Atom-fullerene hybrid photoionization mediated by coupled d -states in Zn@C_{60}

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Strong hybridization, resulting in symmetric and antisymmetric mixing of the Zn $3d$ state and the C_{60} $4d$ state of π symmetry, is found in the jellium based local density approximation (LDA) structure of Zn@C_{60} ground state. Using the time dependent LDA method to include electron correlations, the photoionization of these $d-d$ hybrid states are computed for the first time. Ionization cross sections of these states exhibit effects of plasmon resonances coupled with the diffraction type oscillations induced by localized emissions of C_{60} electrons. We detect significant interference effects in the hybrid ionization from the atom-fullerene coherent mixing.

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I. INTRODUCTION

Photoionization of atomic endofullerenes - compounds made of a fullerene molecule and an atom sequestered inside it [1] - is an active field of research. The primary impetus of such is underpinned by a broad scope of applications that these materials espouse, ranging from quantum computations [2] to photovoltaics [3] to the drug delivery [4]. Besides, endofullerenes are great “laboratories” to develop fundamental insights in the spectroscopy of atoms in confinement as well as of fullerenes endohedrally doped. Some success in the synthesis of these materials has spawned inspiring recent experiments [5–7].

Among various theoretical models of photoionization studies [8–13], the most complete approach is our jellium-based local density functional technique [14], that allows for probing the ground state and dynamical interactions of combined atomic and fullerene electrons active in the ionization process, including significant aspects of correlation. As a consequence of this ability, calculations using this method have predicted (i) a phenomenal boost in the atomic photoresponse from the host fullerene’s plasmonic activities [15–17] and (ii) atom-fullerene hybrid levels with novel ionization behavior [14, 18]. The latter feature is of particular interest, since this leads to the possibilities of covalent type bondings of the fullerene with the guest atom and their influence on the ionization response of the compound to electromagnetic radiations or charged-particle impacts.

From the orthogonality property of the spherical harmonics of single electron orbitals, only the atomic and fullerene orbitals of same angular-momentum (ℓ) can hybridize. However, from a perturbation theory point of view, both the overlaps of the participating “unperturbed” wavefunctions and the proximity of their bind-

ing energies are proportional to the strength of hybridization, since the former guarantees a large numerator and the later ensures a small denominator of the coupling term. These conditions *vis-à-vis* the known energy range of C_{60} single-electron π band (band with wavefunctions having one node that extend toward the central atom) [13], suggest that the atomic valence and sub-valence levels are the possible candidates to hybridize. For Xe@C_{60} a powerful $s-s$ hybridization between Xe $5s$ and a C_{60} s -level of π character was predicted [18]. Moving to higher angular momentum, we now discover a strong $d-d$ hybridization in endofullerenes with group IIB metals. Considering Zn@C_{60} we calculate the photoionization cross sections of the hybrid levels that exhibit broad structural diversities from effects of plasmons and oscillatory modulations in the emission process. For a detailed scrutiny of the mechanism we further examine the role of the interference in atom-fullerene coherent coupling to alter the hybrid cross sections.

II. GROUND STATES AND HYBRIDIZATION

Non-relativistic density functional theory was used to describe the electronic structure of the C_{60} cage; the details of the methodology is given in Ref. [13]. Previous works (i) explained the measured oscillations in the valence photoelectron intensities of neutral C_{60} [19] and (ii) agreed well with a recent experimental study of the surface plasmon as well as a new higher-energy plasmon resonance in the photoionization of C_{60} cations [5]. In the formulation for the C_{60} ground state, the four valence electrons ($2s^2 2p^2$) of each carbon atom are allowed to delocalize while the core C^{4+} ions (each consisting of a carbon nucleus plus two very-tightly-bound $1s$ electrons) are represented by a classical spherical jellium shell (with a radius $R=3.54\text{\AA}$, a thickness Δ), and a constant potential depth V_0 [20]. We place Zn at the center of the sphere which is a realistic approximation as indi-

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FIG. 1: (Color online) (a) The average radial LDA ground state potential of Zn@C_{60} . C_{60} single-electron occupied band, $3d$ Zn and $4d$ C_{60} unperturbed levels, and two hybrid levels are shown; (b) Four radial wavefunctions corresponding to unperturbed and hybrid states are presented. The scaled wavefunction of the symmetric hybrid is also shown; see text for details.

cated by an *ab initio* Hartree-Fock study using a molecular orbital basis [21]. The Kohn-Sham equations for the system of 270 electrons (30 from Zn and 240 delocalized electrons from the C_{60} cage) are then solved to obtain the ground state in the local density approximation (LDA). We have employed a widely used parametric formulation [22] to approximately treat the electrons' exchange-correlation interactions. V_0 and Δ are determined by requiring charge neutrality and by producing the experimental value, -7.54 eV, of the first ionization potential. The width Δ is found to be $1.5\text{\AA}$, which agrees well with experimentally derived value of the molecular width [19]. Further, although the jellium core ignores the truncated-icosahedral C-structure, similarities of our LDA ground state near the HOMO and HOMO-1 levels with known quantum chemical calculations [23] were noted in Ref. [13].

