Vacancy decay in endohedral atoms: the role of an atom’s non-central position

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Abstract

We demonstrate that the Auger decay rate in an endohedral atom is very sensitive to the atom’s location in the fullerene cage. Two additional decay channels appear in an endohedral system: (a) the channel due to the change in the electric field at the atom caused by the dynamic polarization of the fullerene electron shell by the Coulomb field of the vacancy and (b) the channel within which the released energy is transferred to the fullerene electron via the Coulomb interaction. The relative magnitude of the correction terms is dependent not only on the position of the doped atom but also on the transition energy $\omega$. Additional enhancement of the decay rate appears for transitions whose energies are in the vicinity of the fullerene surface plasmons energies of high multipolarity. It is demonstrated that in many cases the additional channels can dominate the direct Auger decay resulting in pronounced broadening of the atomic emission lines. The case study, carried out for Sc$^{2+}@C_{80}^{-}$, shows that narrow autoionizing resonances in an isolated Sc$^{2+}$ within the range $\omega = 30–45$ eV are dramatically broadened if the ion is located strongly off the centre. Using the developed model, we carry out the quantitative analysis of the photoionization spectrum for the endohedral complex Sc$_3$N@C$_{80}$ and demonstrate that the additional channels are partly responsible for the strong modification of the photoionization spectrum profile detected experimentally by Müller et al (2007 J. Phys.: Conf. Ser. 88 012038).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In this paper, we demonstrate that the rate of atomic non-radiative decay in an endohedral system A@C$_N$ strongly depends on the location of the atom inside the fullerene cage. In particular, the width of the Auger decay can be varied by orders of magnitude by increasing the atomic displacement $a$ from the cage centre. As $a$ increases, the most pronounced enhancement of the width occurs for the transitions whose energy lies in the vicinity of the fullerene surface plasmon of high multipolarity.

To analyse the influence of the fullerene electron shell on the atomic decay, we consider two physical mechanisms. The first one accounts for the change in the electric field at the atom due to the dynamic polarization of the shell by the Coulomb field of the transferring atomic electron [2]. This scheme is similar to the one which leads to the modification of radiative and Auger decays in an isolated atom due to the intrashell many-electron correlations [3]. Within the second mechanism the energy, released in the atomic transition, is transferred via the Coulomb interaction to the fullerene electron which becomes ionized. In [4], this mechanism was called interatomic Coulombic decay, thus pointing out its close relationship with the interatomic decay process in various molecular clusters [5–7].

The influence of the fullerene electron shell on the processes of radiative and non-radiative decays of a vacancy in the atom was analysed for spherically symmetric endohedral systems A@C$_{60}$, in which the atom A is placed at the centre of the spherical cage of the C$_{60}$ fullerene [2, 4]. It was noted
that the interatomic Coulombic decay leads to a dramatic increase of the atomic decay rate, especially in the case when a non-radiative transition in the isolated atom is energetically forbidden. The estimates presented in the cited papers show that the interatomic decay mechanism in A@C_{60} can increase the radiative decay rate by a factor $10^5$–$10^6$. On the other hand, the impact of the dynamic polarization of the fullerene on the atomic Auger width was found to be negligibly small for the at-the-centre location of the atom [2].

Another prediction made in [2] concerns the modification of the atomic Auger width due to the interference between a direct wave of the electron emitted in the Auger process and its waves scattered from the cage. This effect is identical to the one in the photoionization (PI) process of an endohedral atom, where the interference of the direct and scattered photoelectron waves can lead to the so-called 'confinement resonances' [8] in the PI cross section. In recent years, a number of theoretical predictions have been made on the properties of the confinement resonances in various spherical endohedral systems (see, e.g., [9]). However, so far many of these predictions have not been supported experimentally. The explanation of the discrepancy between the predictions and the earlier experimental results was presented recently [10]. It was shown that the structure of confinement resonances in the PI cross section of an endohedral atom is very sensitive to the mean displacement $\langle a \rangle$ of the atom from the cage centre. The resonances are strongly suppressed if $2\langle a \rangle$ exceeds the photoelectron half-wavelength. A decrease in the amplitude of the confinement resonances with the increase of the doped-atom displacement from the cage centre was also noted in [11]. Taking into account the similar nature of the confinement resonances in the PI and Auger decay processes, we can state that the interference effects will not affect the Auger widths if the emitted electron wavelength satisfies the criterion formulated above.

The experimental data on the PI of A@C_{60} are sparse due to the difficulty to produce sufficient amounts of purified endohedrals for the gas phase experiments [1, 12]. The cross sections in the region of giant atomic resonances were measured for Dy@C_{82} [13], Ce@C_{82} [14], Pr@C_{82} [15] and Ce@C_{82}^{+} [1, 12, 16]. No confinement resonances were detected. The first ever observation of the confinement resonances has been reported recently [17] for the PI of Xe@C_{80}.

Apart from these, the measured cross sections for the PI of the endofullerene Sc_{3}N@C_{80} in the photon energy range 30–45 eV were reported in [1]. These data are of prime interest in connection with the topic of this paper. Indeed, as was shown theoretically [18, 19] and also confirmed experimentally [20], the cross section of the PI of an isolated ion Sc^{3+} in the indicated energy range is dominated by a set of narrow resonances due to the excitations of the 3p electrons to intermediate autoionizing states. Hence, taking into account that each scandium atom in Sc_{3}N@C_{80} carries a positive charge $q \approx +2e$ [21], it is natural to expect the manifestation of the autoionizing resonances in the PI of the endofullerene. However, such distinct structure has not been seen in the experiment [1]. Instead, the presence of the endohedral molecule Sc_{3}N resulted in a single wide peak (of 6 eV full-width at half-maximum) in the PI curve of Sc_{3}N@C_{80}. In [1], it was mentioned that such a dramatic modification can be due to the presence of the fullerene cage which could cause significant broadening of any atomic resonance features in PI.

The intriguing experimental results of [1] have stimulated our current study on the dependence of the atomic non-radiative decay processes on the doped-atom displacement from the cage centre. For doing this, we developed a formalism which allows one to determine the corrections to the atomic Auger width due to the dynamics of the fullerene electrons. Within the framework of the formalism, which is presented in section 2, one accounts for the off-the-centre position of the doped atom and expresses the corrections in terms of the fullerene multipole dynamic polarizabilities of the second kind. On the basis of the developed formalism in section 3, we carry out the quantitative analysis of the dependence of the autoionizing width on the displacement $\alpha$. This is carried out for the Sc^{3+} ion encaged in the fullerene C_{80}. The obtained data are used further to calculate the PI spectrum for the endohedral complex Sc_{3}N@C_{80} in the photon energy range 30–45 eV. In the appendix, we discuss different types of polarizabilities of the hollow objects and present the model description of the dynamic multipole polarizabilities of a fullerene.

The atomic system of units is used throughout the paper.

2. The formalism

2.1. The Auger width in an isolated atom

For the sake of clarity and consistency of the notations and terminology adopted below in the paper, let us outline the basic formalism related to the calculation of the Auger width in an isolated atom. The Auger decay of the vacancy in an isolated atom can be illustrated by the diagram presented in figure 1(a). The inner vacancy $f$ is filled by the electron from the outer state $i$. Due to the interelectron Coulomb interaction $v = 1/|r - r'|$, the released energy $E_i - E_f$ is transferred to another electron from the state $j$ which becomes ionized ($p$ stands for the...
asymptotic moment of the outgoing electron). The energy conservation implies \( \epsilon_i + \epsilon_j = \epsilon_f + \epsilon \), where \( \epsilon = p^2/2 \).

The amplitude \( A^\Lambda_{ij\rightarrow fp} \) of the process from figure 1(a) is proportional to the two-electron Coulomb matrix element \( \langle fp|p|ji \rangle \). Presenting the wavefunctions of single-electron states \( i, j, f \) as products of angular and radial parts, and using the standard multipole expansions of \( v \) and of the outgoing electron wavefunction, one derives the analytical expression for \( A^\Lambda_{ij\rightarrow fp} \) (the subscript ‘\( \Lambda \)’ stresses that the quantity refers to the isolated atom). Although the formalism developed in our paper is applicable to the Auger transitions of an arbitrary fullerene, we focus on the dipole transitions \( i \rightarrow f \) and \( j \rightarrow p \). As is discussed further, the presence of the fullerene cage, whose radius noticeably exceeds that of the endohedral atom, most strongly affects the dipole Auger transitions. This refers, in particular, to the case of \( \text{ScC}_8\text{N}@\text{C}_60 \), since, as already mentioned, the PI of an isolated ion \( \text{Sc}^{2+} \) is dominated by the presence of the fullerene. Thus, one can expect that in those cases the atomic Auger decay process can be strongly influenced due to the excitations (real or virtual) of the fullerene electrons [18–20].

In the dipole approximation, the amplitude can be written as follows:

\[
A^\text{dip,}\Lambda_{ij\rightarrow fp} = -\delta_{jx} \delta_{sx} \sqrt{\frac{8\pi^3}{p}} \sum_{l=|j|+1}^{\infty} i^{-d} \epsilon^k \gamma^{(1)}_{\nu_{i}\nu_{j},\nu_{f}} \left( -1 \right)^{m_{j}+m_{j}} \times \left( \begin{array}{ccc} l_{j} & 1 & l_{j} \\ -m_{j} & 1 & m_{j} \end{array} \right) \sum_{\mu} \left( \begin{array}{ccc} l_{f} & 1 & l_{f} \\ -m_{f} & 1 & m_{f} \end{array} \right) Y_{\mu m}(p),
\]

(1)

where \((a \ b \ c)\) is the 3j-symbol. The subscripts \( a = i, j, k \) denote the atomic states. The notation \( \nu_{a} = (n_{a}, l_{a}) \) stands for the set of principal and orbital quantum numbers, and \( \delta_{\nu_{a}} \) denotes the spin projection. The quantities \( p, v \equiv (\epsilon, l) \), \( s \) and \( \delta_{\nu} \) (the scattering phaseshifts) refer to the outgoing electron. The factors \( \delta_{jx} \delta_{sx} \) take into account that within the non-relativistic framework the spin projections \( s \) are not changed in the transitions \( i \rightarrow f \) and \( j \rightarrow p \). The quantity \( \gamma^{(1)}_{\nu_{i}\nu_{j},\nu_{f}} \) denotes the dipole radial Coulomb matrix element:

\[
\gamma^{(1)}_{\nu_{i}\nu_{j},\nu_{f}} = \Pi_{l_{b},l_{b}} \left[ \left( \begin{array}{ccc} l_{j} & 1 & l_{j} \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_{f} & 1 & l_{f} \\ 0 & 0 & 0 \end{array} \right) \right],
\]

(2)

where \( \Pi_{l_{b}l_{b}} \cdots = \sqrt{(2l_{a}+1)(2l_{b}+1)(2l_{c}+1)\cdots} \).

Equation (1) has been derived in a single-electron approximation. To account for the electron correlations, one substitutes \( \gamma^{(1)}_{\nu_{i}\nu_{j},\nu_{f}} \) with the corresponding matrix element of the effective interaction (see, e.g., [22]).

