Random phase approximation with exchange for the photoionization of confined atoms: Xe in C\textsubscript{60} fullerene

Zhifan Chen and Alfred Z. Msezane

Center for Theoretical Studies of Physical Systems, and Department of Physics
Clark Atlanta University, Atlanta, Georgia 30314, U. S. A.

ABSTRACT

Photoionization of a Xe atom confined inside C\textsubscript{60} has been studied using the random phase approximation with exchange (RPAE) method. The C\textsubscript{60} fullerene has been described by an attractive short range spherical well with potential \( V(r) \), given by \( V(r) = -V_0 \) for \( r_i < r < r_0 \), otherwise \( V(r) = 0 \) where \( r_i \) and \( r_0 \) are respectively, the inner and outer radii of the spherical shell. The radial parts of the wave function in the three regions \( r < r_i \), \( r_i < r < r_0 \) and \( r > r_0 \) have been obtained by solving the Schrödinger equation using both regular and irregular solutions and the continuous boundary conditions at \( r_i \) and \( r_0 \). The photoionization cross sections for the Xe 4\textit{d}, 5\textit{s} and 5\textit{p} electrons in the Xe@C\textsubscript{60} endohedral molecule have been evaluated and compared with those of the photoionization for the free Xe atom and other previous calculations for the Xe@C\textsubscript{60} fullerene. Our method surmounted the weaknesses of the previous model potential calculations and demonstrated significantly stronger correlated confinement resonances for the Xe@C\textsubscript{60} photoionization.

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1 Introduction

In recent years the photoionization of an atom confined by a C\textsubscript{60} fullerene has received both extensive and intensive research [1-21], because of its importance to the development of nanotechnology. Endohedral C\textsubscript{60} molecules can be prepared by accelerating ions of atoms and implanting them into the C\textsubscript{60} cage [22] and by a surgical method [23]. In the former method the ions should have just enough energy to open up the cage and enter. The endohedral C\textsubscript{60} molecules can also be achieved by co-evaporation of the carbon and the metal in an arc discharge chamber [24]. If the dopant remains neutral, it normally stays in the centre of the cage, which will greatly simplify the theoretical treatment of the photoionization process. In the past several years there have been a number of theoretical studies of the photoionization of endohedral atoms [1-6,11-21], and only very few experimental studies [10] have been reported. The confining effect of the C\textsubscript{60} cage in the theoretical studies is usually modeled by a potential well, such as a δ-like potential [11-17] or a spherical, short range attractive well [18-21]. It should be noted, however that in reality the whole space has been divided by the C\textsubscript{60} potential into several regions. In these regions the solution of the Schrödinger equation for a confined atom is usually different from that of a free atom. If only the boundary condition is changed in solving the Schrödinger equation for the confined atom, the solution is kept the same as that of the free atom, the continuum wave function will not have the phase shift due to the photoelectron scattered by the C\textsubscript{60} potential well [12]. Because of this care must to be taken to obtain the appropriate wave functions by solving the Schrödinger equation.

The δ-like potential, which is not zero only in an infinitely thin spherical layer, is not a good approximation to the C\textsubscript{60} shell. A potential well, which models the confining effect of the C\textsubscript{60} cage has been optimized through the study of C\textsubscript{60} photoionization [25] and employed in studies of photoionization [20-21]. This potential well has an inner radius of 5.75 a.u. which is approximately equal to the radius of the C\textsubscript{60} molecule and the thickness of the well is approximately 1.89 a.u. The depth of the well is -0.3028 a.u. [9, 14].

In this paper we have performed a random phase approximation with exchange (RPAE) calculation for the photoionization of the Xe 4d, 5s and 5p electrons in the Xe@C\textsubscript{60} endohedral molecule. The results have been compared with those of previous calculations for the Xe@C\textsubscript{60} and with both the theoretical and experimental data for the free Xe atom.
2 Theory

We study the photoionization process of a Xe atom located in the center of the C\textsubscript{60} fullerene shell, Xe@C\textsubscript{60}. The wave function of an optical electron of the Xe atom in this spherically symmetrical well has the standard form $\psi(r) = [P(r)/r]Y_{lm}(\theta, \phi)$. As $r_i$ is much larger than the electron shell of the Xe atom, the wave function of an optical electron in the ground state can be considered approximately to coincide with the corresponding wave function of a free Xe atom [14]. However, the continuum wave function will be quite different from that of the free atom. The continuum wave function, $P(r)$, satisfies the radial Schrödinger equation,

$$\frac{1}{2}[P''(r) - \frac{l(l + 1)}{r^2} P(r)] + \left[\frac{k^2}{2} - V(r) - U(r)\right] P(r) = 0,$$

