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Response of metal clusters to elastic electron impact

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We perform a theoretical study of the response of neutral and ionized metal clusters to the elastic impact of slow electrons. We center our attention on Na_{40} and Na_{41}^+ closed-shell clusters. A phase-shift analysis is performed for both systems. The total cross section for the neutral cluster presents resonances related with the existence of quasibound states when studied as a function of incident energy. For the ionized cluster we show the calculated ratio of the angular distribution to the Rutherford differential cross section, near and far from a resonance. The existence of resonances as well as the associated energies are very sensitive to the mean interaction potential. As a consequence, elastic scattering of slow electrons on clusters could be a useful tool in the study of the electronic structure of clusters.

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I. INTRODUCTION

The understanding of how atomic and molecular properties evolve into the bulk solid is one of the motivations which has driven the research on metal clusters during recent years. Many experiments have addressed aspects of cluster physics such as cluster stability, ionization potentials, and plasmon resonances (see, e.g., [1]). The theoretical calculations of those magnitudes were successful in predicting and reproducing, within reasonable limits, the experimental measurements (see, e.g., [2]). Most of the theoretical descriptions of the electronic structure of metal clusters start from a shell model description of their valence electrons, in which the electrons move independently in an average potential. Based on this single particle scheme, magic numbers, ionization potentials, and plasmon resonance frequencies have been evaluated. The calculations are sensitive to the details of the average potential. More sophisticated theoretical calculations corroborate this independent particle picture [3–5].

In this paper we present an alternative way of gaining information on the average potential of clusters and other related properties, that is, by studying the scattering of electrons by metal clusters. Elastic collisions of slow electrons with neutral and ionized metal clusters, if performed, will yield information on the cluster structure, thereby providing information on size effects, as well as detailed information on the long and short range properties of the electron-cluster interaction.

The experimental study of electron-cluster collisions is difficult, mainly due to the very low signal of size-selected clusters in a molecular beam [6]. However, some experiments of low energy electron scattering on small metal clusters are being performed [7], encouraging us to investigate theoretically elastic scattering of slow electrons by metal clusters. For low incident electron energies, elastic dispersion will be the dominating process; at larger incoming energies, inelastic processes, such as ionization, fragmentation, mass and energy transfer, must be incorporated.

The first theoretical study of elastic electron scattering by clusters used a semiclassical approximation [8]. Recently we carried out a fully quantum mechanical study [9] of the neutral clusters Na_8 and Na_{20} by solving the scattering Schrödinger equation. Pure quantum mechanical effects, such as the appearance of resonances in the elastic cross sections (when studied as a function of the incident electron energy) have been obtained. These resonances correspond to quasibound states of the system. In this paper we apply the quantum mechanical treatment of Ref. [9] to the scattering of electrons by larger sodium clusters, not only neutral but also positively ionized. In this way, we treat systems which are easier to produce experimentally. The paper is organized as follows. In Sec. II, we review the formalism, whereas Sec. III is devoted to the presentation and discussion of the results obtained. Conclusions are collected in Sec. IV.

II. FORMALISM

Let V_{tot} be the local total effective potential between the incoming electron and the cluster. For closed-shell clusters this potential is usually assumed to be spherically symmetric and therefore we may use the partial wave expansion of the scattering wave function

$$\Psi = r^{-1} \sum_{\ell=0}^{\infty} u_\ell(k,r) P_\ell(\cos\theta) . \tag{2.1}$$

The radial equation to be solved for the partial wave u_ℓ is

$$\left\{\frac{d^2}{dr^2}+k^2-\frac{2\mu V_{tot}(\ell,r)}{\hbar^2}\right\}u_\ell(k,r)=0\ , \qquad (2.2)$$

where $k^2=2\mu E/\hbar^2$, E is the incident energy, and μ is the reduced electron mass.

The total effective potential between the incident electron and the target cluster should be evaluated through a many-body calculation and its more general expression is nonlocal in space and time. More elaborate calculations [3–5] indicate the validity of the quasiparticle picture, the main effect of the many-body effects being a sizable renormalization of the quasiparticle energies, without a significant change in the associated wave functions. In the following, we will not incorporate these many-body effects.

