathbf{r_a})}{|\mathbf{r} - \mathbf{r_a}|} \approx \frac{1}{r} \approx \frac{1}{R}, \tag{50}$$

where ρ_n is the electron density in state n and $\mathbf{r_a}$ and $\mathbf{r}$ are the coordinates of the atomic electron and of that in the FS.

Thus the final-state wave function can be written as

$$\Phi_0(\mathbf{r}) = \sum_\ell \frac{N_\ell}{V'} Y_{\ell m}(\Omega), \tag{51}$$

with

$$V' = V + \frac{3}{2}\frac{1}{RU_0}. \tag{52}$$

Employing Eqs. (46) and (51), we obtain

$$\langle \Phi_0 | \Psi_0 \rangle = 1 - \frac{3}{4}\frac{1}{RU_0}. \tag{53}$$

Assuming, following [14], that the values of the FS parameters for the fullerene C_{60} are

$$R = 6.02, \quad \Delta = 1.25 \tag{54}$$

(in this case $N = 240$), we find

$$1 - \langle \Phi_0 | \Psi_0 \rangle = 0.046, \quad \langle \Phi_0 | \Psi_0 \rangle^2 = 0.91. \tag{55}$$

The numerical results do not depend strongly on the actual values of the parameters. For example, taking $R = 5.75$ a.u. and $\Delta = 1.89$ a.u. [15], we find

$$1 - \langle \Phi_0 | \Psi_0 \rangle = 0.060, \quad \langle \Phi_0 | \Psi_0 \rangle^2 = 0.88.$$

For the fullerene C_{20} we can put, following [16], $R = 3.89$, $\Delta = 1.8$, providing

$$\langle \Phi_0 | \Psi_0 \rangle^2 = 0.80. \tag{56}$$

Some additional data can be obtained by studying the distributions of the electrons ejected from the FS.

IV. PARTIAL-WAVE ANALYSIS

Here we consider the energies for which $N\xi^2 \ll 1$, and thus the perturbative treatment of the FSI is possible. We must include both FSI and SO mechanisms. The ratio $r(E)$ given by Eq. (31) can be written as the sum of the contributions of the partial waves,

$$r(E) = \sum_{n\ell} |\langle \Phi_{n\ell} | \Psi_0 \rangle|^2 + \xi^2 \sum_{n\ell} |\langle \Phi_{n\ell} | \Lambda | \Psi_0 \rangle|^2$$
$$- \xi^2 \sum_{n\ell} \langle \Psi_0 | \Phi_{n\ell} \rangle \langle \Phi_{n\ell} | \Lambda^2 | \Psi_0 \rangle, \tag{57}$$

with the sum carried out over the excited states $n \neq 0$. There are certain limits on the values of ℓ for any particular state n.

The first and the third terms on the RHS obtain nonzero values only for $\ell = 0$. For the second one we can employ expansion in terms of the Legendre polynomials,

$$\ln(1 - t) = \sum_\ell a_\ell P_\ell(t),$$

$$a_\ell = \frac{(2l + 1)}{2} \int_{-1}^{1} dt \, P_\ell(t) \ln(1 - t), \tag{58}$$

$$a_0 = \ln 2 - 1, \quad a_{\ell \geqslant 1} = -\frac{2\ell + 1}{\ell(\ell + 1)}. \tag{59}$$

Introducing

$$A_{n\ell} = \langle \Phi_{n\ell}^r | \Psi_0^r \rangle, \tag{60}$$

with Ψ^r and Φ^r being the radial parts of the wave functions, we can write for the matrix element in the second term on the

RHS of Eq. (57)

$$\langle \Phi_{n\ell} | \Lambda | \Psi_0 \rangle = A_{n\ell} \langle \ell m | \Lambda | 00 \rangle \tag{61}$$

since

$$\langle \ell m | \ln(1 - t) | 00 \rangle = \delta_{m0} \frac{a_\ell}{(2\ell + 1)^{1/2}}, \tag{62}$$

with $\langle \ell m |$ denoting the state with definite values of the angular momentum ℓ and its projection m, while a_ℓ are defined by Eq. (34). We can present Eq. (57) in the form

$$r(E) = \sum_n \left(\delta_{\ell 0} A_{n0}^2 - \xi^2 N \delta_{\ell 0} A_{n0}^2 + \xi^2 N \sum_{\ell=1} b_\ell A_{n\ell}^2 \right), \tag{63}$$

with the sum carried out over the excited states of the FS,

$$b_\ell = \frac{2\ell + 1}{\ell^2(\ell + 1)^2}. \tag{64}$$

The first term on the RHS of Eq. (63) is caused by SO, the second one comes from the interference between the SO and the FSI, and the last one corresponds to FSI.

