Photoionization of bonding and antibonding-type atom-fullerene hybrid states in Cd@C₆₀ vs Zn@C₆₀

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Abstract
Powerful hybridization of the Cd 4d state with the d-angular momentum state of C₆₀ π symmetry is found in the local density approximation (LDA) structure of Cd@C₆₀ ground state. The photoionization of the resulting symmetric and antisymmetric levels are computed using the time dependent LDA method to include electron correlations. Cross sections exhibit effects of the C₆₀ plasmonic motion coherently coupled to the diffraction-type cavity oscillations induced by local emissions from C₆₀. The Cd@C₆₀ results exhibit a substantial difference from our previous results for Zn@C₆₀.

Keywords: photoionization, endofullerene, hybridization

(Some figures may appear in colour only in the online journal)

1. Introduction
Photoionization of atoms caged in fullerenes is an active field of current research [1, 2]. These endofullerene materials have a broad scope of applications from quantum computation [3] to photovoltaics [4] to drug delivery [5]. Also, endofullerenes are excellent natural laboratories to develop fundamental insights into the spectroscopy of atoms in confinement, as well as of doped fullerenes. Some success in the synthesis of these materials has spawned inspiring recent experiments [6–9].

Our jellium-based time-dependent local density functional technique [10] is one of the most complete approach among various theoretical models of photoionization studies [11–18]. Because the scheme incorporates the ground state, excited states and dynamical interactions of all atomic-electrons and active fullerene electrons in the same computational footing, including significant aspects of correlation. Using this method, we have already found (i) a strong enhancement in the atomic photoresponse from the host fullerene’s plasmon dynamics [19–21] and (ii) atom-fullerene hybrid levels with novel ionization behavior [10, 22]. The latter feature is quite interesting, since these hybrid levels lead to possibilities of covalent-type bonding of the fullerene with the trapped atom and their influence on the ionization response of the compound to electromagnetic radiation or charged-particles impact. In general, spectroscopic examination of such hybrids paves the route to probe wavefunction mixing in other spherical dimer composites, such as buckyonions or clusters trapped in fullerene cages.

Only the atomic and fullerene orbitals of the same angular momentum hybridize. This is because the orthogonality property of the spherical harmonics makes the other terms zero. Also, from a perturbation theory viewpoint, to have strong hybridization, not only good overlap of the unperturbed wave functions is needed but the binding energies of those levels have to be close, since they respectively guarantee a large numerator and a small denominator of the coupling term. These conditions applied to the known energy levels of the C₆₀ π band [23] suggest that the atom’s valence and subvalence levels are susceptible to hybridization. For Xe@C₆₀ a strong s-s hybridization between Xe 5s
and a C\(_{60}\) s level of \(\pi\) character was predicted [22]. Also in the case of Zn@C\(_{60}\) strong \(d-d\) hybridization has been found between Zn 3d and a C\(_{60}\) d level [24]. Here we investigate the same phenomenon in Cd@C\(_{60}\) to explore how much the detail shapes of its hybrid wavefunctions alter from the corresponding Zn@C\(_{60}\) hybrids given an extra node in Cd 4d. The photoionization cross sections of these hybrid levels exhibiting structures over a broad energy range from effects of plasmons and oscillatory modulations in the emission process are calculated. In addition, the results are compared and contrasted with the earlier Zn@C\(_{60}\) results to examine the extent of their differences from differing emission responses of Zn and Cd.

2. Ground-state hybridization

As in the Zn@C\(_{60}\) study [24], we employ nonrelativistic density functional theory to describe the electronic structure of the C\(_{60}\) cage: the details of the method can be found in [23]. In order to make the present paper somewhat self-contained, some of the discussion of [24] is repeated. Earlier studies using this methodology explained the oscillations measured in the valence cross sections of neutral systems in their symmetric and antisymmetric correlation interactions.

This omission the truncated-icosahedron C-structure, similarities of our LDA ground state near the HOMO and HOMO-1 levels with quantum chemical calculations [30] were earlier noted [23].