The total effective potential V_{tot} is given by

$$V_{tot}(\ell,r)=V(r)+V_{pol}+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\ . \qquad (2.3)$$

Here the mean field potential $V(r)$ is obtained in the *local density approximation* (LDA) to *density functional theory* (DFT), via the solutions of the Kohn-Sham equations for the target cluster [10]. The three main contributions to $V(r)$ are (i) a direct Coulomb term accounting for the interaction between the N valence electrons and the incident electron, (ii) a jellium contribution where the N_i ions of the cluster (N_i+1 in the case of the positive ionic cluster) are replaced by a uniform rigid background of positive charge, and (iii) the LDA exchange-correlation contribution. For neutral closed-shell clusters, due to the important screening effects between the first two contributions, the mean field arises mainly from the exchange-correlation terms which fall off exponentially with r. For positively ionized closed-shell clusters, the Coulomb cancellation is not complete, and the average potential will decay as $1/r$. The ionic background of the cluster is treated as a uniform sphere (for closed-shell clusters) of radius $R=a_0r_sN_i^{1/3}$, where a_0 is the Bohr radius, $r_s=4$ is the bulk Wigner-Seitz radius for sodium, and N_i is the number of atoms (ions) in the cluster.

According to the fact that neutral or ionic cluster targets are polarized by the electric field of the incoming electron, we introduce an additional second order term accounting for this effect [11] which behaves as $1/r^4$ at large distances. For this polarization potential we use the adiabatic approximation [12]

$$V_{pol}(r)=-\frac{\alpha e^2}{2(d^2+r^2)^2} \qquad (2.4)$$

where α is the static dipole polarizability of the cluster target and d a cutoff parameter which is of the order of the cluster size.

As mentioned before, many-body effects are not included here. Among them, dynamical corrections, which may lead to a small absorption, may be relevant at larger bombarding energies. We defer the study of these effects in these regimes to a future study.

To solve Eq. (2.2) we numerically integrate the wave function from $r=0$ up to a matching radius, where

$$u_\ell(k,r)\underset{r\to\infty}{\longrightarrow}H_\ell^{(-)}(k,r)+\exp(2i\Delta_\ell)H_\ell^{(+)}(k,r) \qquad (2.5)$$

with

$$H_\ell^{\pm}=\exp(\mp i\sigma_\ell)\{F_\ell\pm iG_\ell\}$$

and $\Delta_\ell=\sigma_\ell+\hat{\delta}_\ell$. F_ℓ and G_ℓ are the regular and irregular spherical Coulomb functions and σ_ℓ is the Coulomb phase shift. The additional phase shift $\hat{\delta}_\ell$ is due to the short range and polarization components of the potential. For the dispersion of electrons by neutral clusters, the functions F_ℓ and G_ℓ are replaced (within a factor $\rho=kr$) by the spherical Bessel functions j_ℓ and η_ℓ and a new phase shift $\Delta_\ell=\delta_\ell$ has to be determined.

The general scattering amplitude is $f(\theta)=f_c(\theta)+\hat{f}(\theta)$, where $f_c(\theta)$ is the Coulomb scattering amplitude and $\hat{f}(\theta)$ is given by

$$\hat{f}(\theta)=(2ik)^{-1}\sum_{\ell=0}^{\infty}(2\ell+1)\exp(2i\sigma_\ell)\times\{\exp(2i\hat{\delta}_\ell)-1\}P_\ell(\cos\theta)\ .$$

For the case of ionized clusters the expression to be evaluated is the ratio

$$\frac{(d\sigma/d\Omega)}{(d\sigma_{Ruth}/d\Omega)}=\left|1+\frac{\hat{f}(\theta)}{f_c(\theta)}\right|^2\ . \qquad (2.6)$$

Whereas for the ionized target the total cross section diverges, for the neutral case a simple expression can be found. One can write

$$\sigma_{tot}(k)=\frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell(k)\ . \qquad (2.7)$$

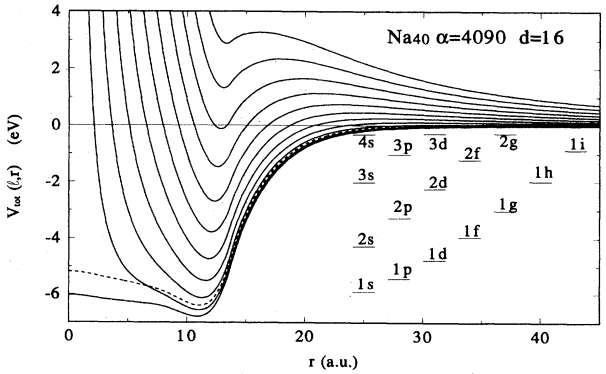

FIG. 1. Effective potentials for Na_{40} from $\ell=0$ up to $\ell=10$. The solid lines include the contributions from the mean field, the polarization, and the centrifugal term. The potential without the polarization correction is shown only for $\ell=0$ (dashed line). On the right-hand side of the figure, the single particle bound states are shown for the total potential (polarization included).

