

Quantum theory of fast electron impact ionization of C_{60} : application of the spherical jellium model

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Abstract

Integrated and differential cross-sections for the ionization of the fullerene C_{60} by electrons with energies of more than 100 eV have been calculated in the plane-wave Born approximation using a spherical jellium shell model to describe the target electron states. The results are compared with measured absolute integrated and relative triply differential cross-sections. For high energies, reasonable agreement between theory and experiment is found. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The total and partial cross-sections for the production of various charged fragments by inelastic electron scattering from the fullerene C_{60} are experimentally well known [1–3], but the theoretical understanding of these data is still in its infancy. In fact, only two attempts to calculate the total cross-section for the single ionization of C_{60} (i.e. the cross-section for emission of one electron accompanied by production of any combination of fragments), have been reported so far. Using a Mulliken population analysis, Deutsch et al. [4] extended a semi-empirical formula for estimating cross-sections for electron impact ionization of atoms [5] to the case of C_{60} . Results obtained from a modified additivity rule have been quoted in Ref. [3]. Neither the energy dependence nor the absolute values of the measured cross-section could be reproduced by these calcula-

tions. Thus, in particular, the remarkable fact that this cross-section does not show the pronounced maximum at small energies familiar from atomic ionization cross-sections, has not yet been explained.

From the experimental partial cross-sections [1], it is evident that the curve shape just mentioned is due to the dominant direct single ionization reaction $e^- + C_{60} \rightarrow 2e^- + C_{60}^+$. In this Letter, we report on a quantum mechanical calculation of the corresponding integrated cross-section for the case of fast electron impact (kinetic energies in excess of 100 eV), based on the plane-wave Born approximation. The bound and continuum states of C_{60} are described in the spherical jellium model. To validate this description, we also discuss the triply differential cross-sections measured in a recent ($e,2e$) experiment [6].

2. Theoretical model

The spherical jellium shell model of C_{60} was first proposed in Refs. [7,8] as a means to analyse the

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optical response of fullerenes. This model approximates the potential generated by the carbon nuclei and the 1s core electrons by a spherical potential well (radius, 6.7 Å; thickness, 5.6 Å). The depth of this well is defined in the spirit of the jellium model of metal clusters [9]. To obtain the effective single-particle orbitals from this model, we self-consistently solved the corresponding Kohn–Sham equations of density functional theory [10] with this external ionic potential. The exchange–correlation energy functional in the local density approximation (using the Vosko–Wilk–Nusair parametrization of the correlation energy density [11]) was employed. A Latter correction was applied to force the proper $-1/r$ asymptotic behaviour of the self-consistent effective potential. Due to the spherical symmetry, the resulting ground state wavefunction is represented by only 15 effective one-electron orbitals, with quantum numbers in the range of $n = 1, 0 \leq l \leq 9$ and $n = 2, 0 \leq l \leq 4$. Each of these orbitals is $2 \cdot (2l + 1)$ -fold degenerate, so that the closed-shell system would accommodate 250, rather than 240, electrons [8]. In our calculations, we therefore assume that all m levels of the most weakly bound ($n = 1, l = 9$) state have fractional occupation number 28/38.

To describe the ionization process, we use the plane-wave Born approximation (PWBA) first used by Bethe [12] and reviewed in Ref. [13]. In this high-energy model, the projectile electron is described by plane waves, and the electron–electron scattering process is treated in first-order perturbation theory. Exchange effects are neglected. In our calculations, we represent the final continuum state of the ejected electron by a scattering solution (with incoming spherical wave boundary conditions) of the Schrödinger equation with the self-consistent effective potential described above. This choice renders bound and scattering states orthogonal so that there is no contribution of elastic projectile–jellium background scattering to the Born series [14]. The Latter correction ensures that the asymptotic form of the effective potential is that of the residual singly charged ion.

The implementation of the PWBA model for a general spherical potential is straightforward. The only technical complication is that the ejected electron wavefunction is only known in terms of a partial wave series. Corresponding explicit formulae for

differential and integrated cross-sections are given, e.g. in Ref. [15]. In the present computations, convergence of the partial wave expansion was slow due to the large size of the C_{60} molecule: up to 110 partial waves had to be used. For atomic systems, the PWBA is known to be unreliable if the impact energy is smaller than about five times the binding energy [16]. We therefore restricted our calculations for fullerenes to impact energies greater than 100 eV.