One can calculate the width, which defines the probability (per unit time) of the Auger transition, starting from the following general formula:

\[
\Gamma_{ij\rightarrow fp} = \frac{p}{8\pi^{2} E_{f}} \sum_{m_{j}m_{j}m_{f}} \sum_{i,j} \int dr \rho(r) \rho(r)^{2} P_{\nu_{i}}(r) P_{\nu_{j}}(r) \left| \gamma^{(1)}_{\nu_{i}\nu_{j},\nu_{f}} \right|^{2} \left( \frac{\epsilon_{i}^{2}}{r^{2}+1} \right),
\]

(3)

where \( \Gamma_{ij\nu_{i},\nu_{j},\nu_{f}} \) stands for the partial width of the transition \( \nu_{i}\nu_{j} \rightarrow \nu_{f}\nu \).

Using (1) in (3), one derives the following expression for the partial width of the dipole Auger transition in the isolated atom:

\[
\Gamma_{ij\nu_{i},\nu_{j},\nu_{f}}^{\text{dip,}\Lambda} = \frac{4\pi}{3\Pi_{l_{j}}^{2}} \left| \gamma^{(1)}_{\nu_{i}\nu_{j},\nu_{f}} \right|^{2}.
\]

(4)

2.2. Correction to the width of the Auger decay in the endohedral atom

If the atom is encaged in a fullerene \( \text{C}_{N} \), the atomic decay process can be strongly influenced due to the excitations (real or virtual) of the fullerene electrons [2, 4].

To start with we mention that the atomic Auger decay can occur via the additional channel, the diagrammatical representation of which is given in figure 1(b) [2]. Here, the energy \( \omega_{if} = \epsilon_{i} - \epsilon_{f} \) released in the transition \( i \rightarrow f \) is transferred to the electron \( j \) not directly, as in the process from figure 1(a), but via the virtual excitation of the fullerene. The diagrams in figure 1(b) constitute the correction term, \( \Delta A^{\text{Aug,C}}_{ij\rightarrow fp} \), to the amplitude of the Auger decay. Hence, the total amplitude of the Auger decay in the encapsulated atom reads

\[
A^{\text{Aug,C}}_{ij\rightarrow fp} = A_{ij\rightarrow fp}^{\Lambda} + \Delta A^{\text{Aug,C}}_{ij\rightarrow fp}.
\]

(5)

Physically, the virtual excitation implies that the Coulomb interaction between two atomic electrons, \( i \) and \( j \), is modified due to the polarization of the fullerene shell. The polarization is dynamic, i.e. it depends on the transition energy \( \omega_{ij} \), so that \( \Delta A^{\text{Aug,C}}_{ij\rightarrow fp} \) is proportional to the dynamic susceptibility of the fullerene. Thus, one can expect that in those \( \omega_{ij} \)-regions, where the modulus of susceptibility is large enough, the additional channel can modify noticeably the width of the transition \( ij \rightarrow fp \).

In [2], the additional channel of the dipole Auger decay was analysed for an atom placed at the centre of a spherically symmetric fullerene. Assuming the atomic radius \( R_{a} \) to be much smaller than the fullerene radius \( R \), the authors expressed the amplitude \( \Delta A^{\text{dip,}\text{Aug,C}}_{ij\rightarrow fp} \) in terms of dynamic dipole polarizability of the fullerene. Then, carrying out the order-of-magnitude estimate, they found that \( \Delta A^{\text{dip,}\text{Aug,C}}_{ij\rightarrow fp} \sim (R_{a}/R)^{3} \), i.e. the correction is much smaller that the Auger amplitude in the isolated atom in the whole range of \( \omega \).

Below in the paper we demonstrate that the relative magnitude of the correction term is governed not only by \( \omega \) (this has been already noted in [2, 4]) but also is strongly dependent on the position of the atom inside the cage. The parameter, which defines this dependence, is the ratio \( a/R \), where \( a \) stands for the displacement of the atom from the cage centre. Below in this section we demonstrate that the correction term as a function of both \( \omega_{ij} \) and \( a/R \) varies by orders of magnitude. This can result in the dominance of the additional channel over the direct Auger decay (see the case study presented in section 3.1).
Figure 2. Illustrative picture of the atom located inside the spherical fullerene shell. The shell average radius and width are noted as $R$ and $\Delta R$, respectively. The atomic nucleus (the charge $Z_a$) is displaced by the vector $a$ from the centre. The position vectors of the fullerene, $e_a$, and the atomic, $e_s$, are noted as $r$ and $\rho$.

Let us outline the derivation of the correction term $\Delta A_{ij \rightarrow fp}^{\text{dip}, \text{A} \text{C}_n}$ for the dipole Auger transition occurring in the atom (nucleus charge $Z_a$, average radius $R_a$), located inside spherically symmetric fullerene (average radius of the cage $R$, average width of the shell $\Delta R$) and displaced by $a$ from the cage centre, see figure 2.

The two diagrams in figure 1(b) correspond to the analytic expression:

$$
\Delta A_{ij \rightarrow fp}^{\text{dip}, \text{A} \text{C}_n}(a) = \delta_{ij} \delta_{\Delta A} \sum_{n} \left[ \left\langle f; n|V|0; i \right\rangle \left\langle p|V|n; j \right\rangle \right] \omega_{0n} \omega_{n0} + \omega_{nf} + \omega_{fn} + \omega_{n0} + \omega_{nf} + \omega_{fn}
$$

(6)

The sum is carried out over the complete spectrum of the fullerene excited states (the integration over the continuous spectrum is implied), and $\omega_{0n} = \omega_{n0}$ is the energy of the virtual transition $0 \rightarrow n$.

The quantity $V = \sum_{\rho_a} 1/|r_c - \rho_a|$, stands for the Coulomb interaction between the atomic and fullerene electrons, see figure 2. Assuming the fullerene electrons to be located farther from the centre than atomic electrons, i.e. $r > |a + \rho|$, and choosing the $z$-axis along $a$, one expresses $V$ in terms of multiple series [23, 24]:

$$
V \approx \sum_{l=0}^{\infty} \sum_{l_1} \sum_{l_2} \sum_{m_1} \sum_{m_2} \frac{2l + 1}{\sqrt{\Gamma(2l + 1)}} \frac{\sqrt{\Gamma(2l_1 + 1)}}{\sqrt{\Gamma(2l_2 + 1)}} \frac{\Gamma(l_1)}{\Gamma(l_2)} \frac{\Gamma(l)}{\Gamma(l_3)} \frac{\Gamma(l_3)}{\Gamma(l_4)}
$$

$$
\times C_{lm}(r_{\rho_a}) Q_{lm}(\rho_a).
$$

(7)

Here, the quantity $Q_{lm}(\rho_a)$, defined as

$$
Q_{lm}(\rho_a) = \sqrt{\frac{4\pi}{2l + 1}} \frac{Y_{lm}(\rho_a)}{r_{\rho_a}^l}
$$

(8)

is commonly termed as the operator of $2l$-pole electric moment of the atom (the sum is carried out over atomic electrons). The quantity

$$
C_{lm}(r_{\rho_a}) = \sqrt{\frac{4\pi}{2l + 1}} \frac{Y_{lm}(r_{\rho_a})}{r_{\rho_a}^l}
$$

(9)

also is related to the multipole expansion of the electrostatic field created by the electron charge distributed in the fullerene shell (the sum is carried out over the fullerene electrons). To distinguish $C_{lm}$ from $Q_{lm}$, we call the former the operator of ‘interior 2l-pole moment’ of the fullerene (see appendix A.1 for details).

The argument $a$ on the left-hand side of (6) is added to stress that the amplitude is dependent on the displacement from the centre.

Inserting (7) into (6), one carries out the intermediate algebra and arrives at the following expression for the amplitude of the dipole $i \rightarrow f$ and $j \rightarrow p$ transitions:

$$
\Delta A_{ij \rightarrow fp}^{\text{dip}, \text{A} \text{C}_n}(a) = \delta_{ij} \delta_{\Delta A} \sum_{l=0}^{\infty} \sum_{l_1} \sum_{l_2} \sum_{m_1} \sum_{m_2} \frac{2l + 1}{\sqrt{\Gamma(2l + 1)}} \frac{\sqrt{\Gamma(2l_1 + 1)}}{\sqrt{\Gamma(2l_2 + 1)}} \frac{\Gamma(l_1)}{\Gamma(l_2)} \frac{\Gamma(l)}{\Gamma(l_3)} \frac{\Gamma(l_3)}{\Gamma(l_4)}
$$

$$
\times \left( \frac{\Gamma(l_1)}{\Gamma(l_2)} \frac{\Gamma(l)}{\Gamma(l_3)} \frac{\Gamma(l_3)}{\Gamma(l_4)} \right) \left( \frac{\Gamma(l_1)}{\Gamma(l_2)} \frac{\Gamma(l)}{\Gamma(l_3)} \frac{\Gamma(l_3)}{\Gamma(l_4)} \right) \left[ \left\langle f; n|V|0; i \right\rangle \left\langle p|V|n; j \right\rangle \right] \omega_{0n} \omega_{n0} + \omega_{nf} + \omega_{fn} + \omega_{n0} + \omega_{nf} + \omega_{fn}
$$

(10)

Here, $d_{iA}^{\text{A}}(a)$ and $d_{fA}^{\text{A}}(a)$ stand for the radial matrix elements of the atomic dipole moment, $d_{iA}^{\text{A}}(a)$ is the fullerene’s dynamic $2l$-pole polarizability of the second kind. This type of polarizability appears when one is interested in the modification of the electric field inside the fullerene due to its polarization under the action of the $2l$-pole external field whose source is also located in the fullerene interior. This is in contrast to the ‘conventional’ polarizability $d_{iA}^{\text{C}}(a)$ which is responsible for the same effect but in the case where both the source and the observation point are located outside the fullerene (see the appendix for more details).

Summing (10) and (10), one constructs the total amplitude $A_{ij \rightarrow fp}^{\text{dip}, \text{A} \text{C}_n}$ of the dipole Auger decay. Then, using $A_{ij \rightarrow fp}^{\text{dip}, \text{A} \text{C}_n}$ in (3), one derives the following set of expressions, which defines the partial width of the transition $\nu_i \rightarrow \nu_j \rightarrow \nu_f \nu V$ in the encaged atom:

$$
\Gamma_{\nu_i \nu_j \nu_f \nu V}^{\text{dip}, \text{A} \text{C}_n}(a) = \Gamma_{\nu_i \nu_j \nu_f \nu V}^{\text{dip}, \text{A}} F_{\nu_i \nu_j \nu_f \nu V}(a).
$$

(11)

The factor $F_{\nu_i \nu_j \nu_f \nu V}(a)$, which depends on the atom’s displacement, takes into account the width modification due to the presence of the fullerene (for an isolated atom $\Gamma_{\nu_i \nu_j \nu_f \nu V}^{\text{dip}, \text{A}}(a) = 1$). It can be written in the form

$$
F_{\nu_i \nu_j \nu_f \nu V}(a) = 1 - 2\kappa_{\nu_i \nu_j \nu_f \nu V} \left( \sigma_{\nu_i \nu_f; a} \right)^2
$$

(12)

The factor $\kappa_{\nu_i \nu_j \nu_f \nu V}$ is constructed from the atomic characteristics only:

$$
\kappa_{\nu_i \nu_j \nu_f \nu V} = \left( \frac{\Gamma_{\nu_i \nu_f}^{\text{dip}, \text{A}}}{\Gamma_{\nu_i \nu_f}^{\text{dip}, \text{A}}} \right)^{1/2}
$$

(13)

where $\Gamma_{\nu_i \nu_f}^{\text{dip}, \text{A}}(a)$ is the partial radiative width of the transition $\nu_i \rightarrow \nu_f$; $\sigma_{\nu_i \nu_f; a}$ is the partial cross section of the PL of the subshell $\nu_f$; and $\Gamma_{\nu_i \nu_f}^{\text{dip}, \text{A}}$ is given by (4).
The quantities $\Sigma_{1,2}(\omega_f; a)$ are dependent on the displacement $a$ and on the fullerene’s dynamic multipole polarizabilities of the second kind:

$$
\begin{align*}
\Sigma_1(\omega_f; a) &= \frac{3}{8\pi} \sum_{l=0}^{\infty} \frac{c^2}{4l^2} \left[rac{1}{l(l+1)} - \frac{1}{(l-1)}\right] \alpha^{(2)}(\omega_f) \alpha^{(0)}(\omega_f), \\
\Sigma_2(\omega_f; a) &= \frac{3}{8\pi} \sum_{l=0}^{\infty} \frac{c^2}{4l^2} \left[rac{1}{l(l+1)} - \frac{1}{(l-1)}\right] \alpha^{(2)}(\omega_f) \alpha^{(0)}(\omega_f),
\end{align*}
$$

(14)

where $c \approx 137$ is the light velocity in the atomic units. As a function of the fullerene cage radius $R$, the polarizability $\alpha^{(2)}(\omega_f)$ scales as $R^{2l-4}$ (see (A.7) and (A.12)). Therefore, the expansion parameter in the series (14) is $(a/R)^2$.