To correct the asymptotic behavior of the LDA ground-state potential we added a self-interaction correction as done by Perdew and Zunger [24]. Likewise, for the excited states we used a similar implementation [25]. Consequently, this correction in the LDA frame renders the single electron potentials orbital specific. Thus, an effective radial potential, averaged over the orbitals and

weighted by their occupancies, is presented in Fig. 1(a). A powerful hybridization between the free (unperturbed) Zn $3d$ state and empty C_{60} $4d$ (π) state occurs. (Standard Coulomb notations are used for to label both Zn and C_{60} orbitals.) In general, states hybridized in any arbitrary proportion of two constituent states $|\phi_{3d\text{Zn}}\rangle$ and $|\phi_{4d\text{C}_{60}}\rangle$ of free systems can be given by characteristic symmetric and anti-symmetric combinations:

$$3d4d_+ = |\phi_+\rangle = \sqrt{\alpha}|\phi_{3d\text{Zn}}\rangle + \sqrt{1-\alpha}|\phi_{4d\text{C}_{60}}\rangle \quad (1a)$$

$$3d4d_- = |\phi_-\rangle = \sqrt{1-\alpha}|\phi_{3d\text{Zn}}\rangle - \sqrt{\alpha}|\phi_{4d\text{C}_{60}}\rangle, \quad (1b)$$

that embody the bonding and antibonding Zn- C_{60} interactions; to preserve normalization α must be between zero and one. Energies [Fig. 1(a)] and radial wavefunctions [Fig. 1(b)] of the two reactant-levels of pristine systems and their hybrid products are shown. Note also in Fig. 1(b) that multiplying the $3d4d_+$ wavefunction by a factor of $\sqrt{2}$ reproduces the Zn $3d$ and C_{60} $4d$ wavefunctions at their respective regions. This suggests that the states hybridize to the effect that produces a practically 50-50 admixture in respective electron densities which determines α in Eqs. (1) to be $\frac{1}{2}$. Surprisingly, such a powerful hybridization emerges even though the overlap between Zn $3d$ and C_{60} $4d$ [see Fig. 1(b)] is so small, which must then be due to the near-degeneracy of the participant levels. This property alone puts the featured states, along with the states predicted before [18], in a different league compared to the known hybrids [26] from the physical contact of a larger atom packed in a smaller fullerene.

III. PHOTOIONIZATION: A SUCCINCT ACCOUNT

A time-dependent LDA (TDLDA) method [13] is employed to calculate the dynamical response of the system to the external dipole field. The perturbation z , the dipole interaction for linearly polarized light, induces a frequency-dependent complex change in the electron density arising from dynamical electron correlations. This can be written, using the LDA susceptibility χ_0 , as

$$\delta\rho(\mathbf{r};\omega) = \int \chi_0(\mathbf{r},\mathbf{r}';\omega)\delta V(\mathbf{r}';\omega)d\mathbf{r}', \quad (2)$$

in which

$$\delta V(\mathbf{r}';\omega) = z + \int \frac{\delta\rho(\mathbf{r}';\omega)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \left[\frac{\partial V_{\text{xc}}}{\partial\rho}\right]_{\rho=\rho_0} \delta\rho(\mathbf{r};\omega), \quad (3)$$

where the second and third term on the right hand side are, respectively, the induced change of the Coulomb and the exchange-correlation potentials. Obviously, besides containing the external perturbation z , δV also includes

FIG. 2: (Color online) Photoionization cross sections calculated using single-electron LDA and correlated TDLDA methods for the hybrid states are shown. Autoionizing resonances for inner shell excitations from C_{60} , appearing at lower photon energies, and from $3p@$ and $3s@$ states of Zn are identified. C_{60} low (LEP) and high energy plasmon (HEP) regions are indicated.

