Revivification of confinement resonances in the photoionization of $A@C_{60}$ endohedral atoms far above thresholds

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It is discovered theoretically that significant confinement resonances in an $nl$ photoionization of a multielectron atom $A$ encaged in carbon fullerenes, $A@C_{60}$, may re-appear and be strong at photon energies far exceeding the $nl$ ionization threshold, as a general phenomenon. The reasons for this phenomenon are unravelled. The Ne $2p$ photoionization of the endohedral anion Ne$@C_{60}^{-}$ in the photon energy region of about a thousand eV above the $2p$ threshold is chosen as case study.

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Endohedral fullerenes $A@C_{60}$, where an atom $A$ is confined (encaged) inside a hollow carbon cage $C_{60}$, are modern frontline targets of research in chemistry and physics. This is in view of their novelty in basic science and importance to various applied sciences and technologies. In particular, many efforts have been undertaken to unravel trends in the response of $A@C_{60}$ confined atoms $A$, referred to as $A@$ for brevity, to external perturbations, such as the incoming photoionizing radiation (see Refs. [1, 2, 3, 4] and references therein) and fast charged-particles [5]. One of outstanding inherent features of the corresponding spectra is the presence of resonances, termed confinement resonances [1, 2, 4]. New aspects of confinement resonances are the subject of this paper.

Much of the current understanding of the nature and origin of confinement resonances in spectra of confined atoms $A@C_{60}$ is based on modeling the $C_{60}$ cage by a short-range attractive spherical potential $V_c(r)$ of inner radius $r_0 = 5.8$ a.u., depth $U_0 = -8.2$ eV, and either the zero thickness, i.e., $V_c(r) = -U_0 \delta(r - r_0)$ [4], or finite thickness $\Delta = 1.9$ a.u. [1, 2, 3, 4, 6] (and references therein):

$$V_c(r) = \begin{cases} 
-U_0 < 0, & \text{if } r_0 \leq r \leq r_0 + \Delta \\
0, & \text{otherwise.}
\end{cases}$$

(1)

The formation of the $A@C_{60}$ system is completed by placing the neutral atom $A$ at the center of the cage. For small sized, compact atoms there is no charge transfer to the cage, so that the confined atom $A@$ retains the structure of the free atom $A$. In the framework of such modeling, confinement resonances in partial $nl$ ionization cross sections of the $A@$ atom occur due to the interference of the ejected photoelectron waves emerging directly from the confined atom, and those scattered off the confining $C_{60}$ cage.

According to the thus accumulated database of calculated data, confinement resonances in a partial $nl$ ionization cross section of a $A@C_n$ system have been known to rapidly vanish with increasing energy of the outgoing photoelectron, ceasing to exist at only some tens eV above the $nl$ threshold, not to mention thousands eV above the threshold. This is in line with a theory of scattering of particles off a potential well/barrier. Indeed, starting from a sufficiently high energy of the outgoing electron, the corresponding coefficient of reflection off a finite potential well/barrier decreases with increasing energy of the electron. As a result, the interference effect between the outgoing and scattered electron waves becomes weaker, with increasing energy of the electron, and so are the associated confinement resonances. For the case of $A@C_{60}$ photoionization, the confining potential, Eq. (1), and, thus, the $C_{60}$ cage itself, become invisible to an outgoing $nl$ photoelectron at energies that are only some tens eV above the $nl$ threshold. This is because the confining potential $V_c(r)$ is shallow, being only a few eV deep. Consequently, the $nl$ photoionization cross sections of the confined and free atoms become virtually identical at these energies, and they previously have been thought to remain nearly identical at all higher energies.

We show in this paper that, contrary to the existing understanding of the behavior of confinement resonances as a function of ejected photoelectron energy, the importance of the shallow confining potential, or the cage itself, generally re-emerges at high photoelectron energies, for confined multielectron atoms. As a result, confinement resonances manifest, i.e., revive, in the $nl$ photoionization spectra of a confined multielectron atom $A@$ in a region far above the threshold energy. We term this effect the *revivification of confinement resonances*. This revivification causes the corresponding spectra of the free and confined atom be much different from each other, as they are near threshold. The prediction and study of the revivification of confinement resonances effect constitutes the quintessence of the present paper. To qualitatively explain, and quantitatively study this effect, we consider the $2p$ photoionization of Ne@$ from a quintuply-charged endohedral fullerene anion Ne@C$_{60}^-$. near the Ne@$ 1s$ threshold; we deem this case study a most illustrative one among other possibilities.

