Exchange effects in the transition amplitude for inelastic electron-cluster collisions

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The effect of the electronic exchange in the calculation of the scattering amplitude for inelastic electron-cluster collisions is evaluated. The target cluster initially in the ground state is excited, by means of the Coulomb forces, into a particle-hole state. An antisymmetrized transition amplitude is evaluated in the scope of the distorted-wave Born approximation. A comparison is made with a calculation in which the exchange is taken into account by adding to the direct interaction a Coulomb exchange term in the Slater approximation. The treatments are applied to the closed-shell Na_8 cluster for incident energies up to 5 eV. [S1050-2947(97)00404-6]

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A theoretical study of the elastic scattering of low-energy electrons by closed-shell metal clusters [1,2] and the excitation of a single-particle–hole state in inelastic collisions [3] was recently presented. In both cases, the total cross section as a function of the incident energy exhibits resonances that are connected to quasibound states of the electron-cluster system. These studies showed that the position and magnitude of those resonances depend on the approaches used in the evaluation of the mean-field potential. Therefore, a comparison with experiments might yield valuable information about the electronic structure of clusters and justifies continuing efforts in refining the previous theoretical treatments in order to get more reliable predictions. The present report focuses on the exchange effects between the incoming electron and the valence electrons of the cluster in scattering problems, in particular, the excitation of particle-hole states through inelastic electron collisions.

To evaluate the transition amplitude (including exchange effects) we make use of the distorted-wave Born approximation. The use of target wave functions (distorted waves) instead of plane waves works better for low incident electron energies. On the other hand, this Born approach is valid for the one-step process analyzed in the present paper in which a single particle-hole state is excited in the cluster. We may thus write

$$T_{\alpha\to\beta}=\int \chi_f^{(-)*}(\vec{k}_f,\vec{R})\,\phi_\beta^*(\vec{r})\,\frac{e^2}{|\vec{R}-\vec{r}|}[\phi_\alpha(\vec{r})\chi_i^{(+)}(\vec{k}_i,\vec{R}) - \phi_\alpha(\vec{R})\chi_i^{(+)}(\vec{k}_i,\vec{r})]\,d\vec{R}\,d\vec{r}. \tag{1}$$

Here $\vec{R}$ and $\vec{r}$ describe the position of the incoming and valence electrons with respect to the center of mass of the system before exchange, χ_i and χ_f are the relative motion wave functions of the incident and outgoing electrons, and ϕ_α and ϕ_β are the initial and final internal bound wave functions of the valence electrons involved in the excitation. The wave vectors $\vec{k}_i$ and $\vec{k}_f$ are evaluated by taking into account the kinetic-energy differences in both channels. This difference, due to the transfer of energy from the incident electron to the target cluster, is very important for the low incoming energies under consideration.

We expand the scattering wave functions $\chi_i^{(+)}$ and $\chi_f^{(-)}$ in partial waves

$$\chi_i^{(+)}(\vec{k}_i,\vec{R})=\frac{\sqrt{4\pi}}{k_iR}\sum_{l=0}^{\infty}\hat{l}i^l f_l(k_i,R)Y_{l0}(\hat{R}), \tag{2}$$

$$\chi_f^{(-)*}(\vec{k}_f,\vec{R})=\frac{4\pi}{k_fR}\sum_{l',m'} i^{-l'}f_{l'}^*(k_f,R) \times Y_{l'm'}(\Theta,\Phi)Y_{l'm'}^*(\hat{R}), \tag{3}$$

with (Θ,Φ) being the scattering angles. For electron-cluster collisions the mean field (together with a polarization correction) determines the relative motion of the target and projectile and also the single-particle states of the valence electrons. The radial wave functions f_l are obtained by integrating numerically the scattering radial Schrödinger equation with an optical potential

$$V_{\rm op}=V_{\rm MF}+V_{\rm pol}. \tag{4}$$

For metal clusters the mean field $V_{\rm MF}$ has three main contributions: (i) the electron-core interaction, usually described by a jellium approximation; (ii) the direct Coulomb electron-electron interaction, and (iii) an exchange and correlation term. This last contribution dominates since the first two terms almost cancel each other. To evaluate the mean-field potential we use the solution of the Kohn-Sham equations in the local-density approximation (LDA) to density-functional theory.

