

Quantum and classical features of the photoionization spectrum of C_{60}

A. V. Verkhovtsev,^{1,2,3,*} A. V. Korol,^{1,4} and A. V. Solov'yov^{1,†}

¹Frankfurt Institute for Advanced Studies, Ruth-Moufang-Strasse 1, 60438 Frankfurt am Main, Germany

²St. Petersburg State Polytechnic University, Politekhnickeskaya ul. 29, 195251 St. Petersburg, Russia

³A. F. Ioffe Physical-Technical Institute, Politekhnickeskaya ul. 26, 194021 St. Petersburg, Russia

⁴Department of Physics, St. Petersburg State Maritime Technical University, Leninskii prospekt 101, 198262 St. Petersburg, Russia

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By considering photoionization of the C_{60} fullerene, we elucidate the contributions of various classical and quantum physics phenomena appearing in this process. By comparing the results, based on the *ab initio* and model approaches, we map the well-resolved features of the photoabsorption spectrum to single-particle and collective excitations which have a different physical nature. It is demonstrated that the peculiarities arising in the photoionization spectrum of C_{60} atop the dominating plasmon excitations have a quantum origin. In particular, we demonstrate that a series of individual peaks can be assigned either to the optically allowed discrete transitions or to the ionization of particular molecular orbitals of the system. The analysis performed gives detailed information on the nature of numerous features in the photoabsorption spectrum of C_{60} .

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I. INTRODUCTION

The dynamics of electron excitations and dynamical processes of fullerenes and other carbon-based nanoscale systems have been the topic of intensive experimental and theoretical research for more than several decades (see, e.g., Refs. [1–3] for review). Special attention has been paid to the study of ionization processes of these systems by means of the photon, electron, and ion impact [3–12].

Photoionization of fullerenes, as well as other nanoscale systems, represents a complex phenomenon and involves a number of features which can be studied by means of various theoretical methods. Being by its nature a quantum phenomenon, the photoionization process can be described within the *ab initio* framework based on the time-dependent density-functional theory (TDDFT) [13]. It deals with the time-dependent Schrödinger equation and allows one to obtain information on the excited-state properties of a complex many-electron system. However, it is well established that photoionization of nanoscale carbon systems, fullerenes in particular, as well as various metallic clusters and nanoparticles, takes place through plasmons—collective excitations of delocalized valence electrons that are induced by an external electric field. The plasmon excitations correspond to oscillations of the electron density with respect to the positively charged ions [14,15]. Such collective excitations, appearing in many-electron systems, are well known in classical electrodynamics and are described in classical physics terms [14–16].

When a fullerene is ionized either by a photon or by a projectile particle, various types of collective excitations, which are characterized by prominent resonantlike structures in the ionization spectra, are formed in the system. The most prominent structure, positioned in the excitation energy range from 20 to 30 eV, is formed due to collective oscillations of both σ and π delocalized electrons of a system, while a

smaller narrow peak in the low-energy region of the spectrum (below 10 eV) is attributed to the collective excitation of only π electrons. The σ and π electrons occupy, respectively, σ and π orbitals of a fullerene, which are formed due to the sp^2 hybridization of carbon atomic orbitals. The resonance peaks in the ionization spectra are described by some characteristic widths, Γ , which have a quantum origin and appear due to the decay of the collective excitation modes into the incoherent sum of single-electron excitations. Although the exact calculation of the plasmon widths should be performed within the quantum-mechanical framework, they can be estimated using a relation similar to the Landau damping of plasmon oscillations [3]. Such an estimate results in $\Gamma \sim Av_F/R$, where v_F is the velocity of the fullerene electrons on the Fermi surface, R describes a characteristic width of the electron density distribution in the fullerene, and A is a factor on the order of unity.

In most cases, the excitation spectra, calculated within the *ab initio* framework, can be obtained in a broad range of excitation energies range only for small molecules or clusters consisting of a few atoms. For larger system, such as, for instance, fullerenes, a vast majority of contemporary software packages for *ab initio*-based calculations can describe accurately only a limited number of low-lying excited states located below or just above the ionization threshold. A detailed structure of the spectrum at higher excitation energies, where the plasmon excitations dominate the spectrum, could be hardly revealed due to significant computational costs. An alternative approach for the description of electron excitations in many-electron systems is based on the jellium model [17]. During recent years, this approach has been used to calculate the photoionization spectra of fullerenes and atoms endohedrally confined inside the fullerene cages (see, e.g., Refs. [3,18–20]).

An effective tool for evaluation of the contribution of plasmon excitations to the ionization spectra is based on the plasmon resonance approximation [21–23]. The advantage of this approach is that it provides a clear physical explanation of the resonantlike structures in the photoionization [15,24] and inelastic scattering cross sections [12,21–23,25] on the basis of excitation of plasmons by the photon or electron impact.

*verkhovtsev@fias.uni-frankfurt.de

†On leave from A. F. Ioffe Physical-Technical Institute, Politekhnickeskaya ul. 26, 194021 St. Petersburg, Russia.