(1)

where $k$ is the momentum of the photoelectron, $k^2 = 2E$, $E$ is the energy of the photoelectron and $l$ is the orbital angular momentum. $U(r)$ is the self-consistent field created by the atomic nucleus and all the atomic electrons, acting upon the optical electron and $V(r)$ is the model potential of the C\textsubscript{60} fullerene:

$$V(r) = \begin{cases} -V_0, & r_i < r < r_o \\ 0, & r < r_i \text{ or } r > r_o \end{cases}$$

(2)

where $V_0 = 0.3028$ a.u. [20], which is obtained from the experimental electron affinity energy for the negative C\textsubscript{60}~ ion [26] and a spherical shell model potential for the C\textsubscript{60} electrons [14].

Equation (1) is a second order differential equation. The general solution is a linear combination of a regular solution $u_{kl}(r)$ and an irregular solution $v_{kl}(r)$. In this paper the regular solution is obtained from reference [27]. The irregular solution is evaluated using equation (9.3-23) of reference [28]. In the region $r < r_i$, $r_i < r < r_0$ and $r > r_0$ the general solutions of equation (1) are given by:

$$P(r) = \begin{cases} A \ast u_{kl}(r) & r < r_i \\ B \ast u_{kl}(r) + C \ast v_{kl}(r) & r_i < r < r_0 \\ u_{kl}(r) \ast \cos \delta_l - v_{kl}(r) \ast \sin \delta_l & r > r_0 \end{cases}$$

(3)

where $q = \sqrt{k^2 + K_0^2}$, $K_0^2 = 2V_0$ and $\delta_l$ is the phase shift due to the photoelectron scattering by the potential of the C\textsubscript{60} fullerene. $u_{kl}$ is the wave function corresponding to $V(r) = 0$, which can be obtained by the package of Ref. [27]. For the Xe $4d-\epsilon f$ transition we create three excited states and forty continuum
wave functions. Each radial wave function was represented by 1000 points. The intrashell correlations can occur among all these excited and ionized states. \( u_{ql} \) is treated similarly; however, \( k^2 \) is replaced by \( q^2 \) in Eq. (1).

The coefficients \( A, B, C, \cos \delta_l, \) and \( \sin \delta_l \) in equation (3) have been obtained through the use of the continuous boundary conditions of the wave functions and their logarithmic derivatives at \( r = r_i \) and \( r = r_0 \), leading to

\[
B = \frac{u_{kl}(r_0) \cos \delta_l - v_{kl}(r_0) \sin \delta_l}{u_{ql}(r_0) + \frac{D}{F} v_{ql}(r_0)} \quad (4)
\]

\[
A = B \times \frac{u_{ql}(r_i) + \frac{D}{F} v_{ql}(r_i)}{u_{kl}(r_i)} \quad (5)
\]

\[
C = \frac{D}{F} \times B \quad (6)
\]

\[
\sin \delta_l = \frac{G}{\sqrt{G^2 + H^2}} \quad (7)
\]

\[
\cos \delta_l = \frac{H}{\sqrt{G^2 + H^2}} \quad (8)
\]

where \( D, F, G \) and \( H \) are given by

\[
D = u_{kl}(r_i) u_{ql}'(r_i) - u_{kl}'(r_i) u_{ql}(r_i) \quad (9)
\]

\[
F = u_{kl}'(r_i) v_{ql}(r_i) - u_{kl}(r_i) v_{ql}'(r_i) \quad (10)
\]

\[
G = (u_{ql}(r_0) + \frac{D}{F} v_{ql}(r_0)) * u_{kl}'(r_0) - (u_{ql}'(r_0) + \frac{D}{F} v_{ql}'(r_0)) * u_{kl}(r_0) \quad (11)
\]

\[
H = (u_{ql}(r_0) + \frac{D}{F} v_{ql}(r_0)) * v_{kl}'(r_0) - (u_{ql}'(r_0) + \frac{D}{F} v_{ql}'(r_0)) * v_{kl}(r_0) \quad (12)
\]

The symbol \( (') \) means taking the derivative with respect to \( r \). After creating the wave functions, the random phase approximation with exchange method [27] was used to obtain the photoionization cross sections for the Xe \( 4d \), \( 5s \) and \( 5p \) electrons in the Xe@C\(_{60}\) endohedral molecule. The cross sections are also evaluated by the approximate formula [11, 12]

\[
\sigma_{Xe@C_{60}} = A^2 \times \sigma_{\text{Free-atom}}. \quad (13)
\]

where \( \sigma_{\text{Free-atom}} \) is the photoionization cross section for a free atom.

