

Confinement and electron correlation effects in photoionization of atoms in endohedral anions: $\text{Ne}@C_{60}^{z-}$

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Abstract. Trends in resonances, termed confinement resonances, in photoionization of atoms A in endohedral fullerene anions $A@C_{60}^{z-}$ are theoretically studied and exemplified by the photoionization of Ne in $\text{Ne}@C_{60}^{z-}$. Remarkably, above a particular nl ionization threshold of Ne in *neutral* $\text{Ne}@C_{60}$ ($I_{nl}^{z=0}$), confinement resonances in corresponding partial photoionization cross sections σ_{nl} of Ne in any charged $\text{Ne}@C_{60}^{z-}$ are not affected by a variation in the charge z of the carbon cage, as a general phenomenon. At lower photon energies, $\omega < I_{nl}^{z=0}$, the corresponding photoionization cross sections of *charged* $\text{Ne}@C_{60}^{z-}$ (i.e., those with $z \neq 0$) develop additional, strong, z -dependent resonances, termed Coulomb confinement resonances, as a general occurrence. Furthermore, near the innermost 1s ionization threshold, the 2p photoionization cross section σ_{2p} of the outermost 2p subshell of thus confined Ne is found to inherit the confinement resonance structure of the 1s photoionization spectrum, via interchannel coupling. As a result, new confinement resonances emerge in the 2p photoionization cross section of the confined Ne atom at photoelectron energies which exceed the 2p threshold by about a thousand eV, i.e., far above where conventional wisdom said they would exist. Thus, the general possibility for confinement resonances to resurrect in photoionization spectra of encapsulated atoms far above thresholds is revealed, as an interesting novel general phenomenon.

1. Introduction

Endohedral fullerenes $A@C_{60}$, where the atom A is encapsulated inside the hollow interior of the carbon cage C_{60} , are of the highest interest and importance both to the basic and applied sciences and technologies, as new modern building blocks of materials and devices with unique properties. Therefore, they have attracted much attention of many investigators in recent years. In particular, the photoionization, as a basic phenomenon in nature, of atoms A encapsulated in fullerenes $A@C_{60}$ has become a topical research subject both for theorists for some years now (see a review paper [1] as well some latest works [2, 3, 4] on the subject and references therein) and, since only very recently, experimentalists [5, 6]. Among the performed photoionization studies of thus confined atoms, only works [1, 7] have provided the initial understanding of how the photoionization spectrum of an atom could be modified by the environment of a negatively charged carbon cage C_{60}^{z-} . The understanding was exemplified by trends in photoionization of the innermost 1s subshell of Ne in $\text{Ne}@C_{60}^{z-}$ with various z 's. However, how these and other possible trends might show up, as general phenomena, in spectra of intermediate and outer subshells of atoms A in $A@C_{60}^{z-}$ has remained unstudied. The present paper expands further

the investigation started in [7] to the intermediate 2s and outermost 2p subshells of the confined Ne with the aim to reveal which new aspects of these spectra of endohedral anions are most interesting, as general phenomena.

2. Brief description of theoretical concepts

Following previous works, see, e.g., [1, 2, 7] and references therein, the neutral C_{60} cage is modelled 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 finite thickness $\Delta = 1.9$ a.u.

$$V_c(r) = \begin{cases} U_0, & \text{if } r_0 \leq r \leq r_0 + \Delta \\ 0 & \text{otherwise.} \end{cases} \quad (1)$$

A neutral endohedral fullerene $A@C_{60}$ is formed by placing the atom A at the center of the cage. For small sized, compact atoms A there is no charge transfer to the cage, so that the confined atom A retains the general structure of the free atom A . Alternatively [1, 7], an endohedral anion $A@C_{60}^{z-}$ is modelled by the sum total of the potential V_c and the Coulomb potential $V_z(r)$ of an excessive negative charge on the cage C_{60} . Assuming that the charge z is uniformly distributed over the entire outer surface of C_{60} ,

$$V_z(r) = \begin{cases} \frac{z}{r_0 + \Delta}, & \text{if } 0 \leq r \leq r_0 + \Delta \\ \frac{z}{r} & \text{otherwise.} \end{cases} \quad (2)$$

Next, the sum total of these two potentials is added to nonrelativistic Hartree-Fock (HF) equations for a free atom. Solutions of these new HF equations, i.e., electronic energies and wavefunctions of the confined A atom, are used in well-known expressions for nl photoionization amplitudes, angle-differential and/or angle-integrated nl photoionization cross sections, *etc.*, for free atoms; see [8] for the latter. To account for interchannel coupling in the photoionization of a confined atom, the *random phase approximation with exchange* (RPAE) [8] is utilized to meet the aim. This is because RPAE, which uses a HF approximation as the zero-order approximation, has proven to be a very reliable methodology over the years. Accordingly, for the sake of “theoretical” consistency, HF values of ionization thresholds of free and confined Ne atoms are used in the present study.

