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LETTER TO THE EDITOR

Effects of geometry in elastic scattering and capture of free electrons by C_{60} molecules

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Abstract. In this paper the influence of C_{60} geometry on low-energy elastic scattering and attachment of free electrons is studied. Strong resonances in the total capture cross sections are found for energies corresponding to negative-ion resonances. The resonance structure is shown to be very sensitive to the actual geometry of the molecular core, the icosahedral symmetry of which is completely taken into account.

In recent years, intensive investigations of free-electron interaction with the fullerene molecule C_{60} has been carried out. The experimental and theoretical study of these processes supplies additional information about the electronic structure of the target, which cannot be obtained from photoabsorption measurements.

Low-energy electron scattering is of particular interest because in this energy range there are no core electron excitations, and electron attachment to C_{60} is the most effective process which yields long-lived anions C_{60}^-. The capture process was observed experimentally within a remarkably broad electron energy region, ranging from near zero up to 13–14 eV (Lezius *et al* 1993, Jaffke *et al* 1994, Huang *et al* 1994, Elhamidi *et al* 1997). Theoretically this process was studied within models treating the fullerene molecule as a spherically symmetric target (Tosatti and Mannini 1994, Matejcik *et al* 1995). Similar models were used for the calculations of the optical response of a C_{60} molecule. They revealed reasonable agreement with experimental data and showed the dominant role of collective effects (Wang *et al* 1993, Alasia *et al* 1994). One could expect collective effects to also be very important in electron–fullerene collision processes. However, at electron energies below the plasmon resonance energy, the influence of the target structure is expected to be more important or comparable with the influence of collective resonance and polarization effects. The goal of this letter is to exhibit the role of the fullerene structure in low-energy electron attachment.

It was found for electron attachment to C_{60} that the probability of capture is proportional to the cross section for elastic electron scattering (Tosatti and Mannini 1994, Matejcik *et al* 1995), though it is well known that the near-threshold cross section behaviour of these processes should normally differ. Therefore in the present work we study the capture through elastic collisions of free electrons with fullerenes in the range of projectile energies up to 6 eV. The present calculations are performed within the local density approximation (LDA) using both the simple spherical model and the approach accounting for the icosahedral

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symmetry of C_{60} molecules. The comparison between these two calculations has shown that the target structure significantly affects the cross section behaviour of elastic scattering and capture processes, respectively.

The mean-field potential in which the extra electron moves is calculated by taking into account the 240 delocalized electrons of neutral C_{60} within the LDA by solving the Kohn–Sham equations (Kohn and Vashita 1983) for the target ground state. The centrifugal potential together with electron–cluster interaction form a potential barrier which, in turn, leads to the appearance of quasi-stationary states of the incident electron.

Theoretical approach

In the present work, to describe the C_{60} valence electrons we use the following Kohn–Sham equation (Kohn and Vashita 1983)

$$(T + U^{\mathrm{Loc}}(\boldsymbol{r}, [\rho]))\, \psi_k(\boldsymbol{r}) = \epsilon_k\, \psi_k(\boldsymbol{r}) \tag{1}$$

with the local potential

$$U^{\mathrm{Loc}}(\boldsymbol{r}, [\rho]) = V_{\mathrm{ee}}(\boldsymbol{r}, [\rho]) + V_{\mathrm{xc}}(\boldsymbol{r}, [\rho]) + V_{\mathrm{ext}}(\boldsymbol{r}). \tag{2}$$

Here, V_{ee} is the Hartree Coulomb potential, and the exchange-correlation potential $V_{\mathrm{xc}}(\boldsymbol{r}, [\rho])$ is used in the LDA following the parametrization of Perdew and Zunger (1981). The object of interest of our work is the effect of the geometry of the external potential formed by $N = 60$ positive carbon ions disposed on the truncated icosahedron:

$$V_{\mathrm{ext}}(\boldsymbol{r}) = \sum_{i=1}^{N} u^{\mathrm{Loc}}_{\mathrm{pseudo}}(|\boldsymbol{r} - \boldsymbol{R}_i|). \tag{3}$$

Here, $\boldsymbol{R}_i$ are the equilibrium positions of the carbon nuclei with respect to the centre of the molecule, and $u^{\mathrm{Loc}}_{\mathrm{pseudo}}(r)$ is the local part of the pseudo-potential caused by the two tightly bound 1s core electrons of each carbon atom.

