Signature of electronic correlation in multi-electron emission from C_{60}

O. Kidun, N. Fominykh, J. Berakdar *

Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

Received 16 March 2005; in final form 17 May 2005
Available online 16 June 2005

Abstract

Contrasting single to double-particle transition probabilities induced by a one-particle perturbation yields information on the strength of (two-particle) correlation in a system. Here, we calculate single and double ionization probabilities for a C_{60} molecule upon the absorption of a single photon. We employ the Hartree–Fock and the frozen-core approximations for single-particle states and the random-phase approximation for the screened Coulomb interaction. Energy and angular dependencies of total and differential cross-sections are analyzed and the signature of the geometry of the fullerene and its charge-density response are pointed out.

1. Introduction

The impact of electronic interaction on the physical properties of materials has been the subject of research since the early days of modern physics. The interest in this topic is not only driven by the complexity and the intellectual challenge in describing interacting, many electron systems. In fact, electronic correlation is a key factor for understanding a variety of observable physical phenomena: Wannier excitonic states in wide-band semiconductors, and the insulating (magnetic) ground states of narrow band materials, such as 3d transition metal oxides, rare earths, and actinides are just few examples. The role of electronic correlation in molecular and polymeric materials has been as well in the focus of research. The discovery that C_{60} doped with alkalis may turn superconducting [1] initiated an ongoing investigation of the role of the electron–electron (e–e) interaction in fullerenes: The analysis of the KVV C_{60} Auger results [2] indicated that doped C_{60} has the properties of a strongly correlated system, e.g., it has been argued that K_{3}C_{60} is a half-filled Mott-Hubbard insulator. A theoretical study of the nature of the e–e interaction in solid (ordered) phase of C_{60} concluded that the screened on-site molecular Coulomb integral $U$ is $U \approx 2.1$ eV [3]. On the other hand, as confirmed by a range of spectroscopic studies (photoemission, inverse photoemission, and soft X-ray absorption [4]), the electronic structure of C_{60} remains essentially intact when a solid is formed. Therefore, it is of interest to study the nature of e–e interaction in isolated C_{60}. In this Letter, we propose to study the e–e interaction of the valence electrons by means of photo-induced single and double electron-removal spectroscopy. The significance of this proposition can be appreciated from the lowest-order (in the e–e interaction) diagram describing the double photoelectron emission (DPE) (cf. Fig. 1): A photon with energy $\hbar \omega$ [5] excites a valence state $\phi_{\nu}$ to the (vacuum) scattering state $\psi_{q}$ which is identified by the wave vector $q$ (the index $\nu$ stands for a collective set of quantum numbers (including spin) characterizing the orbital $\phi_{\nu}$). Measuring the electron emission probability at a specified $q$ yields information on the

* Corresponding author. Fax: +49 345 5511223.
E-mail addresses: okidun@mpi-halle.de (O. Kidun), jber@mpi-halle.de (J. Berakdar).
Fig. 1. (a) DPE described by the lowest-order diagram in the electron–
electron interaction $W$. (b) Calculated single $\sigma_1$ (solid curve) and
double (dashed curve) photoionization cross-sections of the highest
occupied molecular orbital (HOMO) of C$_{60}$ vs. photon energy. Open
circles are experimental absolute partial $\sigma_1$ of HOMO of C$_{60}$[14]. Inset
shows the Fourier transform of $\sigma_1(q)$, where $q = \sqrt{2(\omega + \epsilon_{\text{HOMO}})}$ is the
photoelectron wave vector.