3. Results and discussion

3.1. Conventional confinement resonances: irrelevance of a charged state of C_{60}^{z-}

RPAE calculated photoionization cross sections σ_{2p} of Ne in variously z -charged $Ne@C_{60}^{z-}$ are displayed in figure 1. Corresponding photoionization cross sections σ_{2s} and σ_{1s} are depicted in figure 2. In these calculations, interchannel coupling in the atom was accounted for at an intra-shell approximation level, as the first step in the study. One can see that, above the 2p threshold $I_{2p}^{z=0} \approx 23$ eV of Ne in *neutral* $Ne@C_{60}^{z=0}$ (i.e., to the right of a vertical line marked with $z = 0$), all σ_{2p} ’s oscillate about the 2p photoionization cross section of free Ne, as do σ_{2s} above $I_{2s}^{z=0} \approx 53$ eV and σ_{1s} above $I_{1s}^{z=0} \approx 892$ eV, respectively. The oscillations are due to the interference between the outgoing nl photoelectron wave and those scattered off the confining potential of C_{60}^{z-} . When the constructive interference occurs, there emerge maxima, i.e., resonances in σ_{nl} ’s, termed confinement resonance [1, 2, 4, 7]. Furthermore, one can see that confinement resonances in *all* σ_{nl} ’s are nearly z independent above related $I_{nl}^{z=0}$ thresholds (previously [7], the same was noted in the 1s spectrum of Ne in $Ne@C_{60}^{z-}$). This is because the energy ϵ of an outgoing nl photoelectron in any charged $Ne@C_{60}^{z-}$ exceeds by far the Coulomb potential barrier of the charged carbon cage, at $\omega \geq I_{nl}^{z=0}$. This is clearly seen in figure 3 where direct (Hartree) parts of the potentials “seen” by the ϵp and ϵs photoelectrons (due

to the $2p \rightarrow \epsilon p, \epsilon s$ transitions) are displayed. Hence, the presence of the Coulomb potential barrier is inconsequential for the outgoing nl photoelectrons at photon energies $\omega \geq I_{nl}^{z=0}$. Correspondingly, at $\omega \geq I_{nl}^{z=0}$, confinement resonances in any nl photoionization spectrum of the encapsulated atom will chiefly be governed by details of the confining potential well V_c , equation (1), as in neutral $\text{Ne}@\text{C}_{60}$. Thus, the resonances will nearly be z -independent. We term such confinement resonances as *conventional confinement resonances*.

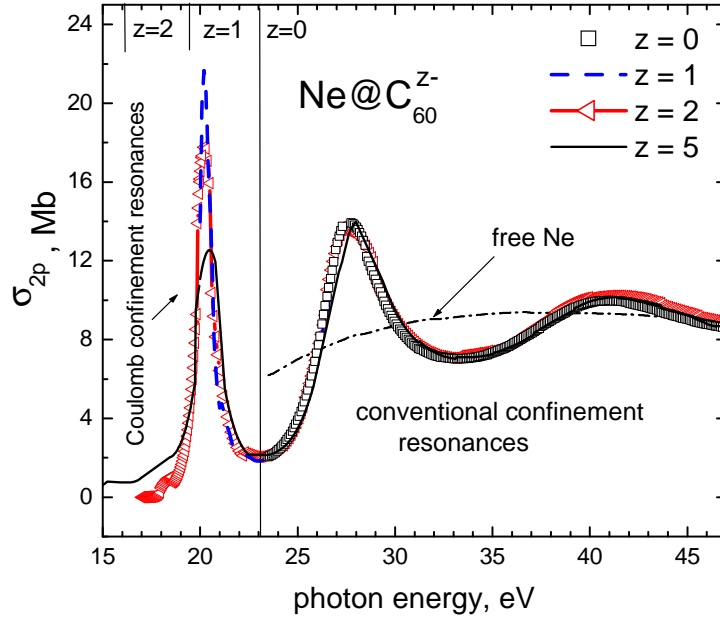


Figure 1. RPAE calculated data, at an intra-shell interchannel coupling approximation level, for the σ_{2p} photoionization cross section of Ne in $\text{Ne}@\text{C}_{60}^{z-}$ for $z = 0, 1, 2, 5$ as well as for free Ne, as marked. Vertical lines with marks $z = 0, z = 1$ and $z = 2$, show positions of the Ne $2p$ thresholds $I_{2p}^{z=0} \approx 23.1$, $I_{2p}^{z=1} \approx 19.6$, $I_{2p}^{z=2} \approx 16.1$ and $I_{2p}^{z=5} \approx 5.5$ eV in corresponding $\text{Ne}@\text{C}_{60}^{z-}$.