As was done in the Zn@C\(_{60}\) calculation, the asymptotic form of the LDA ground-state potential was improved by employing a self-interaction correction as adopted by Perdew and Zunger [31], along with a similar implementation for the excited states [32]; this correction yields orbital-specific single-electron potentials. Thus, the effective radial potential, averaged over the orbitals and weighted by their electron occupation numbers, is presented in figure 1(b). Significant hybridization between the free (unperturbed) Cd 4d state and C\(_{60}\) 4d \((\pi)\) state takes place. (Routine Coulomb notation is used to label both Cd and C\(_{60}\) orbitals.) States hybridized in any arbitrary proportion of two constituent states \(|\psi_\alpha\rangle\) and \(|\psi_\beta\rangle\) of free systems in their symmetric and antisymmetric combinations are written as

\[
4d4d_+ = |\psi_+\rangle = \sqrt{\alpha} |\psi_{4dCd}\rangle + \sqrt{1-\alpha} |\psi_{4dC_{60}}\rangle \quad (1a)
\]

\[
4d4d_- = |\psi_-\rangle = \sqrt{\alpha} |\psi_{4dCd}\rangle - \sqrt{1-\alpha} |\psi_{4dC_{60}}\rangle, \quad (1b)
\]

that realize the bonding and antibonding Cd-C\(_{60}\) coupling; \(\alpha\) is between zero and one, since the hybrid states must be normalized. The radial hybrid wavefunctions are shown in figure 1(a), and energies of the two reactant-levels of pristine

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\(\text{Figure 1.} \) (a) Four radial wavefunctions for bonding and antibonding hybrid states of both Cd@C\(_{60}\) and Zn@C\(_{60}\). (b) The average radial LDA ground state potential of Cd@C\(_{60}\). C\(_{60}\) single-electron occupied band, 4d Cd and 4d C\(_{60}\) unperturbed levels, and two Cd@C\(_{60}\) hybrid levels are shown. Similar hybrids in Zn@C\(_{60}\) are included for comparison.
systems and their hybrid products in figure 1(b). Multiplying the $4d4d_e$ wavefunction by $\sqrt{2}$ reproduces the Cd $4d$ and C$_{60}$ $4d$ wavefunctions (not shown) in their respective regions—a fact that implies that the hybrid states are roughly a 50–50 admixture of the electron densities so that $\alpha$ in equations (1) is about 0.5. It is surprising that so strong a hybridization occurs even though the overlap between Cd $4d$ and C$_{60}$ $4d$ wavefunctions (not shown) is found to be small, as in Zn@C$_{60}$ [24]; thus, it must be due to the near-degeneracy of the participant levels (figure 1(b)), since the separation between Cd $4d$ and C$_{60}$ $4d$ energies also plays a role with the closest states suffering maximal mixing owing to the energy denominator in the mixing matrix element. This property puts these hybrid states, along with those predicted earlier [22, 24], in a different league than the known hybrids [33] from physical contacts of a larger atom packed in a smaller fullerene.

Radial wavefunctions that emerged from Zn $3d$ hybridized with C$_{60}$ $4d$ in the Zn@C$_{60}$ compound [24] are also displayed in figure 1(a). Comparison reveals differences between wavefunctions of the two compounds for each of bonding and antibonding symmetries, which is owing to the node that Cd $4d$ has whereas Zn $3d$ is nodeless. In fact, this distinction is also the reason why $4d4d_e$ is less bound than $4d4d_e$ in Cd@C$_{60}$ (figure 1(b)); in each case, the binding energy of the hybridized state with the larger number of nodes is decreased, as must happen.