valence single-particle spectrum (which is the aim of
single photoelectron spectroscopy SPE [6]). However,
there is a finite probability for the excited electron with
the wave vector $q$ to interact with a second valence
state $\phi_{\mu}$, leading asymptotically to two vacuum electron
states $\psi_{k_1}$ and $\psi_{k_2}$ with wave vectors $k_1$ and $k_2$. These
states can be verified in a coincidence experiment. The
(UV) photon couples to a single particle only. Hence,
the emission of two photoelectrons can only be
mediated by the valence e–e interaction [5]. Obviously, mea-
suring the angular and energy correlation between the
two excited electrons yields valuable details that are
encompassed in the averaged energetic weight $U$ of the
e–e interaction. In C$_{60}$ the electrostatic e–e
Coulomb interaction $u$ acts in the presence of an inho-
mogeneous polarizable surrounding. Thus $u$ will be
dynamically (and non-locally) screened. In a linear re-
response approach the screened e–e interaction $W$ is
$W = u \varepsilon$, where $\varepsilon = \varepsilon(\omega, q - k_2)$ is the dielectric func-
tion. For sufficiently screened $u$ the diagram shown in
Fig. 1 is dominant over higher order diagrams that
account for further multiple scattering events (in $W$).
Recent theoretical calculations using $W$ within the ran-
dom phase approximation with exchange (RPAE) [7]
indicated a surprisingly strong screening of $u$ in C$_{60}$
[8,9]. This encouraged us to evaluate the SPE and
DPE probabilities using the diagram Fig. 1. Besides,
the recent experimental activities in realizing DPE from (free and surface-deposited) C$_{60}$ [10,11] make
the enormous computational efforts in calculating
DPE cross-sections worthwhile and desirable. The
application of the present theory for the description
of the emission of more than two electrons from C$_{60}$
is currently computationally not possible. Therefore,
we introduced in a recent work [13] a statistical pho-
ton-energy deposition model for the treatment of the
total ionization cross-sections for many-electron emis-
sion. A purely statistical treatment (see also related ref-
ences in [13]) is, however, inappropriate to deal with
the simultaneous one-photon two-electron transitions,
in particular as far as the two-particle energy and
angular correlations are concerned.

2. Theoretical approach

The photon absorption and the electrons emission
proceed fast on typical time scales of the ground-state
molecule. Hence, degrees of freedom other than those
of the valence electrons are frozen during the emission
process. The fully differential SPE cross-section
\[ \frac{d\sigma_1(\omega)}{d^3q} \]
we evaluate within the dipole approximation as (unless
otherwise stated we use atomic units (a.u.) throughout)
\[ \frac{d\sigma_1(\omega)}{d^3q} = 4\pi^2 \omega \sum_{\epsilon_i < E_F} |\langle \psi_{\mu} | e \cdot r | \phi_{\nu} \rangle|^2 \delta(\omega + \epsilon_i - E_q), \] (1)
where $e$ is the (linear) polarization vector of the light, $\epsilon_i$
the energy of the occupied state $\phi_{\nu}$. $E_F$ is the highest
occupied molecular state (HOMO), $E_q$ is the photoelec-
tron energy and $\alpha$ is the fine-structure constant. The
total SPE cross-section is obtained by integrating
numerically over $q$. The SPE has been already calculated
by a number of authors (e.g., [24,23,13] and references
therein). An example of the partial $\sigma_1$, from HOMO is
shown in Fig. 1 (determining $\omega$ and $E_q$ pins down $\epsilon_i$ in
Eq. (1)). The fully differential double ionization cross-
sction $\frac{d\sigma_2(\omega)}{d^3k_1d^3k_2}$ is evaluated as
\[ \frac{d\sigma_2(\omega)}{d^3k_1d^3k_2} = \sum_{\mu,\nu \neq k_1} \int d^3q |\langle \Psi_{k_1,k_2} | W | \phi_{\mu} \phi_{\nu} \rangle|^2 \frac{d\sigma_1(\omega)}{d^3q} \times \delta(E_q + \epsilon_\mu - E_1 - E_2), \] (2)
where $\Psi_{k_1,k_2}$ is an anti-symmetrized two-electron scatter-
ing wave function constructed from the one-electron
states $\psi_k$ and $\psi_k'$. Thus, $\langle \Psi_{k,k'} | W | \phi_p \phi_q \rangle$ contains a direct and an exchange term which we will treat as in our previous work [8] on electron-impact ionization. The direct amplitude $\langle \psi_k, \psi_k' | W | \phi_p \phi_q \rangle$ is determined by solving full numerically the integral RPAE equation (similarly we calculate the exchange term)

$$
\langle \psi_k, \psi_k' | W | \phi_p \phi_q \rangle = \langle \psi_k, \psi_k' | t | \phi_p \phi_q \rangle + \sum_{p, \phi_p \neq \phi_q, k, \psi_k > E_p} \left( \frac{\langle \phi_p \psi_k' | W | \phi_p \phi_q \rangle \langle \phi_p \psi_k | t | \psi_q \phi_p \rangle}{E_q - (e_p - e_0 - i\delta)} - \frac{\langle \phi_q \psi_k' | W | \phi_q \phi_p \rangle \langle \phi_q \psi_k | t | \psi_q \phi_p \rangle}{E_q + (e_p - e_0 - i\delta)} \right),
$$