the dynamical field produced by important electron correlations. The photoionization cross section is then calculated as the sum of independent partial cross sections $\sigma_{n\ell \rightarrow k\ell'}$, corresponding to a dipole transition $n\ell \rightarrow k\ell'$:

$$\sigma_{PI}(\omega) = \sum_{n\ell} \sigma_{n\ell \rightarrow k\ell'} \sim \sum_{n\ell} 2(2\ell + 1) |\langle \phi_{k\ell'} | \delta V | \phi_{n\ell} \rangle|^2. \quad (4)$$

The method of calculating photoelectron continuum wavefunctions, $\phi_{k\ell'}$, is detailed in Ref. [13]. Clearly, replacing δV in Eq. (4) by z yields the LDA cross section that entirely omits the correlation.

IV. RESULTS AND DISCUSSION

The single-electron LDA photoionization cross sections, as a function of the photon energy, for the two hybrid states $3d4d_{\pm}$ are presented in Fig. 2 which are dramatically different, both in magnitudes and structures, from the cross sections of Zn $3d$ and C_{60} $4d$ levels, shown in Fig. 3. The structure includes characteristic oscillations, the mechanism of which can be described by the *acceleration* gauge formalism of the dipole photoionization matrix element which will be discussed later in the following.

Cross sections of the hybrid levels calculated in TDLDA, that includes electron correlations, provide a realistic estimate which can be compared with future measurements. These results are also shown in Fig. 2.

FIG. 3: (Color online) LDA and TDLDA cross sections for $3d$ of free Zn and $4d$ of empty C_{60} . Autoionizing resonances due to Zn $3p$ excitations are identified.

First, note that the TDLDA curves feature C_{60} autoionizing resonances at low energies as well as Zn $3p@ \rightarrow ns@, nd@$, $3s@ \rightarrow np@$ autoionizing resonances at high energies; we use the symbol $n\ell@$ to denote the levels of the confined atom and likewise use $@n\ell$ to represent the levels of the doped C_{60} . Far more dramatically, the TDLDA results in Fig. 2 modify LDA results over the fullerene's low energy plasmon (LEP) region centered around 16 eV and also over a broader region of the high energy plasmon (HEP), showing the differences as high as up to 80 eV. Obviously, in the TDLDA results of hybrid ionizations, correlation-driven many-electron plasmonic enhancement from C_{60} couples with the single-electron oscillation effects seen in LDA. The following diagnostics help in better interpreting the results.

The general correlation-modified (TDLDA) matrix element, in the framework of the first-order perturbation theory based interchannel coupling, of the dipole photoionization of $3d4d_{\pm}$ levels can be written as [17],

$$\mathcal{M}_{\pm}(E) = \mathcal{D}_{\pm}(E) + \sum_{n\ell} \int dE' \frac{\langle \psi_{n\ell}(E') | \frac{1}{|\mathbf{r}_{\pm} - \mathbf{r}_{n\ell}|} | \psi_{\pm}(E) \rangle}{E - E'} \mathcal{D}_{n\ell}(E') \quad (5)$$

where the single electron (LDA) bound-continuum matrix element

$$\mathcal{D}_{\pm}(E) = \langle kp(f) | z | \phi_{\pm} \rangle \quad (6)$$

and $|\psi\rangle$ is the $n\ell \rightarrow k\ell'$ channel wavefunction.

We consider Eqs. (1)] for $\phi_{\pm}$ with arbitrary α to deduce results for a general mixing. Consequently, the hybridiza-

tion of the channel wavefunctions in Eq. (5) becomes

$$|\psi_+\rangle = \sqrt{\alpha}|\psi_{3d@Zn}\rangle + \sqrt{1-\alpha}|\psi_{@4dC_{60}}\rangle \quad (7a)$$

$$|\psi_-\rangle = \sqrt{1-\alpha}|\psi_{3d@Zn}\rangle - \sqrt{\alpha}|\psi_{@4dC_{60}}\rangle. \quad (7b)$$

In Eqs. (7) we used subscripts $3d@$ and $@4d$ to include

the modifications of the continuum waves of, respectively, the confined Zn and the doped C_{60} .