Presenting

$$\frac{2\ell + 1}{\ell^2(\ell + 1)^2} = \frac{1}{\ell^2} - \frac{1}{(\ell + 1)^2}, \tag{65}$$

we see that

$$\sum_{\ell=1}^{\infty} b_\ell = 1. \tag{66}$$

This is the consequence of the closure of angular functions. Using Eq. (62), we can write

$$\sum_{\ell m} |\langle \ell m | \ln(1 - t) | 00 \rangle|^2 = \sum_\ell \frac{a_\ell^2}{(2\ell + 1)}. \tag{67}$$

On the other hand,

$$\langle 00 | \ln^2(1 - t) | 00 \rangle = (\ln 2 - 1)^2 + 1. \tag{68}$$

Thus

$$(\ln 2 - 1)^2 + 1 = a_0^2 + \sum_{\ell=1} b_\ell, \tag{69}$$

leading to Eq. (66). Recall, however, that for any excited state n the possible values of ℓ are limited by a certain value ℓ_{max}, i.e., $\ell \leqslant \ell_{max}$. Since all $b_\ell > 0$, we find

$$\sum_{\ell=1}^{\ell_{max}} b_\ell < 1. \tag{70}$$

Since both $\xi^2 N$ and $A_{n\ell}^2$ are small, we can write in the lowest order

$$r(E) = 1 - A_{00}^2 + \xi^2 N \sum_n \sum_{\ell=1} b_\ell A_{n\ell}^2, \tag{71}$$

with the dipole term thus providing more than 3/4 of the FSI contribution. The amplitude of the dipole transition to a particular excited state n is proportional to the overlap of the radial wave functions $\langle \Phi_{n1}^r | \Psi_0^r \rangle$. Thus investigating the spectrum of the electrons ejected from the FS would provide the data which are complimentary to that

obtained from the studies of direct photoionization of the fullerenes [17,18].

Recall that these results are true if $\xi^2 N \ll 1$. This means that $E \gg 5$ keV for the fullerene C_{60} and $E \gg 1.7$ keV for C_{20}. At such energies all N electrons of the fullerene C_N can participate in the process.

V. TOTAL CROSS SECTION

Now we can trace the energy dependence of the cross section of absorption by the FS in this process. Employing Eqs. (32) and (33), we find that closure can be used at $E \geqslant 50$ eV. If the energy E is smaller than the ionization potential of the core 1s electrons $I_c \approx 315$ eV, the ratio $r(E)$ is determined by Eq. (39) with $N = N_v$, where N_v is the number of valence electrons, $N_v = 240$ for C_{60}, and $N_v = 80$ for C_{20}. At E close to I_c we find $1 - r(E) \approx 2 \times 10^{-5}$ for C_{60} and $r = 0.97$ for C_{20}.

At $E > I_c$ the core electrons are involved in the process as well. Thus $N = 360$ for C_{60} and $N = 120$ for C_{20}. While E is of the order of I_s, their contribution cannot be calculated by employing closure since some of the excited states cannot be reached due to restrictions imposed by the energy conservation law. However, Eq.(39) with $N = N_v$ provides the upper limit for the value of $1 - r(E)$ at these energies.

At larger energies $E \gg I_c$ the ratio $r(E)$ is determined by Eq. (41) with the core electrons included. At $E = 2$ keV we find $1 - r(E) \approx 0.09$ for C_{60}, i.e., $r(E)$ is still very close to unity. At $E = 5$ keV, $r(E) \approx 0.62$ for C_{60}, dropping as $1/E$ at larger energies, following Eq. (31). For C_{20} this value is reached at $E = 1.7$ keV. The FSI and the SO contributions to the ratio $r(E)$ expressed by Eq. (39) have the same order of magnitude at $E \geqslant 50$ keV in the case of C_{60} and at $E \geqslant 8$ keV for C_{20}. The dependence $r(E)$ of the endohedral atoms $A@C_{60}$ and $A@C_{20}$ is shown in Fig. 1.