where $\phi_p$ and $\phi_q$ are, respectively, the intermediate particle and hole states and $\delta$ is a small positive real number. Neglecting the influence of the charge-density fluctuations amounts to using the first term on the RHS of Eq. (3) only (referred to below as w/o RPAE). Neglecting altogether the correlation between the two photoelectrons, i.e., setting $W = \text{constant}$, the double ionization cross-section vanishes (in our calculations scattering and bound states belong to the same Hamiltonians and hence they do not overlap). The various integral cross-sections are obtained from Eq. (2) by a numerical integration (using a Monte Carlo procedure) over the appropriate variables ($E_1$, $E_2$, $k_1$, $k_2$).

3. Numerical procedure

The single-particle states of the fullerene are obtained from self-consistent Hartree–Fock calculations using an implementation of the non-local variable phase method [15,16]. Hence, we incorporate in the initial state (ground state) the mean-field part of the electron–electron interactions and exchange effects. As done in various studies on the electronic properties of C60 we employ a spherical shell model potential $V_{\text{ion}}(r)$ for the 240 valence electrons ([17,18] and references therein), i.e., $V_{\text{ion}}(r) = V_0$ for $R - \delta < r < R$, and $V_{\text{ion}}(r) = 0$ elsewhere. In determining the model potential $V_{\text{ion}}$ one needs the experimental radius of C60 ($R \approx 6.65$ a.u.), the (average) distance between the neighboring carbon sites (which enters as the thickness of the well $\delta \approx 2.69$ a.u.) and the affinity energy of the electron to the singly charged fullerene [18]. The number of the valence electrons (240) and the experimentally determined first ionization potential of C60 (7.6 eV [20,21]) fix then the potential depth $V_0 \approx 108$ eV. Here we do not discuss the resulting ground-state electronic structure for space limitation and refer to [19] which uses a similar model and where the ground-state spectral properties of C60 are compared to experiments. Our procedure produces results numerically similar to [19].

4. Results and interpretations

A notable feature of the photoionization cross-sections $\sigma_1$ and $\sigma_2$ shown in Fig. 1 is the oscillations as a function of $\omega$. As discussed in [14,22–24], the origin of the oscillations in $\sigma_1$ lies in an interference effect of the photoelectron waves emitted from parts of the potential that scatter particularly strong. In practice, these sites are the potential discontinuities at the carbon nuclei positions which enter in our model as the width $\delta$ of the confining ionic potential, whereas the C60 icosahedral symmetry is approximated by a spherical one. Therefore, the two characteristic lengths $R$ and $\delta$ of our model are manifested in $\sigma_1$ as two resonant frequencies and two satellites corresponding to $R - 3\delta$, $R$ and $R + 3\delta$, as shown in the inset of Fig. 1. It should be stressed, however, that this simple explanation is not generally viable even in the present model calculations [25] because in addition to the confining potential, the electrons are also subject to the (non-local) Hartree–Fock and the centrifugal potential. The results in Fig. 1 indicate, however, that in this particular case the confining potential plays the key role, as far as the oscillations in $\sigma_1$ are concerned. The oscillation appears in $\sigma_2$ for the following reason: Inspecting the diagram Fig. 1 we conclude that only in the photon absorption step the energy $h\omega$ must be converted into momentum $q$ by a strong scatterer in the absorption region. In contrast, the e–e scattering potential $W$ can in general mediate momentum and energy exchange and therefore the cross-section for this process is not expected to show any oscillations (when varying $\omega$). This is in fact confirmed theoretically [8] and experimentally [26,27] by the electron-impact ionization of C60. In addition, the particle–hole (de)excitations, as incorporated in Eq. (3) have been shown to flatten the e–e scattering probability [8]. That is, as far as $\sigma_2(\omega)$ vs. $\omega$ is concerned, in Eq. (2) the term $\int \frac{d^2k_1 d^2k_2}{C^{25}} | \Psi_{k_1,k_2} | W | \phi_p \phi_q \rangle |^2$ acts as a smooth flat function of $\omega$ and hence $\sigma_2(\omega)$ exhibits the oscillations present in $\sigma_1$ as well as qualitatively the same slope. The ratio of $\sigma_1(\omega)$ to $\sigma_2(\omega)$ at a particular $\omega$ is a general indicator of the strength of $W$ (lim $W \rightarrow 0 \sigma_2 \rightarrow 0$ as clear from Fig. 1). At present, we cannot compare directly with the (initial-state non-resolved) experiments [10–12] due to computational limitations. Experimentally, Reinköster et al. [11] reported a ratio of 1/7 between angle- and energy-integrated double and single ionization events at a photon energy of 45 eV, whereas Kou et al. [10] find a ratio of about 2/3. A different ratio is found in the condensed phase [12], however, the cross-sections are then measured for a certain electron emission angle.