In the limit $a = 0$ (atom at the centre) only dipole terms with $l = 1$ contribute to the sums (14). Hence, one finds

$$
\Sigma_2(\omega_f; 0) = 0
$$

and

$$
\Sigma_1(\omega_f; 0) = \frac{3}{8\pi} \frac{c^2}{\alpha^{(1)}(\omega_f)} \approx \frac{3}{8\pi} \frac{c^2}{\alpha^{(0)}(\omega_f)} \frac{\alpha^{(2)}(\omega_f)}{R^6},
$$

(15)

where $\alpha^{(0)}(\omega_f)$ is the dynamic dipole polarizability of the fullerene. (The transformation from $\alpha^{(2)}(\omega_f)$ to $\alpha^{(1)}(\omega_f)$, which leads to the approximate equality, is explained in appendix A.6.) As a result, factor (12) reduces to

$$
F_{\nu i,\nu j}(0) \approx 1 - \kappa_{\nu i,\nu j} \sqrt{\frac{3}{8\pi} \frac{c^2}{\alpha^{(0)}(\omega_f)} \frac{\alpha^{(2)}(\omega_f)}{R^6}}.
$$

(16)

Expression (16) was obtained in [2]. The authors, estimating the magnitude of the correction term in the parentheses as $(R_a/R)^3 \ll 1$, derived $F_{\nu i,\nu j}(0) \approx 1$. Thus, it was tacitly concluded that the additional channel of the atomic Auger decay, figure 1(b), does not affect the decay rate if the atom is placed at the centre.

However, as the displacement $a$ from the cage centre increases, the larger contribution to the sums from (14) comes from the terms with higher $l$. This leads to a noticeable increase in the magnitude of the factor $F_{\nu i,\nu j}(a)$ not only in the vicinity of the fullerene giant plasmon resonance but in a much wider range of transition energies $\omega_fi$. Potentially, the atomic Auger decays with $\omega_fi$ within the interval $10–40$ eV can be affected.

To illustrate this statement, in figure 3 we plot the dependences of $f_1(\omega; a) \equiv -2\text{Re} \Sigma_1(\omega; a)$ and $f_2(\omega; a) \equiv |\Sigma_1(\omega; a)|^2 + |\Sigma_2(\omega; a)|^2/2$ (right panel) on the transition energy $\omega$ calculated for various $a/R$ values as indicated (see equations (12) and (14)). The data refer to the fullerene $C_{60}$ (see appendix A.5) and explanations in the text.

Figure 3. Dependences $f_1(\omega; a) \equiv -2\text{Re} \Sigma_1(\omega; a)$ (left panel) and $f_2(\omega; a) \equiv |\Sigma_1(\omega; a)|^2 + |\Sigma_2(\omega; a)|^2/2$ (right panel) on the transition energy $\omega$ calculated for various $a/R$ values as indicated (see equations (12) and (14)). The data refer to the fullerene $C_{60}$ (see appendix A.5) and explanations in the text.
pronounced in the profile of the dipole polarizability of the second kind $\tilde{\alpha}_i^{(3)}(\omega)$ (see figure A1). As the multipolarity $l$ increases, the resonance energies move towards each other and their intensities gradually equalize. For $l \gg 1$, the resonances merge at $\omega \approx 30$ eV. This explains the increase of $f_1(\omega; a)$ and $f_2(\omega; a)$ with $a$: as the displacement increases, the terms with $l \gg 1$ contribute more to series (14).

Therefore, a good candidate for the Auger width modification due to the mechanism from figure 1(b) would be an atom whose Auger spectrum has pronounced peaks in the range $\omega \approx 30$–40 eV, and which, being encaged, is located far off the centre. The molecule Sc$_3$N@C$_{80}$ is a good example of this sort. Indeed, three scandium atoms are symmetrically located far from the centre being displaced by $a \approx 2$ Å [31, 32]. In this complex, each scandium atom donates two electrons to the fullerene cage. Hence, the theory developed above in this section can be applied to the Auger transitions in the ion Sc$_3^+$, for which the Auger spectrum has been investigated both experimentally [20] and theoretically [18, 19, 33]. In section 3.1, we consider the modification of the Auger widths in Sc$_3^+$ due to the presence of the C$_{80}$ shell. The obtained results are applied further in section 3.2 to calculate the PI spectrum of the Sc$_3$N@C$_{80}$ molecule. The results of our calculations are compared with a recent experiment [1].

2.3. Additional channel of the Auger decay in the endohedral atom

In addition to the modification of the atomic Auger decay via the change of the electric field at the atom, the presence of the fullerene shell opens another channel of the Auger decay, which is absent in the isolated atom [2, 4, 5]. The diagrammatical representation of this process is given in figure 4. The energy $\omega_{i f}$, released in the atomic transition $i \rightarrow f$, is transferred, by means of the Coulomb interaction, to the fullerene electron which becomes ionized. In [4], the process was called interatomic Coulomb decay, thus pointing out its similarity with the interatomic decay in smaller systems (e.g., in neon dimer [6]).

It was pointed out in [2, 4] that this decay channel in the endohedral atom becomes especially important if the non-radiative transition $i \rightarrow f$ is energetically forbidden in the isolated atom. In this case, one compares the additional Auger decay width $\Gamma_{i f}^{\text{Aug}}$ and the width of the radiative decay, $\Gamma_{i f}^{\gamma A}$. The estimates, carried out in [2, 4] for atoms placed at the centre of the C$_{80}$ cage, show the dramatic increase of the decay rate (by the factor $\Gamma_{i f}^{\text{Aug}} / \Gamma_{i f}^{\gamma A} \sim 10^5$–$10^9$) for the transitions with $\omega_{i f}$ lying in the vicinity of the giant plasmon resonance at 20 eV.

In this section, we demonstrate that for off-the-centre atoms the increase of the decay rate can become even more pronounced and in a much wider range of the transition energies.

To construct the amplitude of the process presented in figure 4, we use the approximate formula (7) for the atom–fullerene Coulomb interaction. The amplitude is used further in (3) to derive the width. Restricting ourselves to the dipole transitions $v_i \rightarrow v_f$, we obtain the following expression for the partial width of the transition as a function of the atom displacement:

$$\Gamma_{v_i v_f}^{\text{Aug}, \text{A@C}_8}(a) = F(\omega_{i f}; a) \Gamma_{v_i v_f}^{\gamma A}. \quad (17)$$

The factor $F(\omega_{i f}; a)$ stands for the ratio of the Auger decay width in the endohedral atom to the radiative width in the isolated atom. It depends on the displacement and the transition energy and can be written as follows:

$$F(\omega_{i f}; a) = \frac{c^3}{2a_0^3} \sum_{l=1}^{\infty} (2l + 1) a^{2l-2} \text{Im} \tilde{\alpha}_l^{(1)}(\omega_{i f}). \quad (18)$$

Similar to the series from (14), the expansion parameter is $(a/R)^2$.

Placing an atom at the centre and accounting for the approximate relation (A.19), one derives $F(\omega_{i f}; 0) = (3c^3/2a_0^3) \text{Im} \tilde{\alpha}_1^{(1)}(\omega_{i f}) \approx (3c^3/2R^6\omega_{i f}^3) \text{Im} \sigma_1^{(1)}(\omega_{i f})$. Using the latter expression in (17), one arrives at the formula derived in [2].

Dependence of the ratio $F(\omega; a)$ on the transition energy, calculated for several $a/R$ values, is presented in figure 5. The data refer to C$_{80}^-$. The parameters of the fullerene cage and of the dynamic polarizabilities $\tilde{\alpha}_i^{(3)}(\omega)$ are given in appendix A.5.

It is worth noting the change in the $F(\omega; a)$ profile with the increase of the displacement $a$. For the at-the-centre atom (or slightly off-the-centre) the behaviour of $F(\omega; a)$ is determined...
by the imaginary parts of $\tilde{\alpha}_l^{\text{CN}}(\omega)$ with $l \approx 1$ (see the lower-left graph in figure A1). As a result, there is a pronounced maximum at $\approx 20 \text{ eV}$—the energy of the first surface plasmon excitation. In the vicinity of the second surface plasmon peak ($\approx 36 \text{ eV}$), the value of $F(\omega; a)$ is an order of magnitude lower.

As the displacement increases, the higher-$l$ terms contribute to the right-hand side of (18). For $l \gg 1$ both plasmon modes merge, so that for each $l$ the dependence $\text{Im} \alpha_l^{\text{CN}}(\omega)$ has a single peak at $\omega \approx 30 \text{ eV}$. Hence, in this energy range the ratio $F(\omega; a)$ acquires additional enhancement. The curves with $a/R = 0.4$–0.6 show that a large enhancement can be achieved in a wide interval of energies: $\omega \approx 20–40 \text{ eV}$.

Therefore, we conclude that the decay channel, presented in figure 4, can be additionally intensified (by more than the order of magnitude) if the endohedral atom is located sufficiently far away from the cage centre.

2.4. The radiative decay in the endohedral atom

The radiative decay $i \rightarrow f + \gamma$ in an isolated atom is represented by the first diagram in figure 6. The correction due to the virtual polarization of fullerene under the joint action of the Coulomb interaction and the photon field is illustrated by the other two diagrams in the figure. For a centrally positioned atom, this process was considered in [2].

