

The role of fullerene shell upon stuffed atom polarization potential

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We have demonstrated that the polarization of the fullerene shell considerably alters the polarization potential of an atom, stuffed inside a fullerene. This essentially affects the electron elastic scattering phases as well as corresponding cross-sections. We illustrate the general trend by concrete examples of electron scattering upon endohedrals Ne@C₆₀ and Ar@C₆₀. To obtain the presented results, we have suggested a simplified approach that permits to incorporate the effect of fullerenes polarizability into the Ne@C₆₀ and Ar@C₆₀ polarization potential. By applying this approach, we obtained numeric results that show strong variations in shape and magnitudes of scattering phases and cross-sections due to effect of fullerene polarization upon the endohedral polarization potential.

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1. At first glance, the addition of a single relatively small atom inside a fullerene should not affect essentially the electron elastic scattering cross-section of the latter, since the presence of an additional atom inside alters negligibly the total size of the system under consideration. As it was demonstrated recently in [1, 2], the quantum interference changes the situation impressively, so that the total phase $\delta_l^{A@C_N}$ of the partial wave l of an electron scattered upon endohedral A@C_N is with good accuracy equal to the sum of scattering phases δ_l^A and $\delta_l^{C_N}$ of electrons upon atom A, stuffed inside the fullerene C_N, and the C_N itself. It means, counterintuitively, that a single atom contribution is quite big as compared to the background of C_N cross-section.

In [1] we have performed calculations, assuming that the incoming electron feels the Hartree–Fock $\hat{V}_{\text{HF}}(r)$ potential of the atom A, as well as the static $W_{\text{F}}(r)$ and polarization $V_{\text{F}}^{\text{pol}}(r)$ potentials of the C_N. The inclusion of $V_{\text{F}}^{\text{pol}}(r)$ proved to be very important, since C_N is a highly polarizable object, as compared to the atom A.

However, we know that the polarization potential of the atom A itself modifies essentially its scattering phases and respective cross-sections. Since the contribution of the atom's A phase is clearly reflected in $\delta_l^{A@C_N}$, one has to investigate the effect of atom A polarization potential $\hat{V}_A^{\text{pol}}(r)$ upon $\delta_l^{A@C_N}$. Therefore, we investigate this effect here. This is the first aim of the present Letter.

Moreover, since the fullerene is a highly polarizable object, it can affect the atom's A polarization potential leading to a potential that accounts for the modification of $\hat{V}_A^{\text{pol}}(r)$ by the fullerene's shell that we denote $\hat{V}_{\text{FA}}^{\text{pol}}(r)$. Investigation of the changes that happen when $\hat{V}_A^{\text{pol}}(r)$ is substituted by $\hat{V}_{\text{FA}}^{\text{pol}}(r)$ is the second aim of this Letter.

As concrete objects of calculations we choose almost ideally spherical fullerene C₆₀ and endohedrals Ne@C₆₀ and Ar@C₆₀ with centrally located quite small and spherical atoms Ne and Ar.

It is in place to remind one general property of the behavior of scattering phases upon a static potential U . Let the phases $\delta_l(E)$ as functions of energy E be normalized in such a way that $\delta_l(E \rightarrow \infty) \rightarrow 0$. If the target consists of electrons and nuclei and exchange between incoming and target electrons are taken into account, an expression $\delta_l(0) = (n_l + q_l)\pi$ proved to be valid. Here q_l is the number of bound electron states with the angular momentum l in the target itself, while n_l is the number of bound electron states with angular momentum l in the system $e + U$ [3, 4].

Therefore, the behavior of phases as functions of E is qualitatively different in cases when we treat the target with and without taking into account the exchange, e.g. in Hartree or Hartree–Fock (HF) approximations. Note that in these two cases the phases deviate from each other (in numbers of π) although the strength of the potential is almost the same.