3. Photoionization: brief theory

By using the time-dependent LDA (TDLDA) methodology [10], the response of the system to the photon is obtained. The dipole perturbation $\chi$ by the linearly polarized photon induces an energy-dependent complex change in the electron density arising from dynamical correlations. This can be expressed, using the LDA susceptibility $\chi_0$, as

$$\delta \rho (r; \omega) = \int \chi_0 (r, r'; \omega) \delta V (r'; \omega) dr', \quad (2)$$

in which

$$\delta V (r; \omega) = z + \int \frac{\delta \rho (r'; \omega)}{|r - r'|} dr' + \left[ \frac{\partial V_0}{\partial \rho} \right]_{\rho = \rho_0} \delta \rho (r; \omega). \quad (3)$$

where the second and third term on the right hand side are, respectively, the induced change of the Coulomb and the exchange-correlation potentials. Clearly, besides containing the perturbation $\chi$, $\delta V$ also incorporates the dynamical field induced by important correlations. One can then construct the following photoionization cross section as the sum of independent partial cross sections $\sigma_{nl \rightarrow kl'}$, corresponding to a transition $nl \rightarrow kl'$ with $l' = \ell \pm 1$.

$$\sigma_{nl \rightarrow kl'} (\omega) = \sum_{n'l'} (2l' + 1) \left| \langle \phi_{n'l'} | \delta V | \phi_{nl} \rangle \right|^2. \quad (4)$$

Note that replacing $\delta V$ in equation (4) with $\chi$ yields the independent particle LDA cross section that entirely omits the correlation.

4. Results and discussion

The LDA photoionization cross sections for the two hybrid states $4d4d_e$, as a function of the photon energy, are presented in figure 2. They are seen to be substantially different,
both in structures and magnitude, from the LDA cross sections of Cd $4d$ and C$_{60}$ $4d$ levels in figure 3. This is the effect of the wavefunction mixing merely via hybridization as the correlation is omitted in LDA. The mechanism of the oscillatory structure seen can be described by the acceleration gauge form of the dipole matrix element which will be discussed below. Cross sections of the hybrid levels, obtained using TDLDA and shown in figure 2, should be rather realistic quantitatively, since they include correlation effects. The TDLDA cross sections exhibit C$_{60}$ autoionizing resonances at low energies, along with Cd $4p@ \rightarrow ns@$, $n4d@$, 4 $s@ \rightarrow np@$ autoionizing resonances at higher energies; the symbol $nl@$ is used to represent the levels of the confined Cd and $nl'$ to denote the levels of the doped C$_{60}$. These TDLDA results in figure 2 dramatically modify the LDA cross sections in the fullerene’s low energy plasmon (LEP) region roughly centered at 17 eV (figure 3), and also over a wider region of the high energy plasmon (HEP), exhibiting considerable quantitative differences as high as up to about 50 eV. Obviously, in the TDLDA results for hybrid ionization, correlation-driven collective plasmon enhancements from C$_{60}$ couple with the single-electron oscillation effects seen in LDA. The following discussions are useful to better understand the results. In the framework of the first-order perturbation theory based interchannel coupling, the general correlation-modified (TDLDA) matrix element of the dipole photoionization of $4d4d_z$ can be written as [21],

$$M_{\pm}(E) = D_\pm(E) + \sum_{nl} \int \frac{\langle n\ell |d'|E'\rangle}{E-E'} \left| D_{nl}(E') \right|^2 (5)$$

in which the single electron (LDA) matrix element

$$D_\pm(E) = \left\{ kp(f) \left| \frac{\partial}{\partial \varphi} \psi_\pm \right. \right\}$$

and $|\psi\rangle$ is the wavefunction of the $nl' \rightarrow kl'$ channel. Taking the hybridization into account, the channel wavefunctions in equation (5) become

$$\psi_+ = \sqrt{\alpha} |\psi_{4d\oplus Cd}\rangle + \sqrt{1-\alpha} |\psi_{4d\ominus C_{60}}\rangle \quad (7a)$$

$$\psi_- = \sqrt{1-\alpha} |\psi_{4d\oplus Cd}\rangle - \sqrt{\alpha} |\psi_{4d\ominus C_{60}}\rangle \quad (7b)$$