In this paper, we elucidate the contributions of various classical and quantum physics phenomena appearing in the ionization process. By comparing the *ab initio* TDDFT results with those based on the plasmon resonance approximation, we map the well-resolved features of the photoabsorption spectrum of the C₆₀ fullerene to different types of single-particle and collective electron excitations having different physical natures. We demonstrate that the peculiarities arising in the spectrum atop the dominating plasmon excitations have a quantum origin. In particular, we demonstrate that a series of individual peaks in the continuous part of the excitation spectrum can be assigned to particular single-electron transitions and are caused by ionization of inner molecular orbitals of the fullerene. It is also demonstrated that the results of the *ab initio*- and model-based calculations are in close agreement with the experimental results on the photoabsorption of C₆₀.

The atomic system of units, $m_e = |e| = \hbar = 1$, is used throughout the paper.

II. THEORY

A. Time-dependent density-functional theory

In the present study we utilize the TDDFT approach to calculate precisely the photoabsorption spectrum of C₆₀. Being a generalization of density-functional theory (DFT) [26], TDDFT allows one to introduce time-dependent Kohn-Sham equations [13] and to study various single-particle properties of a many-electron system as a function of time. Within the TDDFT approach the response function of the system can be calculated either in the time domain or in the frequency domain. In the former case, one uses the real-time propagation method [27,28] to study the evolution of the dipole moment due to an initial impulsive distortion of the system. The main limitation of this approach is that stable integration of the time-dependent Kohn-Sham equations requires a very small time step, $\sim 10^{-3}$ fs, which decreases with increasing the number of grid points [29] and, therefore, is very demanding from a computational viewpoint. Within the alternative method [29,30] based on the frequency representation of the response function, it is possible to calculate the full photoabsorption spectrum in a broad energy range without repeating time-consuming operations for different excitation frequencies. In this approach, the response function is represented by a matrix element of the resolvent of the Liouvillian operator (see Refs. [30,31] for details). This approach has been used recently to study photoionization of noble gas atoms encapsulated in C₆₀ [32,33].

In the present study the *ab initio* TDDFT calculations are performed in the linear regime within the dipole approximation. The linear response theory aims to study the variation of a given physical observable due to the application of a weak external perturbation to a many-particle system. Within this framework, the external potential acting on the system can be represented as a sum of a time-independent part, $v_{\text{ext}}^0(\mathbf{r})$, and a time-dependent perturbation, $v'_{\text{ext}}(\mathbf{r}, t)$:

$$v_{\text{ext}}(\mathbf{r}, t) = v_{\text{ext}}^0(\mathbf{r}) + v'_{\text{ext}}(\mathbf{r}, t). \quad (1)$$

Application of the external perturbation leads to variation of the electron density of the system. Therefore, the time

evolution of the electron density can be represented as a sum of two terms, $\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}, t)$, where $\rho_0(\mathbf{r})$ is the unperturbed ground-state density and $\delta\rho(\mathbf{r}, t)$ describes variation of the electron density due to the perturbation $v'_{\text{ext}}(\mathbf{r}, t)$.

In order to consider the response of a system to an external perturbation in the frequency representation, one performs the Fourier transformation of time-dependent quantities. In the linear regime, the Fourier transform of $\delta\rho(\mathbf{r}, t)$ reads

$$\delta\rho(\mathbf{r}, \omega) = \int \chi(\mathbf{r}, \mathbf{r}', \omega) v'_{\text{ext}}(\mathbf{r}', \omega) d\mathbf{r}', \quad (2)$$

where $v'_{\text{ext}}(\mathbf{r}', \omega)$ is the Fourier transform of the external perturbation $v'_{\text{ext}}(\mathbf{r}, t)$ and $\chi(\mathbf{r}, \mathbf{r}', \omega)$ is the generalized frequency-dependent susceptibility of the system.

For the external perturbation $v'_{\text{ext}}(\mathbf{r}, \omega) = -\mathbf{E}(\omega) \cdot \mathbf{r}$ due to a uniform electric field, the Fourier transform of the induced dipole moment reads as follows:

$$d_i(\omega) = \sum_j \alpha_{ij}(\omega) E_j(\omega), \quad (3)$$

where i and j denote the Cartesian components, $\alpha_{ij}(\omega)$ is the dynamical polarizability tensor which describes the linear response of the dipole to the external electric field,

$$\alpha_{ij}(\omega) = - \int r_i \chi(\mathbf{r}, \mathbf{r}', \omega) r'_j d\mathbf{r} d\mathbf{r}', \quad (4)$$

and r_i and r'_j are the components of the position operators \mathbf{r} and \mathbf{r}' . The photoabsorption cross section is related to the imaginary part of $\alpha_{ij}(\omega)$ through

$$\sigma(\omega) = \frac{4\pi\omega}{3c} \sum_j \text{Im}\alpha_{jj}(\omega), \quad (5)$$

where c is the speed of light, and the summation is performed over the diagonal elements of the polarizability tensor.