For a non-central position, applying the approximations described above, one derives the following formula which relates the partial widths of the (dipole) radiative decay in the endohedral atom and in the isolated one:

$$\Gamma_{\gamma; \lambda; \text{CN}} = D(\omega_{if}) \Gamma_{\gamma; \lambda}^{\lambda \text{CN}},$$

(19)

where

$$D(\omega_{if}) = |1 - \beta_{1,\lambda}^{\text{CN}}(\omega_{if})|^2.$$  

(20)

Here, $\beta_{1,\lambda}^{\text{CN}}(\omega_{if})$ stands for the dipole shielding factor of the fullerene. This quantity determines the modification of the electric field inside the fullerene due to its polarization under the action of the external uniform electric field (see the appendix for more details). Using the approximate relationship between $\beta_{1,\lambda}^{\text{CN}}(\omega_{if})$ and the dipole polarizability of the fullerene, $\beta_{1,\lambda}^{\text{CN}}(\omega_{if}) \approx \alpha_{1,\lambda}^{\text{CN}}(\omega_{if})/R^3$ (see (A.19)), one reduces the right-hand side of (19) to the formula derived in [2] for the atom at the centre.

The quantity $D(\omega)$ is a so-called dynamical screening factor [28, 29, 34]. It is equal to the ratio of the intensity of the total electric field $E_{\text{tot}}$ at the atom to the intensity of the external field $E_0$ applied to the endohedral system A@CN. The total electric field $E_{\text{tot}} = E_0 + \Delta E$ contains an additional term $\Delta E$ which is due to the shell polarization. In the cited papers, it was demonstrated that $D(\omega)$ defines the increase of the photoabsorption rate of the atom due to the presence of the fullerene shell. The radiative decay is the inverse process for the photoabsorption. Therefore, the same dynamical screening factor relates the radiative width in the encaged and isolated atoms.

The factor $D(\omega)$, as defined by (20), does not depend on the distance $d$ from the cage centre. This is a consequence of the approximation made to derive equation (20). Namely, when calculating the additional electric field $\Delta E$, we ignored the reciprocal effect of the polarized atom on the shell. Thus, it was assumed that the shell is polarized only under the action of the uniform field $E_0(\omega)$ of the dipole photon. The field $E_0(\omega)$ gives rise to a uniform polarization of the field inside the cavity of the fullerene. As a result, the dynamical screening factor is not sensitive to the position of the endohedral atom [28, 34]. Such an approximation must be modified if the atomic dynamic dipole polarizability $\alpha_{1,\lambda}^{\text{CN}}(\omega)$ is large enough to cause a noticeable additional polarization of the shell. In this case, as was demonstrated in [29, 35], the dynamical screening factor acquires dependence on the displacement vector $\alpha$. In this paper, for the sake of simplicity, we ignore this reciprocal effect of the polarized atom on the shell.

The dependence of the dynamical screening factor on the photon energy is presented in figure 7. The calculations, performed for $C_{80}$, were carried out within the PRA, see appendix A.4. The profile of this dependence, characterized by a powerful peak in the vicinity of the symmetric surface plasmon energy and with the extended right shoulder due to the activation of the antisymmetric plasmon excitation, is similar to those reported earlier for other spherically symmetric fullerenes of finite thickness [28, 35]. Thus, one can expect the order-of-magnitude increase in the decay rate magnitude for radiative transitions within the $\approx 20–25 \text{ eV}$ range, and less than that for $\omega \approx 25–35 \text{ eV}$. 

Figure 6. The radiative decay $i \rightarrow f$ in an isolated atom (the first diagram) and the correction due to the virtual excitation $0 \rightarrow n$ of the fullerene (two last diagrams). The dashed line depicts the emitted photon, other notations as in figure 1. The energy conservation law implies $\omega = \omega_{if}$.

Figure 7. Dynamical screening factor $D(\omega) = |1 - \beta_{1,\lambda}^{\text{CN}}(\omega)|^2$ for the fullerene $C_{80}$. 

\[ \text{Figure 7. Dynamical screening factor } D(\omega) = |1 - \beta_{1,\lambda}^{\text{CN}}(\omega)|^2 \text{ for the fullerene } C_{80}. \]
To conclude this section, let us note that the applicability of the PRA for the dynamical screening factor was tested in [29, 35, 36] against the TDLDA calculations [37, 38]. A good quantitative agreement between these two approaches was reported.

3. Numerical results

In this section, we apply the above-described approach to carry out the model calculations of the PI cross section of the endohedral complex Sc3N@C60 in the photon energy range 30–45 eV. Within this range of photon energies, the PI spectrum of an isolated ion Sc2+ is dominated by autoionizing resonances (of the widths less than 1 eV) due to 3p excitations [18–20]. However, recent experiments by Müller et al [1] demonstrated that a distinct resonance structure is absent in the endohedral complex Sc2+@C78. Deduced by digitalizing figures 9 and 10 of [20].

In what follows, we start with the quantitative analysis of the dependence of the autoionizing widths in the encaged Sc2+ on the displacement of the ion from the cage centre due to the mechanisms discussed in sections 2.2 and 2.3. The obtained data are used further to calculate the PI spectrum of the endohedral complex.

3.1. Auger widths in Sc2+ and Sc2+@C60

Cross sections for the PI of Sc2+ ions were measured by employing the merged ion–photon beams technique [20]. It was noted (see also [19]) that in addition to a direct PI pathway, the process can proceed via an intermediate resonance state according to the scheme

\[ h\omega + \text{Sc}^{2+} \rightarrow (\text{Sc}^{2+})^* \rightarrow \text{Sc}^{3+} + e^- . \]  (21)

The intermediate state decays via (super-)Coster–Kronig transition resulting in a resonance line in the PI spectrum.

The Sc2+ ion beam, used in the experiment, contained ions in the ground state (the configuration [Ne]3s23p63d22P3/2) and in the first two excited, metastable states ([Ne]3s23p63d22D5/2 and [Ne]3s23p63d24s21S1/2) as well. This leads to a variety of the intermediate states (Sc2+) and, as a result, to a number of measured peaks in the spectrum within the photon energy range 30–45 eV. The parameters of the experimentally measured peaks are given in the tables and figures of [20]. Theoretical data on the resonances together with the theory-versus-experiment discussion can be found in [19] (see also [33]).

For our case study, we restrict ourselves to the transitions from the ground state only. In table 1, the data are presented on the most pronounced PI resonances within the interval \( \omega = 31–42 \) eV. For each excited state (Sc2+)*, the following information is included: the resonance energy \( \omega_{21} \) (subscripts ‘1’ and ‘2’ mark the ground and the excited states, respectively), peak value \( \sigma \) of the PI cross section, the Auger width \( \Gamma^{(\text{Sc}^{2+}*)} \), peak area \( S \), radiative width \( \Gamma_{2\rightarrow1}^{\gamma} \), and the parameter \( \kappa = (\Gamma^{(\text{Sc}^{2+}*) \sigma / \Gamma_{2\rightarrow1}^{\gamma})^{1/2} \) calculated in accordance with (13).

The values of \( \omega_{21} \), \( \sigma \), \( \Gamma^{(\text{Sc}^{2+}*)} \) and \( S \) were deduced from the data presented in table II and figures 4, 5, 8–10 of [20].

### Table 1. Transition energies \( \omega_{21} \) from the excited state (Sc2+) to the ground state Sc2+(D1/2), peak widths \( \Gamma^{(\text{Sc}^{2+}*)} \), peak values of the PI cross section \( \sigma \), peak areas \( S \), radiative widths \( \Gamma_{2\rightarrow1}^{\gamma} \), and parameters \( \kappa \) (see equation (13)).

| \( \text{(Sc}^{2+}*)^{a} \) | \( \omega_{21} \) (eV) | \( \Gamma^{(\text{Sc}^{2+}*)} \) (meV) | \( S \) (eV Mb) | \( \sigma \) (Mb) | \( \Gamma_{2\rightarrow1}^{\gamma} \) (10^-6 eV Mb) | \( \kappa \) |
|-----------------|-------------|------------------|-------------|-------------|------------------|-----|
| 3d2 2F5/2       | 31.66       | 0.87             | 4.88        | 0.15        | 4.71 x 10^-4     |
| 3d4s 2F3/2      | 33.22       | 4.22             | 12.72       | 0.70        | 3.10 x 10^-3     |
| 3d4s 2F5/2      | 34.73       | 5.40             | 6.49        | 1.13        | 7.02 x 10^-3     |
| 3d4s 2P3/2      | 37.14       | 7.29             | 36.00       | 11.4        | 4.17 x 10^-3     |
| 3d2 3P1/2       | 39.63       | 11.5             | 10.14       | 8.24        | 0.120            |
| 3d2 3P3/2       | 39.72       | 11.3             | 9.00        | 0.65        | 1.36 x 10^-2     |
| 3d2 3D3/2       | 40.22       | 2.8              | 4.50        | 0.45        | 5.60 x 10^-2     |

\( a \) [Ne]3s23p3 is omitted in the excited-state designation.
\( b \) Calculated from the Lorenz profile (see explanation in the text).
\( c \) Deduced by digitalizing figures 9 and 10 of [20].

When indicated, the Auger width (or the cross section \( \sigma \)) was calculated assuming the Lorentz profile of the peak. This was carried out using the relation \( \sigma = 2\pi/\Gamma \). Thus, in our calculations we ignored the asymmetry seen in the experimentally measured peaks.

The radiative width of the transition \( 2 \rightarrow 1 \) was calculated as follows:

\[ \Gamma_{2\rightarrow1}^{\gamma} = \frac{2\sigma_{21}}{\Gamma_{1}} \frac{g_{1}}{g_{2}} f_{1\rightarrow2} \]  (22)

where \( g_{1} = 4 \) and \( g_{2} \) are statistical weights of the ground and the excited states, respectively, and \( f_{1\rightarrow2} \) is the oscillator strength of the transition \( 1 \rightarrow 2 \). For a given transition, \( f_{1\rightarrow2} \) is related to the PI peak area \( S \) through \( f_{1\rightarrow2} = (c/2\pi)^{3} S \).

Once the values of \( \Gamma_{2\rightarrow1}^{\gamma} \) and \( \kappa \) are established, one can use them in (11), (12), (17) and (19) to calculate the total widths of the excited states for the ion Sc2+ encaged in a fullerene. The results of such calculations, carried out for the system Sc2+@C60, are presented in table 2.

The first three columns in table 2 are identical to those from table 1 and are reproduced for the sake of convenience only. The present values of the total width \( \Gamma_{\text{tot}}^{(\text{Sc}^{2+})*} \) were obtained by summing three terms, calculated from (11), (17) and (19) for several values of the \( a/R \) ratio as indicated.

For each excited state (Sc2+)*, the upper line presents the values of \( \Gamma_{\text{tot}}^{(\text{Sc}^{2+})*\sigma} \) obtained using the data on \( \Gamma_{2\rightarrow1}^{\gamma} \) and \( \kappa \) from table 1. The lower line was obtained using the \( \Gamma_{2\rightarrow1}^{\gamma} \) and \( \kappa \) values corrected due to the recommendation made by Sossah et al [19].

In the cited paper, the theoretical calculations of the PI cross section of Sc2+ were performed for photon energies from threshold to 68.0 eV. The calculation results were compared to the experimental data from [20]. One of the results of this comparison concerns the discrepancy in the calculated and measured values of the total oscillator strength of the 3p0 shell, which must be equal to 6 in accordance with the Thomas–Reiche–Kuhn sum rule. On the basis of physical

\[ \text{3} \] The contribution of the modified radiative width, equation ([19]), to \( \Gamma_{\text{tot}}^{(\text{Sc}^{2+})*\sigma} \) is negligible compared with the other two terms. It is mentioned for the sake of consistency only.

