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On the interactions of the high energy photoelectrons with the fullerene shell

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The probability that photoionization of the caged atom in an endohedral system is accompanied by excitation of the fullerene shell is shown to be close to unity in broad intervals of the photoelectron energies. This is obtained by summation of the perturbative series for the interaction between the photoelectron and the fullerene shell. The result can be verified in experiments. As an outcome, interaction between the photoelectron ejected from the cage atom and the fullerene shell cannot be described by a static potential, since inelastic processes become decisively important.

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In the present paper we demonstrate that in a broad region of photon energies ω the ionization of an atom caged by a fullerene is accompanied with almost unit probability by excitation or ionization of the fullerene electrons. It is assumed that ω is so large that the energy of the photoelectron E exceeds strongly the characteristic binding energies of the fullerene.

Interaction of the high energy photons with endohedral atoms attracts much attention nowadays [1–4]. The inelastic processes in the fullerene shell (FS) caused by the electrons created in photoionization of the caged atom is one of the main subjects of these studies. The calculations of these processes require understanding of the mechanism of interaction between the photoelectron and the electrons of the FS. In the present Letter we find the sum of the cross section of inelastic processes in the FS focusing on the energy behavior of the ratio

$$r(E) = \frac{\sigma_A(E)}{\sigma_\gamma(E)}. \tag{1}$$

Here σ_γ and σ_A are the cross sections of photoionization of the isolated atom, and of the same process in the caged atom accompanied by inelastic processes in the FS. Thus $\sigma_A(E)$ is the total absorption cross section. We demonstrate that in the broad intervals of the values of E the ratio $r(E)$ is close to unity. Hence the probability that photoionization of the caged atom is followed by an inelastic process in the FS is close to unity.

In the first step we find the general expression for the amplitude of transition of the FS to a state $|\Phi_x\rangle$ with the low excitation energy, i.e. with that of the order of FS electrons binding energy. Since, as we shall see, these very states saturate the closure condition, we can sum the cross section over the excited states $|\Phi_x\rangle$, without specifying their nature and structure. This enables to obtain quantitative results.

At the first glance this result looks surprising since the two main mechanisms [5] of excitation and ionization of the FS are determined by small parameters. In the shake-off (SO) the electronic shell is moved to an excited state by the sudden change of the effective field caused by the incoming photon. Since FS is far from the caged atom, i.e. the FS radius R is large

$$R \gg 1, \tag{2}$$

the SO contribution is of the order $1/R^2 \ll 1$. (We employ the atomic system of units with $e = m = \hbar = 1$). The final state interaction (FSI) between the photoelectron and the bound ones is determined by its Sommerfeld parameter $\xi = 1/v$ with v being the relative velocity of the photoelectron and the bound electrons [6]. At high energies we can put

$$\xi^2 \approx 1/2E \ll 1. \tag{3}$$

Note however that while in SO the electronic shell reacts on creation of the hole as an entire body, each bound electron is affected by FSI separately. Hence, the FSI parameter is rather $\xi^2 N$ with N being the number of the bound electrons, while the SO effects do not depend on N directly. Thus, for light atoms $\xi^2 N \ll 1$

already at the energies higher than several hundred eV. However in the endohedral atoms, which are fullerenes stuffed with an atom inside, the number of electrons N is much larger and the FSI become weak at much larger energies. For example, there are $N = 360$ electrons in the fullerene C_{60}, and $\xi^2 N \ll 1$ only for $E \gg 5\,\text{keV}$.

Fortunately, for the endohedral atoms one can sum the FSI power series in $\xi^2 N$ without assuming this parameter to be small. This is due to the large size of these systems – Eq. (2). Localization of FS electrons in a thin layer

$$R \le r \le R + \Delta, \tag{4}$$

enabled us to calculate the sum of the power series in $\xi^2 N$ in a model-independent way.

We employ the model in which we assume that the electrons of the caged atom and those of the FS move in independent way, while the FS ones are localized in a thin layer (Eq. (4)) far away from the caged atom (Eq. (2)). This model proved itself to be a realistic one, e.g. by the prediction of the confinement resonances in the endohedral atoms [7] confirmed recently in the experiment [8]. It was shown, however [9–11] that in some cases this approach may not be true for the outer electrons, since their mixing with those of the FS becomes important (hybridization). In this case our analysis, which does not include the hybridization effects, is valid for inner subshells of the caged atom.