Using Eqs. (1) and (7) in Eq. (5), and recognizing that the overlap between a pure Zn bound state and a pure C_{60} bound state is negligible, we can conveniently separate the atomic and fullerene regions of integration to obtain the TDLDA matrix element of the symmetric hybrid $3d4d_+$ as

$$\begin{aligned} \mathcal{M}_+(E) = & \sqrt{\alpha} \left[\mathcal{D}_{3d@Zn}(E) + \sum_{n\ell(Zn)} \int dE' \frac{\langle \psi_{n\ell}(E') | \frac{1}{|\mathbf{r}_+ - \mathbf{r}_{n\ell}|} | \psi_{3d@Zn}(E) \rangle}{E - E'} \mathcal{D}_{n\ell}(E') \right] \\ & + \sqrt{1-\alpha} \left[\mathcal{D}_{@4dC_{60}}(E) + \sum_{n\ell(C_{60})} \int dE' \frac{\langle \psi_{n\ell}(E') | \frac{1}{|\mathbf{r}_+ - \mathbf{r}_{n\ell}|} | \psi_{@4dC_{60}}(E) \rangle}{E - E'} \mathcal{D}_{n\ell}(E') \right] \end{aligned} \quad (8)$$

$$= \sqrt{\alpha} \mathcal{M}_{3d@Zn}(E) + \sqrt{1-\alpha} \mathcal{M}_{@4dC_{60}}(E). \quad (9)$$

Likewise, the TDLDA matrix element of the asymmetric hybrid level can be obtained as

$$\mathcal{M}_-(E) = \sqrt{1-\alpha} \mathcal{M}_{3d@Zn}(E) - \sqrt{\alpha} \mathcal{M}_{@4dC_{60}}(E). \quad (10)$$

A. The LDA context

Within the LDA framework, that omits electron correlations, both the integrals on the right-hand-side of Eq. (8) will vanish to automatically simplify Eqs. (9) and (10) to

$$\mathcal{D}_+(E) = \sqrt{\alpha} \mathcal{D}_{3d@Zn}(E) + \sqrt{1-\alpha} \mathcal{D}_{@4dC_{60}}(E) \quad (11a)$$

$$\mathcal{D}_-(E) = \sqrt{1-\alpha} \mathcal{D}_{3d@Zn}(E) - \sqrt{\alpha} \mathcal{D}_{@4dC_{60}}(E), \quad (11b)$$

which, of course, can also be directly obtained by substituting Eqs. (1) in Eq. (6).

In LDA the mechanism producing the oscillations can be best explained in the *acceleration gauge* formalism in which the dipole matrix element, Eq. (6), can be equivalently expressed as,

$$\mathcal{D}_{\pm}(E) \sim \left\langle kp(f) \left| \frac{\partial V}{\partial r} \right| \phi_{\pm} \right\rangle, \quad (12)$$

which engenders the notion that the electron in the potential $V(r)$ requires a force $\partial V/\partial r$ to escape the system. This ionizing force offered by the average radial potential [Fig. 1(a)] of the compound produces local peaks at the inner and the outer edges, R_i ($= 2.79$ Å) and R_o ($= 4.29$ Å), of the C_{60} hull, suggesting photoemissions from these locations. Note further in Fig. 1(a) that a strong force is also available at the central atomic region where the

potential continuously changes. Therefore, since the hybrid wavefunctions $\phi_{\pm}$ are finite over all these force-sites [Fig. 1(b)], the photoemissions will occur from all three sites, significantly interfering with each other from the coherence. To further enrich the interference, the part of the amplitude emanated from the Zn region will reflect from the hull edges as a consequence of the modified continuum of Zn due to the surrounding C_{60} potential.

The detailed expressions of the general structure of this LDA matrix element is already derived earlier [27, 28]. Following Ref. [28], we can then identify the results below:

$$\begin{aligned} \mathcal{D}_{3d@Zn} \sim & \mathcal{D}^{\text{atom}}(k) \\ & + A^{\text{refl}}(k) \left[e^{-ikD_o} e^{-iV_0 \frac{2\Delta}{k}} - e^{-ikD_i} \right] \end{aligned} \quad (13a)$$

$$\mathcal{D}_{@4dC_{60}} \sim A^{\text{hull}}(k) e^{-i \frac{V_0}{k}} [a_i e^{-ikR_i} - a_o e^{-ikR_o}], \quad (13b)$$

in which the photoelectron momentum $k = \sqrt{2(E - \epsilon_{\pm})}$ in atomic units, V_0 is the average depth of the hull potential, and a_i and a_o are the values of $\phi_{\pm}$ at, respectively, R_i and R_o . In Eq. (13a), $\mathcal{D}_{\pm}^{\text{atom}}$ are the contributions to the matrix element from the atomic region and the second term on the right hand side denotes the reflection induced oscillations in momentum coordinate with frequencies D_i and D_o , the inner and the outer diameter of the hull. Eq. (13b) represents the portion of the overlap integral over the hull region, producing two collateral emissions from the hull edges, where non-zero ionizing forces exist; as evident, these contributions oscillate in two frequencies, R_i and R_o . The later effect is similar to the *diffraction in momentum space* where oscillations (fringes) are connected to the fullerene radii.