In equations (7a) the subscripts $4d\oplus$ and $4d\ominus$ are used to include the modifications of the continuum waves of, respectively, the confined Cd and the doped C$_{60}$. Substituting equations (1) and (7a) in equation (5), and noting that the overlap between a pure Cd and a pure C$_{60}$ bound state is almost negligible, we can separate the atomic and fullerene contributions to the integral to get the TDLDA matrix element for the symmetric hybrid $4d4d_z$ level as

$$M_+(E) = \sqrt{\alpha} \left[ D_{4d\oplus Cd}(E) \right] + \sum_{nl\oplus(Cd)} \int \frac{\langle n\ell |d'|E'\rangle}{E-E'} \left| D_{nl}(E') \right|^2 (8a)$$

$$+ \sqrt{1-\alpha} \left[ D_{4d\ominus C_{60}}(E) \right] + \sum_{nl\ominus(C_{60})} \int \frac{\langle n\ell |d'|E'\rangle}{E-E'} \left| D_{nl}(E') \right|^2 (8b)$$

Similarly, the TDLDA matrix element for the asymmetric hybrid level is

$$M_-(E) = \sqrt{1-\alpha} M_{4d\ominus Cd}(E) - \sqrt{\alpha} M_{4d\oplus C_{60}}(E). \quad (10)$$

### 4.1. LDA multi-path interference oscillations

Within the LDA framework, where correlations are omitted, the integrals on the right-hand side of equation (8) will disappear and simplify equations (9) and (10) to

$$D_+(E) = \sqrt{\alpha} D_{4d\oplus Cd}(E) + \sqrt{1-\alpha} D_{4d\ominus C_{60}}(E) \quad (11a)$$

$$D_-(E) = \sqrt{1-\alpha} D_{4d\ominus Cd}(E) - \sqrt{\alpha} D_{4d\oplus C_{60}}(E). \quad (11b)$$

Of course, the above equations can be directly obtained by substituting equations (1) in equation (6).

In LDA the production of the confinement oscillations is easily explained in the acceleration gauge frame where the dipole matrix element, equation (6), is expressed as,

$$D_\pm(E) \sim \left\{ kp(f) \left| \frac{\partial}{\partial \varphi} \psi_\pm \right. \right\},$$

which underpins the notion that the electron in the potential $V(r)$ needs a force $\partial V/\partial r$ to escape. This ionizing force produced by the average radial potential (figure 1(a)) of the compound peaks at the inner and the outer edges, $R_1 (= 2.79\tilde{A})$ and $R_2 (= 4.29\tilde{A})$, of the C$_{60}$ shell, suggesting strong emission from the edge regions where the potential changes rapidly. Furthermore, figure 1(a) shows that a strong force also exists in the central atomic region where the Coulombic part of the potential ensures a continuous gradient. Thus, since the hybrid wavefunctions $\psi_\pm$ are finite over these force-sites (figure 1(b)), emission will take place from all three regions, significantly interfering with each other through the coherence. The effect further enriches, since the part of the amplitude emanated from Cd reflects from the shell as a result of the continuum modified by the surrounding C$_{60}$ potential.

The general structure of this LDA matrix element has been discussed previously [34, 35]. Following [35],

$$D_{4d\oplus Cd} \sim D_{\text{atom}}(k) + A^{\text{eff}}(k) \left[ e^{-ikD_1} - e^{-ikD_2} \right]$$

(13a)
\[ D_{\text{4d}C_{60}} \sim A_{\text{shell}}(k) e^{-i\frac{V_0}{k}} \left[ a_i e^{-ikR_i} - a_o e^{-ikR_o} \right], \]

where the photoelectron momentum \( k = \sqrt{2(E - e_\text{F})} \) in atomic units, \( a_i \) and \( a_o \) are the values of \( \phi_{\text{F}} \) at \( R_i \) and \( R_o \), and \( V_0 \) is the average depth of the shell potential. In equation (13a), while \( D_{\text{atom}} \) is the contribution from the atomic region, the second term denotes that the reflection-induced oscillations in momentum coordinate with frequencies \( D_i \) and \( D_o \) the inner and outer diameters of the shell. Equation (13b) presents the portion of the overlap integral from the shell region, producing two collateral emissions from the edges, where non-zero ionizing forces exist; these contributions oscillate in two frequencies, \( R_i \) and \( R_o \). The latter effect is akin to the *diffraction in momentum space* where oscillations (fringes) are connected to the fullerene radii.