To calculate the one-electron set of electronic bound and continuous wavefunctions and energies, as well as photoionization amplitudes of thus confined Ne, we follow a step-to-a-step, the methodology described in details in [2]. In short, the $C_{60}$ is simulated by the potential $V_c(r)$, Eq. (1). The excessive negative charge $q = -5$ on $C_{60}$ is evenly distributed over the entire outer spherical
surface of the cage. The excessive charge on the C_{60} cage brings up an extra Coulomb potential \( V_q(r) \) in addition to the neutral cage potential \( V_s(r) \):

\[
V_q(r) = \begin{cases} 
\frac{e^2}{r_0 + \Delta}, & \text{if } 0 \leq r \leq r_0 + \Delta \\
\frac{e^2}{r}, & \text{otherwise}. 
\end{cases}
\]

The sum total of these two potentials, \( V(r) = V_s(r) + V_q(r) \), is added to nonrelativistic Hartree-Fock (HF) equations for a free closed shell atom, thereby turning the “free atom” HF equations into “confined” HF equations. Calculated HF electronic energies and wavefunctions of the confined Ne atom are used for calculating dipole \( nl \) photoionization amplitudes of the atom. To account for interchannel interaction/coupling in the Ne@ photoionization, the random phase approximation with exchange (RPAE) [10] is utilized with HF employed as the zero-order approximation. RPAE has proven to be a very reliable methodology over the years [10].

With the thus calculated RPAE photoionization amplitudes and their phase shifts, dipole angle-integrated partial photoionization cross sections \( \sigma_{N@C_{60}}^{Ne}(\omega) \) and dipole angular asymmetry-parameters \( \beta_{N@C_{60}}^{Ne}(\omega) \) of photoelectrons ejected from Ne@ are determined. The corresponding expressions for these quantities of an \( A@ \) photoionization are exactly the same as those for any free closed shell atom \( A \), see, e.g., Ref. [10]. When accounting for interchannel coupling in the Ne@ 2p photoionization, RPAE calculations have to include coupling between all possible photoionization channels \( 1s \rightarrow p, 2s \rightarrow p, 2p \rightarrow d, \) and \( 2p \rightarrow s \), since it is expected, on the basis of free Ne data [11], that none of these channels can be discarded in the photon energy region of interest. Finally, in RPAE calculations, we use HF calculated ionization thresholds instead of experimental ones, just for the sake of “theoretical” consistency. For 2p, 2s, and 1s ionization thresholds of free Ne these are \( I_{Ne}^{1s} \approx 894, I_{Ne}^{2s} \approx 53, \) and \( I_{Ne}^{2p} \approx 23 \) eV versus \( I_{Ne}^{1s} = 874, I_{Ne}^{2s} = 35, \) and \( I_{Ne}^{2p} = 5.5 \) eV for Ne confined in C_{60}. A notable difference between the \( I_{nl}^{1s} \) and \( I_{nl}^{2s} \) ionization thresholds is due chiefly to the Coulomb potential brought about inside the C_{60} cage by the excessive negative charge on the cage, Eq. (2).

RPAE results for \( \sigma_{N@C_{60}}^{Ne}(\omega) \) and \( \beta_{N@C_{60}}^{Ne}(\omega) \), above the 1s threshold, are depicted in Fig. 1 along with corresponding data for free Ne. One can see that both \( \sigma_{N@C_{60}}^{Ne}(\omega) \) and \( \beta_{N@C_{60}}^{Ne}(\omega) \) show the two noticeable resonances emerging above the \( I_{N@C_{60}}^{1s} \) threshold (\( \approx 874 \) eV), whereas there is nothing even remotely similar in \( \sigma_{Ne}^{2p} \) and \( \beta_{Ne}^{2p} \) of free Ne. Thus, the confinement, i.e., the charged C_{60} cage itself, represented by the sum total of the potentials \( V_s(r) \) and \( V_q(r) \), surprisingly starts mattering again, and quite appreciably, at the 2p photoelectron energy which is of the order of a thousand eV above the small confining potential; this, as well, may be termed as reemerging confinement effect. Hence, the resonances in \( \sigma_{N@C_{60}}^{Ne}(\omega) \) and \( \beta_{N@C_{60}}^{Ne}(\omega) \) are confinement resonances in origin, since they are brought about by the confinement, thereby illustrating the revivification of confinement resonances in the high energy region of the 2p spectrum.