3 Results

Figure 1 shows the photoionization cross sections versus photon energy for the Xe \( 4d \) electron of the Xe@C\(_{60}\) endohedral molecule. The solid and dashed curves are respectively, the results from the RPAE calculation and equation (13). The
calculations included only the $4d - \epsilon f$ channel. Both calculations are reasonably close to each other. Similar results were found for the Xe $5s$ and $5p$ electrons of the Xe@C$_{60}$ endohedral molecule. This indicates that equation (13) is a good approximation to the RPAE calculation if only intrashell correlations are included in the calculation.

The peak at 92.7 eV is partly caused by the reflection effect of the C$_{60}$ potential. The reflected wave combined with the initial wave reaches a large maximum inside the C$_{60}$. At photon energy of 92.7 eV the combined radial part of the $\epsilon f$ wave function has a maximum which is about 2.2 times larger than that of the same wave function but photoionized from the free Xe atom. Therefore the dipole matrix element reaches a maximum 1.9, at 92.7 eV.

Using equation (13) implies that we consider the photoionization processes occurring only inside the C$_{60}$ shell. However, the RPAE calculation involves the intrashell correlations occurring both inside and outside of the C$_{60}$. Therefore the peak, which shifts from 92.7 eV (dashed curve obtained from equation (13)) to 90.9 eV (solid curve, RPAE) in Fig. 1, demonstrates the importance of the intrashell correlations occurring outside the C$_{60}$.

Figure 2 displays the Xe $4d$ photoionization cross section versus photon energy when five channels, Xe $4d - \epsilon f$, $4d - \epsilon p$, $5s - \epsilon p$, $5p - \epsilon s$ and $5p - \epsilon d$ are included in the RPAE calculation. The solid curve and the dotted curve represent respectively, the Xe $4d$ photoionization from the Xe@C$_{60}$ endohedral molecule and the free Xe atom. The black dots are the experimental data for the free Xe atom [29]. The dotted curve has a large and broad maximum, so called the giant resonance. The peak of the solid curve in Fig. 1 has been reduced from 121.5 Mb to 65.4 Mb because of the intershell correlations among the $4d$, $5s$ and $5p$ sub-shells. Since the giant resonance of the $4d - \epsilon f$ transition is a shape resonance, the resonance amplitude is mainly determined by the shape of the potential and will not be greatly affected by the intershell correlations in the photoionization of the free Xe atom. The dashed curves in Fig.1 and Fig.2 have changed a little, the peak is reduced from 137.7 Mb in Fig. 1 to 117.3 Mb in Fig. 2. Therefore by comparing the dashed curve, which is the result of equation (13), and the solid curve of Fig. 2 we found that equation (13) is no longer a good approximation to the RPAE calculation. A method, which incorporates the intershell correlation in the calculation, such as the RPAE has to be employed to evaluate the peak position and the amplitude of the cross section in the multichannel calculation.
Figure 3 compares the photoionization cross sections versus photon energy for the Xe 4d electron confined in C_{60}. The solid, dashed and dotted curves represent, respectively the results from this paper, the calculation of δ-like potential, and other spherical, short range attractive well [18]. The δ-like potential and our results have similar resonance structure but different peak positions and amplitudes. Ref. [18] under estimates the resonance effect. The calculation using delta-like potential correctly solved the Schrödinger equation using both regular and irregular solutions in the region outside the C_{60}. However, their δ-like potential used an infinitely thin spherical layer, which is geometrically not a good approximation to the C_{60} shell to describe the C_{60} fullerene. The photoionization cross sections obtained using this model are evaluated by an equation similar to equation (13) of this paper. Therefore, their cross sections do not include the intershell correlations within the confinement condition. Ref. [18] improved on the δ-like potential by using a potential, V_0 for r_0 > r > r_i and 0 otherwise. However, their solutions of the Schrödinger equation did not include the irregular solution (∞ at the origin) in the region outside of the C_{60} and in the C_{60} shell. Therefore their wave function could not reflect the phase shift due to the photoelectron scattered by the C_{60} potential well [12].

Our calculation used a model potential V_0 for r_0 > r > r_i, otherwise 0; and the regular (0 at the origin) and irregular (∞ at the origin) solutions as well to solve the Schrödinger equation in both the C_{60} shell and outside the shell. After creating the wave function a RPAE calculation was performed to obtain the photoionization cross section. Our method surmounted the weaknesses of both the δ-like potential and the other spherical short range attractive well [18].