The LDA cross sections in figure 2, obtained by squaring the modulus of equation (11), hence involve interferences among atomic, reflective and shell ionization modes yielding multitude of oscillations. It was previously shown [10] by Fourier transforming the cross sections of a multitude of oscillations. It was previously shown [10] by Fourier transforming the cross sections of \( \text{Xe}@C_{60} \) that the dominant frequencies correspond \( D_i \), \( D_o \) from the reflective and \( R_i \), \( R_o \), from the diffractive emissions.

### 4.2. Cd@C\text{60} coherence in TDLDA

The TDLDA cross sections of the hybrid ionization are obtained by squaring the modulus of equations (9) and (10):

\[
\sigma_+ = a_1 \sigma_{4d@Cd} + (1 - a_1) \sigma_{4d@C_{60}} + \sqrt{\alpha - \alpha^2} M_{4d@Cd} \otimes M_{4d@C_{60}}
\]

\[
\sigma_- = (1 - a_1) \sigma_{4d@Cd} + a_1 \sigma_{4d@C_{60}} - \sqrt{\alpha - \alpha^2} M_{4d@Cd} \otimes M_{4d@C_{60}}
\]

where \( M_+ \otimes M_- = M^*_+ M_- + M^*_- M_+ \) represents dynamical interferences between \( \text{Cd} \) and \( C_{60} \) amplitudes that superpose coherently.

The many-electron contribution from the \( \text{Cd} \) region of the compound, the first integral on the right hand side of equation (8), is weak. This is evident from the small differences between \( \text{Cd} 4d \) LDA and TDLDA results in figure 3. However, both these \( 4d \) curves are significantly stronger than \( C_{60} 4d \) curves at higher energies. On the other hand, the differences between LDA and TDLDA predictions for \( C_{60} 4d \) (figure 3) are huge over the LEP and HEP regions from the plasmonic boosts via the second integral in equation (8). These enhancements can even mask the reflection effect in equation (13a), while far stronger diffraction oscillations, equation (13b), persist. Consequently, the large value of \( M_{4d@C_{60}} \) at lower energies and that of \( M_{4d@Cd} \) at higher energies result in strong \( \text{Cd}-C_{60} \) coherent-mixing in \( 4d/4d \) TDLDA cross sections over a broad energy range as seen in figure 3.

The total TDLDA cross section of \( \text{Cd} \) agrees well with the experiment [36] in the energy range where the \( 4d \) result (figure 3) completely dominates. We also find that the sum (integral) of the TDLDA oscillator strength distribution up to 150 eV for \( \text{Cd} 4d \) is 8.0, as expected from the general rule for atoms that the total sum will be roughly equal to the number (10) of electrons in a \( d \)-subshell. For \( C_{60} 4d \), on the other hand, this sum yields 17.1 which is higher than the \( d \)-occupancy number. This is not surprising as the ionization of LEP and HEP uses a great bulk of the total 240 oscillators in TDLDA. The hybrid \( 4d/4d \) channels are then expected to share between them at least a strength of 25.1 (=8.0 + 17.1) available jointly from the two independent channels of \( \text{Cd} 4d \) and \( C_{60} 4d \). It turns out, however, that the hybrid channels exhaust, respectively, 17.8 and 12.9 which add up to 30.7, which is an excess of 5.6. This is because the ionization thresholds of the hybrids situated close to the peak energy of LEP (figure 1(b)) enable the emergence of a larger amount of plasmon-driven strength through the hybrid channels. This means at least near LEP both hybrids are also interacting with other continuum channels of \( C_{60} \), going beyond the simple picture of two-channel coherence.