In Eq. (4) $V_{\rm pol}$ accounts for the polarization induced in the cluster electron cloud by the incoming electron. For this term the parametrization of Mittleman and Watson [4] will be used

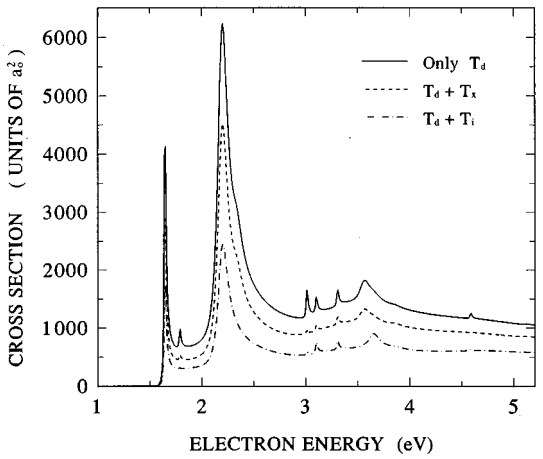

FIG. 1. Total integrated cross sections for the e-Na_8 system as a function of the incident electron energy. The solid line shows the direct angle-integrated cross section and the dashed and dot-dashed lines correspond to cross sections including T_x and T_i in the transition amplitude, respectively. All the allowed particle-hole transitions are considered. The units of the cross sections are expressed in the Bohr radius a_0.

$$V_{\rm pol} = -\frac{\alpha e^2}{2(R^2+d^2)^2}. \tag{5}$$

In Eq. (5) α is the static electric polarizability and d is a cutoff parameter of the order of the cluster size. In Ref. [1] the choice of the real optical interaction given by Eq. (4) and the parameter dependence of the polarization contribution were discussed. In particular, if the polarization term is neglected the position of the elastic resonances is shifted. The LDA plus the polarization potential used in this work and the energies of the LDA single-particle bound states for the Na_8 cluster are shown in Fig. 1 of Ref. [3].

The bound single-particle wave functions ϕ_j can be written as

$$\phi_j(\vec{r}) = \frac{u_{n_j l_j}(r)}{r} Y_{l_j m_j}(\theta,\phi) \quad (j=\alpha,\beta) \tag{6}$$

and are evaluated by diagonalization of the mean-field potential. When bound-state wave functions are evaluated, in the calculation of the mean field we include the self-interaction correction (SIC) since, as shown in Ref. [5], this improves the results. Small changes in the position of the single-particle energies are obtained. We also include the polarization correction, which modifies the energies of the SIC calculation.

Substituting the expansions (2) and (3) and Eq. (6) into the expression for the transition amplitude and using the expansion in λ multipoles for the Coulomb interaction, one finds for the direct T_d and exchange T_x contributions to the $\alpha=(n_\alpha,l_\alpha,m_\alpha)\rightarrow\beta=(n_\beta,l_\beta,m_\beta)$ transition the expressions

$$T_d(\Theta,\Phi) = \frac{(4\pi)^{3/2}}{k_f k_i} \sum_{l,l',\lambda,\mu} \hat{l}^2 \hat{l}' \hat{l}_\alpha \hat{l}_\beta \, i^{l-l'} \times (-1)^{m_\beta} \begin{pmatrix} l_\alpha & \lambda & l_\beta \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_\alpha & \lambda & l_\beta \\ m_\alpha & \mu & -m_\beta \end{pmatrix} \times \begin{pmatrix} l & \lambda & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & \lambda & l' \\ 0 & \mu & -\mu \end{pmatrix} Y_{l'-\mu}(\Theta,\Phi) \times \int_0^\infty dR f_l(k_i,R) B^\lambda_{\alpha\beta}(R) f_{l'}(k_f,R) \tag{7}$$

and

$$T_x(\Theta,\Phi) = -\frac{(4\pi)^{3/2}}{k_f k_i} \sum_{l,l',\lambda,\mu} \hat{l}^2 \hat{l}' \hat{l}_\alpha \hat{l}_\beta \, i^{l-l'} \times (-1)^{\mu} \begin{pmatrix} l & \lambda & l_\beta \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & \lambda & l_\beta \\ 0 & m_\beta & -m_\beta \end{pmatrix} \times \begin{pmatrix} l' & \lambda & l_\alpha \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & \lambda & l_\alpha \\ \mu & -m_\beta & m_\alpha \end{pmatrix} Y_{l'-\mu}(\Theta,\Phi) \times \int_0^\infty dR f_{l'}(k_f,R) C^\lambda_{l\beta}(R) u_{n_\alpha l_\alpha}(R). \tag{8}$$

