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Nonadiabatic response in a C_{60} ion collision: A real-time quantum approach

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Abstract. We use a large N-electron determinant-basis method to calculate the excitation energy of valence electrons in a C^+–C_{60} collision without fragmentation at energy K. We study a central collision in the range $50\,\mathrm{eV} < K < 15\,\mathrm{keV}$. The electronic excitation energy of π electrons displays two main maxima at 1.15 and 5 keV. They are interpreted as resonance effects. We calculate by two independent approaches in real time the electron densities of the sites and the currents of the bonds. We show that the valence electrons tend to form a wake following the incident ion at the same velocity.

PACS. 36.40.Cg Electronic and magnetic properties of clusters

1 Introduction

We study the electronic response of a C_{60} cluster colliding with a fast incident ion. We only consider a collision without fragmentation, a physical situation encountered in recent experiments. For example, in Ar^{8+}–C_{60} collisions [1], the production of C_{60}^{p+} with p varying from 1 to 5 has been observed.

A two-step description of the process can be proposed. First, a relatively large excitation energy of the valence electrons is stored, because of their interaction with the rapid incident charge; then the system de-excites through autoionization or photoemission. In this paper, we concentrate on the first step (the storage of excitation energy during the collision); we do not study the second aspect of the phenomenon (the various de-excitation modes). We consider a C^+–C_{60} collision without fragmentation in the range of energies $50\,\mathrm{eV} \leq K \leq 1.5 \times 10^4\,\mathrm{eV}$.

As it is often assumed in this kind of model, we suppose that during the collision, the C_{60} nuclei remain frozen on their sites. This is justified by a comparison between the interaction time, $\sim 10^{-14}$ s, and the phonon frequency, $\sim 10^{-13}$ s. The previous assumption becomes questionable for low K energies: $K \lesssim 100\,\mathrm{eV}$ (for $K = 100\,\mathrm{eV}$ the crossing time is 2×10^{-14} s). In this range, the nuclei move significantly throughout the interaction and this motion can contribute to the total excitation energy. This point warrants a more precise description.

If the nuclei is frozen and the incident particle is noninteracting with C_{60} at large times, as we assume, then the final electronic ground state is the same as the initial electronic state. For very low velocity collisions, where practically no electron-hole excitations are created, the wave function will be described by the Hamiltonian ground state (i.e., the adiabatic wave function); this process is called adiabatic. For relatively large K values, electron-hole excitations are produced, and our calculation can be considered as measuring the nonadiabatic character of the phenomenon.

We also suppose that the charge of the incident particle is constant. Here again, this approximation is mainly valid for large K values, because for low K values, a possible electron capture by the incident ion cannot be excluded. An improvement in this area of the model is discussed at the end of the paper.

Let us recall why it is necessary in N-electron time-dependent problems for one to use a determinant basis. Indeed, once the solution of the one-electron Hamiltonian has been performed at any time, nothing is known about the occupancy of the one-electron states. The solution that would consist in populating the one-electron states with the lowest energies is arbitrary, and can lead to important errors. For example Friedel [2,3], Anderson [4], and Nozières *et al.* [5] show that when a large N-electron gas is submitted to a sudden change of local potential, the N-electron state built by populating the lowest energies of one-electron states is strictly empty. The system is projected only on excited states. This phenomenon leads in particular to the edge- singularity effect observed in metal X-ray spectra.

Our method, which will be presented in Sect. 2, leads to a real-time quantum description of the interaction between the impinging charge and the aggregate valence electrons. In Sect. 3, we apply our method to a central collision. In addition to the total electronic excitation energy in the collision, we calculate the time dependence of the populations on each site and the currents in the aggregate.

Similar problems have been investigated by the use of other methods. Guet *et al.* [6,7] use a semiclassical limit of a time-dependent Hartree–Fock (TDHF) description. Also of note is the recent work of Reinhard *et al.* [8] who use a time-dependent density functional theory. We come back to these works below.

2 The model

In this paper, we limit the calculation to the excitation of the π electrons; the role of the σ electrons is also briefly discussed at the end of the paper.