Notes:
[33] A V Korol and A V Solov'yov J. Phys. B: At. Mol. Opt. Phys. 44 (2011) 085001
arguments, presented on pp 7–8 of [19], the authors indicate that ‘...the total oscillator strength in the π cross section of Sc2+ from threshold to 68 eV should be a bit under 6...’. They noted further that the calculated total oscillator strength is 5.29, whereas the one which follows from the experimental data equals 3.24, which is too low. The conclusion, which is drawn by the authors, is as follows: ‘Thus we believe that the overall magnitude of the measured cross section is too small and should be multiplied by a factor of 5.29/3.24 = 1.63 to bring the oscillator strength to a reasonable value’.

One easily verifies that such multiplication increases $\Gamma_{2\to1}^{\gamma}$ and $\kappa$ by the same factor of 1.63. The lower lines in table 2 were obtained using these enhanced values.

The data in table 2 illustrate the sensitivity of the width $\Gamma_{tot}^{(Sc^{2+})^{\gamma}\@C_5^m}(a)$ both on the atom displacement and on the excited state. While for all excited states $(Sc^{2+})^+$ the widths increase with $a$, the increase rate is quite different for different states. It can be quite moderate as $a/R$ varies from 0 to 0.6 (e.g., the increase by approximately 50% in the case of $3d^2 2F_{5/2}$ at $a_{21} = 31.66$ eV) or very sharp (up to $10^3$ increase for the $3d^2 2P_{1/2}$ state).

Let us briefly describe the relative contribution of the two mechanisms, presented by figures 1(b) and 4, to the total width $\Gamma_{tot}^{(Sc^{2+})^{\gamma}\@C_5^m}(a)$. With the exception for the $3d^4 2P_{1/2}$ excited state, the contribution due to the diagram in figure 1(b) dominates by the factor from 2 to 20 depending on the state and the $a/R$ value. In the case of $3d^4 2P_{1/2}$ both channels contribute to the total width almost equally.

In figure 8, the dependence $\Gamma_{tot}^{(Sc^{2+})^{\gamma}\@C_5^m}(a)$ is plotted for the excited $3d^2 2F$ state (excitation energy $\omega_{21} = 37.14$ eV) which is responsible for the widest peak in the PI cross section from the ground state of Sc$^{2+}$ [20]. In the encaged ion, the width can attain noticeably larger values than in the isolated ion (the horizontal line in the graph), and this influences the profile of the PI spectrum.

### Table 2. Total widths $\Gamma_{tot}^{(Sc^{2+})^{\gamma}\@C_5^m}(a)$ for several $a/R$ ratios. For each transition the upper line is due to the $\Gamma_{2\to1}^{\gamma}$ and $\kappa$ data from table 1, and the lower line was obtained accounting for the correction due to Sossah et al [19] (see explanation in the text).

| $(Sc^{2+})^+$ | $\omega_{21}$ | $\Gamma_{tot}^{(Sc^{2+})^{\gamma}\@C_5^m}$ (eV) | $a/R = 0$ | $a/R = 0.4$ | $a/R = 0.5$ | $a/R = 0.55$ | $a/R = 0.6$ |
|-------------|-----------|-----------------|----------|-----------|-----------|-----------|-----------|
| $3d^2 2F_{5/2}$ | 31.66 | 116 | 0.116 | 0.118 | 0.127 | 0.141 | 0.177 |
| $3d^4 2P_{1/2}$ | 33.22 | 45 | 0.048 | 0.071 | 0.117 | 0.183 | 0.351 |
| $3d^4 2F_{5/2}$ | 34.73 | 53 | 0.062 | 0.114 | 0.215 | 0.361 | 0.761 |
| $3d^2 2F_{5/2}$ | 37.14 | 847 | 1.027 | 1.343 | 1.829 | 2.432 | 3.849 |
| $3d^2 2P_{1/2}$ | 39.63 | 11.5 | 0.118 | 0.363 | 0.931 | 1.875 | 4.769 |
| $3d^2 2P_{3/2}$ | 39.72 | 11.3 | 0.018 | 0.028 | 0.044 | 0.066 | 0.122 |
| $3d^2 2D_{5/2}$ | 40.22 | 2.3 | 0.008 | 0.020 | 0.044 | 0.082 | 0.195 |

Figure 8. Total width $\Gamma_{tot}^{(Sc^{2+})^{\gamma}\@C_5^m}(a)$ of the excited $3d^2 2F$ state (excitation energy $\omega_{21} = 37.14$ eV) versus $a/R$. The dashed curve was calculated using the $\Gamma_{2\to1}^{\gamma}$ and $\kappa$ data from table 1. The chained curve accounts for the 1.63-correction due to Sossah et al [19] (see explanation in the text). The horizontal solid line marks the width in the isolated ion Sc$^{2+}$. The vertical line marks the ratio $a/R = 0.55$ which can be estimated as the largest available for Sc$^{2+}$ in Sc$_8$N@C$_{60}$ (see section 3.2).

To analyse the influence of the fullerene cage on the PI spectrum of Sc$^{2+}$, one can use the following simple model. The cross section $\sigma_{Sc^{2+}}(\omega; a)$ is calculated as the sum of resonance terms corresponding to the intermediate excited states $(Sc^{2+})^+$ listed in tables 1 and 2. Each term is approximated by a symmetric Lorentzian line profile. Thus, the model does not account for the asymmetry of the peaks (see the discussion in [20]). Hence, $\sigma_{Sc^{2+}}(\omega; a)$ can be written as follows:

$$
\sigma_{Sc^{2+}}(\omega; a) = \frac{1}{2\pi} \sum_{j=1}^{7} \frac{S_j \Gamma_j}{(\omega - \omega_j)^2 + \Gamma_j^2/4},
$$

(23)
where \( j \) enumerates the excited states. For each \((\text{Sc}^{2+})^j\), the values of resonance frequency \( \omega_j \), peak area \( S_j \), and peak width (for the isolated ion as well as for the encaged one) are given in the tables.

Figure 9 presents the dependence of \( \sigma_{\text{Sc}^{2+}}(\omega; a) \) on \( \omega \) calculated for the isolated scandium ion (thin solid curve) and for \( \text{Sc}^{2+} \) encaged in \( \text{C}_{60}^- \) at different distances from the centre. To calculate the resonance terms in (23) we used, for each indicated value of the ratio \( a/R \), the resonance terms \( \Gamma_{\text{tot}}^{j} \) (isolated) listed in the upper lines of table 2. Within the model framework, we assumed the peak areas \( S \) (see the third column in table 1) to be independent of \( a \). Also, we disregarded the possible redistribution of the ionic oscillator strength due to the presence of the fullerene shell [12].

The focus of our study is on the modification of the PI spectrum profile due to the Auger widths broadening. From this viewpoint, the comparison of different curves in figure 9 is quite illustrative. For moderate values of \( a/R \), similar to the case of the isolated ion, the spectrum is dominated by well-separated lines. As \( a \) increases, the lines, loosing in the peak values and gaining in the widths, become less accentuated. For \( a/R = 0.5 \sim 0.6 \) (this range of the \( a/R \) ratio is quite realistic, see section 3.2) the spectrum noticeably flattens. This effect is most pronounced for \( \omega \lesssim 35 \sim 37 \text{ eV} \), where the effect of the fullerene shell polarization on the ionic Auger decay is very strong (see figures 3 and 5).

### 3.2. PI spectrum of \( \text{Sc}_3\text{N}@\text{C}_{60}^+ \)

In [1], the experimental results for the PI cross section were reported for \( \text{Sc}_3\text{N}@\text{C}_{60}^+ \). To carry out the theoretical investigation of the PI process of this endohedral system, we assume that both its electronic structure and isomeric form are close to those of the neutral compound \( \text{Sc}_3\text{N}@\text{C}_{60} \), which is a member of a family of the tri-metallic-nitride endohedral system [39]. These objects are rather curious in that often both of the two subsystems are unstable in isolation. When these two subsystems are combined into an endohedral fullerene, there is a series of electron transfers between various components of the subsystem that results in a mutual stabilizing effect [40].

Electronic structure of \( \text{Sc}_3\text{N}@\text{C}_{60} \)-metallofullerene was discussed in [21]. Each scandium atom donates two electrons to the fullerene cage. Additionally, a partial charge of 0.4 is donated to the nitrogen atom. The endohedral complex is therefore \((\text{Sc}^{2+})_2\text{N}^{1.2+}@\text{C}_{60}^0\). For the purposes of this paper, we ignore the partial charges in all intermediate stages of the calculations. Hence, each scandium ion is treated as doubly ionized, \( \text{Sc}^{2+} \), and the nitrogen is considered as a neutral atom. At the final stage, when constructing the PI cross section of the compound \( \text{Sc}_3\text{N}@\text{C}_{60}^+ \) the partial charges will be accounted for following the phenomenological arguments presented in [1].

The isomeric form of the \( \text{C}_{60}^- \) cage becomes of the \( I_h \) type, i.e. ‘nearly spherical’. Based on the study of Nakao et al. [25] (see also [41]) one can use the value \( R = 4.15 \text{ Å} \) for the average radius of the isomer.

All four atoms of the \( \text{Sc}_3\text{N} \) complex lie in a single plane [31, 32]. The nitrogen atom forms the central part of the structure, and the three scandium atoms are positioned at an average separation of 2.0 Å. Therefore, had the nitrogen atom resided at the cage centre, the (average) displacement of each \( \text{Sc}^{2+} \) would be \( a \approx 2 \text{ Å} \), i.e. \( a/R \approx 0.5 \). However, analysing the NMR spectra of \( \text{Sc}_3\text{N}@\text{C}_{60}^0 \), Stevenson et al. [32] indicated that the complex is not localized in any particular site in the fullerene. Therefore, it is meaningful to estimate the largest displacement \( a_{\text{max}} \) which can be experienced by \( \text{Sc}^{2+} \) in the \( \text{C}_{60}^- \) cage. Calculating the density of the electron cloud in the ground state of \( \text{Sc}^{2+} \) (for example, by means of the Hartree–Fock code [42]), one finds that \( R_{\text{Sc}^{2+}} \approx 1.1 \text{ Å} \) is a good estimate for the radius of the ion. Taking into account that the thickness of the fullerene electron cloud is 1.5 Å [43] for \( \text{C}_{60}^- \), we find the shortest distance between \( \text{Sc}^{2+} \) and the cage as \( 1.1 + 0.75 = 1.85 \text{ Å} \). This value suggests that the largest displacement of \( \text{Sc}^{2+} \) from the centre is \( a_{\text{max}} \approx R - 1.85 \text{ Å} = 2.3 \text{ Å} \), yielding \( a_{\text{max}}/R \approx 0.55 \).

Hence, to estimate the increase in the Auger widths in \( \text{Sc}^{2+} \) due to the excitation of the plasmon oscillations in the fullerene shell, one can use the \( a/R \) ratio from the range 0.5–0.55 (see table 2 and figures 8 and 9).