3. Triply differential ionization cross-section

The strongest test of any theory of electron impact ionization is the comparison of the results with data from so-called $(e,2e)$ experiments, in which the two continuum electrons emerging from the collision are detected in coincidence, and all electron momentum components are measured, so that the experiment is kinematically complete (note that the observed cross-section is commonly called ‘triple differential’ because the solid angles are counted as only one variable, and one component is defined by energy conservation). For the case of fullerene targets, such an $(e,2e)$ experiment has been carried out by Vos et al. [6]. These authors used a scattering arrangement characterized by high energies of all continuum electrons (impact energy, 20.8 keV; electron observation energies, ≈ 19.6 and ≈ 1.2 keV). For these experimental conditions, a first-order description using a representation of all continuum electron states in terms of (non-relativistic) plane waves, the so-called plane-wave impulse approximation (PWIA), is adequate. The corresponding triply differential cross-section factorizes into the spin-averaged free electron–electron scattering cross-section f_{ee} (that depends on the incoming electron momentum \mathbf{k}_0 and the outgoing electron momenta \mathbf{k}_1 and \mathbf{k}_2) and the momentum density of the ionized electron in its initial state (energy eigenvalue, E_b) $|\psi_{E_b}\rangle$:

$$\frac{d^3\sigma^{\text{PWIA}}}{d\Omega_1 d\Omega_2 dE} = (2\pi)^4 \frac{k_1 k_2}{k_0} f_{ee}(\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2) \times |\langle \mathbf{q} | \psi_{E_b} \rangle|^2 \quad (1)$$

where $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_1 - \mathbf{k}_2$ is the momentum of the recoil ion [17]. The squared matrix element is equiv-

alent to the energy-momentum density $\rho(E_b, \mathbf{q})$ of the initial state, hence such experiments can be considered as an ‘electron momentum spectroscopy’ (see e.g. [17,18]), In principle, such $(e,2e)$ measurements allow us to obtain the complete quantum mechanical information on the effective single-electron orbitals, although in practice, only the spherical average $\rho(E_b, |q|)$ can be measured for atoms and molecules. The data of Ref. [6] are therefore ideally suited to assess the validity of the spherical jellium shell model of C_{60} .

Fig. 1 shows the experimental results of Ref. [6] (we refer to this work for further details of the somewhat intricate scattering kinematics) in comparison with corresponding data from a jellium shell model PWBA calculation. We have also carried out a PWIA calculation that yields practically identical

results. This indicates the validity of the PWIA factorization concept that allows us to relate our results directly to the description of the initial bound state. To facilitate comparison, the theoretical data have been convoluted with a Gaussian of 1 eV half width simulating the finite experimental energy resolution.

The most striking observation is that the calculated $(e,2e)$ spectrum is concentrated on the few orbital eigenvalues of the spherical jellium shell model, rather than being a continuous function of E_b . Of course, this is a direct consequence of the massive artificial degeneracies introduced by assuming spherical rather than icosahedral symmetry. It is also obvious that the jellium model mispredicts the eigenvalues of the most strongly bound effective one-particle orbitals.