Within the approach introduced in Refs. [29,30], the electron density variation, $\delta\rho(\mathbf{r}, \omega)$, is expressed via the so-called Liouvillian operator \mathcal{L} ,

$$(\omega - \mathcal{L}) \delta\rho(\mathbf{r}, \omega) = [v'_{\text{ext}}(\mathbf{r}, \omega), \rho_0], \quad (6)$$

whose action onto $\delta\rho(\mathbf{r}, \omega)$ is defined as

$$\mathcal{L} \delta\rho(\mathbf{r}, \omega) = [H_0, \delta\rho(\mathbf{r}, \omega)] + [v'_H(\mathbf{r}, \omega), \rho_0] + [v'_{\text{xc}}(\mathbf{r}, \omega), \rho_0], \quad (7)$$

where H_0 is the ground-state Kohn-Sham Hamiltonian calculated within the DFT approach and $v'_H(\mathbf{r}, \omega)$ and $v'_{\text{xc}}(\mathbf{r}, \omega)$ stand for the linear variations of the frequency-dependent electrostatic and exchange-correlation potentials, respectively [30]. The polarizability tensor $\alpha_{ij}(\omega)$ is defined then by the off-diagonal matrix element of the resolvent of the Liouvillian \mathcal{L} :

$$\alpha_{ij}(\omega) = -\langle r_i | (\omega - \mathcal{L})^{-1} [r_j, \rho_0] \rangle, \quad (8)$$

which is calculated using the Lanczos recursion method (see Refs. [30,31] for details).

As stressed above, the advantage of the utilized approach is that it makes possible to calculate the full photoabsorption spectrum of complex molecular systems in a broad range of excitation energies. However, this approach does not allow one

to get information on partial ionization cross sections which describe ionization of particular molecular orbitals. The reason for this drawback is that only the occupied states are required for performing the calculations and there is no need to calculate any empty states [29,30]. It makes the method, introduced in the aforementioned references, substantially different from Casida's approach [34], which is implemented in many codes for *ab initio* calculations. Within the latter one, it is possible to calculate each individual excitation and to assign it to a specific transition. In general, this operation is feasible only in a limited range of excitation energies, which is not typically larger than 10 eV and depends also on the density of the excitation energies [35]. Alternatively, the method introduced in Refs. [29–31] allows one to compute the absorption spectrum in a broad energy range but a systematic way to assign the transitions is missing.

B. Plasmon resonance approximation

In order to evaluate the contribution of plasmon excitations to the cross section, we utilize the following model approach. The fullerene is represented as a spherically symmetric system with a homogeneous charge distribution within the shell of a finite width, $\Delta R = R_2 - R_1$, where R_1 and R_2 are the inner and the outer radii of the molecule, respectively [12,36–38]. The chosen value of the shell's width, $\Delta R = 1.5 \text{ \AA}$, corresponds to the typical size of the carbon atom [37].

Due to interaction with the uniform external field, $\mathbf{E}(\omega)$, the variation of the electron density, $\delta\rho(\mathbf{r}, \omega)$, occurs on the inner and outer surfaces of the fullerene shell. This variation leads to the formation of the surface plasmon, which has two normal modes, the symmetric and antisymmetric ones [24,36–38]. It has been shown [15,16,24] that only the surface plasmon can occur in the system interacting with a uniform external electric field, as it happens in the photoionization process. When a system interacts with a nonuniform electric field created, for instance, in collision with charged particles, the volume plasmon [39] can also occur due to a local compression of the electron density in the shell interior [25].

Within the plasmon resonance approximation (PRA) [21–23] it is assumed that the main contribution to the cross section comes from the collective electron excitations. Single-particle excitations are not accounted for in the approximation, since the single-particle effects give a small contribution as compared to the collective modes [22,39]. Within this approach the dynamical polarizability $\alpha(\omega)$ has a resonance behavior in the region of frequencies where collective electron modes in a fullerene can be excited. In the present study, we account for the both π and $(\sigma + \pi)$ plasmons, which involve only π or both $\sigma + \pi$ delocalized electrons of the system, respectively. Thus, the photoionization cross section, $\sigma_{\text{pi}}(\omega) \propto \text{Im} \alpha(\omega)$, is defined as the sum of the two plasmons, $\sigma_{\text{pi}}(\omega) = \sigma^\pi(\omega) + \sigma^{\sigma+\pi}(\omega)$, and the contribution of each plasmon is governed by the symmetric and antisymmetric modes:

$$\sigma^i(\omega) = \frac{4\pi\omega^2}{c} \left(\frac{N_s^i \Gamma_s^i}{[\omega^2 - (\omega_s^i)^2]^2 + \omega^2 (\Gamma_s^i)^2} + \frac{N_a^i \Gamma_a^i}{[\omega^2 - (\omega_a^i)^2]^2 + \omega^2 (\Gamma_a^i)^2} \right), \quad (9)$$

where the superscript i denotes the π or $(\sigma + \pi)$ plasmon. Here ω is the photon energy, ω_s^i and ω_a^i are, respectively, the resonance frequencies of the symmetric and antisymmetric modes of the two plasmons, Γ_s^i and Γ_a^i are the corresponding widths of the plasmon excitations, and N_s^i and N_a^i are the number of delocalized electrons which are involved in each collective excitation. These values should obey the sum rule $N_s^{\sigma+\pi} + N_a^{\sigma+\pi} + N_s^\pi + N_a^\pi = N$, where N stands for the total number of delocalized electrons in the fullerene (four valence $2s^2 2p^2$ electrons from each carbon atom result in $N = 240$ in case of C_{60}). The frequencies of the collective excitations are defined as [36–38]

$$\omega_{s/a}^{\sigma+\pi} = \omega_0 + \left[\frac{N_{s/a}^{\sigma+\pi}}{2(R_2^3 - R_1^3)} (3 \mp \sqrt{1 + 8\xi^3}) \right]^{1/2}, \quad (10)$$

$$\omega_{s/a}^\pi = \left[\frac{N_{s/a}^\pi}{2(R_2^3 - R_1^3)} (3 \mp \sqrt{1 + 8\xi^3}) \right]^{1/2},$$

where the signs “–” and “+” correspond to the symmetric and antisymmetric modes, respectively, and $\xi = R_1/R_2$ is the ratio of the inner to the outer radii. The term ω_0 defines the free-electron picture threshold for the $(\sigma + \pi)$ plasmon [37]. Below ω_0 , some of the valence electrons are treated as bound ones and, therefore, are not involved in the formation of plasmon excitations. Following Ref. [37], we use the threshold value $\omega_0 = 14 \text{ eV}$ in the calculations.