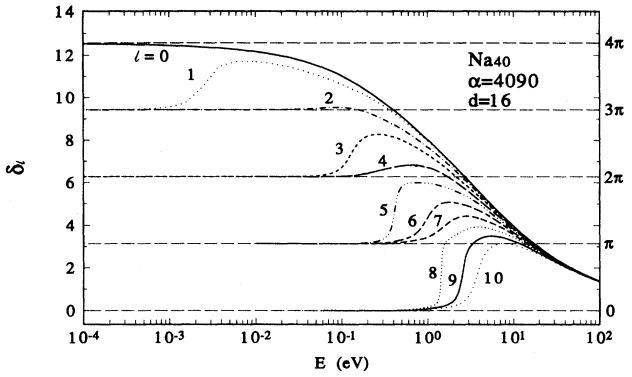

FIG. 2. Phase shifts from $\ell = 0$ up to $\ell = 10$ as a function of incident electron energy for the e^--Na_{40} system.

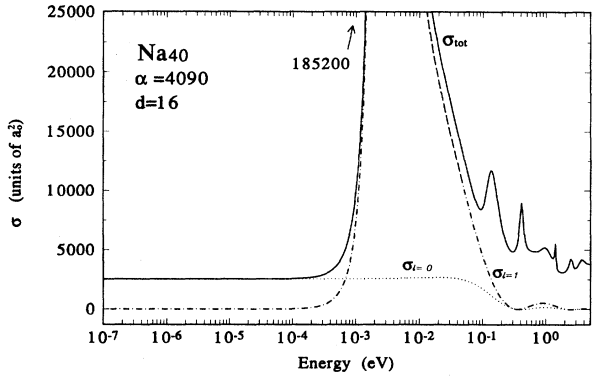

FIG. 4. Total elastic cross section for an extended range of very low incident energies for the e^--Na_{40} system. The figure shows the tendency $\sigma \to$ const when $E \to 0$.

This expression is only valid at low energies, when the phase shifts are real.

III. RESULTS

Figure 1 shows the calculated optical potential V_{tot}, which includes the centrifugal potential, from $\ell = 0$ up to $\ell = 10$, for the e^--Na_{40} system (solid lines). The dashed line gives the interaction potential without the contribution of the polarization term for $\ell = 0$. The value of the polarizability parameter α was taken from experimental results [13]. The remarkable feature is the existence of pockets for $1 \leq \ell \leq 10$ which lead to resonances in the cross sections when the incident energy approaches the energy of a metastable quasibound state. We display, in the same figure, the energies of all the bound states of the system for the mentioned potential (polarization included).

The phase shifts δ_ℓ are plotted in Fig. 2 for $\ell = 0$ up to 10 as a function of the incident energy. For large energies all the phase shifts tend towards zero (the large energy range was selected only to show these convergencies). For small energies the phase shifts approach $n_\ell \pi$, where n_ℓ is the number of bound states of the system for a given angular momentum ℓ (Levinson's theorem) [11].

A characteristic signature of an energy resonance is a rapid increment of the phase shift, over a small energy interval, by a magnitude equal to π. Figure 2 shows that a clear resonance is observed for $\ell = 8$ at $E_r \sim 1.45$ eV. This energy is slightly below the top of the barrier of the $\ell = 8$ effective potential.

The total elastic cross section for the e^--Na_{40} system is shown in Fig. 3 as a function of the energy of the impinging electron. We disentangle the partial contributions due to each angular momentum. The figure shows a rich structure which can be related to the behavior of the phase shifts. The above mentioned resonance at $E \sim 1.45$ eV manifests itself as a well defined peak. The total cross section also has bumps at $E \sim 0.15$ eV and at $E \sim 0.4$ eV. The first is due to a very wide quasistationary state for $\ell = 3$; the second arises from the $\ell = 5$ contribution. At a very low energy ($\sim 3 \times 10^{-3}$ eV), there is a peak in the cross section due to the $\ell = 1$ contribution. This bump, however, is not a resonance; it is due to the fact that a partial cross section always goes