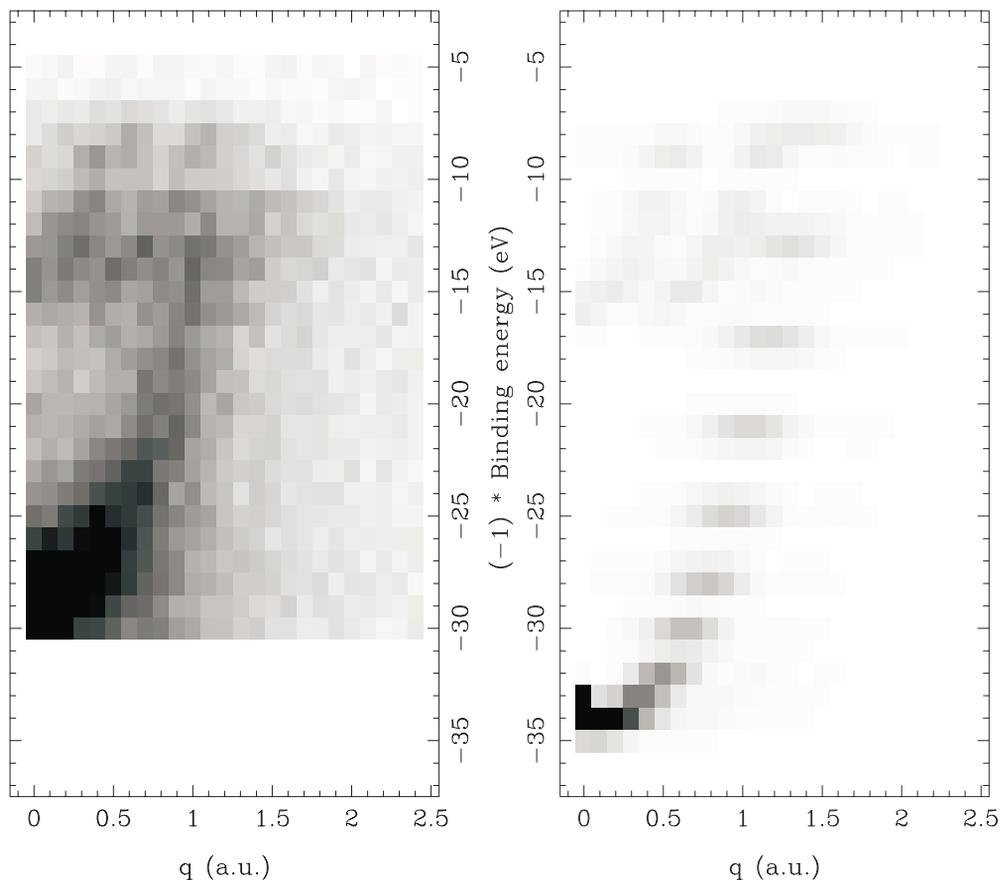


Fig. 1. Triply differential cross-section for $(e,2e)$ process on C_{60} as function of recoil ion momentum q (in a.u.) and binding energy (in eV). Linear gray scale in arbitrary units. Left: experiment [6]; right: PWBA calculation.

On the other hand, if one accepts the model as a discrete representation of the quasi-continuum of valence electron states in C_{60} , it is fair to say that all important features of the observed electron momentum distribution, namely the existence of a parabolic σ band and a less pronounced π band split due to the intrinsic curvature of the fullerene geometry [6], are qualitatively reproduced. Even certain fine details, notably the absence of the maximum at the bottom of the π band expected from structure calculations [6], are confirmed by our calculations. The spherical jellium shell model offers a particularly simple qualitative interpretation of these observations: assuming the electrons to be delocalized over a sphere of some given radius r_0 , the expectation values of energy and momentum are (in a naive approximation treating the ionic potential as a constant) related by $E \sim l(l+1)/r_0^2 \sim q^2/2$ because there is no radial momentum component, hence the parabolic shape of the calculated ‘bands’ (see also Ref. [6]). The splitting of the contributions from $n=2$ states is a direct consequence of the node theorem for the eigenstates of spherically symmetric Hamiltonians.

We therefore conclude that the spherical jellium shell model provides a reasonable starting point for the theoretical study of inelastic electron scattering from fullerenes (note that, at the high excess energies in question, the small deviations from the experimental binding energy range will be of no consequence). More generally, our results explicitly demonstrate that these effective one-electron orbitals capture all the essential features of the momentum space structure of C_{60} , which justifies their use in theoretical studies whenever only a global description of the one electron properties of fullerene is needed. However, a molecular approach will be required whenever the localization of charges on the fullerene cage structure plays a role. See Ref. [19] for further discussion of this problem.

4. Integrated ionization cross-section

As was indicated in Section 2, calculating the integrated electron impact ionization cross-section within the spherical jellium shell model in PWBA is in principle straightforward. However, the electron

continuum of C_{60} supports pronounced shape resonance features that have been observed in the electron attachment cross-section (see Ref. [20] and references therein). These shape resonances also show up in the singly differential ionization cross-section calculated in the spherical jellium shell model [21]. Hence, a very fine grid is required to sample the contributions of these resonances in the integration over final state energy sharings. This fact conspires with the slow convergence of the partial wave series, and the necessity to deal with each of the 15 model orbitals separately, to render the numerical calculations extremely cumbersome, and precludes a high-precision solution. From the comparison of different stages of refinement of our calculations, we estimate the residual error of the present results to be less than 10%.

In Fig. 2, we show our numerical results along with the experimental data of Matt et al. [1], as reconsidered by the same authors in Ref. [2], and recently confirmed by an independent measurement using a different method [3]. Notice that the experimental error bars are too small to show up in this figure [1]. The PWBA results (that have been corrected for the minor contribution of the core electrons using the calculated single atom cross-section) approach the experimental cross-section for the formation of C_{60}^+ ions as the impact energy is increased, and are in reasonable quantitative agreement with the experimental data at the highest energy considered, in contrast to the semi-empirical calculation of Ref. [4]. This suggests that the removal of a single valence electron of C_{60} in a binary collision with a fast projectile electron in most cases leads to formation of a *stable* C_{60}^+ complex.