III. COMPUTATIONAL DETAILS

In order to calculate the photoabsorption spectrum of C_{60} within the *ab initio* framework we utilized a combination of various computer packages. The GAUSSIAN09 package [40] was used to optimize the geometry of the molecule. The optimization procedure was performed by means of DFT within the local density approximation (LDA) using the split-valence triple- ζ 6-311+G(d) basis set with an additional set of polarization and diffuse functions. To account for the exchange and correlation corrections, the Slater exchange functional [26] and the local Perdew functional [41] were used. The photoabsorption spectrum of the optimized system was obtained using the TDDFPT module [42] of the QUANTUMESPRESSO package [43]. The optimized structure of the C_{60} molecule was introduced into a supercell of $20 \times 20 \times 20 \text{ \AA}$. Then, the system of Kohn-Sham equations was solved self-consistently for 240 valence electrons of fullerene to calculate the ground-state eigenvalues using a plane-wave approach [43]. It should be noted that a similar approach was utilized in Refs. [32,33] to study photoionization of noble gas atoms encapsulated in C_{60} . In the present calculations, we used an ultrasoft pseudopotential of the Rappe-Rabe-Kaxiras-Joannopoulos type [44], which substitutes real atomic orbitals in the core region with smooth nodeless pseudo-orbitals [31]. For the plane-wave calculations we used the kinetic energy cutoff of 30 Ry for the wave functions and 180 Ry for the electron densities. The results obtained were validated by performing a series of calculations with different values of the supercell size and the energy cutoff.

It should also be noted that a pseudopotential local-density method, based on *ab initio* principles, was also used earlier to

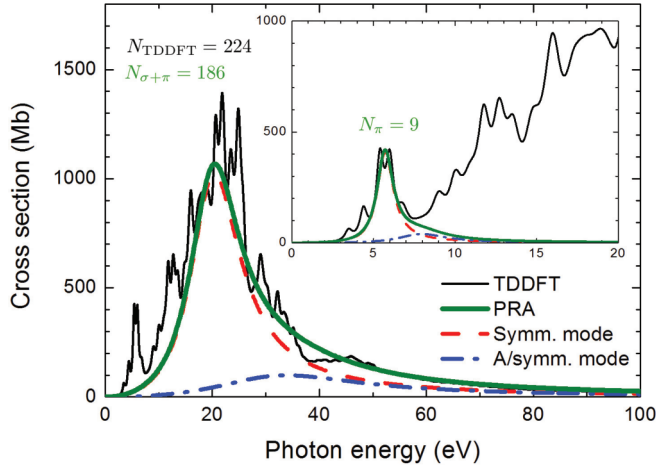


FIG. 1. (Color online) The photoabsorption cross section of C_{60} calculated within the TDDFT method (thin black line) and the plasmon resonance approximation (thick green line). The curves, obtained within the classical approach, describe the dominating plasmon resonance, which is formed due to collective oscillations of $(\sigma + \pi)$ delocalized electrons of the system, and a narrow low-energy peak below 10 eV (shown in the inset) which is attributed to the collective excitation of only π electrons. Contributions of the symmetric and antisymmetric modes of the plasmons are shown by the dashed (red) and dash-dotted (blue) lines, respectively.

calculate the electronic structure of solid C_{60} [45]. The analysis performed showed that the occupied states of C_{60} and some of the empty states can be described as either σ or π states, which are formed due to the sp^2 hybridization of carbon atomic orbitals.

IV. RESULTS

A. Contribution of plasmon excitations

Figure 1 shows the photoabsorption spectrum of C_{60} calculated within the *ab initio* and classical approaches in the photon energy region up to 100 eV. The thin solid (black) line represents the results of TDDFT calculations within the LDA approach, and the thick solid (green) line represents the contribution from the plasmon excitations. The main resonant structure presented in Fig. 1 is formed due to collective oscillations of both σ and π electrons of the system, while a prominent peak in the low-energy region of the spectrum (shown in the inset) is attributed to the collective excitation of only π electrons. The dashed (red) and dash-dotted (blue) lines show, respectively, contributions from the symmetric and antisymmetric modes of the plasmons to the cross section. The resonance frequencies, ω_s and ω_a , for the two modes of the $(\sigma + \pi)$ and π plasmons as well as the corresponding widths, Γ_s and Γ_a , are summarized in Table I. The width $\Gamma_s^{\sigma+\pi} = 11.4$ eV of the symmetric $(\sigma + \pi)$ -plasmon mode corresponds to the experimental values obtained from the photoionization and energy loss experiments on neutral C_{60} [5,11]. For the antisymmetric mode, we used the value $\Gamma_a^{\sigma+\pi} = 33.2$ eV which corresponds to the widths of the second plasmon resonance obtained in the study of photoionization of C_{60}^{q+} ($q = 1 - 3$) ions [8].