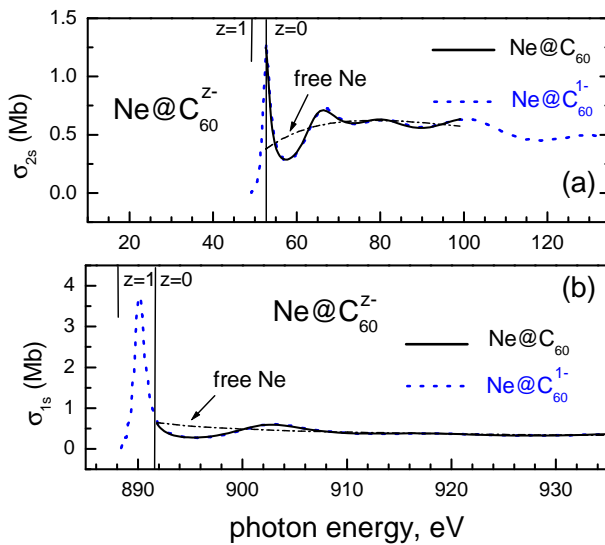


Figure 2. (a): RPAE calculated data, at an intra-shell interchannel coupling approximation level, for the σ_{2s} photoionization cross section of Ne in $\text{Ne}@\text{C}_{60}^{z-}$ for $z = 0$ and 1 as well as for free Ne, as marked. Vertical lines with marks $z = 0$ and $z = 1$ show positions of Ne $I_{2s}^{z=0} \approx 52.5$ eV and $I_{2s}^{z=1} \approx 49$ eV. (b): The same as in (a) but for the Ne $1s$ photoionization ($I_{1s}^{z=0} \approx 892$, $I_{1s}^{z=1} \approx 888$ eV).

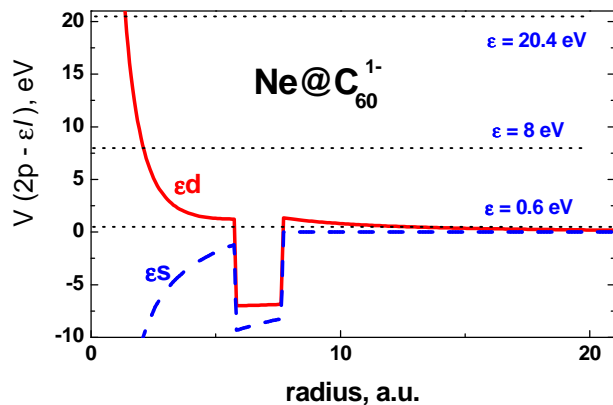


Figure 3. A direct (Hartree) part of the potential $V(2p \rightarrow \epsilon l)$ “seen” by ϵs and ϵp photoelectrons in the $2p \rightarrow \epsilon s$ and $2p \rightarrow \epsilon d$ photoionization transitions in the Ne@C_{60}^{1-} atom, as marked. Horizontal lines show the photoelectron energies $\epsilon \approx 0.6, 8$ and 20.4 eV corresponding to maxima of the resonances in the Ne@C_{60}^{1-} photoionization cross section σ_{2p} (see figure 1) at about 20, 28 and 42 eV of the photon energy, respectively.

To conclude, the above results reveal, and the given explanation proves, that *conventional* confinement resonances in photoionization cross sections of inner, intermediate and outer subshells of an atom A in $A@\text{C}_{60}^{z-}$ appear to be almost z -independent. This is an interesting general phenomenon. Another important observation (see figures 1 and 2) is that conventional confinement resonances vanish quite rapidly with increasing photon (or photoelectron) energy. This is in line with a theory of scattering of particles off a potential well/barrier. Indeed, starting at a sufficiently high energy of the outgoing photoelectron, the coefficient of reflection of the latter off a finite potential well/barrier decreases with increasing energy of the electron. As a result, the interference effect between the outgoing and scattered off the potential well/barrier photoelectron waves weakens, with increasing energy of the electron, and so are the associated conventional confinement resonances. In further, we will term this reasoning as “conventional thinking”.