In the next step, we expand the external potential in spherical harmonics with respect to the centre of gravity of C_{60} (Alasia *et al* 1994)

$$V_{\mathrm{ext}}(\boldsymbol{r}) = \sum_{L=0}^{L_{\max}} \sum_{M=-L}^{L} S_{L,M}\, V_L(r)\, Y_{L,M}(\boldsymbol{r}) \tag{4}$$

with coefficients $S_{LM} = \sum_{i=1}^{N} Y^*_{L,M}(\boldsymbol{R}_i)$ (Alasia *et al* 1994). The radial functions are given by $V_L(r) = 2\pi \int_{-1}^{1} u^{\mathrm{Loc}}_{\mathrm{pseudo}}(y)\, P_L(x)\, \mathrm{d}x$, $y^2 = r^2 + R^2 - 2rRx$, $R = |\boldsymbol{R}_i|$ and $P_L(x)$ is a Legendre polynomial.

Because of the symmetry of the system, we expand the wavefunctions of bound states ψ_k as follows $\psi_k(\boldsymbol{r}) = \sum_{nlm} C^k_{nlm}\, \phi_{nlm}(\boldsymbol{r})$, where $\phi_{nlm}(\boldsymbol{r}) = R_{nl}(r)\, Y_{lm}(\boldsymbol{r})$ and $R_{nl}(r)$ are the solutions of equation (1), taking into account only the spherical component ($L = M = 0$) of U^{Loc}, and correspondingly the partial-wave expansion of the scattered wavefunction Ψ is given as follows:

$$\Psi = \frac{1}{r} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \varphi_l(k, r) Y_{lm}(\boldsymbol{r}). \tag{5}$$

The radial equation for the partial wave $\varphi_l(k, r)$ is

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + k^2 - \frac{2V_{\mathrm{tot}}(l, r)}{\hbar^2} \right) \varphi_l(k, r) = 0 \tag{6}$$

where $k^2 = 2E$ and E is the incident electron energy (atomic units are used $|e| = m_e = \hbar = 1$).

In our model we neglect polarization effects because the investigation of their role in the electron scattering process is not the main subject of this letter, as far as the considered projectile energies are significantly lower than the energies of plasmon resonances in C_{60} molecule (Wang *et al* 1993). The other reason for this simplification is the relatively low static dipole polarizability for C_{60} (Wang *et al* 1993, Alasia *et al* 1994) in comparison with metal clusters (Knight *et al* 1985), where the polarization interaction (Amusia and Cherepkov 1975, Amusia 1990) plays an important role (Ivanov *et al* 1996, Ipatov *et al* 1998a, b). So the total effective potential for the scattered electron is given by

$$V_{\mathrm{tot}}(l, r) = U_{\mathrm{eff}}(r, L_{\max}) + \frac{l(l+1)}{2r^2} \tag{7}$$

where $U_{\mathrm{eff}}(r, L_{\max})$ is determined via the self-consistent solution of the Kohn–Sham equation (1) for the target cluster with maximal angular momentum $L_{\max}$ in expansion (4) as a parameter, and the influence of high harmonics in the external potential on the elastic electron scattering was studied. The potential (7) is used for calculation of the phaseshifts of partial waves and elastic scattering cross sections.

Results and discussion

Partial phaseshifts and elastic scattering cross sections were found by numerical integration of the radial equation (6) for two models: taking into account only the $L = M = 0$ component of $U^{\mathrm{Loc}}(\boldsymbol{r}, [\rho])$, i.e. for the spherical target, and including angular momenta of $V_{\mathrm{ext}}(\boldsymbol{r})$ (4) up to $L_{\max} = 20$. The results of calculations are presented in figures 1–4.