TABLE I. Peak positions and the widths of the two modes of the $(\sigma + \pi)$ and π plasmons used in the present calculations. All values are given in eV.

	ω_s	Γ_s	ω_a	Γ_a
$(\sigma + \pi)$ plasmon	20.3	11.4	33.5	33.2
π plasmon	5.8	1.2	7.9	3.5

The plasmon resonance approximation describes quite well the main features of the spectrum, such as height, width, and position of the plasmon resonance peaks. The spectrum calculated within the TDDFT approach reveals a more detailed structure which is formed atop the plasmon resonances and represents a series of individual peaks. The oscillator strengths, calculated by means of TDDFT and within the plasmon resonance approximation in the photon energy range up to 100 eV, are equal to 224 and 195, respectively. Analysis of the plasmon contribution to the cross section shows that about 9 π electrons are involved in the low-energy collective excitation below 10 eV. This value corresponds to the experimentally evaluated sum rule of the oscillator strength up to the ionization threshold of C_{60} , $I_p \approx 7.6$ eV, which gives a value of 7.8 [6].

In Fig. 2, the theoretical curves are compared to the results of recent experimental measurements of photoabsorption of C_{60} [9] (open squares). The oscillator strength, calculated by means of TDDFT, is very close to the experimentally measured value of 230.5 [9]. It should be noted that the detailed structure of the spectrum, which is described within the TDDFT approach, is not seen in the experimental curve due to a high operational temperature of 500–700 °C [6]. In the experiments, the linewidths of single-electron excitations are broadened in the vicinity of the main plasmon resonance due to the coupling of electron excitations with the vibrational modes of the ionic background [46]. The analysis, performed in the present study, shows that the plasmon resonance approximation gives an

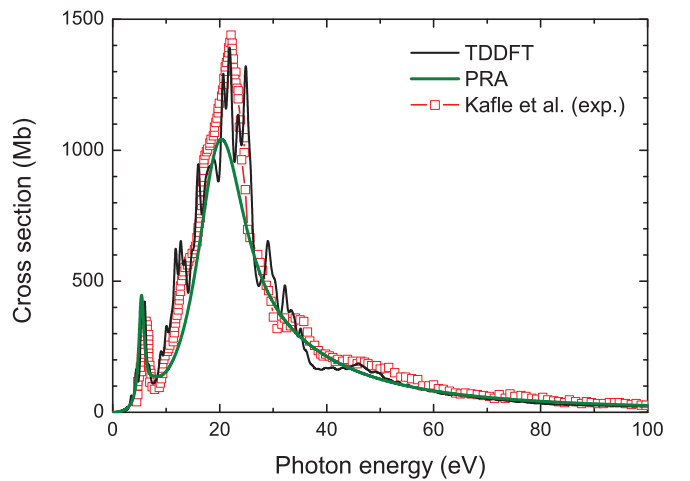


FIG. 2. (Color online) The photoabsorption cross section of C_{60} calculated within the TDDFT method (thin black line) and the plasmon resonance approximation (thick green line). The curve, obtained within the classical approach, describes both the $(\sigma + \pi)$ and π plasmons. Theoretical curves are compared to the experimental data of Kafle *et al.* [9].

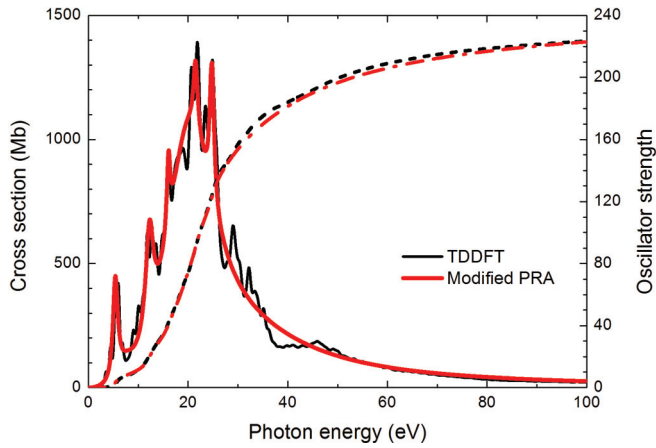


FIG. 3. (Color online) The photoabsorption cross section of C_{60} calculated within the TDDFT approach (thin black line) and the modified plasmon resonance approximation (thick red line), which estimates in a simple way the single-particle contribution [see Eq. (11)]. Dashed (black) and dash-dotted (red) lines represent the integrated oscillator strengths calculated within the TDDFT-based approach and the modified plasmon resonance approximation, respectively.

adequate description of the experimental results. A better agreement can be obtained if one incorporates the broadening of the linewidths of single-electron excitations into the model and uses the calculated values of the widths. This problem requires a separate detailed analysis and will be a subject for a further investigation.