We introduce as H_0 the unperturbed tight binding Hamiltonian of the C_{60} π electrons; then $H(t)$ will be written:

$$H(t) = H_0 + V(t), \tag{1}$$

where $V(t)$ is due to the positive charge of the incident ion located at position $\mathbf{R}(t)$. If $c^+_{r\sigma}$ $(c_{r\sigma})$ is the creation (annihilation) operator of an electron with spin σ on atomic orbital φ_r, we may write:

$$H_0 = \beta \sum_{\sigma,r,s \text{ neigh. } r\neq s} c^+_{r\sigma} c_{s\sigma} + E_{\text{at}} \sum_r c^+_{r\sigma} c_{r\sigma} \tag{2}$$

$$V(t) = \sum_{r,s,\sigma} V_{rs}(t) \left[c^+_{r\sigma} c_{s\sigma} + c^+_{s\sigma} c_{r\sigma} \right] \tag{3}$$

where β, $\beta \sim -1.25$ eV, and E_{at} are respectively the hopping and diagonal terms in the C_{60} tight binding Hamiltonian [9] (the results reported here do not depend on E_{at}).

Formally, for a Z incident charge we have:

$$V_{rs}(t) = -\frac{Ze^2}{4\pi\,\varepsilon_0} \int \varphi^*_r(\mathbf{r}) \varphi_s(\mathbf{r}) \frac{\mathrm{d}^3 r}{|\mathbf{r} - \mathbf{R}(t)|}\,. \tag{4}$$

We suppose that its trajectory is linear and that its v velocity is constant; $K = \frac{1}{2}mv^2$ is the kinetic energy.

At time $t = -\infty$, $V(t) = 0$, and $\Psi(t = -\infty) = \Psi_0$ is the ground state of the unperturbed C_{60} electrons. If we call ϕ_ℓ $(\ell = 1, 2, ...60)$ the one-electron molecular eigenstates of H_0 ordered by increasing energies, the Ψ_0 determinant will be written:

$$\Psi_0 = \det \left(\phi_{1\uparrow} \phi_{1\downarrow} \phi_{2\uparrow} \phi_{2\downarrow} \cdots \phi_{30\uparrow} \phi_{30\downarrow} \right)\,. \tag{5}$$

Now let us consider our working determinant basis. Because the dimension is too large (the dimension is given by the number of possible ways for sharing 30 ↑ and 30 ↓ electrons in 60 ↑ and 60 ↓ states; this gives $\sim 10^{34}$) for practical calculations, a convenient size-limited basis, that we will call basis B with Ψ_i elements, has to be determined.

We choose the Ψ_i elements among the N-electron eigenstates of $H(\tau)$, where τ is a given intermediate time in the process. Let us call $\Psi_{\text{ad}}(t)$ the N-electron adiabatic solution of Hamiltonian $H(t)$, given by:

$$H(t)\,\Psi_{\text{ad}}(t) = E_{\text{ad}}(t) \Psi_{\text{ad}}(t)\,. \tag{6}$$

The Ψ_i elements and the time τ are fixed so that, at any time of the process, $\Psi_{\text{ad}}(t)$ can be accurately developed in basis B. In the calculations presented in Sect. 4, we take $\tau = -t_0^+$ which is the time when the projectile has just entered the C_{60} cage and check that $\Psi_{\text{ad}}(t)$ can be well developed in basis B at various successive times on the trajectory, namely $t = -\infty$, $t = -t_0^+$, $t = 0$, $t = t_0^-$, and $t = +\infty$. We retain the determinants which have the largest weights in the development of $\Psi_{\text{ad}}(t)$ at these times. The size of basis B is $\delta \sim 200$ determinants.

The Schrödinger equation projected on basis B gives a system of 2δ coupled differential equations. We will call $a_i(t)$ the weight of $\Psi(t)$ on Ψ_i:

$$\Psi(t) = \sum_i a_i(t) \Psi_i\,. \tag{7}$$

3 Central collision

We consider a central collision where the incident ion, supposed to be a C^+ ion, enters and leaves the C_{60} cage by crossing two parallel pentagons. The distance between the two pentagons is 6.2 Å.