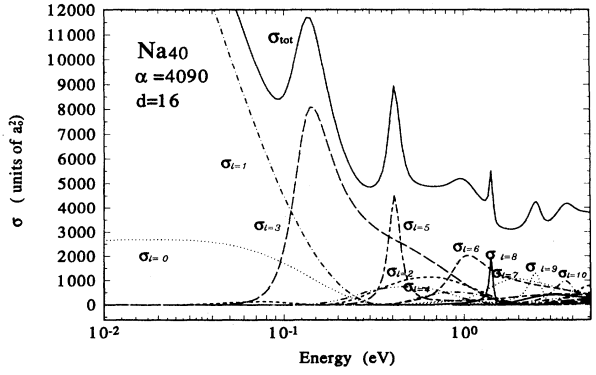

FIG. 3. Total and partial elastic cross sections as functions of the incident energy for Na_{40}.

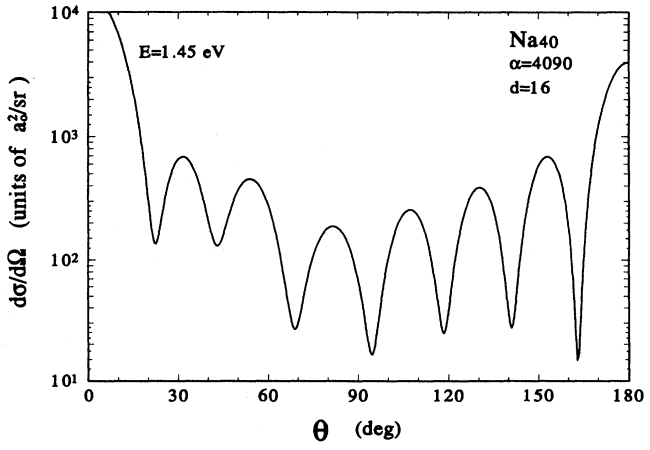

FIG. 5. Differential cross section for the system e-Na_{40} for the incident energy $E = 1.45$ eV.

through a maximum when the phase shift goes through a half integer of π (see Fig. 2). Finally, in Fig. 4 one can observe that, at very low energy ($E \sim 10^{-4}$ eV), the cross section approaches a constant value, only dependent on the $\ell = 0$ partial contribution.

The differential cross section ($d\sigma/d\Omega$) for a given energy also yields information about the resonances. In Fig. 5, the angular distribution for the e^--Na_{40} system is shown for $E = 1.45$ eV. As expected, the theoretical calculation displays minima which coincide approximately with the zeros of the $P_{\ell=8}$ Legendre polynomial (the distortion being due mainly to interference with $\ell = 6$ partial contribution). Thus the experimental observation of the angular distribution gives information about the angular momentum of the metastable state characterizing the resonance.

It can be argued that the polarization correction chosen is an *ad hoc* expression and that the value of the cutoff parameter d may influence the results. We have performed calculations in which this parameter was varied around 10% of the cluster radius. The results show small variations in the amplitude and positions of the peaks, retaining essentially the ℓ character and the position of the resonances.

In order to show the behavior of the total cross sections as a function of the size of the target cluster, we compare, in Fig. 6, the total cross sections for Na_8, Na_{20}, Na_{40}, and Na_{58} for the same region of incoming electron energies. The number of peaks (resonances) increases with increasing N_i and the ℓ value of the resonances also increases with N_i.

We concentrate our attention now on the dispersion of an electron by the ionized cluster Na_{41}^+ which constitutes the target of the collision. In Fig. 7 we display the mean field potential plus the centrifugal term. The main difference from neutral Na_{40} is the Coulomb tail referred to before. This long range attractive Coulomb term dominates at large distances and generates a deeper well inside the cluster. The potential still displays pockets, but for higher angular momenta than in the neutral case. In particular, for $8 \leq \ell \leq 11$ the figure displays the existence of barriers which may give rise to quasistationary states.

