ON THE ROLE OF SCREENING IN METALLIC CLUSTERS

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Abstract This work aims at visualizing the role of the inelastic electron-electron relaxation time in metal cluster. We develop a quantum mechanical model for the description of inelastic electronic collisions from metal cluster and applies it to the ionization of C_{60} by low-energy electrons. The results show evidently that the measured spectrum for the production of C_{60}^{+} depends strongly on the screening of the electron-electron collisions. The value of the screening length we obtain is in accord with previous studies on the relaxation in metal clusters.

Keywords: Interacting electron liquid, metal clusters, electronic correlation, variable phase approach, ionization.

1. INTRODUCTION

In series of seminal papers [1], Pines and Bohm have shown that a dense, interacting electron gas can be described quantum mechanically by expressing the long-range part of the inter-electronic Coulomb interactions in terms of collective fields. These represent organized plasma oscillations of the electron gas as a whole. The total Hamiltonian can then be written in terms of these collective fields and a set of individual electrons which interact with one another via short-range screened Coulomb potentials. There is, in addition, a mixing term for the field-particle coupling which can be eliminated under certain conditions. The short-range part of the electron-electron interaction can be parameterized remarkably well by a Yukawa-type potential (exponentially screened Coulomb potential) with a screening length being on the order of the inter-electronic distances. This insightful knowledge has profound consequences as to how electronic collisions within an interacting electron liquid proceed at energies off the plasma frequencies and how they can be formulated theoretically: Two particles colliding at an impact pa-

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rameter that is larger than the finite range of the potential are not scattered. Therefore, in this case free (unscattered) asymptotic states can be defined (in contrast to the case of infinite-range (unscreened) Coulomb interaction) and standard methods of quantum scattering theory are applicable. In particular, perturbation expansions (for the Green operator, the transition operator or for the wave function) can be applied and are expected to provide a useful mean for description. This brings about a simplification in the treatment of scattering events within a dense electron gas as contrasted to the scattering theoretic treatment of few charged particle collisions. The above remarks give also a first hint that a direct comparison of the outcome of electronic collisions from pure-Coulombnic systems, e.g. atoms, and from an electron gas (e.g. *sp* metals) is to be made cautiously.

To follow up the above idea with calculations on real systems we envisage in this work the ionizing collisions of low-energy electrons from metallic clusters. This case is particularly interesting as the valence electrons of metal clusters can be modeled satisfactorily by an interacting electron gas and experimental studies on the inelastic electronic collisions do already exist. The proper account of such collisions is imperative for a precise estimate of the relaxation time [2] in clusters and hence is of importance for the understanding and description of transport properties.

For the calculations presented in this work we construct the bound states of the cluster by means of the non-local variable phase method [3, 4] and we calculate the total electron-impact ionization cross section from C_{60} by evaluating the transition matrix elements in first order perturbation theory with respect to the electron-electron interaction. We find a decisive effect of the screening length of the electron-electron interaction: The cross section increases monotonically for lower energies and then rather saturates at energies above 100 eV. For C_{60} the theoretical results are in reasonable agreement with the experiment at a screening length of 3 a.u. which is in accord with the predictions of Pines theory for the screening length in metals (see also Ref.[2]). The neglect of screening results in atomic like character of the cross section and is not supported by the experiment.

2. THEORETICAL METHODS

There is a number of experimental studies on the total and partial cross sections for the production of various charged cluster fragments upon inelastic electron scattering from metal clusters[5, 7]. Previous theoretical treatments are based either on a semi-empirical formula [8]

or on an additivity rule [6]. Recently Keller et al [9] report quantum mechanical calculations within the local-density approximation (of the density-functional theory) for the generation of the single-particle orbitals of the clusters. The scattering dynamics has been treated within the a plane-wave impulse approximation. The screening of the electron-electron scattering has not been taken into account. Nevertheless, in contrast to previous methods, the study of Keller et al [9] has some success in explaining the high energy behavior of the measured spectrum but fails evidently at low energies. In particular, it has not been possible to give a reasoning for to the absence of the pronounced peak in the total cross section as observed in the atomic case.

In this work we show that this behavior in metal clusters is due to the screening of the electron-electron interaction induced by the delocalized electrons. For a theoretic formulation we consider a monoenergetic electron beam with momentum $\mathbf{k}_0$ impinging onto a cluster in its ground state ϕ_j, the cluster is ionized and two electrons escape into the vacuum with momenta $\mathbf{k}_1$ and $\mathbf{k}_2$. The transition matrix element for this process reads (unless otherwise stated explicitly we use atomic units [a.u.])

$$T(\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2, \phi_j) = \langle \mathbf{k}_1, \mathbf{k}_2 | (1 + \mathrm{VG}) \mathrm{V}_{12} | \mathbf{k}_0, \phi_j \rangle. \quad (1)$$

Here $G = G_0 + G_0 V G$ is the total Green operator of the projectile-cluster system with the total potential V. The interaction potential between the projectile electron and the cluster electrons is designated V_{12}.