The difference between the oscillator strengths, calculated within the TDDFT approach, and the plasmon resonance approximation is due to the contribution from single-particle excitations, which are neglected in the model. This contribution can be estimated and added to the model-based results by

describing individual peaks in the TDDFT-based spectrum by a number of Lorentzian functions. Then, the total cross section reads as

$$\sigma(\omega) = \sigma_{\text{pl}}(\omega) + \frac{4\pi\omega^2}{c} \sum_j \frac{f_j \Gamma_j}{(\omega^2 - \omega_j^2)^2 + \omega^2 \Gamma_j^2}, \quad (11)$$

where $\sigma_{\text{pl}}(\omega)$ is the contribution from the $(\sigma + \pi)$ and π plasmons, defined by Eq. (9), the index j represents the number of Lorentzian functions used, and f_j stands for the summarized oscillator strength of one or several individual peaks in the TDDFT spectrum, which are modeled by a single Lorentzian function. In order to estimate the single-particle contribution to the cross section in the range from 10 to 25 eV, we introduced four Lorentzian profiles, as it is shown in Fig. 3. The summarized curve, which comprises the contribution from the plasmon excitations and a simple estimate for the single-particle excitations, is shown by the thick red line. Figure 3 represents also the comparison of the integrated oscillator strengths, calculated within the TDDFT-based approach (dashed black curve) and the modified plasmon resonance approximation defined by Eq. (11) (dash-dotted red curve). The analysis of the two curves demonstrates that such a simple estimate for the single-particle contribution covers the difference in the oscillator strengths calculated within the TDDFT and the model approaches. The oscillator strengths, calculated by means of TDDFT and within the modified plasmon resonance approximation in the photon energy range up to 100 eV, are equal to 224 and 223.5, respectively.

B. Quantum nature of individual peaks

Let us focus now on the origin of individual peaks which are formed in the photoionization spectrum of C_{60} atop the plasmon resonances. These peaks can be assigned to discrete transitions between particular molecular orbitals (MOs). The

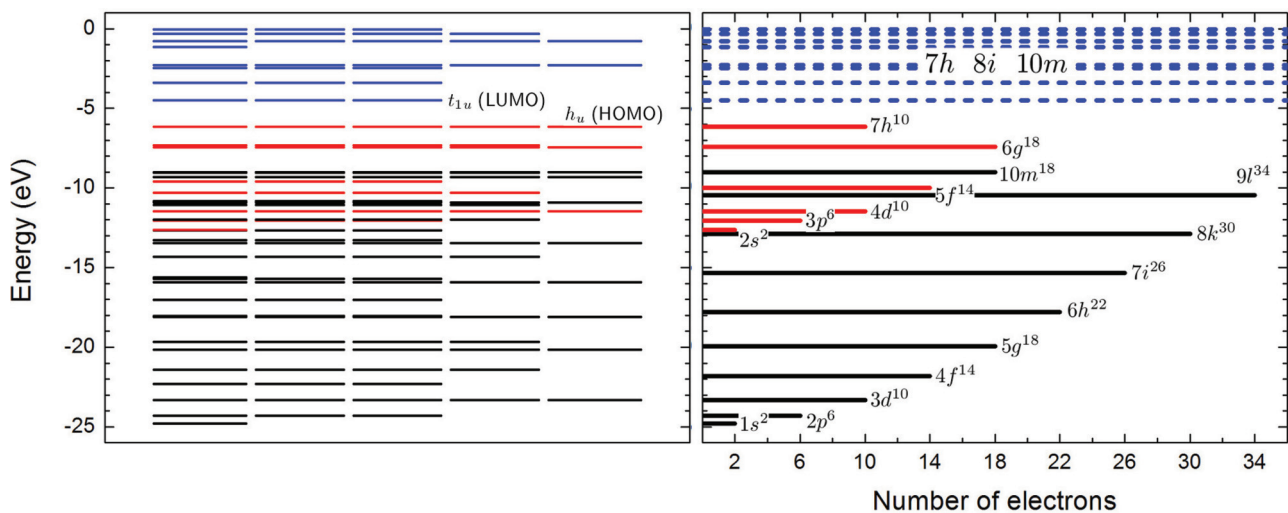


FIG. 4. (Color online) Left panel: The ground-state electronic structure of C_{60} obtained within the *ab initio* framework accounting for the real I_h symmetry of the molecule. Each line corresponds to one molecular orbital which accommodates (or may accommodate) two electrons. Black and red lines (in the range -6 to -25 eV) represent the MOs, which are occupied by 240 delocalized valence electrons of C_{60} . Blue lines (above -5 eV) represent virtual bound states. Right panel: Electronic structure of the corresponding spherically symmetric nl orbitals. The horizontal lines indicate the occupation numbers for each orbital and correspond to the summarized number of electrons which occupy the corresponding MOs.

TABLE II. Molecular orbitals occupied by delocalized electrons of C_{60} (left column) and the corresponding spherically symmetric orbitals which are obtained by the expansion of real MOs in terms of spherical harmonics in the angular momentum l (right column).

a_g	s	($l = 0$)
t_{1u}	p	($l = 1$)
h_g	d	($l = 2$)
$g_u + t_{2u}$	f	($l = 3$)
$h_g + g_g$	g	($l = 4$)
$h_u + t_{1u} + t_{2u}$	h	($l = 5$)
$a_g + t_{1g} + g_g + h_g$	i	($l = 6$)
$h_u + t_{1u} + t_{2u} + g_u$	k	($l = 7$)
$h_g + g_g + t_{2g} + h_g$	l	($l = 8$)
$g_u + h_u + g_u + t_{1u} + t_{2u}$	m	($l = 9$)