For the static dipole polarizability of Na_{41}^+ there are no direct experimental results available. Therefore we used $\alpha = 4330$ deduced from the experimental surface plasmon resonance frequency ω_r of Ref. [14] and the relation $\alpha = R^3(\omega_s/\omega_r)^2$ [15] where $R^3 = (a_0 r_s)^3 N$ and ω_s is the classical surface plasmon frequency (3.4 for

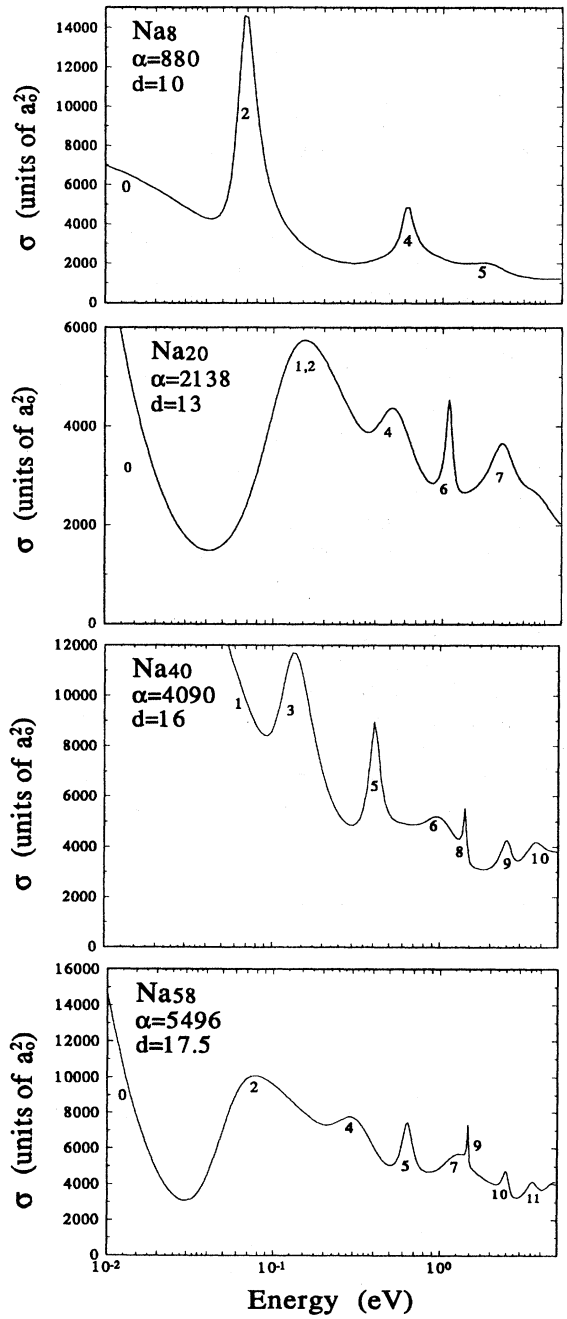

FIG. 6. Total cross sections for the systems e-Na_N with $N = 8, 20, 40, 58$ in the same region of incoming electron energies.

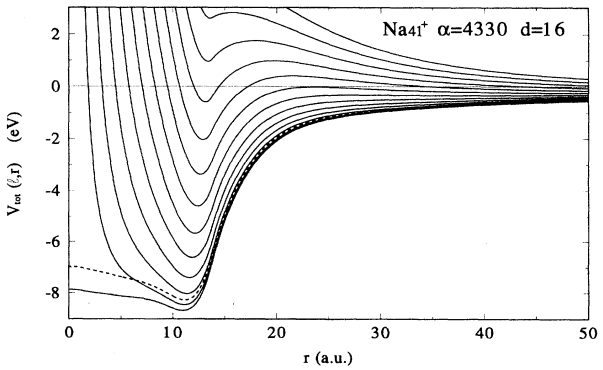

FIG. 7. Effective potentials for Na_{41}^+ for $\ell = 0$ up to $\ell = 12$. The contributions from the mean field, the polarization, and the centrifugal term are disentangled (solid lines). The potential without the polarization correction is shown only for $\ell = 0$ (dashed line).

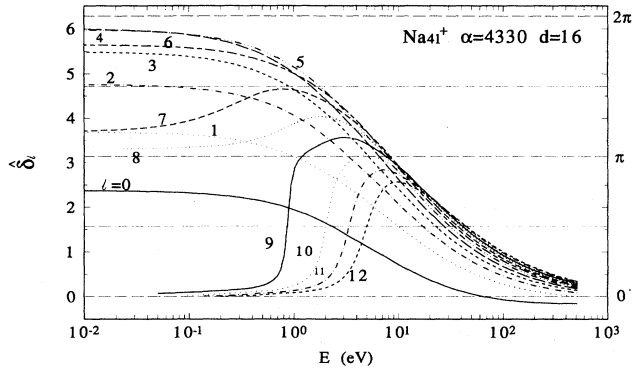

FIG. 8. Phase shifts for $\ell = 0$ up to $\ell = 12$, as a function of the incident electron energy, for the e^--$Na_{41}{}^+$ system.