In the photon energy range 30–45 eV, the PI cross sections of the fullerene cage [1] and of the nitrogen atom [44] are the smooth functions of \( \omega \). Therefore, one would expect that any peculiarity in the cross section \( \sigma_{\text{Sc}^{2+},\text{N}@\text{C}_{60}^0} \) of the endohedral complex is due to the scandium ions. Ignoring the difference in the PI cross section between the \( \text{C}_{60}^- \) and \( \text{C}^{5-} \)-cages, one can write the following approximate relation:

\[
\Delta \sigma(\omega; a) \equiv \sigma_{\text{Sc}_3\text{N}@\text{C}_{60}^+} - \sigma_{\text{C}_{60}^-}(\omega) \approx \sigma_N(\omega) + 3 \sigma_{\text{Sc}^{2+}N}(\omega; a).
\] (24)

The experimental data on \( \sigma_{\text{Sc}_3\text{N}@\text{C}_{60}^+} \) and \( \sigma_{\text{C}_{60}^-}(\omega) \) can be found in figure 3 of [1]. Therefore, to carry out a theory-versus-experiment comparison it is necessary to evaluate the right-hand side of (24). To calculate the term \( \sigma_N(\omega) \), we used...
calculations carried out for Sc$^+$ ions displaced by $a/R$ from the cage centre; the solid curve, which was obtained by using the PI cross sections of the second kind are large enough.

In figure 10, we present the calculated dependences $\Delta \sigma(\omega; a)$ together with the experimental data which were obtained by digitalizing the upper graph in figure 3 of [1]. The fitting, carried out in the cited paper, suggests that the experimental data can be described by a single broad peak of $6 \text{ eV}$ full-width at half-maximum (this profile is not drawn in figure 10). This behaviour clearly differs from that of the thin solid curve, which was obtained by using the PI cross sections for the isolated Sc$^{3+}$ ion in (24).

The correspondence between theory and experiment can be considerably improved by accounting for the shell polarization and placing the scandium ions away from the cage centre. Two thick curves in figure 10 represent $\Delta \sigma(\omega; a)$ calculated for $a = 0.55R = 2.3 \text{ Å}$ from the cage centre; the solid curve obtained without the 1.63-correction due to [19], and the dashed curve when the correction was accounted for. See explanation in the text.


The tabulated data [45]. The calculation of $\sigma_{\text{Sc}^{3+}}(\omega; a)$ was carried out in accordance with (23). Additionally, the obtained $\sigma_{\text{Sc}^{3+}}(\omega; a)$ curves were shifted on the photon energy axis by +1.5 eV. This shift accounts (approximately) for the increase in 3p subshell binding energy of the Sc charge state 2.4+ instead of 2+ [1].

In figure 10, we present the calculated dependences $\Delta \sigma(\omega; a)$ together with the experimental data which were obtained by digitalizing the upper graph in figure 3 of [1]. The fitting, carried out in the cited paper, suggests that the experimental data can be described by a single broad peak of $6 \text{ eV}$ full-width at half-maximum (this profile is not drawn in figure 10). This behaviour clearly differs from that of the thin solid curve, which was obtained by using the PI cross sections for the isolated Sc$^{3+}$ ion in (24).

The correspondence between theory and experiment can be considerably improved by accounting for the shell polarization and placing the scandium ions away from the cage centre. Two thick curves in figure 10 represent $\Delta \sigma(\omega; a)$ calculated for $a = 0.55R = 2.3 \text{ Å}$ from the cage centre; the solid curve obtained by using the $S$ values from table 1 and the upper columns of $\Gamma_{\text{Sc}^{3+}}(\omega; a)$ from table 2. The dashed curve was obtained by obtaining the correction due to Sossah et al. [19]. Within this scheme, the peak areas $S$ were multiplied by 1.63 and the lower values from the $a/R = 0.55$ column of table 2 were used.

Taking into account the approximate framework used to describe the dynamic plasmonic effects in the fullerene shell (the resonance plasmon approximation accompanied by several parameters introduced 'by hand') as well as several simplifying and phenomenological assumptions made to calculate the right-hand side of (24), we would not claim that these curves fully reproduce the experimental data. The main drawback of the calculated profiles is that they still contain several peaks associated with the ionic transitions indicated in table 1. These features have not been seen in the experiment [46]. Nevertheless, the general trend, which was intuitively formulated in [1], is quite clear: the presence of the fullerene cage could result in significant broadening of atomic/ionic resonances in PI. The case study, which has been carried out in this paper and which is illustrated by figure 10, indicates that the impact of the cage polarization on the PI peaks strongly depends on (a) the location of the target atom inside the cage, (b) the energy of the atomic transition and (c) the magnitudes of the radiative and non-radiative width of the transition.

4. Summary

In summary, we have demonstrated that the Auger decay rate in an endohedral atom is very sensitive to the atom’s location in the fullerene cage as well as to the energy $\omega$ released in the decay process.

Two additional decay channels have been considered, which appear in an endohedral system and lead to the modification of the rate. Firstly, there is a correction to the direct Auger decay channel due to the change in the electric field at the atom caused by the dynamic polarization of the fullerene electron shell by the Coulomb field of the decaying vacancy. In principle, this correction can be of either sign (depending on $\omega$), and, thus, can either increase or decrease the decay rate. Within the second channel, the released energy is transferred to the fullerene electron via the Coulomb interaction.

The contributions of both additional mechanisms are expressed in terms of the fullerene dynamic multipole polarizabilities of the second kind. This type of polarizability appears when one is interested in the modification of the electric field in the interior of any hollow object (e.g., a fullerene) due to its polarization under the action of the external field whose source is also located inside the object. This is in contrast to the ‘conventional’ polarizability which is responsible for the same effect but in the case when both the source and the observation point are located in the exterior. Thus, one can expect the modification of the decay rate to be most pronounced in those $\omega$-regions where the polarizabilities of the second kind are large enough.

The relative magnitudes of the correction terms are governed not only by the transition energy but also are strongly dependent on the position of the doped atom. (This feature is absent in the radiative decay processes.) The parameter, which defines this dependence, is the ratio of the off-the-centre atomic displacement $a$ from the fullerene centre to the average radius $R$ of the cage. As $a/R$ increases, the enhancement of the width occurs for the transitions whose energies are in the vicinity of the fullerene surface plasmons energies of high multipolarity.

We have demonstrated that the correction terms as the functions of both $\omega$ and $a/R$ vary by orders of magnitude. This can result in the dominance of the additional channels over the direct Auger decay and can lead to pronounced broadening of the atomic emission lines.

On the basis of the developed formalism, we carried out a case study for the system Sc$^{2+}$@C$_{80}^{-}$. It has been demonstrated...
that narrow resonances in the spectrum of an isolated Sc$^{2+}$ in the energy range $\omega = 30 - 45$ eV are noticeably broadened if the ion is located strongly off the centre ($a/R \approx 0.5$). Our model allowed us to carry out the quantitative analysis of the PI of the endohedral complex Sc$_{2}$N@C$_{60}$. We have demonstrated that due to the the non-central position of the three scandium atoms as well as to the fact that the multipolar surface plasmons’ energies of the fullerene lie within the indicated range, the additional decay channels can be responsible, at least partly, for the strong modification of the PI spectrum profile detected experimentally. The analysis of another reason of the lines broadening, which is also due to the presence of the fullerene shell but different from those discussed in this paper, will be published elsewhere.

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**Appendix. Multipole polarizabilities of hollow objects**

In this appendix, we present general definitions and discuss basic properties of different types of multipole polarizabilities which characterize the response of a ‘hollow object’ to an external electric field. By a hollow object, we will understand any object which has at least one cavity in its interior. A fullerene C$_{N}$, whose (average) radius $R$ greatly exceeds the radius of valence electrons in a carbon atom, can be treated as a hollow object if one neglects the probability of observing electrons in most part of the fullerene interior.

**A.1. Definitions**

Any system of electric charges becomes polarized if exposed to an external electric field. The polarization of this object leads to an additional electric field whose potential depends on the multipolarity of the external field, on the distance from the system to the observation point, and on the (multipole) polarizability, i.e. the quantity which describes the system’s response to the external field.

If an object has no internal cavity (e.g., an atom, a simple molecule), it is natural to assume that a source of the external field (e.g., a point-like charge) is located outside the object. Then, one can distinguish two different cases: the observation point is located (i) outside or (ii) inside the object. The different quantities are responsible for the system’s response in these two cases. Conventionally (see, e.g., [47]), the characteristic associated with case (i) is called a polarizability, whilst case (ii) is described by the quantity termed ‘a shielding factor’.

As discussed below, the response of a hollow object to the action of an external electric field can be described in terms of three different quantities. In addition to the two mentioned ones, the third quantity corresponds to the situation when both the external charge and the observation point are located inside the object.

Let us briefly discuss the quantum formalism which one can apply for a quantitative description of these quantities. For the sake of simplicity, we consider the following model hollow object (called below ‘a fullerene’): a system of $N_e$ electrons located in the vicinity of the spherically symmetric ionic cage of the radius $R$. Let the fullerene be exposed to the field of a point charge $q$ located in some point with the position vector $\mathbf{r}_q$.

Expanding the operator of the Coulomb interaction $V = -\sum_{i=1}^{N_e} q_i / |\mathbf{r}_i - \mathbf{r}_q|$ between $q$ and the fullerene electrons in spherical harmonics, one presents it in the form $V = -q \sum_{lm} \phi_{lm}(\mathbf{r}_q, \{r_j\})$. The multipole potentials $\phi_{lm}(\mathbf{r}_q, \{r_j\})$ depend on whether the charge $q$ is located in the fullerene exterior ($r_q \gg \{r_j\}$) or interior ($r_q \ll \{r_j\}$):

$$\phi_{lm}(\mathbf{r}_q, \{r_j\}) = \frac{4\pi}{2l+1} \left( \begin{array}{c} Y_{lm}^*(\mathbf{r}_q) \frac{r_q^{l+1}}{r_j} Q_{lm}(\{r_j\}) \\ \{r_q^{l+1} Y_{lm}^*(\mathbf{r}_q) C_{lm}(\{r_j\}) \end{array} \right)$$

(A.1)

where

$$Q_{lm}(\{r_j\}) = \frac{4\pi}{2l+1} \sum_{j} r_j^{l+1} Y_{lm}(r_j),$$

$$C_{lm}(\{r_j\}) = \frac{4\pi}{2l+1} \sum_{j} Y_{lm}(r_j).$$

(A.2)

The first one of these quantities, $Q_{lm}(\{r_j\})$, is expressed in terms of the so-called regular solid harmonics $r_j^{l+1} Y_{lm}(r)$ (see, e.g., [48, 49]), and is commonly associated with the 2'-pole moment of a system of point unit charges (in quantum-mechanical terms, it is the operator of the 2'-pole moment). This quantity allows one to calculate the multipole potential created by the system in its exterior. The second quantity, $C_{lm}(\{r_j\})$, written in terms of irregular solid harmonics $r_j^{-l-1} Y_{lm}(r)$ [49], determines the multipole potential in the system’s interior (see [48]). To avoid ambiguity we call this quantity the ‘interior 2'-pole moment’.