To explain the failure of the semi-empirical calculation of Ref. [4], it has been suggested that the electron impact C_{60} breakup reaction at high energies might primarily be due to a binary electron–electron collision leading to an *unstable* C_{60}^+ complex subsequently decaying into one of the many fragmentation channels [1]. If this picture was valid, the calculated cross-section for removal of one electron should approach the counting cross-section for production of any charged fragments, rather than the cross-section for observing C_{60}^+ ions. Hence, the fact that in the high-energy region (where the PWBA theory can be expected to describe the binary colli-

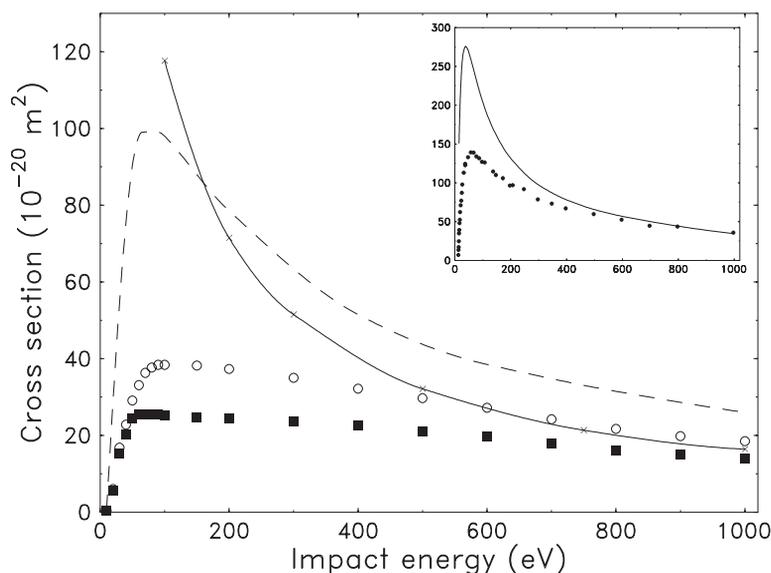


Fig. 2. Integrated cross-section for electron impact single ionization of C_{60} as function of projectile energy. Full symbols: experimental cross-section for production of C_{60}^+ ions [1,2]; open symbols: total counting cross-section [1,2]; dashed line: result of semi-empirical model calculation [4]; crosses: present PWBA calculation (line is to guide the eye). Inset: Integrated cross-section for electron impact ionization of atomic carbon, multiplied by 60. Symbols: experimental data [22], full curve: PWBA calculation (this work).

sion ionization step adequately) our calculated cross-section is significantly smaller than the measured counting cross-section, implies that multiple inelastic scattering of the projectile might play an important role in C_{60} fragmentation up to very high energies.

The spherical jellium shell model completely disregards the ionic substructure of the fullerene. The opposite extreme would be to ignore the global cage structure of C_{60} and describe it as an ensemble of 60 independent carbon atoms. It is therefore instructive to consider the ionization cross-section for this hypothetical system as well (Fig. 2, inset). Evidently, simply scaling the experimental total cross-section for ionization of atomic carbon results in a massive overestimation of the experimental data for C_{60} . This result explicitly demonstrates the crucial importance of the fullerene geometry. It is also consistent with the conclusion, drawn by Deutsch et al. [4] from the failure of their calculation, that calculational schemes based on adding atomic cross-sections are inherently unsuited to describe the ionization of the C_{60} molecule.

The PWBA calculation quantitatively describes the experimental data for atoms only at impact ener-

gies of more than 500 eV, and mispredicts the shape of the cross-section maximum at lower energies, much like in the jellium model case. These observations suggest that the failure of the PWBA–jellium shell approach at intermediate impact energies might be due to the inadequacy of the plane-wave description of the projectile rather than to the breakdown of the jellium shell model. This would imply that the distinct flat shape of the total cross-section for electron impact C_{60}^+ formation is due to elastic rescattering of the projectile electron in the fullerene cage structure.

5. Conclusions

The present results show that the spherical jellium shell model can be used to quantitatively describe electron impact ionization of the C_{60} molecule at impact energies greater than a few hundred eV, and that the plane-wave Born approximation is applicable in this regime. However, the experimental results at lower energies, most notably the unusual flat shape of the total cross-section function, cannot be explained to date. The acceptable qualitative agree-

ment between theoretical and experimental electron momentum spectra, and the energy dependence of the calculated absolute cross-section function, suggest that the description of the scattering process, rather than that of the target states, needs to be improved to describe these experimental data quantitatively. Work in this direction is in progress.

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