Due to the icosahedral symmetry of C_{60} the coefficients $S_{L,M} = (-1)^M S_{L,-M}$ are different from zero only for selected values of the angular momenta (Alasia *et al* 1994) $L = 0, 6, 10, 12, 16, 18, 20$, etc. From angular expansion of the Kohn–Sham equation for

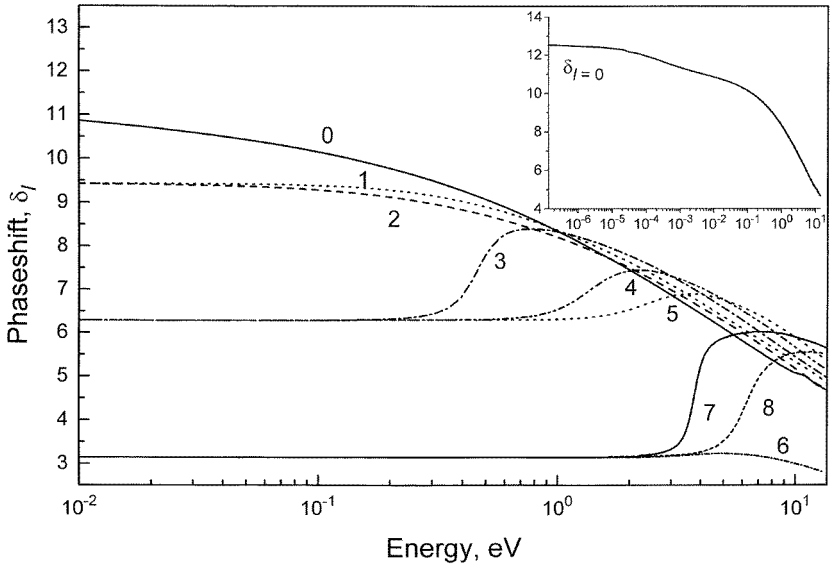

Figure 1. Partial phaseshifts δ_l for $l = 0$ to 8 as a function of the incident electron energy for the e–C_{60} system calculated within the spherical target model ($L_{\max} = 0$).

the incident electron (5) it is easy to find that only $L = M = 0$ harmonics of U^{Loc} (2) and V_{ext} and the higher harmonics of V_{ext} with $S_{L,M} = -S_{L,-M}$ make a contribution to the effective potential V_{tot} (7). So for the incident partial waves with $l = 0, 1, 2$, the influence of the non-spherical target geometry on the scattering cross sections reflects only the changes in Hartree and exchange-correlation parts of (2), i.e. the sensitivity of the ground state electron system to the higher harmonics of the core potential (4).

Figure 1 presents the partial-wave phaseshifts δ_l as functions of the incident electron energy calculated within the spherical approximation for the target electron system. The low-energy asymptotic behaviour of the s-wave phaseshift is shown in the inset. For small energies, the phaseshifts go to the $n_l\pi$ values, where n_l (in accordance with Levinson's theorem (Joachain 1983)) is the number of bound states for the angular momentum l. The inset displays the asymptotic behaviour $\delta_0 \stackrel{k\to 0}{\longrightarrow} 4\pi$ meaning that four s-states are bound.

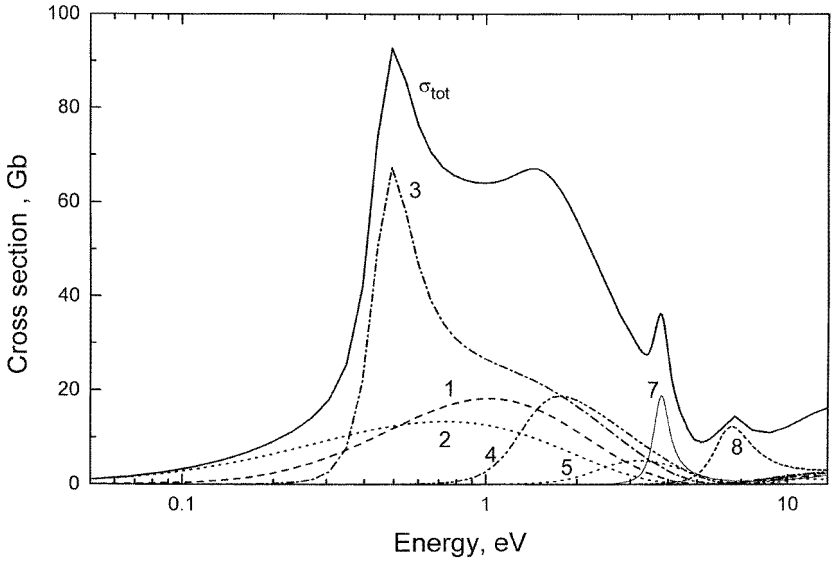

Figure 2. Partial and total free-electron capture cross sections as functions of the incident electron energy for the e–C_{60} system within the spherical target model ($L_{\max} = 0$). Curves 1–8 correspond to l-wave contributions.