We determine the basis according to the method described before. As the Ψ_i determinants are eigenstates of $H(-t_0)$, we get for the average total energy $E(t)$:

$$E(t) = \langle \Psi(t) \,| H(t) |\, \Psi(t) \rangle = \sum_i a^*_i(t)\, a_i(t)\, \varepsilon_i + \sum_{i,j} a^*_i(t)\, a_j(t) \,\langle \Psi_i \,| V(t) - V(-t_0) |\, \Psi_j \rangle\,. \tag{8}$$

We obtained the results reported in this paper by making some simplifying assumptions: (1) We suppose that the electrostatic potential is "felt" by the electrons only when the incident charge is inside the cage $(-t_0 \leq t \leq t_0)$. In other words, we suppose that the π electrons behave as metallic electrons that screen the external fields. (2) In the V_{rs} matrix given by formula 4, we retain only diagonal elements; this is justified by the small overlap between ϕ_r and ϕ_s wave functions that exists when $r \neq s$. (3) We use for $V_{rr}(t)$ a simple formula, which is exact in the limit of strongly localized φ_r wave functions:

$$V_{rr}(t) \sim \frac{\vartheta}{\|\mathbf{R}_r - \mathbf{R}(t)\|}\,.$$

The same formula gives, at $t = -t_0$, for one of the atoms of the first crossed pentagon (say atom 1):

$$V_{11}(-t_0) = \frac{\vartheta}{\|\mathbf{R}_1 - \mathbf{R}(t)\|}.$$

We will not take for ϑ the Coulombic value (deduced from (4)) because screening effects must be taken into account. They can be estimated from a previous study of 1s photoemission spectra in C_{60} [10]. This work shows that the average value of the potential energy "felt" by π electrons

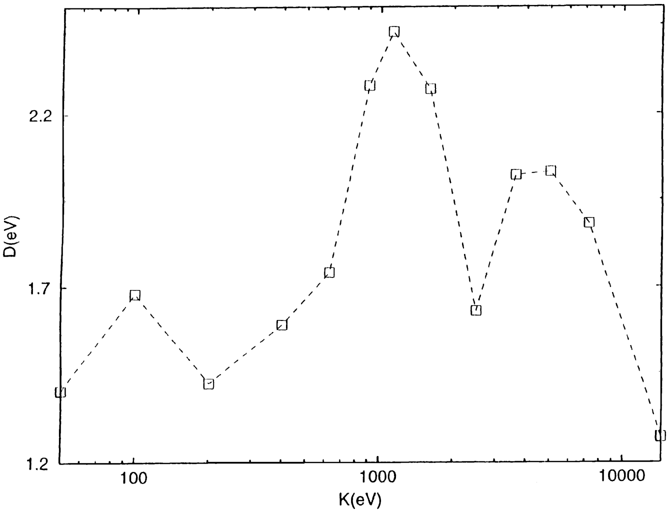

Fig. 1. D excitation energy transferred to π electrons in a central $C^+ \rightarrow C_{60}$ collision versus the K kinetic energy. At low K energies, the crossing time of the C_{60} cage is about 20% of a typical phonon frequency (more precisely, the crossing time is 2×10^{-14} s for $K = 100$ eV). As a consequence, in this range of K values, the assumption that the atoms remain frozen on their sites loses a part of its validity.