In this work we report on the calculation of the first order term of Eq.(1) which can be written as

$$\begin{aligned} T(\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2, \phi_j) &= \langle \mathbf{k}_1, \mathbf{k}_2 \, | \mathrm{V}_{12} | \, \mathbf{k}_0, \phi_j \rangle = \\ &= (2\pi)^{-3/2} \cdot \langle \mathbf{k}_0 - (\mathbf{k}_1 + \mathbf{k}_2) \mid \phi_j \rangle \, \langle \mathbf{k}_0 - \mathbf{k}_1 \mid \mathrm{V}_{12} \rangle \quad (2) \end{aligned}$$

The differential electron-impact ionization cross section is to be summed over ionization events from all the initial bound states accessible within the energy conservation law, i.e.

$$\frac{\mathrm{d}^6\sigma}{\mathrm{d}^3\mathbf{k}_1 \mathrm{d}^3\mathbf{k}_2} = \frac{(2\pi)^4}{k_0} \sum_j |T(\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2, \phi_j)|^2 \, \delta(E_0 - (\epsilon_j^{ion} + E_1 + E_2)). \quad (3)$$

As clear from Eqs.(2,3) an expression for the scattering potential V_{12} is needed for the calculation of the cross sections. Recently [2], there has been an attempt to estimate the importance of electron-electron collision for the relaxation in metal clusters. A crucial input for this estimation is the effective electron-electron cross section whose evaluation requires the knowledge of the screened electron-electron potential. To calculate

the latter the consideration has been restricted to the static screening and the screened potential have been computed. The results can be fitted well by a Yukawa potential with a screening length comparable to that known for metals (3 [a.u.] for sodium clusters). Thus we follow this work and assume for V_{12} the form

$$V(r_{12}) = \frac{\exp(-\lambda r_{12})}{\epsilon\, r_{12}}. \tag{4}$$

Here, ϵ is the dielectric function and the screening length is $1/\lambda$. For the present calculations we adopt $\epsilon = 1$. The Fourier components of the potential (4) are given by the form factor

$$V(|\mathbf{k}_1 - \mathbf{k}_0|) = \sqrt{\frac{2}{\pi}} \frac{1}{|\mathbf{k}_1 - \mathbf{k}_0|^2 + \lambda^2}. \tag{5}$$

The quantum states of the fulleren cluster are constructed within the Hartree-Fock approximation and within the spherical jellium model. The potential of C_{60}, which is a superposition of atomic potentials, is replaced by a simple model potential of a fulleren shell. This shell is formed by delocalized valence electrons that move within the potential well

$$V(r) = \begin{cases} V_0 & R - \Delta R < r < R + \Delta R \\ 0 & \text{elsewhere.} \end{cases} \tag{6}$$

Here, $R \approx 6.7\, a_0$ is the radius of the fulleren, the thickness of the shell is taken as $2\Delta R \approx 2\, a_0$ where a_0 is being the Bohr radius.

With this potential the bound state wave functions are calculated in the frame of the non-local variable phase approach [3, 4]. We developed the implementation of the latter formalism in order to use it for the case of non-spherical potentials in future.

We consider the scattering of a spinless particle with an energy $E = k^2$ and an orbital angular momentum ℓ subject to the nonlocal potential $V(r, r')$. The radial motion of this particle is described by the Schrödinger equation

$$\frac{d^2}{dr^2} u_\ell(r) + \left(k^2 - \frac{\ell(\ell+1)}{r^2} \right) u_\ell(r) = \int_0^\infty dr' V_\ell(r, r') u_\ell(r'). \tag{7}$$

In the variable phase approach one replaces the radial part $u_\ell(r)$ of the wave function by amplitude and phase functions $\alpha_\ell(r)$ and $\delta_\ell(r)$ according to the parameterization

$$u_\ell(r) = \alpha_\ell(r)\, F(\delta_\ell(r)) \tag{8}$$

$$du_\ell(r) = \alpha_\ell(r)\, dG(\delta_\ell(r)). \tag{9}$$

Here the functions F and G are given as

$$F(\delta_\ell(r)) = \cos\delta_\ell(r) j_\ell(kr) - \sin\delta_\ell(r) n_\ell(kr) \tag{10}$$

$$dG(\delta_\ell(r)) = \cos\delta_\ell(r) dj_\ell(kr) - \sin\delta_\ell(r) dn_\ell(kr). \tag{11}$$