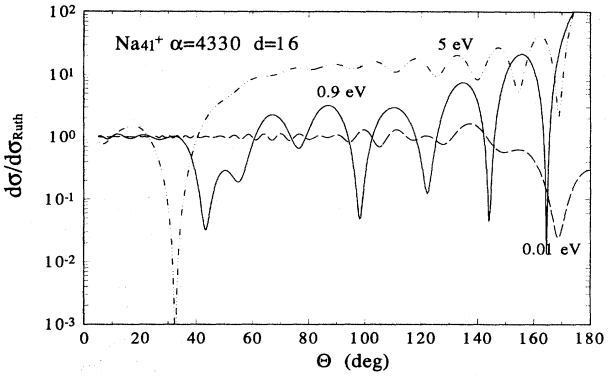

FIG. 9. Ratio of the elastic and Rutherford differential cross sections, $d\sigma/d\sigma_{Ruth}$, for incident energies near to and far from the $E = 0.9$ eV resonance.

Na). We have also computed the α value using the well known time-dependent local density approximation (TDLDA) within the spherical jellium model [16] obtaining $\alpha = 3175$. The corresponding TDLDA value for Na_{40} is $\alpha = 3328$. This value underestimates the experimental polarizability $\alpha = 4090$ by roughly 20%. Assuming that the TDLDA leads to similar deviations in the cation case, we corrected the theoretical results by the same amount, leading to the extrapolated value of $\alpha = 3900$. However, we would like to point out that, for $Na_{41}{}^+$, due to the dominance at large distances of the long range Coulomb over the polarization term, we find a very small dependence of the results on the value used for α in the range mentioned above.

We also note that what is truly relevant is that, for α, the screening of the external field is properly included, as is the case when we use either the experimental values or the extrapolated theoretical TDLDA results. Indeed, by neglecting screening, therefore allowing for an independent response of the valence electrons, we would overestimate the static polarizability by essentially one order of magnitude (in the jellium model, the independent particle static polarizability is 30 200 for Na_{40} and 29 650 for $Na_{41}{}^+$).

The phase shifts $\hat{\delta}_\ell$ for $\ell = 0$ to $\ell = 12$ are plotted in Fig. 8 as a function of the incident electron energy. For large energies the phase shifts approach zero, as in the case of neutral clusters, but the behavior for low energies differs since, for an attractive long range potential that decays as $1/r$, there exists no equivalent of Levinson's theorem.

For ionized clusters the total cross section diverges. However, resonances are observed when the differential cross section, divided by the Rutherford cross section, is plotted. As can be seen from Fig. 9, for an energy of 0.9 eV the ratio $d\sigma/d\sigma_{Ruth}$ has minima which approximately correspond to the zeros of the $P_{\ell=9}$ Legendre polynomial (despite some interferences with $\ell = 7$ and $\ell = 8$ terms). This is a manifestation of the $\ell = 9$ resonance that the system has at that energy (see also Fig. 8). Far from a resonance energy (for example, at 0.01 and 5 eV), the ratio of the cross sections shows no well defined structure.

IV. CONCLUSIONS

In this paper we have studied the elastic scattering of slow electrons by metal clusters, both neutral and singly ionized. Due to the occurrence of resonances, the total cross sections exhibit a marked structure when studied as functions of the energy of the incident electrons. These resonances are associated with quasibound states of the system which appear at specific values of the angular momentum. The positions and widths of these resonances depend sensitively on the average potential used in the calculation, thereby providing a useful tool to test experimentally the shell structure of valence electrons in clusters. We have also shown that the same kind of analysis can be extended to ionized clusters used as targets. In this case the asymptotic behavior of the partial wave function is a linear combination of regular and irregular Coulomb functions and the total cross section diverges. However, one can still obtain information on the resonance structure by measuring the differential cross section near a resonance energy. We have found that, as the cluster size increases, higher angular momenta contribute to the resonances, the cross section displaying a more pronounced structure.

The present method is expected to be accurate at low bombarding energies where the absorption of flux from the elastic channel is negligible. We believe that this study constitutes a good starting point for the analysis of elastic dispersion of electrons by metal clusters, and we hope to promote experiments in this field.

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