C_{60} fullerene belongs to the icosahedral (I_h) symmetry group; therefore its MOs can be classified according to the I_h irreducible representations. The icosahedral symmetry allows the maximum orbital degeneracy equal to 5. Thus, the MOs can be singly (a_g, a_u), triply (t_{1g}, t_{1u}), (t_{2g}, t_{2u}), fourfold (g_g, g_u), and fivefold (h_g, h_u) degenerated. The subscripts “g” and “u” denote, respectively, symmetric (“gerade”) and antisymmetric (“ungerade”) MOs with respect to the center of inversion of the molecule. Due to the quasispherical structure of the molecule, the MOs can be expanded in terms of spherical harmonics in the angular momentum l [47] (see Fig. 4). Thus, the innermost a_g, t_{1u} , and h_g MOs in the I_h symmetry represent, respectively, the s, p , and d orbitals, which correspond to $l = 0, 1$, and 2. The orbitals which correspond to higher angular momenta are constructed as a combination of several MOs. The correspondence between the MOs of C_{60} and the spherically symmetric orbitals with a given value of angular momentum l is given in Table II.

In the spherical representation of C_{60} , the delocalized electrons are considered as moving in a spherically symmetric central field. Therefore, one can construct the ground-state electronic configuration described by the unique set of quantum numbers $\{n, l\}$, where n and l are the principal and orbital quantum numbers, respectively [48]:

$$1s^2 2p^6 3d^{10} 4f^{14} 5g^{18} 6h^{22} 7i^{26} 8k^{30} 9l^{34} 10m^{18} \\ 2s^2 3p^6 4d^{10} 5f^{14} 6g^{18} 7h^{10}.$$

The superscripts indicate the occupation numbers for each spherically symmetric orbital and correspond to the summarized number of electrons which occupy the corresponding MOs (see the left and right panels of Fig. 4). One may consider the icosahedral symmetry of C_{60} as a perturbation of the spherical one, so the correspondence between the real MOs and the spherically symmetric nl orbitals can be explained in terms of splitting of the latter ones due to reduction of the symmetry.

Using the GAUSSIAN09 package [40], we calculated a number of virtual bound states of C_{60} ($t_{1u}, t_{1g}, t_{2u}, h_g, a_g, h_u, g_u$) which can be assigned in the spherical representation to the unoccupied or partially occupied $7h, 8i$, and $10m$ orbitals (see the blue dashed lines in Fig. 4). The optically allowed discrete transitions should result in the change of the MO’s symmetry ($g \leftrightarrow u$) or satisfy the $l \rightarrow l \pm 1$ selection rule

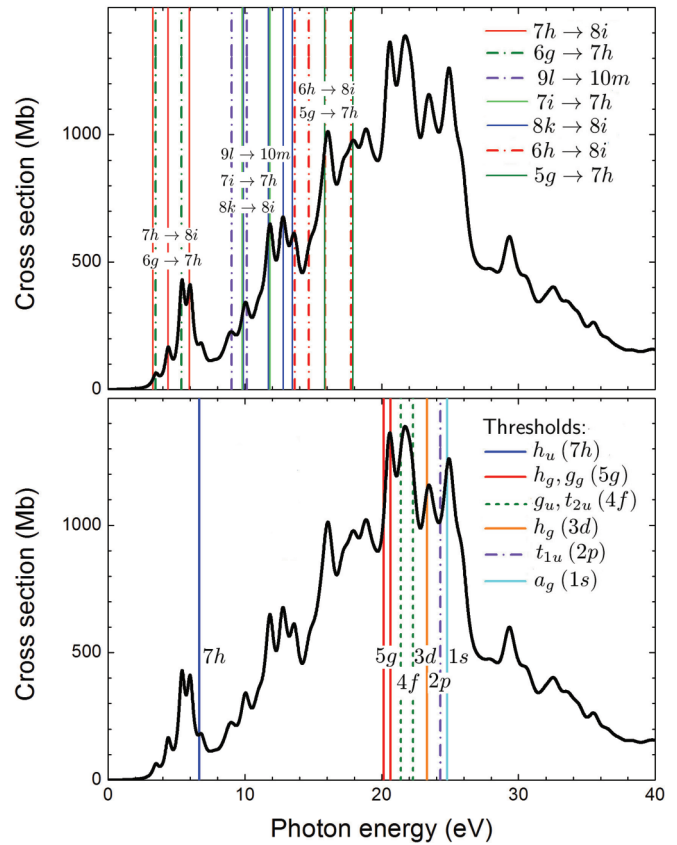


FIG. 5. (Color online) Upper panel: Excitation energies of the optically allowed discrete transitions to the virtual bound states which correspond in the spherical representation of C_{60} to the unoccupied or partially occupied $7h, 8i$, and $10m$ orbitals (see the text for details). Lower panel: Ionization thresholds of the HOMO, h_u (partially occupied $7h$ orbital), as well as of the following innermost valence orbitals: h_g and g_g ($5g$), g_u and t_{2u} ($4f$), h_g ($3d$), t_{1u} ($2p$), and a_g ($1s$). In the LDA calculations, the ionization thresholds for the HOMO (h_u) and the innermost valence (a_g) molecular orbitals are 6.65 and 24.8 eV, respectively.