### 4.3. Cd@C\text{60} versus Zn@C\text{60}

Photoionization of hybrid levels from coupled \( d \)-angular momentum states has recently been studied for \( \text{Zn}@C_{60} \) [24]. Here we compare our current results for \( \text{Cd}@C_{60} \) with \( \text{Zn}@C_{60} \) in figure 4. Comparison reveals a number of significant differences. For each of the symmetric and antisymmetric combinations, the \( C_{60} \) \( d \)-orbital mixes with \( 4d \) \( \text{Cd} \) and \( 3d \) \( \text{Zn} \) by roughly the same amount (figure 1(a)). This allows approximately similar shapes and magnitudes of plasmon-
induced enhancements in the cross sections below 20 eV in figure 4, since the cross section in this region is dominated by the matrix elements from the C₆₀ d-orbital part of the hybridized initial wave function and, hence, coupled to the plasmon resonance.

At energies above 20 eV up to 100 eV, the region of energy-dependent oscillations, strong disagreements between the cross sections of the bonding pair are noted in figure 4. The difference is somewhat weaker for the antibonding pair but is still significant (note the log scale of the cross sections in figure 4). However, the differences in the ground state hybrid wavefunction structure around 2Å between Cd@C₆₀ and Zn@C₆₀ (figure 1(a)) will be largely insensitive to their ionization behavior, since the radial range of this difference coincides with the plateau of the potential (figure 1(a)) where the potential’s derivative (ionizing force) is small. Further, equation (13b) suggests that strengths and relative phases of oscillations depend respectively on the magnitude and sign of hybrid wavefunctions at the shell boundaries. However, for a given hybrid level these quantities are practically equal for the two compounds; see figure 1(a). The mismatch between the cross sections in figure 4 at higher energies then must be due to the differences between 4d and 3d emissions of free Cd and Zn that can alter the atomic contributions in equations (8) and (10). Indeed, as shown in figure 3, significant mismatch between TDLDA Cd 4d and Zn 3d curves, including a more defined shape resonance followed by a Cooper minimum in Cd at 135 eV, exists. Above 100 eV therefore, the remarkable differences between Cd@C₆₀ and Zn@C₆₀ predictions in figure 4 result from the coherent mixing with 4d Cooper minimum in Cd as opposed to the 3d of Zn, which does not have a minimum. This becomes important as the atomic contributions dominate at high energy because the shell contributions fall off much more rapidly with increasing energy, since the shell wave functions have so little amplitude near the atomic nucleus where the matrix element is generated at high energy.

5. Conclusion

In conclusion, a pair of bonding and antibonding orbitals in Cd@C₆₀, originating from the hybridization of outer d-angular momentum states of the free Cd atom and the empty C₆₀ molecule was found. The mixing arises from the near degeneracy of the coupling levels. These hybrid states can be seen as atom-shell spherical analogues of two-center dimer states known among the molecules. Photoionization from these levels shows radically different magnitudes and structures from those of the individual free-system states. Analysis reveals that the coherent superposition between the atomic and C₆₀ ionization engenders sizable effects in the hybrid emission behavior: while the lower photon-energy part of the hybrid cross sections are enhanced by the interaction with the shell’s plasmon response, the higher energy ranges are empowered by the strength of atomic ionization, rendering the effect amenable to measurements over a broad window of photon energy.

The Cd@C₆₀ results are compared to our previous results for Zn@C₆₀. They have roughly the same shape below 20 eV, since the cross section in this region is dominated by inter-channel coupling with the C₆₀ plasmon. However, between 20 and 200 eV and beyond, significant disagreement is seen due to differences in their atomic emissions. Although shape differences in the hybrid wavefunctions are found in the radial zone between the atom and C₆₀ shell, there is almost no contribution to the dipole matrix element from this region, so the differences do not appreciably affect the photoionization. The study suggests that there are substantial differences in the photoionization of outer subshells of chemically similar endohedral atoms, depending upon variations in their free atomic response. We hypothesize that f/d hybrids may exist in some lanthanide and actinide metallofullerenes, the confirmation of which is a subject of future studies.

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