Detailed information on the energy- and angular correlation are accessed by studying the differential cross-sections. For example, Fig. 2 shows, for fixed total energies of the pair $E_{\text{tot}} = E_1 + E_2$, the sharing of $E_{\text{tot}}$
between the two electrons. A strong suppression of \( \frac{d^2\sigma_1}{dE_1 dE_2} \) is observed due charge-density fluctuations, which is consistent with previous conclusions that the screening caused by these fluctuations reduces considerably the effective scattering region and hence the scattering caused by these fluctuations reduces considerably the oscillation in the electron-emission spectra, cf.\[31\] and references therein. For atomic processes the \( 1/k_{1,2} \) divergence of DOS for \( k_{1,2} \to 0 \) removes the kinematical \( k_{1,2} \to 0 \) decrease. In contrast, as outlined above, the \( C_{60} \) single particle potentials do not have \( -1/k_{1,2} \) behaviour and DOS\( (C_{60}) \) is finite at \( k_{1,2} \to 0 \). Thus, due to kinematics \( \frac{d^2\sigma_1}{dE_1 dE_2} \) vanishes for \( E_{1,2} \to 0 \), as seen in Fig. 2.

As to be expected the RPA corrections are frequency dependent and diminish for \( \omega \gg E_F \) in which case the e-e scattering takes place in a much shorter time compared to the characteristic response time of the charge density (in this case \( \lim_{E \to E_F} \sigma \to 0 \)). In Fig. 3 the dependence of \( \frac{d^2\sigma_1}{dE_1 dE_2} \) on \( E_2 \) is plotted for a fixed \( E_1 \) in which case the oscillation akin to photoionisation from \( C_{60} \) emerge. We note the frequency-dependent influence of screening on the oscillations.

Another correlation feature accessible by DPE is the angular correlation of the two electrons, as quantified by \( \frac{d^2\sigma_1}{dE_1 dE_2} \) for fixed \( E_1 \) and \( E_2 \). The general behaviour of this quantity is currently in the focus of discussion in atomic and molecular physics \[28–30\], in particular for simple targets such as noble gas atoms. For \( C_{60} \), even though the assumed spherical symmetry of the problem brings about some simplifications an understanding of all the facets of \( \frac{d^2\sigma_1}{dE_1 dE_2} \) is a challenge. The example in Fig. 4 demonstrates the strong dependence of \( \frac{d^2\sigma_1}{dE_1 dE_2} \) on the charge-density fluctuations (which are negligible for targets with large level spacing). The

---

\[ W(x) = e^{-x^2} \] holds for a homogenous system in the long wavelength limit. \( x \in \mathbb{R}^+ \) is a screening length. FT of \( W \) \( W(k) \propto 1/(k^2 + \frac{1}{\lambda}) \) is constant for \( k \ll \frac{1}{\lambda} \).
reason for these variations with $k_1, k_2$ is the dependence of the dielectric response (described by Eq. (3)) on the momentum transfer during the e-e scattering. Therefore, a measurement of the angular correlation as depicted in Fig. 4 reveals, for a fixed frequency, the anisotropic (momentum-transfer dependent) screening of $W$ in addition to the angular correlation between the electrons. Fig. 4a reveals a smearing of the e-e repulsion for $k_1||k_2$ due to charge-density fluctuations and integrations over $q$ in Eq. (3). In addition, $dW/dq$ has a rich structure which (due to Eq. (2)) is reflected in the peaks observed in Fig. 4a.

5. Conclusions

Summarizing, we present a theory that describes, at the same footing, photo-induced single and double valence-electron removals from clean, isolated C$_{60}$. We demonstrated the power of DPE in revealing the details of the (non-local) frequency-dependent electron–electron interaction in C$_{60}$. In view of the results of [1] on the superconducting properties of alkalis-doped C$_{60}$ it is valuable to extend SPE and DPE studies to doped C$_{60}$.

References

[5] We limit the discussion to photon energies below the threshold for KVV C$_{60}$ Auger transitions.