within the spherical representation. We listed all possible optically allowed discrete transitions and calculated the corresponding transition energies. The results of this analysis are summarized in the upper panel of Fig. 5. The peaks in the TDDFT spectrum can be assigned to $5g, 6g \rightarrow 7h$; $7i \rightarrow 7h$; $6h, 7h \rightarrow 8i$; $8k \rightarrow 8i$, and $9l \rightarrow 10m$ transitions (in order to simplify the analysis we use here the spherical representation of orbitals). The discrete transitions are shown in the upper panel of Fig. 5 by thin solid and dash-dotted vertical lines. The six lowest optically allowed $\pi - \pi^*$ excitations ($h_u \rightarrow t_{1g}$, $h_g \rightarrow t_{1u}$, $h_u \rightarrow h_g$, $g_g \rightarrow t_{2u}$, $h_g \rightarrow t_{2u}$, and $h_u \rightarrow g_g$) [47] from 3 to 6 eV correspond to $7h \rightarrow 8i$ and $6g \rightarrow 7h$ transitions (see solid red and dash-dotted green lines), which are involved in the formation of the π plasmon. The $9l \rightarrow 10m$, $7i \rightarrow 7h$, and $8k \rightarrow 8i$ transitions (violet, aquamarine, and blue lines, respectively) result in the formation of individual peaks in the region from 9 to 14 eV, which are formed atop the $(\sigma + \pi)$ -plasmon excitation. Features in the energy range from 14 to 18 eV are assigned to the single-electron $6h \rightarrow 8i$ and $5g \rightarrow 7h$ transitions from the lower-lying $5g$ and $6h$ orbitals. Thus, accounting for the optically allowed discrete

transitions it is possible to reveal a detailed structure of the photoionization spectrum of C_{60} up to 18 eV. However, one can extend the analysis and characterize a number of subsequent peaks.

In the lower panel of Fig. 5, vertical lines represent the ionization thresholds of several particular orbitals. The highest-occupied molecular orbital (HOMO) (h_u) of C_{60} corresponds in the spherical representation to the partially filled $7h$ orbital. In the present calculations performed within the LDA approach, the h_u ionization threshold is 6.65 eV (solid blue line) which is slightly lower than the experimentally measured ionization potential of C_{60} , approximately equal to 7.6 eV [5]. Since there are no discrete optical transitions with the energy above 20 eV, a series of peaks, arising between 20 and 25 eV, can be assigned to the ionization of the innermost fullerene MOs (the corresponding nl orbitals are given in parentheses), namely, h_g and g_g ($5g$), g_u and t_{2u} ($4f$), h_g ($3d$), t_{1u} ($2p$), and a_g ($1s$). The calculated ionization thresholds of these orbitals are shown in the lower panel of Fig. 5. Within the LDA approach, the threshold of the innermost molecular orbital (a_g) equals 24.8 eV (solid cyan line).

The information, which can be obtained within the *ab initio* framework, allows one to reveal clearly the origin of the individual peaks in the photoionization spectrum of C_{60} for the photon energies up to 25 eV. The nature of several subsequent peaks, located at about and above 30 eV, cannot be explored by the *ab initio* approach and should be investigated by means of the model one. One may suppose that these peaks should be caused by the excitation of particular molecular orbitals to the continuum.

V. CONCLUSION

To conclude, we have performed a detailed theoretical analysis of the photoabsorption spectrum of the C_{60} fullerene and revealed the contributions coming out from single-particle and collective electron excitations. On the basis of the *ab initio* calculations, performed within the TDDFT framework, we

elucidated the origin of various quantum phenomena which manifested themselves atop the plasmon excitations.

We have demonstrated that the individual peaks lying below and above the ionization threshold, in the photon energy region from 3 to 18 eV, are due to optically allowed discrete transitions which are formed atop the collective excitation of $(\sigma + \pi)$ -delocalized electrons. In the spherical representation of molecular orbitals in terms of the angular momentum l , these transitions correspond to the following ones: $5g, 6g \rightarrow 7h$; $7i \rightarrow 7h$; $6h, 7h \rightarrow 8i$; $8k \rightarrow 8i$; and $9l \rightarrow 10m$. The analysis performed shows that the peaks in the vicinity of the dominating $(\sigma + \pi)$ -plasmon resonance, between 20 and 25 eV, are caused by the ionization of the innermost fullerene orbitals, namely, h_g and g_g ($5g$), g_u and t_{2u} ($4f$), h_g ($3d$), t_{1u} ($2p$), and a_g ($1s$). Finally, the peaks around 30 eV and above cannot be explained within the pure *ab initio* framework due to lack of information; therefore one should use some model approaches to explore the origin of these peaks.

The broad resonance peak in the photoabsorption cross section of C_{60} is formed due to the $(\sigma + \pi)$ -plasmon. A number of discrete excitations, lying below and just above the ionization threshold of C_{60} , are attributed to a collective excitation of delocalized π electrons. The spectrum calculated within the model approach is in good agreement with that obtained by means of the more sophisticated TDDFT method and corresponds to the results of experimental measurements. Therefore, the plasmon resonance approximation, utilized in the present work, represents a useful tool for the interpretation of *ab initio* calculations and experimental measurements. A better agreement of the model approach with the experimental data can be obtained if one incorporates the broadening of the linewidths of single-electron excitations into the model and uses the calculated values of the widths. This problem will be a subject for a further investigation.

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