The large probability of inelastic processes in the FS has consequences for the related problem of studying the wave function of the outgoing electron in photoionization of the caged atom. We cannot consider the FS as just a source of external field: inelastic scattering of the photoelectron by FS electrons can be of great importance.

If the photoelectron energy E and thus its momentum p are large enough so that Eq. (3) holds, the first step of the process is the photoionization of the caged atom, which takes place at the distances of the order $r \sim 1/p \ll 1$. After that the photoelectron passes the distances of the order $r \sim R \gg 1$, interacting with the electrons of the FS. Thus, at high energies the amplitude F_x of the process with participation of fullerene shell contains the photoionization amplitude $F_\gamma(E)$ as a factor, i.e. [12]

$$F_x(E) = F_\gamma(E) T_x \tag{5}$$

with T_x being the amplitude of excitation or ionization of FS electrons. The accuracy of this equality is of the order V/E with V being the potential energy of the photoelectron in the field of the FS. Of course, the hybridization effects would break Eq. (5) which employs the independence of motion of the electrons in the caged atom and in the FS.

The zero order (SO) term is

$$T_x^{(0)} = \langle \Phi_x | \Psi_0 \rangle, \tag{6}$$

where $|\Psi_0\rangle$ is the ground state of the FS with the caged atom, while $|\Phi_x\rangle$ is a state of the FS with the caged ion. The lowest order FSI amplitude of can be written as

$$T_x^{(1)} = \langle \Phi_x | U_1 | \Psi_0 \rangle, \tag{7}$$

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

$$U_1(\mathbf{r}^{(k)}) = \frac{1}{c} \int \frac{d^3 f}{(2\pi)^3} G(\mathbf{f}) g(f) e^{i(\mathbf{f}\mathbf{r}^{(k)})}, \tag{8}$$

where c is the speed of light and

$$G(\mathbf{f}) = -\frac{1}{\mathbf{pf} - i\nu}; \quad \nu \to +0 \tag{9}$$

is the free electron propagator in which only the term proportional to the large momentum p is kept in the denominator, $g(f) = 4\pi/(f^2 + \lambda^2)$, $\lambda \to 0$. In Eq. (8) for the electron propagator we have neglected the terms of the order f^2. We omitted also the terms proportional to the energy ε_{n0} transferred to the FS, assuming that $f \ll p$ and $\varepsilon_{n0} \ll E$. This means that we included only those final states of the FS, which have the excitation energy of the order of the binding energy I_{FS} in the FS. But these are the very states that saturate closure. The states with $\varepsilon_{n0} \gg I_{\text{FS}}$ require large momentum $f \approx (2\varepsilon)^{1/2}$ to be transferred to the FS. The corresponding amplitude drops as $1/\varepsilon_{n0}$ [6], and the contribution of these states to the closure is quenched as $\int d\varepsilon_{n0}/\varepsilon_{n0}^2$. Presenting

$$\frac{1}{2(\mathbf{p}\cdot\mathbf{f}) - i\nu} \cdot \frac{1}{f^2 + \lambda^2} = \\ = \int_0^1 \frac{dx}{\left[2(\mathbf{p}\cdot\mathbf{f})(1-x) + q^2 x + \lambda^2 x - i\nu\right]^2},$$

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

$$\int \frac{d^3 f}{(2\pi)^3} \frac{4\pi e^{i(\mathbf{f}\cdot\mathbf{r})}}{(f^2 - b^2 - i\nu)^2} = \frac{1}{2b}\frac{\partial}{\partial b}\frac{e^{ibr}}{r} = i\frac{e^{ibr}}{2b};$$

$$b^2 = p^2 y^2 - \lambda^2$$

we find

$$U_1(\mathbf{r}^{(k)}) = -\frac{i}{c}\int_0^\infty \frac{dy}{b(y)} e^{ib(y)r^{(k)} - i(\mathbf{p}\cdot\mathbf{r}^{(k)})y} = \\ = i\xi\Big[\ln\frac{(r^{(k)} - r_z^{(k)})\lambda}{2} + C_E\Big], \quad (10)$$

with $C_E \approx 0.577$ the Euler constant. Since the last term is of the order $1/R$, we can write [12]:

$$U_1 = i\xi\Lambda; \quad \Lambda = \sum_k \ln(r^{(k)} - r_z^{(k)})\lambda. \quad (11)$$

We shall see that the terms containing parameter λ form the Coulomb phase of the $e{-}e$ scattering and will cancel in the final step.