Partial and total cross sections for elastic scattering of electrons are plotted in figure 2. For very low projectile energies the main contribution to the cross section arises from the s-wave part (see also curve 1 in figure 3) where we have the zero-energy resonance with extremely large scattering length $\bar{a} = 255$ au defined by $\sigma^{\mathrm{tot}}_{k\to 0} = 4\pi\bar{a}^2$. The $l = 3$ resonance gives rise to a well defined peak in the cross section at the energy $E \approx 0.5$ eV. A broad peak at $E \approx 1.5$ eV is due to mutual contributions of partial waves with $l = 1, 2, 4$. More narrow resonances are also revealed for $l = 7$ ($E = 3.7$ eV) and $l = 8$ ($E \approx 6.5$ eV). Resonance scattering for the partial wave with $l = 6$ is practically negligible. Waves with higher angular momenta are not considered here, because their contribution is only important for higher energies of the incoming electron where the resonance structure is affected by inelastic processes (Huang *et al* 1994, Elhamidi *et al* 1997).

Figure 3 illustrates the sensitivity of the s-wave partial cross section to the higher harmonics in the core potential (4). As long as the effective potential (7) is more attractive

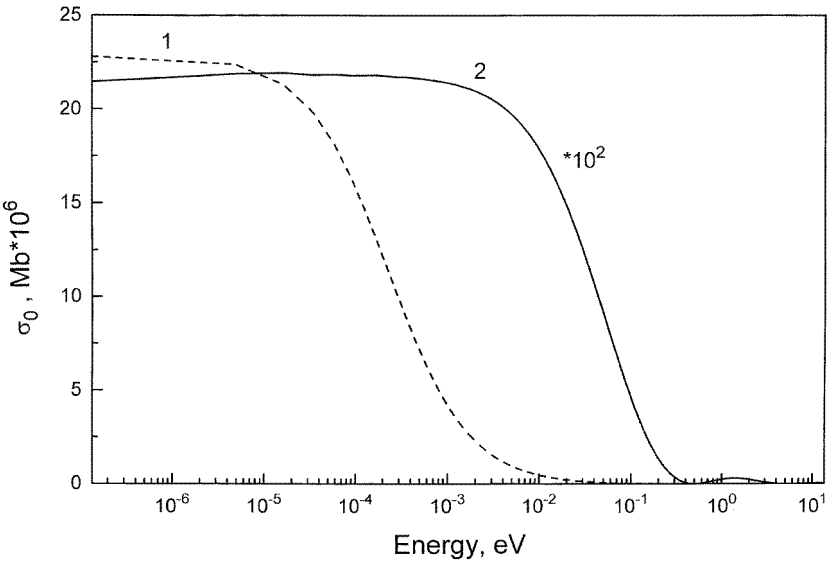

Figure 3. Partial s-wave elastic electron scattering cross sections: 1, $L_{\max} = 0$; 2, $L_{\max} = 20$.

due to the ground state electronic charge redistribution, the strong s-wave resonance becomes much smaller with the corresponding scattering length of $\bar{a} = 25$ au, but nevertheless dominates in the low-energy region. The latest experiments have observed the s-wave contribution to the free-electron capture cross section of C_{60} molecules (Elhamidi *et al* 1997), but because of the absence of a direct proportionality between scattering and attachment and symmetry properties, this contribution may be significantly lower than it is in elastic scattering cross section.

The comparison of the calculated partial (figure 4(*a*)) and total (figure 4(*b*)) cross sections, within the spherical model and with account of higher potential harmonics ($L_{\max} = 20$) brings out the redistribution of resonance strengths taking place for higher values of the angular momentum l, as well as the corresponding shift of the peaks to lower projectile energies. The strongest f-wave resonance peak ($E \approx 0.27$ eV) is significantly higher and narrower than for $L_{\max} = 0$ (figure 2). A similar effect is seen also for $l = 7$ ($E \approx 3.2$ eV) and $l = 8$ ($E \approx 5.7$ eV) whose contribution to the total cross section becomes more pronounced (see figure 4(*b*)) than in the spherical approximation. The position of the broad peak at $E \approx 1.5$ eV does not change. The results obtained are in reasonable agreement with part of the experimentally observed peaks in the total electron capture spectrum (Elhamidi *et al* 1997). The other part of the experimentally detected resonance peaks could be attributed to the influence of target polarization effects and splitting of the resonance peaks due to interaction of the electron quasi-bound states with different core oscillation modes.