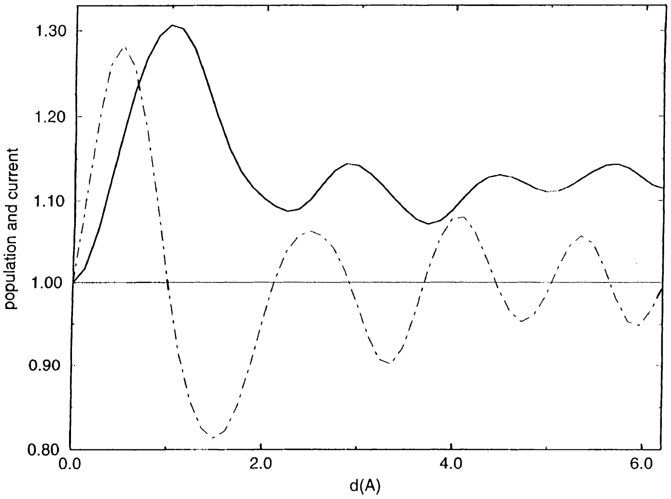

Fig. 2. The case of kinetic energy $K = 1.15$ keV. The C_{60} atoms are grouped in 8 planes perpendicular to the C^+ central trajectory; atom 1 belongs to the first crossed pentagon (first plane), and atom 6 is the atom 1 neighbour belonging to the second plane. We plot the atom 1 electronic population (full line) versus the length d travelled inside the C_{60} cage. The dashed and dotted line is related to the $i_{6,1}(d)$ current. In order to get a clear figure, we plot $\alpha\, i_{6,1}(d) + \alpha'$ with $\alpha = 3$ and $\alpha' = 1$. As a consequence, the plotted quantity is always positive, but one must keep in mind that $i_{6,1}(d)$ continuously oscillates from positive to negative values.

located on a given atom when a deep $1s$ hole appears on the same site is $\sim 3\beta$ (the average distance between the electrons and the hole is ~ 0.7 Å). Here the distance is larger $\|\mathbf{R}_1 - \mathbf{R}(-t_0)\| \sim 1$ Å, so the value $V_{11}(-t_0) = 2\beta$ appears as likely. The previous assumptions can be summarized in the following formula:

$$V_{rs}(t) = \delta_{rs} 2\beta \frac{\|\mathbf{R}_1 - \mathbf{R}(-t_0)\|}{\|\mathbf{R}_r - \mathbf{R}(t)\|} \tag{9}$$

We are mainly interested in the excitation energy D at the end of the process that is a function of the kinetic energy K:

$$D = E(t = \infty) - \varepsilon_0$$

This quantity is plotted, in Fig. 1, versus K for $50\,\text{eV} < K < 1.5 \times 10^4$ eV. The curve will be discussed below. In the range $K \lesssim 100$ eV, as mentioned in the Fig. 1 caption, the assumption that the atoms remain frozen on their sites loses a part of its validity.

It is interesting to follow how the C_{60} electrons react to the incident ion potential in real time. We have calculated the population $n_r(t)$ on a given site r and the electronic current $I_{r,s}(t)$ between two r and s neighbours (from r to s). The current operator is given by:

$$I_{r,s}(t) = \langle \Psi(t) | J_{r,s} | \Psi(t) \rangle$$

with

$$J_{r,s} = jI \sum_k c_r^+(k) c_s(k) - c_s^+(k) c_r(k)\,. \tag{10}$$

In this formula, I is a real constant with the dimension of a current, $j = \sqrt{-1}$, and the summation is made over the 60 k electrons. Finally, one gets:

$$I_{r,s}(t) = I i_{r,s}(t)$$

where $i_{r,s}(t)$ is the dimensionless quantity plotted on Figs. 2 and 3.

Our results are given for two sites belonging to the pentagons crossed respectively on entering (site 1) and on leaving the cage (site 60). Instead of the time t, we use an equivalent variable d, given by the distance traveled by the incident ion inside the cage: $d = v(t + t_0)$ $(-t_0 \leq t \leq t_0)$. As expected, the populations and the currents have correlated variations. In particular, $n(t)$ maxima (minima) systematically occur when $i_{r,s}(t)$ becomes negative (positive).

We observe in the figures that the charge in excess appearing on the sites is related to the incident ion position. For the first pentagons (Fig. 2), the largest population appears at $d \sim 1$ Å, *i.e.* a short time after entering the cage, and for the last pentagon (Fig. 3), the largest population is reached at $d \sim 6.2$ Å, almost when the incident charge leaves the cage. We may deduce from the previous results that the C_{60} valence electrons tend to form a wake following the positive charge and that this mobile screen propagates in C_{60} at the same velocity as the incident charge. This screen displacement happens with loss of electrons, since the excess charge on the last pentagon is smaller than on the first one.