Figure 4 shows the photoionization cross sections for the Xe 5s electron. Curves in Fig. 4 have the same meaning as in Fig. 2. When a 5s electron interacts with the 4d electron in the energy range far from the 5s threshold, where the cross section is already small, the 4d giant resonance, which has a large and broad cross section with a peak of 121.5 Mb, at 90.9 eV, causes the 5s photoionization cross section to reach the peak of 6.4 Mb at 91.6 eV. The results of equation (13) and of the free Xe atom are both much smaller than that of the solid curve. The solid and the dashed curves are not close to each other; particularly the dashed curve does not have a large peak around 91.6 eV. This again demonstrates the failure of equation (13) if there exists strong intershell correlations in the photoionization processes. Therefore, similar
equations in Refs. [11, 12] and their applications in the \( \delta \)-like potential [13-17] should not be expected to predict the correct resonance character in the confinement multichannel situation.

Figure 5 compares the photoionization cross sections versus photon energy for the 5\( s \) electron of the Xe atom confined in a C\(_{60}\) fullerene. The curves have the same meaning as in Fig. 3. The dashed curve from a \( \delta \)-like model does not have the peak around 91.6 eV. This is because their formula [14] to calculate the photoionization cross section can not include strong coupling between the Xe 4\( d \) - \( \epsilon f \) and 5\( s \) - \( \epsilon s, \epsilon d \) transition in the confinement condition. Ref. [18] also underestimates the confined resonance effect as their 4\( d \) photoionization has a little peak around 90 eV. By comparing Fig. 1 of Ref. [14] and Fig. 2 of Ref. [18] we found that a second maximum around 50 eV has been missed in Ref. [18]. This might indicate that more points may be needed in that calculation. Since the resonance is sharp and only exists in a very narrow energy region a careful numerical calculation with sufficient points has to be performed to obtain the correct resonance structure. Because of this it might not be surprising that several authors may plot the different resonance structures with different peak positions and amplitudes when their calculations use different energy points.

Figure 6 shows the photoionization cross sections for the Xe 5\( p \) electron. The RPAE calculation involves all five channels. Curves have the same meaning as in Fig. 4. The dotted curve has a broad maximum in the energy region of the Xe 4\( d \) giant resonance, which is similar to the situation of the 5\( s \) electron in Fig. 4 and is caused by the intershell coupling with the Xe 4\( d \) - \( \epsilon f \) channel. Both the solid and the dashed curves show the confinement resonances. However, the amplitudes and the positions of the confinement resonances are quite different in the two calculations, particularly the dashed curve does not have the characteristic peak of 4.2 Mb around 89.5 eV.

## 4 Conclusion

In conclusion, we have performed RPAE calculations for the 4\( d \), 5\( s \) and 5\( p \) photoionization of the Xe atom confined in a C\(_{60}\) fullerene. Our method has surmounted the weaknesses of both the \( \delta \)-like potential [11-17] and the other spherical short range attractive well [18]. The comparison with those of previous model potential calculations demonstrated significantly stronger correlated confinement resonances for the Xe@C\(_{60}\) fullerene. The comparison also shows
that equation (13) is a suitable approximation for the photoionization process if only intrashell correlations are important. In the multichannel calculation, the RPAE method or other similar methods should be employed to obtain the correct resonance character for the atom confined in a C\textsubscript{60} fullerene.

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Figure Captions

Fig. 1. Comparison of our RPAE results (solid curve) with the data evaluated with equation (13) (dashed curve) for the Xe 4d photoionization in the Xe@C$_{60}$ endohedral molecule when only the 4d – $\epsilon_f$ channel is considered in the scattering processes.

Fig. 2. Effects of the intershell correlations in the photoionization of the Xe 4d electron. The solid, dashed and dotted curves represent respectively, the 4d photoionization cross sections in the Xe@C$_{60}$ endohedral molecule calculated by the RPAE method and equation (13) and for the free Xe atom evaluated by the RPAE calculation when the five channels are included in the calculation. The black dots are the experimental data [29] for the 4d photoionization of the free Xe atom.

Fig. 3. Comparison of our RPAE results (solid curve) with those of the $\delta$-like potential (dashed curve) and Ref. [18] (dotted curve) for the 4d photoionization in the Xe@C$_{60}$ endohedral molecule.

Fig. 4. Same as in Fig. 2 but for the 5s photoionization.

Fig. 5. Same as in Fig. 3 but for the 5s photoionization.

Fig. 6. Same as in Fig. 2 but for the 5p photoionization.