The second order amplitude is $T_x^{(2)} = \langle\Phi_x|U_2|\Psi_0\rangle$, where U_2 is given by

$$U_2 = \frac{1}{c^2}\sum_{k_1k_2}\int \frac{d^3f_1}{(2\pi)^3}\frac{d^3f_2}{(2\pi)^3} \times \\ \times G(\mathbf{f}_1)g(f_1)G(\mathbf{f}_1+\mathbf{f}_2)g(f_2)e^{i(\mathbf{f}_1\mathbf{r}^{(k_1)})}e^{i(\mathbf{f}_2\mathbf{r}^{(k_2)})}. \quad (12)$$

Using Eq. (9) for the Green function G and putting in the integrand $G(\mathbf{f}_1)G(\mathbf{f}_1+\mathbf{f}_2) = [G(\mathbf{f}_1)G(\mathbf{f}_1+\mathbf{f}_2) + G(\mathbf{f}_2)G(\mathbf{f}_1+\mathbf{f}_2)/2 = G(\mathbf{f}_1)G(\mathbf{f}_2)/2$, we find that $U_2 = U_1^2/2$. One can see that this expression can be generalized for the case of arbitrary number n of interactions between the photoelectron and the FS. Introducing $a_n = (\mathbf{p}\cdot\mathbf{f}_1) + (\mathbf{p}\cdot\mathbf{f}_2) + ... + (\mathbf{p}\cdot\mathbf{f}_n)$ we can write

$$\frac{1}{a_1}\cdot\frac{1}{a_2}\times ...\times\frac{1}{a_n} = \frac{1}{n!}\frac{1}{a_1^n}. \quad (13)$$

This equation, which can be proved by the induction method was used earlier for calculation of the radiative corrections in electromagnetic interactions [13]. Thus $U_n = U_1^n/n!$, and the total amplitude is $T_x = \langle\Phi_x|\sum_{n=0}U_n|\Psi_0\rangle$ $(U_0 = 1)$. Hence

$$T_x = \langle\Phi_x|e^{i\xi\Lambda}|\Psi_0\rangle = \langle\Phi_x|\Pi_k(r^{(k)} - r_z^{(k)})^{i\xi}e^{i\xi\ln\lambda}|\Psi_0\rangle \quad (14)$$

with Λ defined by Eq. (11) includes the SO terms and also all FSI terms with the accuracy of the order $1/R^2$. Employing Eq. (4) we can put $r^{(k)} = R$, thus presenting

$$T_x = \langle\Phi_x|\Pi_k(1 - t^{(k)})^{i\xi}|\Psi_0\rangle, \quad (15)$$

with $t^{(k)} = \mathbf{pr}^{(k)}/pr^{(k)}$. 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. Thus

$$r(E) = 1 - |\langle\Phi_0|\Pi_k(1 - t^{(k)})^{i\xi}|\Psi_0\rangle|^2. \quad (16)$$

Contribution of each electron to the matrix element on the RHS of Eq. (16) is $2^{i\xi}/(1 + i\xi)$, providing

$$r(E) = 1 - \frac{h}{(1+\xi^2)^N} = 1 - e^{-N\ln(1+\xi^2)}h; \\ h = |\langle\Phi_0|\Psi_0\rangle|^2. \quad (17)$$

If the photon energy is so large that $N\xi^4 \ll 1$ (for C_{60} this means that $E \gg 800$ eV), we find

$$r(E) = 1 - e^{-N\xi^2}h. \quad (18)$$

Since $h < 1$ we obtain that $1 - r(E) \ll 1$ up to the energies of about 10 keV for the fullerene C_{60}. Thus the probability of inelastic processes is close to unity. The contribution of the SO to inelastic processes is quenched by the factor $1/R^2$. This happenes because after the ionization of the caged atom the FS sufferes a perturbarion of the order $1/R$. Therefor admixture of the excited states $|\Phi_x\rangle$ $(x \neq 0)$to the state $|\Psi_0\rangle$ is of the order $1/R$. Hence, the inelastic processes are mainly due to the FSI. Since $1 - h \sim 1/R^2 \ll 1$, one can put $h = 1$ for the estimations.