In this way Schrödinger's second order differential equation transforms into a system of first-order Riccati-type differential equations

$$\begin{aligned} \frac{d}{dr}\delta_\ell(r) &= \left(-\tfrac{2}{k}\right) F^2(\delta_\ell(r)) \int_0^r dr' V(r,r') \exp\left[-\int_{r'}^r \frac{dG(\delta_\ell(r''))}{F(\delta_\ell(r''))}\right] \\ \frac{d}{dr}\alpha_\ell(r) &= \alpha_\ell(r) \frac{\sin\delta_\ell(r)\cdot j_\ell(kr) + \cos\delta_\ell(r)\cdot n_\ell(kr)}{F(\delta_\ell(r))} \frac{d}{dr}\delta_\ell(r). \end{aligned} \tag{12}$$

The Riccati-Bessel functions $j_\ell(kr)$ and $n_\ell(kr)$ are regular and irregular solutions of the free Schrödinger equation. For the local potential $\frac{1}{2}V(r) = \int_0^r V(r')\delta(r-r')dr'$, $\delta_\ell(r)$ and $\alpha_\ell(r)$ have clear physical interpretation: They are the asymptotic scattering phase and scattering amplitude of the wave function $u_\ell(r)$ of the cutoff (at the point r) potential.

The eigenenergies are calculated by finding the poles of the partial scattering amplitude in the imaginary half-axis of the wave vector $k = i\kappa$, (κ is pure real). The scattering amplitude is related to the scattering phase by the relation $f_\ell = \frac{1}{k} e^{i\delta_\ell} \sin\delta_\ell$ and is determined from the Volterra-type equation for f_ℓ

$$\begin{aligned} \frac{d(i\cdot f(r))}{dr} &= \left(-\frac{2}{\kappa}\right)\cdot \frac{1}{\beta^2} F^2(f(r)) \int_0^r dr' V(r,r') \times \\ &\times \exp\left\{\int_{r'}^r \frac{i\cdot f(r'')\cdot dq(\kappa r'') + \beta^2 dp(\kappa r)}{F(f(r''))}\right\} \quad ; \end{aligned} \tag{13}$$

$$F(f(r)) = i\cdot f(r)\cdot q(\kappa r) + \beta^2 p(\kappa r) \quad ,$$

where p_ℓ and q_ℓ are modified Riccati-Bessel functions of the real argument κr and $\beta = (i)^{\ell+1}$.

The initial condition for the integration is $f_\ell(r=0) = 0$.

Due to the spherical symmetry we have only 7 one-electron orbitals, the lowest five of these have the orbital momenta $0 \le \ell \le 4$ and the two highest occupied orbitals $0 \le \ell \le 1$. Each orbital is $2(2\ell+1)$ fold degenerate. All shells are closed and the total number of the electrons is equal to 60.

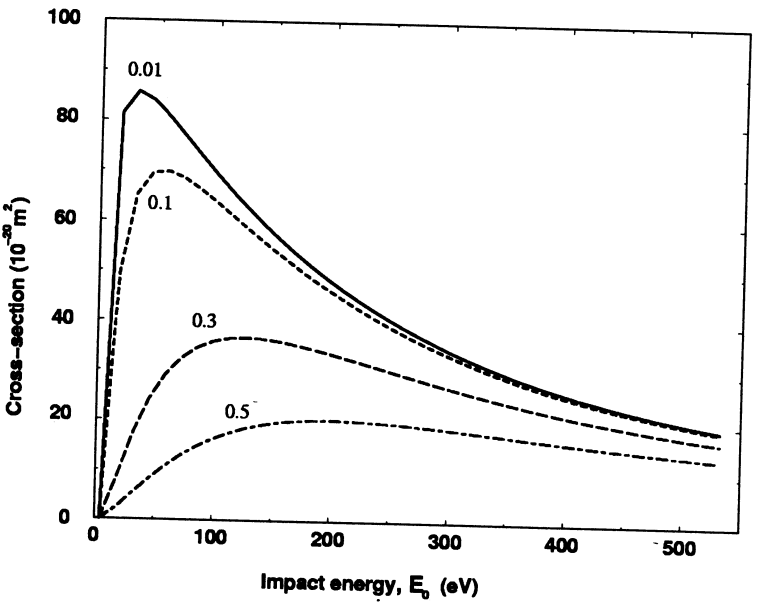

Figure 1 The total ionization cross-section for the electron scattering from C_{60} as function of the projectile energy $E_0\,[eV]$. The cross section is evaluated for various values of λ shown on the figures (cf. Eq.(4)). The screening length $1/\lambda$ is estimated to be $3\,a.u.$ in Ref.[2].