Under the action of the multipolar field $-q\phi_{lm}(\mathbf{r}_q, \{r_j\})$, the electron cloud in the fullerene becomes polarized. This polarization causes the change in the potential, $\delta\phi_{lm}(\mathbf{r})$, created by the electrons. Applying standard perturbation theory, one finds that $\delta\phi_{lm}(\mathbf{r})$ is given by the following second-order matrix element:

$$\delta\phi_{lm}(\mathbf{r}) = q \sum_{n \neq 0} \frac{2(0)[\phi_{lm}(\mathbf{r}_q, \{r_j\})][n]}{\omega_{0n}} [n|\phi_{lm}^*(\mathbf{r}, \{r_j\})|n].$$

(A.3)

Here, $\phi_{lm}(\mathbf{r}, \{r_j\})$ stands for the (operator of) multipole potential created by the electrons in the point $\mathbf{r}$. Its explicit form follows from (A.1) by means of the substitution $r_q \rightarrow r$. The sum is carried out over the complete spectrum of the fullerene’s excited states $n$ (the ground state $0$ is excluded) including the excitations into continuum; $\omega_{0n} = \varepsilon_n - \varepsilon_0$ is the excitation energy.
The explicit form of the expression on the right-hand side of (A.3) depends not only on the location of the external charge \( q \) with respect to \( \langle r_j \rangle \), but also on the location of the observation point \( r \). Considering different cases, one derives

\[
\delta \phi_{lm}(r) = g_0 \frac{4\pi}{\omega^n} Y^{*}_{lm}(r_q) Y_m(r) \left( \frac{r}{\langle r_j \rangle} \right) \bar{\alpha}_l \bar{\beta}_l \bar{\gamma}_l \left( \frac{r}{\langle r_j \rangle} \right) \left( \frac{r}{\langle r_j \rangle} \right),
\]

or \( \frac{r}{\langle r_j \rangle} \gg \langle r_j \rangle \),

\[
\delta \phi_{lm}(r) = \frac{2\pi}{\omega^n} Y^{*}_{lm}(r_q) Y_m(r) \alpha_l \beta_l \gamma_l \left( \frac{r}{\langle r_j \rangle} \right) \left( \frac{r}{\langle r_j \rangle} \right),
\]

\( \frac{r}{\langle r_j \rangle} \gg \langle r_j \rangle \gg r \).

(A.4)

The quantities \( \alpha_l \), \( \beta_l \) and \( \gamma_l \) are given by

\[
\alpha_l = \sum_{n \neq 0} \frac{2|\langle Q_{lm} | n \rangle|^2}{\omega^2_n}, \quad \beta_l = \sum_{n \neq 0} \frac{2|\langle C_{lm} | n \rangle|^2}{\omega^2_n}, \quad \gamma_l = \sum_{n \neq 0} \frac{2|\langle C_{lm} | n \rangle|^2}{\omega^2_n}.
\]

(A.5)

The first two of these are well known in atomic physics (see, e.g., [47]). The (static) polarization \( \alpha_l \) defines the change in the field, created by a system, in the case when both the source charge and the observation point are located in the system’s exterior. The quantity \( \beta_l \) is called a shielding factor, and it defines the change in the field in the system’s interior due to the charge re-distribution under the action of \( q \) located in the exterior. Atomic shielding factors appear when one analyses the change of the field at the nucleus due to the polarization of the outer shells’ electrons under the action of external electric field.

It is the third term, \( \gamma_l \), which additionally appears when a hollow system is exposed to the external field. In this case, both the source charge \( q \) and the observation point can be located in the cavity. To distinguish between \( \alpha_l \) and \( \gamma_l \), we call the latter quantity the polarizability of the second kind.

The polarizability of the second kind naturally appears in the processes which involve the interaction of a subsystem \( I \) embedded by a hollow subsystem \( II \). An example would be an endohedral complex \( A@C_N \), where \( A \) stands for an atom.

It can be shown that the dipole polarizability of the second kind \( \bar{\alpha}_l \) determines the van der Waals interaction between the fullerene and the centrally placed atom [50, 51]. More general treatment of the van der Waals interaction between \( C_N \) and the atom, arbitrary placed in the fullerene interior, involves the polarizabilities \( \bar{\alpha}_l \) of higher multipoles [52]. Dynamical screening of an endohedral atom (see [28, 34]) is another example of the process in which the polarizabilities \( \bar{\alpha}_l \) (more exactly, the dynamic polarizabilities \( \bar{\alpha}_l(\omega) \), see (A.6)) manifest themselves. In this process, the presence of the fullerene dynamically screens the confined atom from an external electromagnetic field, so that the atom experiences a field that is either enhanced or suppressed depending on the field frequency \( \omega \). It can be shown (see [29]) that to calculate the change in the atomic PI cross section due to the dynamical screening, one has to calculate the shielding factor of the fullerene and the polarizabilities \( \bar{\alpha}_l(\omega) \). Equation (14) in the main text demonstrates that fullerene dynamic polarizabilities of the second kind determine the correction to the Auger decay rate of the endohedral atom.

A.2. Dynamic multipole polarizabilities

The formalism outlined above can be adjusted to the case of the time-dependent external multipolar field. To do this, one carries out the Fourier transform of the external field and then treats each Fourier component separately. As a result, each of the quantities \( \alpha_l \), \( \bar{\alpha}_l \) and \( \beta_l \) acquires the dependence on \( \omega \) (the parameter of the Fourier transform or the ‘frequency’ of the external field). Explicit expressions for the dynamic polarizabilities of all types are as follows:

\[
\alpha_l(\omega) = \sum_{n \neq 0} \frac{2\omega_n |\langle Q_{lm} | n \rangle|^2}{\omega^2_n - \omega^2 - i\omega},
\]

\[
\bar{\alpha}_l(\omega) = \sum_{n \neq 0} \frac{2\omega_n |\langle C_{lm} | n \rangle|^2}{\omega^2_n - \omega^2 - i\omega},
\]

\[
\beta_l(\omega) = \sum_{n \neq 0} \frac{2\omega_n |\langle Q_{lm} | n \rangle|^2}{\omega^2_n - \omega^2 - i\omega}.
\]

(A.6)

In the static limit \( \omega = 0 \), these formulae reduce to (A.5).

Let us evaluate the asymptotic behaviour of \( \alpha_l(\omega) \), \( \bar{\alpha}_l(\omega) \) and \( \beta_l(\omega) \) in the region \( \omega >> Ik \) (\( Ik \) stands for the ionization potential of the most bound electrons in the system). As a first step in deriving the asymptotic expressions, one neglects \( \omega^2_n \) in the denominators. The resulting sums over the complete spectrum of the system are carried out using standard methods of evaluation of the sum rules (see, e.g., [33]). To calculate the gradients of regular \( r^l Y_{lm}(r) \) and irregular \( r^{-l-1} Y_{lm}(r) \) solid harmonics, one can use the formulae from chapter 7.3.6 of [23]. The final result reads

\[
\lim_{\omega \rightarrow Ik} \alpha_l(\omega) = -\frac{1}{\omega^2} \sum_n 2\omega_n |\langle Q_{lm} | n \rangle|^2 = -\frac{N_e}{\omega^2} Tr^{2-2},
\]

\[
\lim_{\omega \rightarrow Ik} \bar{\alpha}_l(\omega) = -\frac{1}{\omega^2} \sum_n 2\omega_n |\langle C_{lm} | n \rangle|^2 = -\frac{N_e}{\omega^2} (l+1) Tr^{2l-4},
\]

\[
\lim_{\omega \rightarrow Ik} \beta_l(\omega) = -\frac{1}{\omega^2} \sum_n 2\omega_n |\langle Q_{lm} | n \rangle| |\langle C_{lm} | n \rangle| = 0.
\]

(A.7)

where \( Tr \) denotes the mean value of \( r^l \) in the ground state.

The first formulae from (A.7) coincides with the one obtained earlier in [26]. In the dipole case, \( l = 1 \), it reproduces the well-known result, related to the Thomas–Reiche–Kuhn dipole sum rule.

A.3. Multipoles polarizabilities of a dielectric spherical shell

For reference, we present explicit expressions for the polarizabilities \( \alpha_l \), \( \bar{\alpha}_l \) and \( \beta_l \) of a model hollow object: a spherical shell made up of a material with the dielectric function \( \varepsilon \). The inner and outer radii of the shell are notated as \( R_1 \) and \( R_2 \), respectively.

To find the polarizability \( \alpha_l \) and the shielding factor \( \beta_l \), one places the external charge \( q \) in the shell exterior \( (r_q > R_2) \) and determines the additional potential \( \delta \phi(r) \) due to the polarization of the shell. Multipolar components \( \delta \phi_{lm}(r) \) of this potential are proportional either to \( \bar{\alpha}_l \) (if \( r > R_2 \)) or \( \beta_l \) (if
the quantities excited in a fullerene when it is considered as a spherical layer
be explained \[30\] in terms of two coupled surface plasmons
nature and are due to the excitations of plasmons by the
example, \[26, 27\] and references therein). In the theory of plasmon resonances in metallic clusters (see,
(A.8) coincides with the formula obtained earlier in \[54\].

Here,
\[D_l = (\varepsilon_l + l + 1)(\varepsilon_l + 1)(\varepsilon_l + 1) - l(l + 1)(\varepsilon_l - 1)^2 \xi^2 l+1,\]
\[\xi = \frac{R_1}{R_2} < 1.\] (A.9)
The expression for the multipole polarizability \( \alpha_l \), presented in (A.8), coincides with the formula obtained earlier in \[54\].

A.4. Multipole polarizabilities of a fullerene within the PRA
PI experiments on \( C_{60} \) and its positive ions reveal two giant
resonances in their PI spectra in the photon energy region
\( \approx 20-40 \) eV \[55, 56\]. These resonances are of a collective nature and are due to the excitations of plasmons by the
photon field \[30, 56, 57\]. The existence of two resonances can be explained \[30\] in terms of two coupled surface plasmons
excited in a fullerene when it is considered as a spherical layer of a finite thickness \[28, 29, 35, 54, 58, 59\].

In this section, we apply this model to express each of
the quantities \( \alpha_l \) and \( \tilde{\alpha}_l \) from (A.8) as a sum of two resonance
terms corresponding to the two surface plasmons modes. We
call this approach as the PRA in accordance with the term used in the
theory of plasmon resonances in metallic clusters (see, e.g., \[26, 27\] and references therein).

Let the fullerene valence electrons be distributed within a
spherical shell whose inner and outer radii are \( R_1 = R - \Delta R / 2 \)
and \( R_2 = R + \Delta / 2 \), with \( R \) standing for the (average) radius
of the ionic core and \( \Delta \) for the width of the electron cloud (see
figure 2). Within the framework of the PRA, one can model
the dielectric function \( \varepsilon \equiv \varepsilon(\omega) \) of the fullerene electrons by a
Lorentz-type dielectric function (see, e.g., \[59\]):
\[\varepsilon = 1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\Gamma \omega},\] (A.10)
where \( \Gamma \) is a damping constant, and the term \( \omega_0^2 \) is included to
go beyond the free-electron gas approximation implied by the
Drude model. The plasma frequency \( \omega_p \) is found from \( \omega_p^2 = 4\pi \varepsilon_0 \omega_0 V / \sqrt{V} \), where \( V = 4\pi (R_2^3 - R_1^3) / 3 \) is the volume of the shell.