In Eqs. (7) and (8) $B^\lambda_{\alpha\beta}(R)$ is the direct and $C^\lambda_{l\beta}(R)$ the exchange radial form factor. They are given by

$$B^\lambda_{\alpha\beta}(R) = \int dr u_{n_\beta l_\beta}(r) \frac{r_<^\lambda}{r_>^{\lambda+1}} u_{n_\alpha l_\alpha}(r) \tag{9}$$

and

$$C^\lambda_{l\beta}(R) = \int dr f_l(k_i,r) \frac{r_<^\lambda}{r_>^{\lambda+1}} u_{n_\beta l_\beta}(r), \tag{10}$$

where $r_<$ is the lesser and $r_>$ the greater of r and R. Both form factors are functions of the radial relative coordinate R between the target and the incoming electron and have physical information about the spatial probability that a given particle–hole excitation occurs by a direct or an exchange mechanism. Let us remark that in Eq. (8) the angular momenta l_α and l_β are no longer coupled by the multipolarity λ as is the case in Eq. (7). In Eq. (8) λ couples the orbital angular momentum of the motion of the valence electron in the initial intrinsic state l_α with the outgoing relative angular momentum l' in the exit channel. The same holds for l_β, the angular momentum of the intrinsic final state, and l, the relative angular momentum in the initial channel. As a consequence, in Eq. (8) λ runs over a set of values different from that corresponding to Eq. (7).

The differential cross section for a given transition $\alpha\rightarrow\beta$ is given by the coherent sum of direct and exchange transitions amplitudes according to

$$\frac{d\sigma_{\alpha\rightarrow\beta}(\Theta)}{d\Omega} = \frac{1}{4\pi^2} \frac{k_f}{k_i} \frac{1}{2l_\alpha+1} \sum_{m_\alpha,m_\beta} |T_d+T_x|^2. \tag{11}$$

The total cross section at an incident electron energy is a sum over all the cross sections corresponding to the bound particle-hole transitions opened at such an energy:

$$\sigma_{\rm tot}(E)=\sum_{\alpha,\beta}\sigma_{\alpha\to\beta}(E)=\sum_{\alpha,\beta}\int d\Omega\,\frac{d\sigma_{\alpha\to\beta}(E)}{d\Omega}. \quad (12)$$

For the spherical Na_8 cluster the possible bound particle-hole transitions are $1s\to1d$, $1s\to2p$, $1s\to2s$, $1p\to1d$, $1p\to2s$, and $1p\to2p$. Reference [3] shows that the $1p\to1d$ transition essentially exhausts the direct total cross section since in this case the energy of the excitation (the Q value of the reaction) matches two elastic quasibound resonant states in the incoming and outgoing channels. This transition is also enhanced due to the fact that it has the lowest particle-hole energy and that there is a strong overlap between the corresponding single-particle wave functions.

The calculation for the total cross sections of electrons scattered by a Na_8 cluster as a function of the incident energy is shown in Fig. 1. The solid line shows the total cross section when only the direct contribution T_d is taken into account in Eq. (12). The dashed line of the same figure shows the result when the term T_x is included. As can be seen, the strength with respect to the direct result is reduced by about 20%, although the general pattern is conserved.

This can be understood by analyzing the direct and exchange contributions T_d and T_x as a function of Θ for a given energy (and for fixed m_α and m_β). Both contributions have the same relative phase. Furthermore, not only the angular distributions but also the angle integrated direct and exchange cross sections exhibit a similar behavior as a function of the bombarding energy. This could be expected since, as shown in Ref. [3], the resonances in the inelastic cross sections are related to quasibound elastic resonances of the incoming and outgoing projectile-cluster systems [1]. The same resonant elastic wave functions appear in both the direct and exchange contributions of the transition amplitude and as a consequence, the total cross sections with and without exchange resemble each other in shape.