3. RESULTS AND DISCUSSION

In Fig.1 the results for the production of C_{60}^+ upon electron impact are shown for various values of the screening length $(1/\lambda)$. The biggest effect of screening is seen at lower electron energies. This can be understood from the form factor of the scattering potential (5). At lower impact energies E_0 the maximum momentum transfer q in Eq.(5) is on the order of $\sqrt{2E_0}$. Thus, for $\lambda \gg \sqrt{2E_0}$ the momentum-space potential V_{12} behaves as $\lim_{\lambda \gg \sqrt{2E_0}} V_{12} \rightarrow \frac{1}{\lambda^2}$ and hence is very much dependent on the value of λ, but otherwise is constant for a fixed value of λ. This explains the saturation effect of the cross section in Fig. 1(a). This behavior is in contrast to the atomic case where the cross section is dominated by events with small momentum transfer ($\lim_{\lambda \rightarrow 0} V_{12} \rightarrow \frac{1}{q^2}$, also compare the inset of Fig.2). At very high energies $E_0 \gg \lambda$ the maximum momentum transfer allowed is much larger than λ and hence the effect of screening diminishes at higher energies. For the case of extremely high screening $\lambda \rightarrow \infty$ we arrive at a hard-sphere-type electron-electron collision and the cross section is then constant.

Compared with the experiment (Fig.2) we see a remarkable agreement with the measured values of the cross section (on an absolute scale) when the screening length given in Ref.[2] is used. Obviously the neglect of screening yields the results of Ref.[9] and is at variance with the experimental data at low energies.

Moreover, in line with the above explanations, a vanishing screening leads to an atomic type-behavior of the cross section, as clearly seen by comparing the cross section for atomic carbon (inset of Fig.2) and for C_{60}. The semi-empirical model [8] fails to give a quantitative description of the measurement.

4. CONCLUSIONS

In this work we developed a quantum scattering theory for the description of the production of C_{60}^+ by electron impact. The cluster has been described on the basis of the Hartree-Fock method and within the variable-phase approach. The cluster potential has been modeled by the spherical jellium model. We calculated the transition matrix element within the first order perturbation theory with regard to the electron-electron interaction. The results shows a marked effect of screening on the measured cross sections. Furthermore, this effect can be explained on the basis of the Fourier components of the electron-electron interactions.

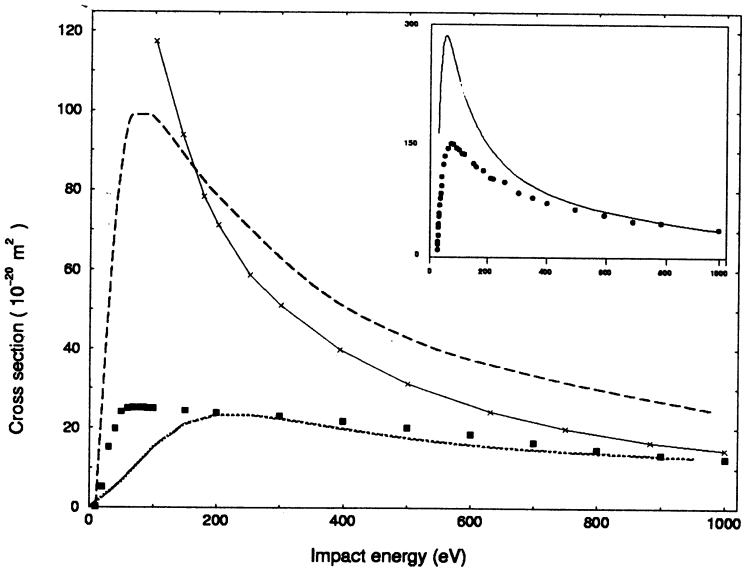

Figure 2 The total cross-section for production of C_{60}^{+} upon the impact of an electron impact with energy E_0 $[eV]$. The experimental cross-section (full dots) [5] are shown along with the result of semi-empirical model [8] (dashed line). The crosses present the calculations of [9](line is to guide the eye). Present results (dotted line) have been obtained using a screening length of $1/\lambda = 3a.u.$. Inset: Integrated cross-section for electron impact ionization of atomic carbon, multiplied by 60. Full symbols are the experimental data of Ref.[10], whereas the full curve is the calculation of Ref.[9].

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