If the binding energy of the ionized state of the caged atom I_a and the photon energy are small enough, both SO and FSI contributions to the cross section are enhanced by the same factor. This happens because the external photon is strongly influenced by the FS due to the polarization of the latter. This effect manifests itself as the factor

$$D(\omega) = 1 - \alpha(\omega)/R^3 \qquad (72)$$

in the amplitude of ionization of the internal atom [19]. Here $\alpha(\omega)$ is the dynamic dipole polarizability of the FS. Since in this region $\alpha(\omega) < 0$, the factor $|D(\omega)|^2$ increases the cross section of the single photoionization [19],

$$\sigma_{pol}^+(\omega) = \sigma^+(\omega)D^2(\omega). \qquad (73)$$

The polarizability $\alpha(\omega)$ has a strong maximum due to FS giant resonance at $\omega \approx 1$ a.u. [19]. The role of polarization diminishes with increasing photon energy. It becomes negligible at $\omega_{max} \approx 2.5$ a.u.; thus here $D^2(\omega) \approx 1$. However, the characteristic binding energy of a FS electron is $I = 7$ eV. If the binding energy of the ionized state of the caged atom is of the same order or smaller, the factor $D^2(\omega)$ increases both SO and FSI contributions to the double-photoionization cross section at the lower limit. Note that the factor $D^2(\omega)$ enters the cross sections of the double and single photoionizations in the same way. Thus it cancels in their ratio $r(E)$.

VI. SUMMARY

We investigated the high-energy photoionization of the endohedral atoms $A@C_N$ followed by inelastic processes in the fullerene shell. We traced the energy dependence of the ratio $r(E)$ of the cross section to that of photoionization of an isolated atom. In a broad interval of values of the photoelectron energies E the ratio is dominated by the final-state interactions and is calculated in a model-independent way beyond the perturbative approach. The ratio is shown to be close to unity until we reach the region where E is several keV. In the case of C_{60} the ratio $r(E) = 0.62$ at $E = 5$ keV; for C_{20} this value is reached at $E = 1.7$ keV. While the nonperturbative approach is important, the multiparticle and the single-particle states of the FS can be excited. The monopole excitations are quenched.

At larger energies the ratio is still determined by the FSI, which can be treated perturbatively. Now only the single-particle state can be excited. The relative probability of the dipole excitations is more than 75%. The monopole excitations are still quenched.

The contributions of the FSI and of the shake-off are the same order at very high energies, $E \approx 50$ keV for C_{60} and $E \approx 8$ keV for C_{20}. The SO leads to excitation of the monopole states of the FS.

One of the results of the present work (see also our earlier publication [10]) is that in a broad interval of the photon energies almost any event of photoionization of the caged atom A is accompanied by a transition in the fullerene shell. Therefore, the measured cross section of one-electron photoionization of the inner atom would appear to be much smaller than that of an isolated atom. The electron spectroscopy method permits us to separate the photoionization cross section of a given subshell nl from all other contributions. As a result, photoionization cross sections of the nl atomic subshell measured for an endohedral atom $A@C_N$ using the electron spectroscopy method in a broad ω region have to be much
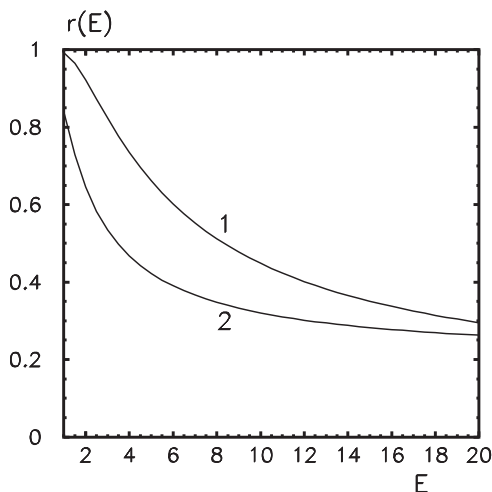

FIG. 1. The ratio $r(E)$ defined by Eq. (5). Lines 1 and 2 are for endohedral atoms $A@C_{60}$ and $A@C_{20}$, respectively. The photoelectron energy E is in keV units.

smaller than the corresponding cross section for an isolated atom A. This prediction is far from being trivial and deserves special experimental verification.

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