Using (A.10) in (A.8), one represents the dynamic polarizabilities \( \alpha_l(\omega) \) and \( \tilde{\alpha}_l(\omega) \) as follows:
\[\alpha_l(\omega) = l \mathcal{A}_l(\omega) \frac{R^{2l-2}}{2l+1},\]
\[\tilde{\alpha}_l(\omega) = (l + 1) \tilde{\mathcal{A}}_l(\omega) \frac{R^{2l-4}}{2l+1},\] (A.11)
The factors \( R^{2l-2} / 2l+1 \) and \( R^{2l-4} / 2l+1 \), which stand for the mean
(2l - 2)th and (2l - 4)th powers of the radius of the
electron cloud (cf. equation (A.7)), conveniently expose the
dependence on \( \alpha_l \) and \( \tilde{\alpha}_l \) on the shell radii
\[\frac{R^{2l-2}}{2l+1} = \frac{3}{2l+1} \frac{1 - \xi^{2l+1}}{1 - \xi^2},\]
\[\frac{R^{2l-4}}{2l+1} = \frac{3}{2l+1} \frac{1}{1 - \xi^2}.\] (A.12)
The \( \omega \)-dependence of the polarizabilities is concentrated in the
factors \( \mathcal{A}_l(\omega) \) and \( \tilde{\mathcal{A}}_l(\omega) \), which have similar resonance structure:
\[\mathcal{A}_l(\omega) = \frac{N_{1l}}{\omega_p^2 + \omega_0^2 - \omega^2 - i\Gamma_{1l}\omega},\]
\[\frac{N_{2l}}{\omega_p^2 + \omega_0^2 - \omega^2 - i\Gamma_{2l}\omega},\]
\[\tilde{\mathcal{A}}_l(\omega) = \frac{N_{1l}}{\omega_p^2 + \omega_0^2 - \omega^2 - i\Gamma_{1l}\omega},\]
\[\frac{N_{2l}}{\omega_p^2 + \omega_0^2 - \omega^2 - i\Gamma_{2l}\omega}.\] (A.13)
Here, \( \omega_{1l} \) and \( \omega_{2l} \) are the surface plasmon frequencies for a
given multipolarity \( l \). These pairs of eigenmodes arise from the
fullerene having a finite thickness and therefore two surface charge densities. The eigenfrequency \( \omega_{1l} \) characterizes the
symmetric mode of coupled oscillations, in which the two
surface charge densities oscillate in phase. The eigenfrequency
\( \omega_{2l} \) (which is larger than \( \omega_{1l} \)) corresponds to the antisymmetric
mode, in which the oscillations are in antiphase \[29, 54\]. These
frequencies are given by
\[\omega_{1l}^2 = \frac{\omega_p^2}{2(l+1)} (2l+1 - p_l) ,\] (A.14)
\[\omega_{2l}^2 = \frac{\omega_p^2}{2(l+1)} (2l+1 + p_l) ,\]
where \( p_l = \sqrt{1 + 4(l+1)^2 \xi^{2l+1}} \). Note that for each
multipolarity, the frequencies \( \omega_{1l} \) and \( \omega_{2l} \) satisfy the relation
\( \omega_{1l}^2 + \omega_{2l}^2 = \omega_p^2 \), which is a consequence of a more general sum
rule for the magnitudes of surface plasmon frequencies \[60\].

The quantities \( N_{1l} \) and \( N_{2l} \) (\( j = 1, 2 \)) are the (multipolar)
oscillator strengths associated with the modes \( \omega_{1l} \) and \( \omega_{2l} \).
They satisfy the relation \( N_{1l} + N_{2l} = N_{1l} + N_{2l} = N_e \), and, thus,
represent the numbers of valence electrons participating in
the symmetric and antisymmetric oscillatory modes. These
numbers are given by
\[N_{1l} = \tilde{N}_{1l} = N_e \frac{p_l + 1}{2p_l} ,\]
\[N_{2l} = \tilde{N}_{2l} = N_e \frac{p_l - 1}{2p_l}.\] (A.15)
Comparing (A.13) and (A.15) one notes that the functions
\( \mathcal{A}_l(\omega) \) and \( \tilde{\mathcal{A}}_l(\omega) \) differ only in the number of oscillators in the
two modes: the expression for \( \tilde{\mathcal{A}}_l(\omega) \) can be obtained from
that for \( \mathcal{A}_l(\omega) \) by means of the substitution \( N_{1l} \leftrightarrow N_{2l} \).

The quantities \( \gamma_{jl} \) (\( j = 1, 2 \)) in (A.13) denote the
half-widths of the surface plasmons multipole excitations. They
determine the decay rate from the collective excitation mode
to the incoherent sum of single-electron excitations. Within
the framework of the PRA, they (as well as the quantity \( \omega_0 \))
are treated as parameters which can be either deduced from
the experimental data or calculated separately \[27, 61\].
Within the PRA, the shielding factor $\beta_l(\omega)$ (see the last line in (A.8)) acquires the form [29, 35]

$$
\beta_l(\omega) = -\frac{3l(l+1)}{2l+1} \frac{1 - \xi^{2l+1}}{1 - \xi^3} \frac{1}{R^2} B_l(\omega). \quad (A.16)
$$

The factor $B_l(\omega)$ has the following resonance structure:

$$
B_l(\omega) = \frac{N_{1l} - N_{2l}}{\omega_{1l}^2 + \omega_0^2 - \omega^2 - i\Gamma_{1l}\omega} - \frac{N_{1l} - N_{2l}}{\omega_{2l}^2 + \omega_0^2 - \omega^2 - i\Gamma_{2l}\omega}.
$$

Note that, in contrast to $A_l(\omega)$ and $\tilde{A}_l(\omega)$, the ‘oscillator strengths’ associated in $B_l(\omega)$ with the symmetric and asymmetric modes are the same and equal to $N_{1l} - N_{2l}$.

### A.5. Dynamic multipole polarizabilities $\alpha_l(\omega)$ and $\tilde{\alpha}_l(\omega)$ of $C_{60}^+$

In this section, we apply the PRA to calculate the dynamic polarizabilities $\alpha_l(\omega)$ and $\tilde{\alpha}_l(\omega)$ for the fullerene ion $C_{60}^+$.  

Taking into account the study of Nakao et al [25], we assume spherical symmetry for the ionic cage and use the value $R = 4.15 \, \text{Å}$ for the cage radius. The thickness $\Delta R$ of the fullerene is set to 1.5 Å, which was obtained in [43] for $C_{60}$. These values of $R$ and $\Delta R$, accompanied by the number of valence electrons $N_e = 326$, lead to $\omega_p = 37.0 \, \text{eV}$ for the plasma frequency and to $\xi = 0.69$ for the inner to outer radii ratio.

The value of $\omega_0$ was chosen so as to equate the frequency of the symmetric dipole resonance (i.e. the resonance frequency of the first term in $A_1(\omega)$, see (A.13)) to the experimentally measured position $\omega_{\text{exp}}$ of the plasma resonance peak in the PI spectrum. Thus, the value $\omega_0 = 13.9 \, \text{eV}$ was calculated from $\sqrt{\omega_{1l}^2 + \omega_0^2} = \omega_{\text{exp}}$, where $\omega_{1l}$ was calculated from (A.14), and we took $\omega_{\text{exp}} = 21 \, \text{eV}$, which corresponds to the experimental maximum of the PI cross section for $C_{60}^+$ [1, 62].

To calculate the half-widths, the following rule was adopted: $\Gamma_{jl} = \gamma_j \omega_{jl} (j = 1, 2)$. For symmetric surface plasmon modes of all multipolarities, the value of $\gamma_1$ was fixed at 0.16, which equals the ratio of experimentally measured half-width $\Gamma_{\text{exp}}$ to the position $\omega_{\text{exp}}$ of the dipole resonance [1, 62]. For the antisymmetric modes, we used the value $\gamma_2 = 0.22$, which corresponds to the $\Gamma_{\text{exp}}/\omega_{\text{exp}}$ ratio measured for the second plasma resonance in the PI of $C_{60}^+$ [56].

The calculated dependences of the real and imaginary parts of $A_l(\omega)$ and $\tilde{A}_l(\omega)$ on the photon energy $\omega$ for several values of $l$ are presented in figure A1.
We mention the following two features of the presented dependences. Firstly, as is seen from equation (A.14), with the growth of $l$ the frequencies $\omega_{1}$ and $\omega_{2}$ approach the same limit: $\omega_{1}$ goes to $\omega/\sqrt{3}$ from below whereas $\omega_{2}$ from above. As a result, the two resonances in both $A_1(\omega)$ and $\tilde{A}_1(\omega)$ merge as $l$ increases. Secondly, the second (antisymmetric) surface plasmon peak is quite pronounced for $\tilde{A}_1(\omega)$ (i.e. in the dynamic polarizability of the second kind) whereas in the case of $A_1(\omega)$ its magnitude relative to the symmetric peak is much smaller. As $l$ increases (and until the peaks merge) the heights of symmetric and antisymmetric resonances nearly equalize in the case of $\tilde{A}_1(\omega)$, whereas for $A_1(\omega)$ the antisymmetric peak quickly disappears. The reason for such a difference in the resonance curves behaviour is related to the different number of valence electrons participating in symmetric and antisymmetric modes, see (A.15). The ratio $N_{2}\omega/\omega_{1}$ rapidly decreases with $l$ (the ratio equals to 0.3 for $l = 1$ and to 0.04 for $l = 10$). Hence, the number of oscillators associated with the antisymmetric mode in $A_1(\omega)$, which is $N_{2}$, rapidly decreases, thus destroying the peak at $\omega_{2}$. In contrast, in $\tilde{A}_1(\omega)$, where the antisymmetric mode is defined by $N_{1}$ oscillators, the relative intensity of its peak increases.

A.6. Approximate relationship between $a_1(\omega)$ and $\tilde{a}_1(\omega)$ for a fullerene

To conclude the appendix, let us mention a transformation which allows one to approximately relate the polarizabilities $\tilde{a}_1(\omega)$ and $a_1(\omega)$. To simplify the algebra we consider the case of a spherically symmetric fullerene with the cage radius $R$ and the thickness $\Delta R$.

Assuming the strong inequality $\Delta R \ll R$, one reduces the interior $2^{-l}$-pole moment $Q_{lm}(|r_1|)$ to the regular solid harmonics $r^l Y_{lm}(r) Q_{lm}(|r_1|)$ (see equation (A.2)) as follows:

$$C_{lm}(|r_1|) = \frac{4\pi}{2l+1} \sum_{j} r^l Y_{lm}(r) Q_{lm}(|r_1|)$$

$$\approx \frac{1}{R^{2+l}} \frac{4\pi}{2l+1} \sum_{j} r^l Y_{lm}(r) = \frac{Q_{lm}(|r_1|)}{R^{2+l}}. \quad (A.18)$$

Using this result in (A.6), one arrives at

$$\tilde{a}_1(\omega) \approx \frac{a_1(\omega)}{R^{2+l}}, \quad \beta_1(\omega) \approx \frac{\alpha_1(\omega)}{R^{2+l}}. \quad (A.19)$$

Sometimes such an approximation is used to estimate the dynamic response of a fullerene to the external field (see, e.g., [21]). However, the accuracy of the approximation is subject to (comparatively) low $l$-values and to a strong inequality $\Delta R \ll R$. Thus, if one considers, for example, the fullerene C$_{60}$, for which $\Delta R/R \approx 0.4$, then equation (A.19) can be used only for the order-of-magnitude estimations and for $l \approx 1$. The accuracy will increase for giant fullerenes (e.g., for C$_{60}$, where $\Delta R/R \approx 0.1$). Additionally, for low $l$-values this approximation neglects the difference between the profiles of symmetric and antisymmetric surface plasmon modes in $\tilde{a}_1(\omega)$, $\beta_1(\omega)$ and $\alpha_1(\omega)$ (to compare the profiles in $a_1(\omega)$ and $\tilde{a}_1(\omega)$, see figure A1).

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