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In calculations presented below we treat the Ne and Ar atom. The polarization potential $\hat{V}_A^{\text{pol}}(r)$ is calculated in the random phase approximation with exchange (RPAE) frame [4], while C_{60} is represented by a static square well potential $W_F(r)$, which parameters are chosen to represent the experimentally known electron affinity of C_{60}^- , and low- and medium energy photoionization cross-sections of C_{60} [5]. Along with $W_F(r)$ we take into account the polarization potential $V_F^{\text{pol}}(r)$ of the fullerene.

We pay special attention to the development of an approximation that permits to calculate the atomic A polarization potential $\hat{V}_{FA}^{\text{pol}}(r)$ inside the fullerenes shell, and corresponding phase-shifts as well as cross-sections.

2. In order to obtain electron scattering phases for a spherical endohedral, one has to solve numerically the following equations for the radial parts of the one-electron wave functions $P_{El}^{A@C_N}(r)$ ²⁾

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \hat{V}_{\text{HF}}(r) + W_F(r) + V_F^{\text{pol}}(r) + \frac{l(l+1)}{2r^2} - E \right] P_{El}^{A@C_N}(r) = 0. \quad (1)$$

Here Z is the inner atom nuclear charge and $\hat{V}_{\text{HF}}(r)$ is the operator of HF non-local potential of the atom A (see the definition in e.g. [6]). The asymptotic of $P_{El}^{A@C_N}(r)$ determines the scattering phase $\delta_l^{A@C_N}(E)$

$$P_{El}^{A@C_N}(r)|_{r \rightarrow \infty} \approx \frac{1}{\sqrt{\pi p}} \sin \left[pr - \frac{\pi l}{2} + \delta_l^{A@C_N}(E) \right]. \quad (2)$$

Here $p^2 = 2E$.

If one neglects $-Z/r + \hat{V}_{\text{HF}}(r)$ in (1), Eqs. (1) and (2) determine scattering function and phase shift of an electron on an empty fullerene, that is denoted as $\delta_l^{C_N}(E)$ and $P_{El}^{C_N}(r)$, respectively, and as ‘‘Hartree’’ on Figures that depict results.

To take into account the atomic polarization potential $\hat{V}_A^{\text{pol}}(r)$ or $\hat{V}_{FA}^{\text{pol}}(r)$, one has to add one of these potentials to $\hat{V}_F^{\text{pol}}(r)$ in (1), thus obtaining equations for the wave functions $P_{El}^{A@C_{NA}}(r)$ and $P_{El}^{A@C_{NFA}}(r)$ as well as scattering phases $\delta_l^{A@C_{NA}}$ and $\delta_l^{A@C_{NFA}}$, respectively.

3. More details on how to obtain scattering phases numerically one can find in [6]. The choice of $W_F(r)$ and $V_F^{\text{pol}}(r)$ is the same as in [1]: for $W_F(r)$ a square

well and for $V_F^{\text{pol}}(r)$ the following expression $V_F^{\text{pol}}(r) = -\alpha_F/2(r^2 + b^2)^2$, where α_F is the static dipole polarizability of a fullerene that for C_{60} and a number of other fullerenes is measured and/or calculated; b is a parameter of the order of the fullerenes radius R . This simple version of $V_F^{\text{pol}}(r)$ is widely used in atomic scattering calculations (see [7] and references therein).

In principal, the polarization potentials are energy-dependent and non-local. We have an experience to determine it for atoms employing perturbation theory in inter-electron interaction and limiting ourselves by second order perturbation theory in incoming and target electrons interaction (see [4] and references therein).

It is then convenient to solve Eq. (1) in the integral form and in energy representation, where for partial wave l it looks in the following way (see Ch. 3 of [4] and references therein):

$$\begin{aligned} \langle El | \hat{\Sigma}^l(E_1) | E'l \rangle &= \langle El | \hat{\Sigma}^l(E_1) | E'l \rangle + \\ &+ \sum_{E''} \langle El | \hat{\Sigma}^l(E_1) | E''l \rangle \frac{1}{E_1 - E'' + i\delta} \langle E''l | \hat{\Sigma}^l(E_1) | E'l \rangle, \end{aligned} \quad (3)$$

where the sum over E'' includes also integration over continuous spectrum.