Let us now evaluate a different approach to the problem. Instead of evaluating the matrix element (1) with antisymmetric electron-cluster wave functions, a simpler alternative consists in adding to the direct Coulomb interaction between the incoming electron and the valence electron a local term accounting for the exchange effect. This approach has been used recently in the collisions analyzed in Ref. [3]. We write

$$T_{\alpha\to\beta}\simeq\int\chi_f^{(-)*}(\vec{k}_f,\vec{R})\,\phi_\beta^*(\vec{r})\left(\frac{e^2}{|\vec{R}-\vec{r}|}+V_x^{(\rm res)}(\vec{r})\,\delta(\vec{R}-\vec{r})\right)\times\phi_\alpha(\vec{r})\chi_i^{(+)}(\vec{k}_i,\vec{R})\,d\vec{R}\,d\vec{r}. \quad (13)$$

Using the Slater approximation for the exchange term V_x [6] of the LDA ground-state potential one obtains [7]

$$V_x^{(\rm res)}=\frac{\partial V_x}{\partial\rho}=-\frac{2}{3}\left(\frac{3}{2\pi}\right)^{2/3}\frac{1}{\rho(r)r_s(\rho)}, \quad (14)$$

with $r_s(\rho)=[3/4\pi\rho(r)]^{1/3}$ being the local value of the Wigner-Seitz radius and ρ the radial density of valence electrons in the cluster calculated by means of the SIC bound-state wave functions of Eq. (6) including the polarization correction in the SIC potential.

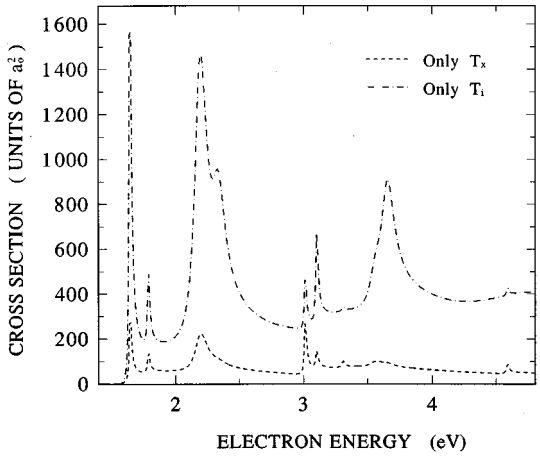

FIG. 2. Total integrated cross sections without the direct contribution T_d, that is, using only T_x (dashed line) and T_i (dot-dashed line) in the transition amplitude.

The total transition amplitude can again be written as a sum of a direct and an exchange term T_d+T_i. The direct term coincides with expression (7) and the (approximate) exchange term T_i has the same form as the direct term, except that the radial form factor B is now replaced by

$$D_{\alpha\beta}^{\lambda}(R)=\frac{2\lambda+1}{4\pi}u_{n_\alpha l_\alpha}(R)\frac{\partial V_x(R)}{\partial\rho(R)R^2}u_{n_\beta l_\beta}(R). \quad (15)$$

The resulting total cross section, with T_x replaced by T_i, is also shown in Fig. 1 by a dot-dashed line. Again, the final result resembles in shape the cross section obtained with only the direct term, but the reduction due to exchange is now of the order of 50%.

Figure 2 displays the resulting cross section for the two different ways of evaluating the exchange effect, in the absence of the direct contribution. The differences in magnitude are substantial. T_i apparently overestimates the exchange effect. This could be explained by keeping in mind that the Slater approach, which is as a local-density approach, underestimates the gap between occupied and unoccupied energy levels. For that reason the residual exchange interaction responsible for the particle-hole excitation through the local exchange approach may be overestimated, thus producing an abrupt reduction of the total cross section. We also note that in this last approach the r dependence of the form factor of Eq. (15) is the same for all λ values, while in the antisymmetrized case previously presented [Eq. (10)] the different multipoles are reduced by a factor $1/r^{\lambda+1}$. Thus the form factor with the local exchange approach is expected to be much more sensitive with respect to high-λ values than in the antisymmetrized calculation.

Similar effects have been previously observed in random-phase approximation calculations, which use the same residual LDA interaction [7] as in Eq. (13). In this case the energy of the plasmon is also overestimated. Detailed experimental data on the low-energy elastic and inelastic scattering of electrons from clusters showing the behavior of emerging electrons, to date not available, would help clarify the questions here considered.

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