In the high energy limit $N\xi^2 \ll 1$ the perturbative approach is valid, and $r(E) \approx N\xi^2 h$, thus dropping with E.

There are more or less detailed investigated fullerenes with the number of atoms $\mathcal{N} = 20, 60, 70, 80$. There are $N_v = 4\mathcal{N}$ valence (collectivized) electrons and $N_c = 2\mathcal{N}$ core electrons. The latter can be treated as the $1s$ electrons bound by the carbon nuclei (also in the field of the valence electrons, the action of which upon $1s$ is small) with the binding energy $I_c \approx 300$ eV. The photoelectron is known to feel the fullerene potential $V \ll 1$. Thus the condition $\xi^2 \ll 1$ enables to use the free propagator presented by Eq. (8). The binding energies I_{FS} of the valence FS electrons satisfy the condition $I_{\mathrm{FS}} \ll I_C$. Employing of the closure condition requires that the photoelectron energy E is large enough to include all important excited states, i.e. E should be much larger than the energy losses $\bar{\varepsilon}$ in the FS. For the energies ε of the excitation of the FS, which exceed strongly the FS binding energies I_{FS} (e.g. $I_{\mathrm{FS}} \approx 7$ eV for C_{60}) the energy distributions drop as $1/\varepsilon^2$. Thus the values of $\bar{\varepsilon}$ for the valence FS electrons are determined by $I_{\mathrm{FS}} \ll \varepsilon \ll E$. The energy distribution at these energies is proportional to $1/\varepsilon^2$ [6]. The energy losses can be estimated as [14]

$$\bar{\varepsilon} \approx \frac{\xi^2 N_v}{4R^2}\ln\frac{E}{I_{\mathrm{FS}}}. \quad (19)$$

As follows from Eq. (19) the closure approximation can be used for $E \gg 50$ eV for all the considered fullerenes. At $E \le I_c$ only the valence electrons can be knocked out by the FSI. In this region $N_v\xi^2 \ge 3.5$ for C_{20} and is even larger for the fullerenes with bigger $\mathcal{N}$. Thus, $r(E)$ is described by Eq. (17) with $N = N_v$. At $E = 300$ eV we find $r = 0.97$ for C_{20} and $r = 0.99997$ for C_{60}. Hence, the cross section σ_A is very close to the cross section of photoionization σ_γ. At $E \sim I_c$ contribution of the core electrons cannot be calculated by employing the closure theorem. However Eq. (17) provides the lower limit for $r(E)$. For $E \gg I_c$ we can employ Eq. (17) with $N = N_v + N_c$. For example, at $E = 1$ keV we find $r = 0.80$ for the fullerene C_{20}, while $r = 0.992$ for C_{60}. The cross section σ_A is again close to σ_γ.

Thus we obtained some quantitative results on the interactions of the high energy photoelectrons with the fullerene shell. Our calculations where based on closure theorem and did not require detailed knowledge of the structure of the FS.

The perturbative behavior requires the energies of the photoelectron to be very large. We find that $N\xi^2 \ll \ll 1$ at $E \gg 1.6\,$keV for the fullerene C_{20}, and at $E \gg 5\,$keV for C_{60}. At the energies of dozens of keV the FSI and SO terms are of the same order and the SO terms should be included.

To summarize, we found the energy dependence of the cross section of photoionization of the caged atom accompanied by inelastic processes in the fullerene shell. In the broad intervals of energies this cross section appeared to be close to that of photoionization of the isolated atom. In other words, the probability that the FS will be excited during photoionization of the caged atom is close to unity. This statement can be checked in inclusive experiments on photoionization of the endohedral atoms by measuring the energy losses of the photoelectrons.

In the related problem of studying the wave function of the outgoing electron in photoionization of the caged atom we cannot consider the FS as just a source of external field. Inelastic processes in the FS are decisively important.

The result was obtained by summation of the power series of interaction between the photoelectron and the FS. The technique of summation can be applied for investigation of other objects with two scales of distances. It can be useful for the systems containing a large number of electrons. These can be, for example, electronic shells of heavy atoms, or of large molecules.

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