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 reappear and be strong at photon energies far exceeding the *nl* ionization threshold, as a general phenomenon. The reasons for this phenomenon are unraveled. The Ne 2*p* photoionization of the endohedral anion $Ne@C_{60}{}^{5-}$ in the photon energy region of about a thousand eV above the 2*p* threshold is chosen as a 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*, to external perturbations, such as the incoming photoionizing radiation (see Refs. [1–5], and references therein) and fast charged particles [6]. One of outstanding inherent features of the corresponding spectra is the presence of resonances termed confinement resonances [1,2,4]. Other 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. [1,2,6–8] (and references therein),

$$V_c(r)=\begin{cases}-U_0<0 & \text{if } r_0\le r\le r_0+\Delta\\ 0 & \text{otherwise.}\end{cases} \qquad (1)$$

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 $A@C_{60}$ 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 or barrier. Indeed, starting from a sufficiently high energy of the outgoing electron, the corresponding coefficient of reflection off a finite potential well or 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 the region far above the threshold energy. We term this effect as 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 2*p* photoionization of the confined atom Ne from a quintuply charged endohedral fullerene anion $Ne@C_{60}{}^{5-}$, near the Ne 1*s* threshold; we deem this case study a most illustrative one among other possibilities.

To calculate the one-electron set of electronic bound and continuous-wave functions and energies, as well as photoionization amplitudes of thus confined Ne, we follow, step-by-step, the methodology described in details in [9]. 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 $V_c(r)$,

$$V_q(r)=\begin{cases}\dfrac{q}{r_0+\Delta} & \text{if } 0\le r\le r_0+\Delta\\[2mm] \dfrac{q}{r} & \text{otherwise.}\end{cases} \tag{2}$$

The sum total of these two potentials $V(r)=V_c(r)+V_q(r)$ is added to nonrelativistic Hartree-Fock (HF) equations for a free closed-shell atom, thereby, turning the "free-atom" HF equations [10] into "confined" HF equations. Calculated HF electronic energies and wave functions of the confined Ne atom are used for calculating dipole nl photoionization amplitudes of the atom. To account for interchannel interaction or coupling in the confined atom 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 $\sigma_{nl}^{[\mathrm{Ne}]}(\omega)$ and dipole angular-asymmetry parameters $\beta_{nl}^{[\mathrm{Ne}]}(\omega)$ of photoelectrons ejected from the confined atom Ne are determined (superscript [Ne] denotes confined atom Ne). The corresponding expressions for these quantities of a confined atom are exactly the same as those for any free closed-shell atom (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 $1s\to p$, $2s\to p$, $2p\to d$, and $2p\to s$ 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 $I_{1s}^{\mathrm{Ne}}=894$, $I_{2s}^{\mathrm{Ne}}=53$, and $I_{2p}^{\mathrm{Ne}}=23$ eV versus $I_{1s}^{[\mathrm{Ne}]}=874$, $I_{2s}^{[\mathrm{Ne}]}=35$, and $I_{2p}^{[\mathrm{Ne}]}=5.5$ eV for Ne confined in $C_{60}{}^{5-}$. A notable difference between the I_{nl} and $I_{nl}^{[\mathrm{Ne}]}$ ionization thresholds is due chiefly to the Coulomb potential brought about inside the $C_{60}{}^{5-}$ cage by the excessive negative charge on the cage [Eq. (2)].

RPAE results for $\sigma_{2p}^{[\mathrm{Ne}]}(\omega)$ and $\beta_{2p}^{[\mathrm{Ne}]}$, above the $1s$ threshold, are depicted in Fig. 1 along with corresponding data for free Ne. One can see that both $\sigma_{2p}^{[\mathrm{Ne}]}$ and $\beta_{2p}^{[\mathrm{Ne}]}$ show the two noticeable resonances emerging above the $I_{1s}^{[\mathrm{Ne}]}$ threshold ($\approx$874 eV), whereas there is nothing even remotely similar in $\sigma_{2p}^{\mathrm{Ne}}$ and β_{2p}^{Ne} of free Ne. Thus, the confinement, i.e., the charged C_{60} cage itself, represented by the sum total of the potentials $V_c(r)$ and $V_q(r)$ surprisingly starts mattering again, and quite appreciably, at the $2p$ photoelectron energy which is on the order of a thousand eV above the small confining potential; this, as well, may be termed as *re-emerging confinement effect*. Hence, the resonances in $\sigma_{2p}^{[\mathrm{Ne}]}$ and $\beta_{2p}^{[\mathrm{Ne}]}$ 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 $\sigma_{1s}^{[\mathrm{Ne}]}$ of Ne@$C_{60}{}^{5-}$. The latter is depicted in the lower panel of Fig. 1 along with the corresponding photoionization cross section of free Ne. The two resonances in $\sigma_{1s}^{[\mathrm{Ne}]}$ are known to be confinement resonances [9]. Their presence in $\sigma_{1s}^{[\mathrm{Ne}]}$ 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 $2p$ photoionization of Ne@$C_{60}{}^{5-}$ can readily be unraveled. Specifically, when the photon energy exceeds the $1s$ threshold energy, the $1s\to p$ photoionization channel opens, and it is dominated by confinement resonances near threshold, as seen above. These confinement resonances are further "funneled" to the $2p\to s$, d channels, via interchannel coupling. Given that the $\sigma_{2p}^{[\mathrm{Ne}]}$ photoionization cross section is much smaller than $\sigma_{1s}^{[\mathrm{Ne}]}$, at these energies, the funneled $1s$ confinement resonances show up strongly as confinement resonances in the Ne $2p$ photoionization as well. Hence, the sig-