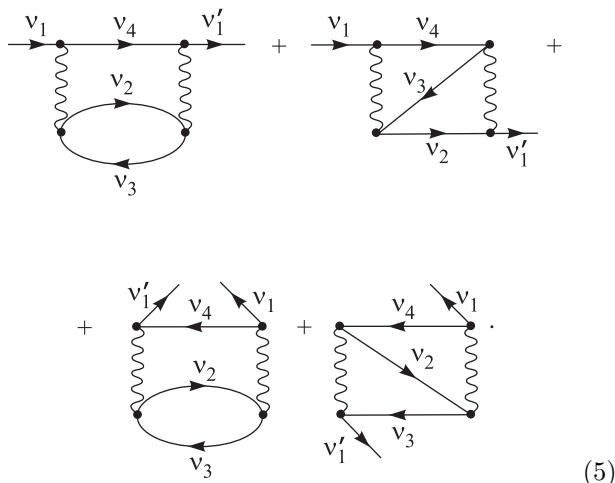
The polarization interaction $\hat{\Sigma}(E)$ leads to an additional scattering phase shift $\Delta\delta_l(E)$ that is connected to the diagonal matrix element of (3):

$$e^{i\Delta\delta_l(E)} \sin \Delta\delta_l(E) = \langle El | \hat{\Sigma}^l(E) | El \rangle. \quad (4)$$

Instead of semi-empirical potentials, we employ here the many-body theory approach with its diagrammatic technique [8, 4]. The matrix elements $\langle El | \hat{\Sigma}^l(E_1) | E'l \rangle$ have the name ‘‘irreducible self-energy part of the one-electron Green’s function’’ [8]. This approach accounts for non-locality and energy dependence of the polarization interaction, but to be accurate enough require inclusion of sufficient number of diagrams’ sequences. Note that the phases determined using Eqs. (1) and (2) or (3) and (4) are the same (see, e.g., [6] and [4]). This was checked by us also pure numerically, by applying both procedures to the case of an empty fullerene that led to identical results.

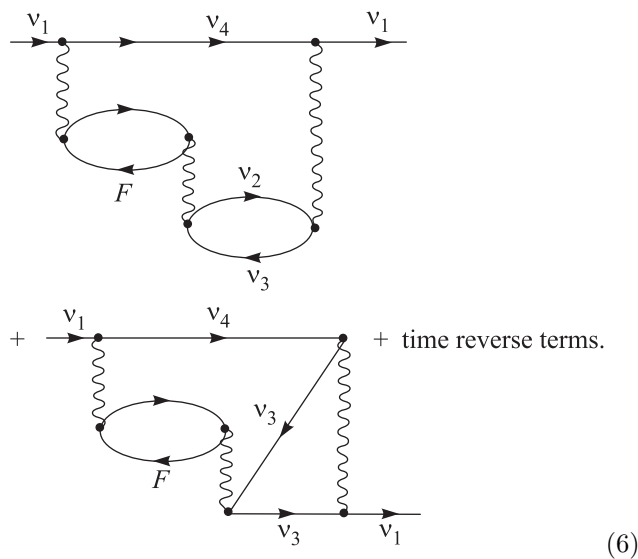
It appeared, however, that at low incoming electron energies, where the polarization interaction is particularly important, in constructing $\langle El | \hat{\Sigma}^l(E_1) | E'l \rangle$ it is sufficient to take into account four diagrams [4] presented by (5).

²⁾We employ the atomic system of units, with electron mass m , electron charge e , and Planck constant \hbar equal to 1.



The wavy line stands for the interelectron interaction. In (5), we use the following notations $\nu_i = E_i l_i$. A line, directed to the right (left), denotes electron (vacancy). These diagrams automatically include some infinite series in electron-vacancy interaction (see Ch. 3 in [4]).

4. When we consider an electron colliding with an endohedral, one has to take into account the contribution of the interaction between atomic and fullerenes electrons. Diagrams (6) present examples of such interaction:



Here F denotes the fullerenes shell virtual excitations.