Concluding remarks

The total cross section of slow electrons elastic scattering by C_{60} clusters exhibits a resonance structure. It is shown that the positions and widths of these resonance peaks associated with quasi-bound extra electron states depend sensitively on the geometry of the target molecule core. The resonance structure obtained is believed to be revealed in the electron attachment

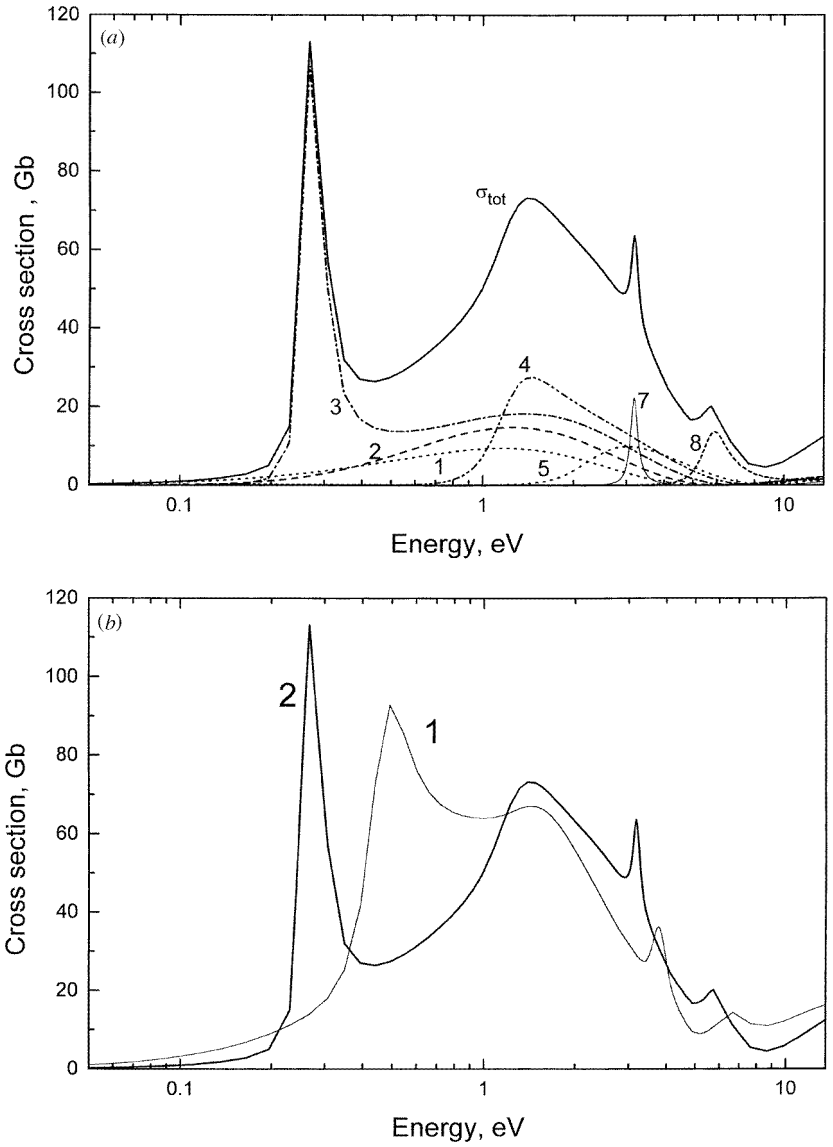

Figure 4. (*a*) Partial and total free-electron capture cross sections as functions of the incident electron energy for the e–C_{60} system calculated taking account of higher harmonics in the core potential ($L_{max} = 20$). Curves 1–8 correspond to *l*-wave contributions. (*b*) Total free-electron capture cross sections for the e–C_{60} system: 1, $L_{max} = 0$; 2, $L_{max} = 20$.

cross section to the fullerene. Comparison with experimental electron capture cross sections shows that the peaks may be attributed to corresponding resonances in elastic scattering.

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