A hint to the physics behind the nature and origin of the revivification of confinement resonances becomes evident when one explores the earlier calculations [9] of the 1s photoionization cross section \( \sigma_{1s}^{Ne}(\omega) \) of Ne@C_{60}. The latter is depicted in lower panel of Fig. 1 along with the corresponding photoionization cross section of free Ne. The two resonances in \( \sigma_{1s}^{Ne}(\omega) \) are known to be confinement resonances [9]. Their presence in \( \sigma_{1s}^{Ne}(\omega) \) is not surprising, at these energies; they emerge only about 20 eV above threshold. There, the probability of reflection of 1s photoelectrons from the confining potential is appreciable, thereby causing the emergence of confinement resonances in the 1s photoionization two of which, the strongest ones, are depicted in Fig. 1. With this understanding of the 1s photoionization in mind, the nature of the two resonances in the corresponding 2p photoioniza-
tion of Ne@ can readily be unraveled. Specifically, when the photon energy exceeds the 1s threshold energy, the 1s → p photoionization channel opens, and it is dominated by confinement resonances near threshold, as seen above. These confinement resonances are further “funneled” to the 2p → s, d channels, via interchannel coupling. Given that the σ_{Ne@}^{2p} photoionization cross section is much smaller than σ_{1s}^{Ne@}, at these energies, the “funneled” 1s confinement resonances show up strongly as confinement resonances in the Ne@ 2p photoionization as well. Hence, the significance of the confining cage reemerges once again, via interchannel coupling with the 1s channel, for high energy photoelectrons. As a consequence, confinement resonances revive in the high energy region of the 2p photoelectron spectrum, thereby driving it significantly away of that of the free atom. To test this conclusion, we have performed a trial calculation with the 1s → p channel excluded from RPAE calculations. The results of the trial calculation (not shown) showed no sign of any confinement resonances at all in the 2p photoionization in the discussed energy region, in accordance with the above conclusion.

Note the fact that the 1s → p channel couples strongly with the 2p → s, d channels near the 1s threshold is not a new idea - for 2p photoionization of free Ne it was illustrated earlier in [11]. Nor is it new that confinement resonances can show up in photoionization cross sections of outer electrons through interchannel coupling. This was demonstrated earlier for Xe 6d photoionization near the Xe 4d threshold of the Xe@C\textsubscript{60} system [2, 12], where the confinement resonances, induced by interchannel coupling, emerge along with the “conventional” Xe 5s confinement resonances (i.e., confinement resonances which are not associated with interchannel coupling). Nevertheless, in the Xe@ case, the correlation confinement resonances emerged in a region of the 5s spectrum where conventional confinement resonances were still expected. The core novelty of the present paper versus Refs. [2, 12] is that we find that confinement resonances reemerge in A@C\textsubscript{60} valence shell confined atom spectra about a thousand eV above threshold, far far above where conventional wisdom said they would exist.

The discovered revivification of confinement resonances effect appears to be an inherent feature of the photoionization of confined multielectron atoms exclusively, whereas in confined single-electron atoms, obviously, only the “conventional” confinement resonances may emerge. Furthermore, the heavier the multielectron atom A, the greater the energy difference between inner and outer subshells in the atom. Therefore, when certain conditions are met (the presence of sizable confinement resonances in inner shell channels along with their strong coupling with outer shell channels), confinement resonances in outer shell spectra of A@C\textsubscript{60} may revive even at tens keV above threshold. And, clearly, the same type of confinement resonances may emerge in other types of ionization processes, such as the ionization of A@C\textsubscript{60} atoms by fast charged-particles, as a general phenomenon. Accordingly, a revised understanding of the behavior of various types of ionization spectra of an A@C\textsubscript{60} confined atom with increasing photon energy should be adopted. Namely, initially, on the scale of tens of eV above threshold, the amplitudes of the confinement resonances in the nl photoionization cross section of the confined atom will be diminished to nearly a zero. However, at higher photon energies, i.e., hundreds or thousands of eV above threshold, the corresponding cross section must generally start exhibiting confinement resonances again. This will happen at photon energies which correspond to opening of inner shell photoionization channels whose intensities exceed by far the intensity of transitions from the outer subshell of the confined atom and which are strongly coupled with the inner-shell transitions.

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