Considering the insertion of fullerenes shell virtual excitation and estimating the corresponding contributions, one has to have in mind that between the essential for the scattering process projectile distance r_p , the fullerene radius, R_F and the atomic radius, r_A , the following inequality exists $r_p > R_C > r_A$. To simplify the problem of taking into account the mutual influence of atomic and fullerenes electron, we enforce this inequality into $r_p \gg R_C \gg r_A$. This permits to limit ourselves

by correcting the dipole interelectron interaction only, substituting the Coulomb interelectron potential in the following way: $1/|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \mathbf{r}_1 \mathbf{r}_2 / r_2^3$ for $r_1 \ll r_2$.

The variation of the long-range dipole interelectron interaction V_1 matrix elements is taken into account similarly to the inclusion of the polarization factor in photoionization of endohedrals as it was demonstrated in [9]. So, we correct them approximately, substituting $|V_1|^2$ by

$$|V_1|^2 \rightarrow |V_1[1 - \alpha_F(E_{\nu_1} - E_{\nu_4})/R_F^3]|^2 \quad (7)$$

in the first and third matrix elements of (5). The alteration of the exchange second and fourth terms of (5) requires substitution:

$$|V_1|^2 \rightarrow |V_1[1\alpha_F(E_{\nu_1} - E_{\nu_4})/R_F^3] \times V_1[1 - \alpha_F(E_{\nu_1} - E_{\nu_2})/R_F^2]|. \quad (8)$$

We left unchanged other than dipole components of interaction matrix elements.

5. To perform calculations, we have to choose concrete values for the C_{60} potentials. The potential $W_F(r)$ is represented by a potential well with the depth 0.52 and inner R_1 (outer R_2) radii equal to $R_1 = 5.26$ ($R_2 = 8.17$). Note that $R_F = (R_1 + R_2)/2$. In [9] (see also [4]) we have calculated the polarizability $\alpha_F(\omega)$. Details on how to find $\langle E|\hat{\Sigma}^l(E_1)|E'l \rangle$ and to solve equations (3) and (4) one can find in Chap. 3 of [4].

In Fig. 1 we illustrate the results of calculations of the scattering phases and cross-sections by the cases of $\text{Ne}@C_{60}$ and $\text{Ar}@C_{60}$ (3). In Fig. 1 we present data for the s -phases δ and their contribution to the cross-sections σ of electron scattering upon Ar and $\text{Ar}@C_{60}$. The curves δ^{Ar} and σ^{Ar} represent data for $e + \text{Ar}$ collision that took into account the action of polarization interaction (5). Data δ^F and σ^F for $e + C_{60}$ are obtained by solving (1) with the term $-Z/r + \hat{V}_{\text{HF}}(r)$ neglected. Results of RPAE calculations $\delta^{\text{Ar}@C_{60}}$ and $\sigma^{\text{Ar}@C_{60}}$ for $e + \text{Ar}@C_{60}$ mean combination of calculating separately polarization interaction, described by (5) for an isolated atom Ar with solving (1). RPAE_F denotes results for $\delta^{\text{Ar}@C_{60F}}$ and $\sigma^{\text{Ar}@C_{60F}}$ obtained after solving (3), with account of (5). Here all intermediate states ν_1, ν_2, ν_3 are solutions of (1), i.e. take into account the action of fullerenes electron shell upon atomic A states.

The curves denoted as RPAE_{FA} are results for $\delta^{\text{Ar}@C_{60FA}}$ and $\sigma^{\text{Ar}@C_{60FA}}$ calculations similar to the case of RPAE_F, but with polarization interaction, that along with (5) includes, by using approximations (7) and (8), also diagrams exemplified by (6). Fig. 2 presents similar results, but for p -wave of the electron scattering with Ne and $\text{Ne}@C_{60}$.

