Quantum and classical phenomena in photoionization of carbon nanostructures

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Abstract. We present the results of investigation of electron excitations in various carbon-based nanoscale systems in the process of photoionization. As a case study, we consider a number of highly symmetric fullerenes, namely C20, C60 and C80, as well as aromatic hydrocarbons – benzene (C6H6) and coronene (C24H12). The calculations are performed within the ab initio TDDFT framework and model approach, based on the plasmon resonance approximation. Analysis of the results demonstrates that the main contribution to the photoionization spectra of nanoscale carbon systems is due to collective excitations of delocalized electrons, known as plasmons. Results of the model-based calculations are in close agreement with those of the more accurate quantum-chemical calculations and correspond also to the existing experimental data.

Photoionization of atomic clusters, 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 quantum by its nature, the photoionization process can be described within the ab initio framework based on the time-dependent density-functional theory (TDDFT) [1]. 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 metallic clusters and nanoparticles, takes place through plasmons – collective excitations of delocalized valence electrons, which are induced by an external electric field. The plasmon excitations correspond to oscillations of the electron density with respect to the positively charged ions [2, 3] and are described in the classical physics terms [2–4].

In this paper, we elucidate the contributions of classical and quantum phenomena appearing in the ionization process of various carbon nanosystems. By comparing the TDDFT results with those based on the plasmon resonance approximation (see [3–5] and references therein), we map well-resolved features of the photoionization spectra of fullerenes and polycyclic aromatic hydrocarbons (PAHs) to different types of single-particle and collective electron excitations having the different physical nature. It is demonstrated that the results of the ab initio and...
model-based calculations are in close mutual agreement as well as with available experimental results on photoionization of carbon nanostructures.

In most cases, the ionization spectra, calculated within the \textit{ab initio} framework, can be obtained in a broad range of excitation energies 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 \textit{ab initio} 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 ionization spectrum, could be hardly revealed due to significant computational costs. However, it has become possible recently to calculate optical spectra of complex molecular systems in a broad excitation energy range using the TDDFT methods (see [6,7] and references therein) in the linear regime within the dipole approximation. The method introduced is based on the frequency representation of the response function and allows one to calculate the full photoionization spectrum of complex molecular systems in a broad energy range without repeating time-consuming operations for different excitation frequencies.

An effective tool for evaluation of the contribution of plasmon excitations to the ionization spectra is based on the plasmon resonance approximation. The advantage of this approach is that it provides a clear physical explanation of the resonant-like structures in the photoionization \cite{3,8} and inelastic scattering cross sections \cite{5,9–11} on the basis of excitation of plasmons by the photon or electron impact. Within this approach it is assumed that a contribution from single-particle excitations, which are of the quantum nature, is small as compared to the collective modes \cite{5,12} and, therefore, can be neglected.

![Figure 1](image.png)

\textbf{Figure 1.} The photoionization cross section of C\textsubscript{60} calculated within the TDDFT method (black line) and the plasmon resonance approximation (green line). Contribution of the symmetric and antisymmetric modes of the surface plasmon is shown by the dashed red and dash-dotted blue lines, respectively. Theoretical curves are compared to the experimental data of Kafle \textit{et al.} \cite{16}.

In order to evaluate the contribution of plasmon excitations to the photoionization spectra of carbon nanosystems, we utilize the following model approach. The systems are described by a homogeneous electron density distribution over the shell of a finite width, $\Delta R = R_2 - R_1$, where $R_{1,2}$ are the inner and the outer radii of a system, respectively \cite{10,13–15}. In all case studies considered, except the coronene molecule, carbon atoms are almost equally-spaced from the geometrical center of the system. Therefore, in order to describe fullerenes and the benzene molecule within the model approach, the shell width $\Delta R$ was chosen to be equal to 1.5 Å. The chosen value corresponds to the typical size of a carbon atom \cite{14}. In order to model correctly geometry of the coronene molecule, we used the value $\Delta R = 3.4$ Å.
Figure 2. The photoionization cross section of the C_{20} and C_{80} fullerenes calculated within the TDDFT method (black line) and the plasmon resonance approximation (green line). Contributions of the symmetric and antisymmetric modes of the plasmons are shown by the dashed red and dash-dotted blue lines, respectively.

It is well established (see, e.g. [17]) that a cloud of delocalized electrons in fullerenes and aromatic hydrocarbons is formed due to the contribution of four 2s^22p^2-electrons from each carbon atom. Therefore, we assume that the number of delocalized electrons \( N = 80, 240 \) and 320 in case of the C_{20}, C_{60} and C_{80} fullerenes, respectively, while 24 and 96 electrons contribute to the plasmon excitations in benzene and coronene, respectively.

Due to the interaction with a uniform external field, the electron density variation occurs on the inner and outer surfaces of the spherical shell. This variation leads to the formation of the surface plasmon, which has two normal modes, the symmetric and antisymmetric ones [8,13,14]. It was shown [3, 4, 8], 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 non-uniform electric field created, for instance, in collision with charged particles, the volume plasmon [12] can also occur due to a local compression of the electron density in the shell interior [11].

Figure 1 shows the photoionization spectrum of C_{60} calculated within the \textit{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) one represents the contribution from the plasmon excitations. The main resonant structure presented in the left panel of figure 1 is formed due to collective oscillations of both \( \sigma \) and \( \pi \) delocalized 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 \( \pi \)-electrons. The \( \sigma \)- and \( \pi \)-electrons occupy, respectively, \( \sigma \)- and \( \pi \)-orbitals of a fullerene, which are formed due to the sp^2-hybridization of carbon atomic orbitals [17]. The dashed (red) and dash-dotted (blue) lines show, respectively, contributions from the symmetric and antisymmetric modes of the plasmons to the cross section (see [19] for further details). In the right panel of figure 1, the theoretical curves are compared to the results of recent experimental measurements of photoabsorption of C_{60} [16]. The analysis performed shows that the plasmon resonance approximation gives an adequate description of the experimental results and more precise TDDFT calculations. In particular, the model approach describes the main features of the spectrum, such as height and position of the plasmon resonances [18]. 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. It has been demonstrated recently [19] that the peculiarities arising in the photoionization spectrum of C$_{60}$ atop the dominating plasmon excitations have the quantum origin and can be assigned to the particular discrete single-electron transitions and to ionization of the innermost valence molecular orbitals of the system.

The photoionization spectra of C$_{20}$ and C$_{80}$ fullerenes are presented in figure 2, while figure 3 demonstrates spectra of aromatic hydrocarbons: the simplest one – benzene (C$_6$H$_6$) (left panel), and a more complicated compound – coronene (C$_{24}$H$_{12}$) which consists of six benzene rings (right panel). Similar to the spectrum of the C$_{60}$ molecule, the main contribution to the ionization spectra of other fullerenes and PAHs comes from the collective excitation of both types ($\sigma$ and $\pi$) of delocalized electrons, which is described by a prominent broad peak located at about 15-25 eV. The spectra are also characterized by a single or several much narrower peaks in the low-energy part of the spectrum, which are due to the collective excitation of only $\pi$-electrons.

**Figure 3.** The photoionization cross section of the C$_{20}$ and C$_{80}$ fullerenes calculated within the TDDFT method (thin black line) and the plasmon resonance approximation (thick green line). In case of benzene theoretical curves are compared to the experimental data [20].

**References**

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