Figure 2 also shows that the excess charge on site 1 is maximum when $d \sim 1$ Å. We see in Fig. 3 that the charge on site 60 begins to increase when the incident ion is at about

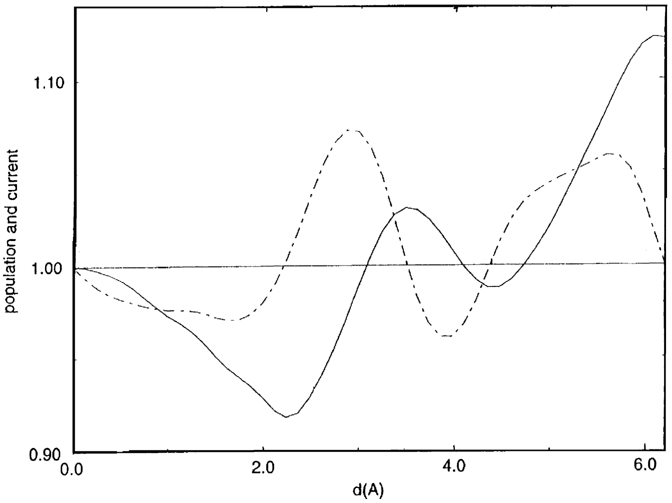

Fig. 3. The case of kinetic energy $K = 1.15\,\mathrm{keV}$. Atom 60 is one of atoms of the last crossed pentagon, and atom 54 is the atom 60 neighbour belonging to the preceding plane (see Fig. 2 caption). We plot the population on atom 60 (full line) and the quantity $\alpha\, i_{54,60}(d) + \alpha'$, (dashed and dotted line). versus the length d travelled inside the cage. As in Fig. 2, we take $\alpha = 3$ and $\alpha' = 1$.

1 Å from the site. Then it seems reasonable to take $d_e \sim 1$ Å as an effective interaction length, which may be defined as the part of the trajectory close to a given site where the perturbative action of the incident ion is effective. This distance is crossed in $t_1 \sim 0.7 \times 10^{-15}$ s for the first main maximum of Fig. 1 ($K = 1.1\,\mathrm{keV}$) and $t_2 \sim 0.35 \times 10^{-15}$ s for the second main maximum ($K = 5\,\mathrm{keV}$). Then let us consider the C_{60} electronic energy spectrum. The two first excitation levels (t_{1u}, t_{1g}) are grouped at about $0.87 \pm 0.13\,\beta$ to which $\hbar/0.87\beta \sim 0.58 \times 10^{-15}$ s corresponds, and the next group of three excited levels (h_g, t_{2u}, h_u) are at about $1.6 \pm 0.16\,\beta$, to which $\hbar/1.6\beta \sim 0.31 \times 10^{-15}$ s corresponds. In spite of the roughness of this evaluation, one may say that there is a correspondence between t_1 and t_2 and the two characteristic excitation times. This leads us to interpret the main excitation energy maxima as a resonance of the first and second groups of excited levels. Other modulations may appear in the curve. In particular, we think that the small maximum at 0.1 keV is not a direct resonance, and may come from a complex coupling between the excited states. It is likely that other maxima will appear at larger K energies corresponding to other groups of excited states.

It is noteworthy that the discrete $D(K)$ structure obtained in this study is related to the high C_{60} spectrum degeneracy. For larger aggregates, the discreteness of the $D(K)$ curve will progressively disappear as the average level separation decreases. Note that no oscillations are observed in the semiclassical models or time-dependent density functional theory mentioned before [8, 11]; for example in [11] $D(K)$ increases continuously with K.

It seems to us that the presence of maxima in the calculated $D(K)$ curve for C_{60} might be experimentally verified. As the C_{60} cage must have a given orientation with respect to the incident ion beam, we suggest the use of solid crystalline C_{60} samples at low temperatures, for which channeling experiments should give minima of the penetration depth for the $D(K)$ energy maxima.

The calculation developed in this paper has to be extended to σ electrons. It is likely that the total excitation energy will be closed to four times the D value, but a precise calculation is necessary.

Let us briefly discuss how the possibility of electron capture by the incident ion can be introduced in the model. This problem is relevant to the ionization problem encountered in SIMS models [9]. The new feature to be introduced in the present calculation is a possible transfer of electrons from C_{60} to the incident ion. We will then obtain a probability of neutralization that depends on the ion position. By using this quantity, a calculation of the average excitation energy can be made using the same method as in this paper. We intend to develop this kind of calculation. Moreover, our investigation of the differential and total excitation cross section, combining a determination of channeling impact parameters (*i.e.* impact parameters for which one may expect nonfragmentation collisions) and of the excitation energy inside these channels, is in progress.

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