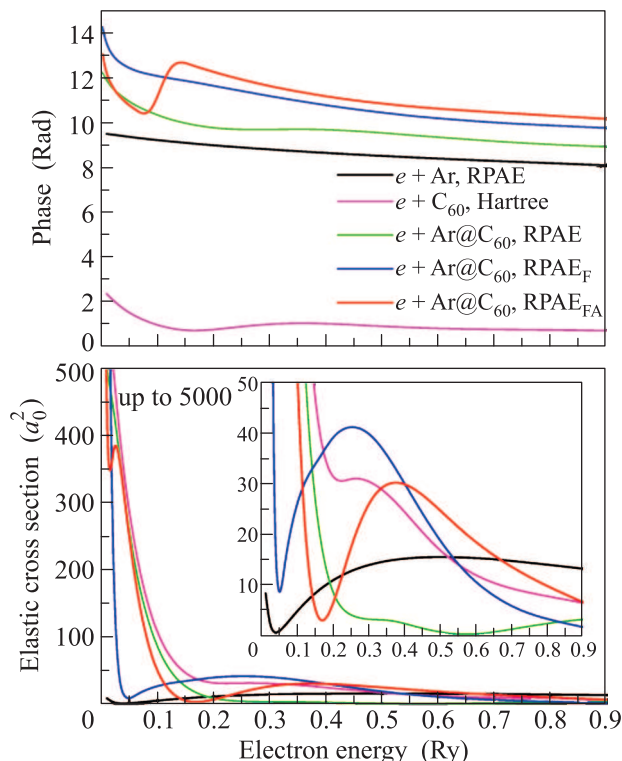


Fig. 1. (Color online) Phases and cross-sections of the s -wave contribution in electron collisions with $\text{Ar}@C_{60}$

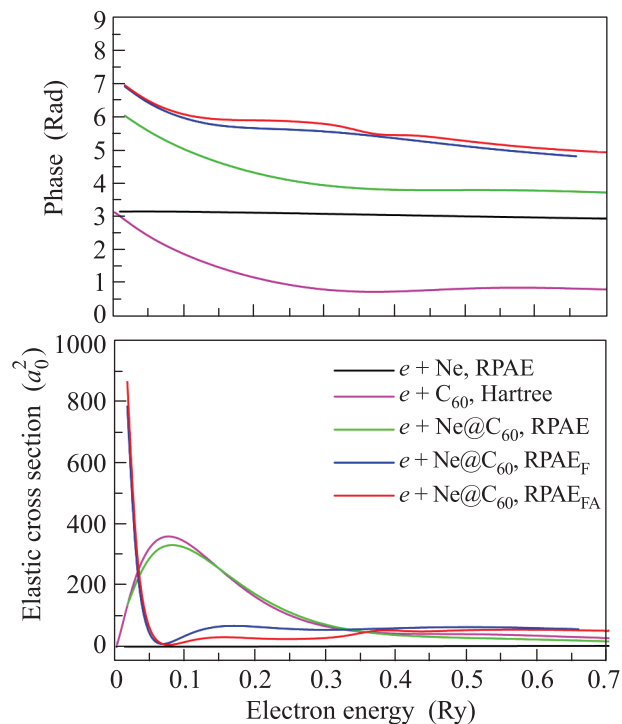


Fig. 2. (Color online) Phases and cross-sections of the p -wave contribution in electron collisions with $\text{Ne}@C_{60}$

Note the difference between RPAE on one hand and RPAE_F and RPAE_{FA} on the other. We see that the inclusion of fullerene action upon the polarization interaction (5) is very important. Not less important for the s -phase is the influence of fullerene polarization exemplified by (6) upon the interaction (5). As to the p -phase presented in Fig. 2, the difference between RPAE_F and RPAE_{FA} results is small.

It is remarkable that the cross-section of $e + C_{60}$ collision rapidly drops down with electron energy growth for both presented in Figs. 1 and 2 phases. Starting from 0.2 Ry the contribution of stuffed atom A became comparable or even bigger than that of the C_{60} itself.