3.2. Coulomb confinement resonances

Above, trends in the Ne nl photoionization cross sections of Ne@C_{60}^{z-} were considered at photon energies ω beyond the corresponding $I_{nl}^{z=0}$ thresholds of Ne in neutral Ne@C_{60} . We now turn the attention to lower photon energy ($\omega < I_{nl}^{z=0}$) parts of figures 1 and 2 (to the left of the $z = 0$ marked line) where we consider photoionization of charged Ne@C_{60}^{z-} ($z \neq 0$). There, the additional resonance in each of σ_{2p} , σ_{2s} and σ_{1s} of Ne@C_{60}^{z-} is seen to emerge. It owes its existence to the Coulomb potential V_z , equation (2), of the charged carbon cage. The V_z potential brings up the Coulomb potential barrier at the outer surface of C_{60} . This engenders reflection of the low-energy continuum photoelectron wave from the Coulomb barrier causing additional resonances one of which is depicted in figures 1 and 2 at photon energies under discussion. Originally, the emergence of this kind of a resonance was noted in the Ne $1s$ photoionization of Ne@C_{60}^{z-} [7], where it was named *Coulomb confinement resonance*, in view of its association with the Coulomb potential barrier of the charged carbon cage. The present paper establishes that the phenomenon emerges in the photoionization of intermediate and outer subshells of the encapsulated atom as well, as a general occurrence. Coulomb confinement resonances appear to be z -dependent, as is clearly exemplified by depicted in figure 1 σ_{2p} ’s. This is because, in this instance, the energy ϵ of the outgoing photoelectron is near or, generally, below the top of the Coulomb potential barrier (see, as illustration, the energy line $\epsilon = 0.6$ eV in figure 3). This makes the photoionization process to be sensitive to details of the latter, and, hence, to a charged state of the carbon cage as well.

To conclude, the established co-existence of z -dependent Coulomb and z -independent conventional confinement resonances in photoionization spectra of endohedral *anions* is an exclusive feature of these systems.

3.3. Correlation confinement resonances: the resurrection of confinement resonances far above thresholds

In the above, the discussion was related to RPAE calculated data for photoionization cross sections $\sigma_{nl}(\omega)$ of the encapsulated Ne atom which were obtained at an intra-shell interchannel coupling approximation level. However [1, 2, 9], the effect of *inter-shell* interchannel coupling in the encapsulated atom may result in the emergence of new confinement resonances, termed *correlation confinement resonances*. These resonances were previously interpreted as resonances which are induced in an outer-shell photoionization spectrum of the encapsulated atom by *conventional confinement resonances* in inner-shell photoionization transitions in the atom, via interchannel coupling. The earlier finding was illustrated by RPAE [1, 9] and recently seconded by relativistic RRPA [2] calculated data for the Xe 5s photoionization of Xe@C₆₀ where interchannel coupling between the 5s and 4d transitions was accounted for. However, the same effect may occur via interchannel coupling with Coulomb confinement resonances as well. It may even be bigger in this case since Coulomb confinement resonances dominate over conventional confinement resonances; see figure 2 for the most illustrative supporting evidence. Furthermore, the effect of interchannel coupling may show up strongly in an outer-shell photoionization spectrum at photoelectron energies which are thousands eV above the threshold, when interchannel coupling involves very deep inner-shell transitions. The effect is going to be strong, because at such big differences in ionization thresholds of the inner and outer subshells, photoionization transitions from the former will be strong whereas those from the latter will be weak, at photon energies above the inner shell threshold. As a result, both inner-shell Coulomb and conventional confinement resonances may be effectively “funneled” through a thousands-eV-distance to the outer-shell spectrum. However, to which extent the “funneled” confinement resonances may indeed perturb the outer-shell spectrum is not clear. To clarify this point, we performed RPAE calculations both of the 2p photoionization cross section σ_{2p} and dipole photoelectron angular-asymmetry parameter β_{2p} for Ne in Ne@C₆₀¹⁻, above the Ne 1s ionization threshold. This time, inter-shell interchannel coupling between the 1s, 2s and 2p transitions was included in the calculations. Thus obtained RPAE calculated data for σ_{2p} and β_{2p} for the encaged Ne are depicted in figure 4 along with data for free Ne.