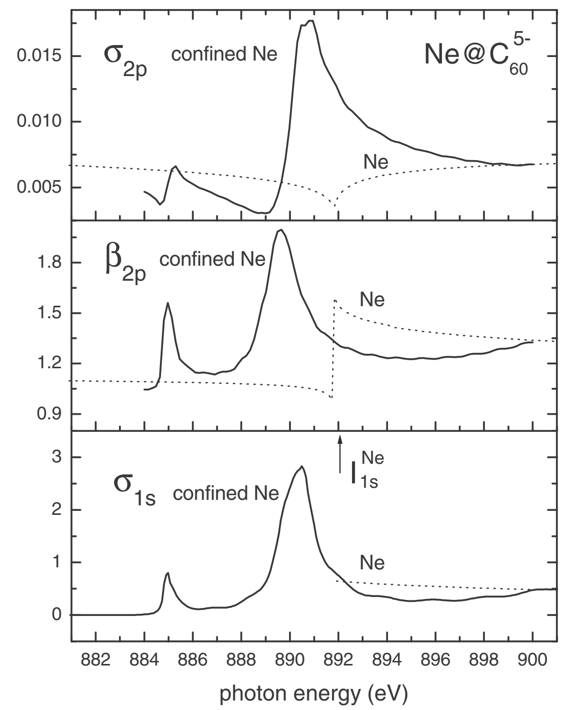

FIG. 1. RPAE data for the partial angle-integrated $2p$ photoionization cross section (Mb) (upper panel) and dipole $2p$ photoelectron angular-asymmetry parameter (middle panel) of confined Ne@$C_{60}{}^{5-}$ (solid lines) and free Ne (dotted lines). Lower panel: RPAE data for the $1s$ photoionization cross section $\sigma_{1s}^{[\mathrm{Ne}]}$ (Mb) of confined Ne@$C_{60}{}^{5-}$ (solid line) and free Ne (dotted line). Note that HF calculated ionization thresholds (see the main text) were used in the calculations. If experimental thresholds were used, the calculated curves would have been shifted by about 22 eV toward lower energies. This is because the HF ($I_{1s}^{[\mathrm{Ne}]}\approx 892$ eV) and experimental ($I_{1s}^{[\mathrm{Ne}]}\approx 870$ eV) values of the $1s$ ionization threshold of free Ne differ from each other by about 22 eV, and so the difference is expected to be in similar confined atom Ne.

nificance of the confining cage re-emerges 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 $1s \rightarrow p$ 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 $1s \rightarrow p$ channel couples strongly with the $2p \rightarrow s, d$ 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 $5s$ photoionization near the Xe $4d$ threshold of the Xe@C_{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 confined atom Xe case, the correlation confinement resonances emerged in a region of the $5s$ spectrum, where conventional confinement resonances were still expected. The core of the present paper versus Refs. [2,12] is that we find that confinement resonances reemerge in A@C_{60} valence shell confined atom spectra about a thousand eV above threshold, 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_{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@$C_{60}{}^{z}$ 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_{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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[1] V. K. Dolmatov, in *Theory of Confined Quantum Sytems: Part Two*, edited by J. R. Sabin and E. Brändas, Advances in Quantum Chemistry (Academic Press, New York, 2009), Vol. 58, pp. 13–68.

[2] R. Govil, A. J. Siji, and P. C. Deshmukh, J. Phys. B **42**, 065004 (2009).

[3] H. S. Chakraborty M. E. Madjet, Jan-M. Rost, and S. T. Manson, Phys. Rev. A **78**, 013201 (2008).

[4] M. Ya. Amusia, A. S. Baltenkov, and L. V. Chernysheva, J. Phys. B **41**, 165201 (2008).

[5] A. Müller, S. Schippers, M. Habibi, D. Esteves, J. C. Wang, R. A. Phaneuf, A. L. D. Kilcoyne, A. Aguilar, and L. Dunsch, Phys. Rev. Lett. **101**, 133001 (2008).

[6] A. S. Baltenkov, V. K. Dolmatov, S. T. Manson, and A. Z. Msezane, Phys. Rev. A **79**, 043201 (2009).

[7] D. M. Mitnik, J. Randazzo, and G. Gasaneo, Phys. Rev. A **78**, 062501 (2008).

[8] A. Lyras and H. Bachau, J. Phys. B **38**, 1119 (2005).

[9] V. K. Dolmatov and S. T. Manson, Phys. Rev. A **73**, 013201 (2006).

[10] M. Ya. Amusia, *Atomic Photoeffect* (Plenum, New York, 1990).

[11] E. W. B. Dias, H. S. Chakraborty, P. C. Deshmukh, S. T. Manson, O. Hemmers, P. Glans, D. L. Hansen, H. Wang, S. B. Whitfield, D. W. Lindle, R. Wehlitz, J. C. Levin, I. A. Sellin, and R. C. C. Perera, Phys. Rev. Lett. **78**, 4553 (1997).

[12] V. K. Dolmatov and S. T. Manson, J. Phys. B **41**, 165001 (2008).