We see that the property of additivity discussed in [1] and [2] is accurate enough only if the effect of the fullerene shell upon atomic polarization interaction presented by (5) is small. It appeared, however, that already inclusion of polarization interaction (5), but with endohedral instead of pure atom's A wave functions, considerably affects the scattering phases and cross-sections.

Fig. 3 presents the total elastic electron scattering

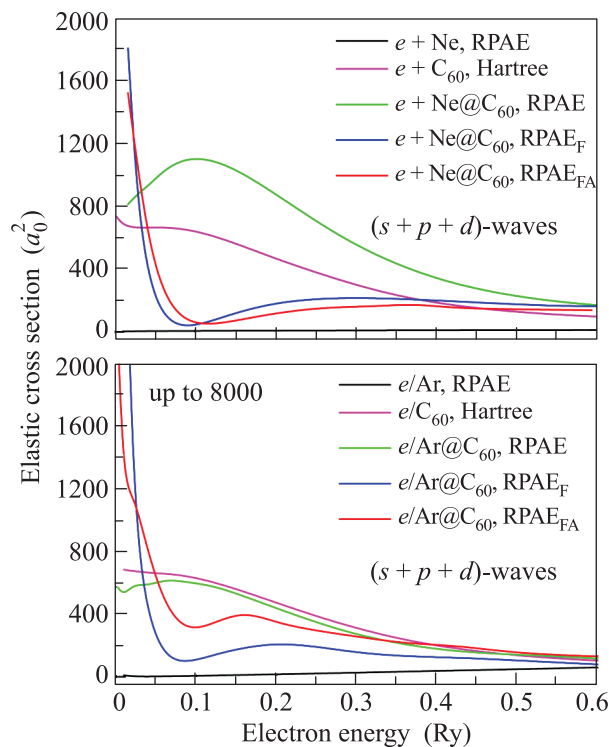


Fig. 3. (Color online) Total cross-section of electron elastic scattering upon $\text{Ne}@C_{60}$ and $\text{Ar}@C_{60}$

cross-sections upon $\text{Ne}@C_{60}$ and $\text{Ar}@C_{60}$. We have calculated first three scattering phases – s , p , and d . For considered energies, particularly below 0.3 Ry the number of included partial waves is sufficient.

Note that as it is evident from Fig. 3, each step in increasing the accuracy of our approach leads to prominent changes in the cross-section.

We see that due to alteration of the inner atom polarization potential by the fullerene, accounted for in the frames of RPAE_F or RPAE_{FA}, the cross-sections acquire a very big resonance at low energy, perhaps even at $E \rightarrow 0$ and a deep minimum at $E \approx 0.1 \text{ Ry}^3$). Note that all this variation of the cross-section does not exist for pure fullerene, or in the RPAE approximation for the endohedral. The RPAE maximum at $E \approx 0.1 \text{ Ry}$ that is particularly big in Ne, transforms in RPAE_F or RPAE_{FA} into a deep minimum. Note, that being qualitatively similar, the RPAE_F and RPAE_{FA} results essentially differ.

6. Using concrete examples we have demonstrated that the elastic scattering of electrons upon endohedrals is an entirely quantum mechanical process, where addition of even a single atom can qualitatively alter the multi-particle cross-section.

Even the crudest account of the fullerene influence upon the caged atom polarization potential (that is achieved by using endohedral's electron wave functions (1) to describe the intermediate states ν_1, ν_2, ν_3 in (5)), alters the phases and cross-sections impressively (compare results for RPAE and RPAE_F in Figs. 1–3).

Surprisingly enough, the fullerenes shell dynamic polarization strongly modifies the stuffed atom polarization potential. This is demonstrated by taking into account the corrections (6)–(8) (compare results for RPAE_F and RPAE_{FA}).

Only further clarification of the polarization potential can permit to make a decisive conclusion on the existence of either a low-energy scattering resonance or an extra bound state between an incoming electron and an endohedral exist.

We do believe that the presented results will stimulate theoretical and experimental research of low-energy elastic scattering of electrons by endohedral atoms.

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³)In atomic scattering such a minimum is called Ramsauer minimum.