FIG. 4: (Color online) The TDLDA cross sections of the hybrid states $3d4d_+$ and $3d4d_-$ along with results of an *ad hoc* calculation using TDLDA cross sections of pristine participating states.

The LDA cross sections in Fig. 2, determined upon squaring the modulus of Eqs. (11), then involves interferences among atomic, reflective and hull ionization modes yielding the oscillations. As shown earlier [14] by Fourier transforming the cross sections of $s-s$ hybrid states in $\text{Xe}@C_{60}$, $\sigma_{\pm}^{\text{LDA}}$ contain dominant frequencies: D_i , D_o from the reflective and R_i , R_o from the diffractive hull-emissions.

B. The atom-fullerene coherence in TDLDA

The TDLDA cross sections of the hybrid photoionization are determined by squaring the modulus of Eqs. (9) and (10) to find

$$\sigma_+ = \alpha\sigma_{3d@Zn} + (1-\alpha)\sigma_{@4dC_{60}} + \sqrt{\alpha - \alpha^2}\mathcal{M}_{3d@Zn} \otimes \mathcal{M}_{@4dC_{60}} \quad (14a)$$

$$\sigma_- = (1-\alpha)\sigma_{3d@Zn} + \alpha\sigma_{@4dC_{60}} - \sqrt{\alpha - \alpha^2}\mathcal{M}_{3d@Zn} \otimes \mathcal{M}_{@4dC_{60}} \quad (14b)$$

where $\mathcal{M}_p \otimes \mathcal{M}_q = \mathcal{M}_p^* \mathcal{M}_q + \mathcal{M}_p \mathcal{M}_q^*$, which represents dynamical interferences between Zn and C_{60} TDLDA ionization-amplitudes from their coherent superpositions.

The many-electron contribution from the Zn-region of the compound, the first integral on the right hand side of Eq. (8), is weak over the energy range considered, as evident from the small differences between Zn 3d LDA and

TDLDA curves in Fig. 3. However, both Zn 3d curves are significantly higher than C_{60} 4d curves at higher energies. On the other hand, the differences between LDA and TDLDA predictions for C_{60} 4d (Fig. 3) is huge over the LEP and HEP regions, indicating the giant enhancements through the second integral in Eq. (8). Over the energy range considered, this enhancement can even mask the reflection effect in Eq. (13a) which is only significant at the LDA level, while far stronger diffraction oscillations, Eq. (13b), will remain. As a consequence, the large value of $\mathcal{M}_{@4dC_{60}}$ at lower energies and that of $\mathcal{M}_{3d@Zn}$ at higher energies must induce very strong Zn- C_{60} interference in $3d4d_{\pm}$ TDLDA cross sections over a broad energy range. This is clearly displayed in Fig. 4 where the hybrid predictions are compared with a curve computed by directly plugging the TDLDA cross sections of Zn 3d and C_{60} 4d in Eqs. (14) and using $\alpha = \frac{1}{2}$ but completely *disregarding the interference term*. As evident, the comparison reveals significant differences which is particularly remarkable for the asymmetric hybrid.

V. CONCLUSION

In summary then, we found a pair of bonding and antibonding orbitals in $\text{Zn}@C_{60}$, originating from the hybridization of outer d -angular momentum states of the free Zn atom and the empty C_{60} molecule. The mixing arises from the near degeneracy of the coupling levels, even though their wavefunction overlap is minuscule. 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 unperturbed free-system states. It is found that while the lower photon-energy part of the hybrid cross sections are strengthened by the shell's plasmon response, their higher energy ranges are empowered by the strength of atomic ionization, making them amenable to future measurements over a broad window of photon energy, *via* photoelectron spectroscopy. Our analysis reveals that the interference between the atomic and C_{60} ionization amplitudes from their coherent superposition allows sizable effects in the emission behavior of these hybrids which is relatively far stronger for the antibonding hybrid. We conjecture that $f-f$ hybrids may as well exist in some of lanthanide and actinide endofullerenes, the confirmation of which is a subject of future calculations. To this end, our research suggests relative abundance of such degeneracy-driven atom-fullerene hybrids across the periodic table which can potentially encourage their experimental studies.

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