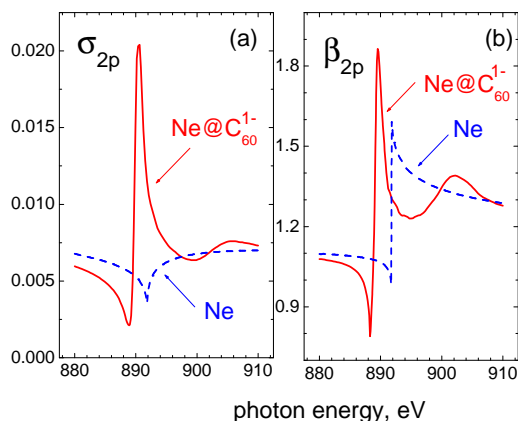


Figure 4. (a): RPAE calculated data for $\sigma_{2p}(\omega)$ (Mb) of Ne in Ne@C₆₀¹⁻ and free Ne near their 1s thresholds, respectively. RPAE calculations included interchannel coupling between transitions from the 1s, 2s and 2p subshells. (b): The same as in (a) but for the dipole photoelectron angular-asymmetry parameter $\beta_{2p}(\omega)$.

One can see that both σ_{2p} and $\beta_{2p}(\omega)$ for the encapsulated Ne atom possess a strong sharp resonance at about 890 eV which is followed by a lower but broader resonance at about 905 eV. As a result, these “encapsulated” σ_{2p} and $\beta_{2p}(\omega)$ differ considerably from the free Ne σ_{2p} and $\beta_{2p}(\omega)$, far above threshold. Thus, the confinement matters in this case, so that the two prominent resonances in “encapsulated” σ_{2p} and $\beta_{2p}(\omega)$ are confinement resonances.

The striking novelty of the above finding is that the resonances emerge far-far above where conventional thinking said they would exist. Indeed, when considering confinement resonances,

one normally thinks in terms of conventional confinement resonances which occur due to the interference between the directly outgoing and reflected off the confining potential photoelectron waves. However, in line with “conventional thinking”, as was discussed above, conventional confinement resonances fade away relative rapidly with increasing energy and do vanish far above threshold. The discovered emergence, or better say resurrection of confinement resonances in the 2p photoionization spectrum of $\text{Ne}@C_{60}^{z-}$ far above threshold implies that, in contrast to “conventional thinking”, a few eV deep/high confining potential well/barrier may, once again, be felt by a far-above-potential-barrier-electron. The effect may as well be called *reemerging confinement effect* for a high-energy scattering electron, as a general phenomenon. This general phenomenon may result in the emergence of far above threshold confinement resonances in the nl photoionization spectrum of a confined atom, as in the above discussed particular example of the Ne 2p photoionization of $\text{Ne}@C_{60}^{1-}$. The latter effect may rightly be termed as *resurrection of confinement resonances* effect. Both the reemerging confinement and resurrection of confinement resonances effects owe their existence to inter-shell interchannel coupling in the encapsulated multielectron atom. Indeed, a trial calculation for $\text{Ne}@C_{60}^{1-}$ showed that removal of the Ne 1s transition (and, thus, associated with it Coulomb and conventional confinement resonances) from RPAE calculations of the Ne 2p photoionization leaves no traces of the two resonances in “encapsulated” σ_{2p} and $\beta_{2p}(\omega)$. As a result, the 2p photoionization spectra of the confined and free Ne atoms become virtually identical far above threshold, as they previously have been thought to remain nearly identical at all high energies, on the basis of “conventional thinking”. Hence, the resurrected confinement resonances in “encapsulated” σ_{2p} and $\beta_{2p}(\omega)$, far above threshold, are due to interchannel coupling with the conventional and Coulomb confinement resonances in the 1s spectrum. The latter are “funneled” to the 2p spectrum via interchannel coupling. This appears to perturb the outer-shell spectrum of the confined atom dramatically.

Clearly, there is nothing particularly special about the $\text{Ne}@C_{60}^{z-}$ system. Therefore, both the reemerging confinement effect and the resurrection of confinement resonances effect are expected to appear in, and be qualitatively similar for, spectra of other endohedrally confined atoms as well. In other words, the two discovered effects step in as novel general features of spectra of endohedrally confined atoms $A@C_{60}^{z-}$ the existence and significance of which has been convincingly proven in the performed study.

In conclusion, neither Coulomb or conventional confinement resonances, not to mention the just discovered resurrected confinement resonances far above threshold, have been experimentally observed yet for technical reasons. We hope that the data presented herein will prompt experimentallists to look into the matter, thereby promoting such developments.

Acknowledgments

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