

LETTER TO THE EDITOR

(e, 2e) spectroscopy of atomic clusters

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Abstract. The potential of applying (e, 2e) spectroscopy to metallic clusters is discussed within the jellium model. It is shown that such experiments would allow the investigation of the analogy between cluster and nuclear structure. Distinct diffractive patterns in the state-selected triply differential ionization cross section as well as in the elastic channel reflect the effective cluster radius. Differences between the triply differential cross section for atomic systems and those for jellium spheres are expected even if the valence electron states are not energetically resolved.

The investigation of cluster properties by suitable experimental probes is one of the growing areas of cluster physics. For instance, a wealth of information on the electronic density of states $\rho(E)$ has been obtained using photoelectron spectroscopy (see, for example, the contributions to chapter 4 of Haberland (1995)). A number of authors (Wassermann and Ekardt 1991, Bernath *et al* 1996, Kroneisen *et al* 1996, Spinella *et al* 1996, 1997) have suggested using *low*-energy elastic and inelastic electron scattering as a tool to determine effective single-particle properties of clusters, which can be extracted from the resonant structure of the cross section.

We suggest considering (e, 2e) spectroscopy (see McCarthy and Weigold 1988, Coplan *et al* 1994 and references therein) as a suitable tool to investigate, for instance, the momentum density $\rho(\mathbf{q})$ (i.e. the modulus squared of the bound-state wavefunction in the momentum representation) of the cluster ground state. For ionization processes induced by *high*-energy electrons (so that first-order perturbation theory is applicable and all continuum electrons can be represented by plane waves) the triply differential cross section in a kinematically complete experiment can be shown to factorize into a kinematical prefactor K and the momentum density of the ionized electron in its initial state $|\psi\rangle$:

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE} = K(\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2) |\langle \mathbf{q} | \psi \rangle|^2 = K(\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2) \rho(\mathbf{q}) \quad (1)$$

where $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_1 - \mathbf{k}_2$ is the recoil momentum, expressed in terms of the initial and final asymptotic momenta \mathbf{k}_i .

It is well known that that high-energy impact ionization of a cluster will most likely lead to fragmentation. In addition, integrated cross sections will be dominated by inner-shell events. The ionization by fast electrons is, however, very sensitive to the initial state in the sense that energy- and angle-resolved detection of both electrons allows the isolation of contributions from individual shells. Therefore neither of the objections, alluded to above, precludes the application of (e, 2e) spectroscopy to clusters.

In this letter we present a first set of calculated $(e, 2e)$ triply differential cross sections with the aim of assessing the potential of $(e, 2e)$ spectroscopy for clusters. Rather than basing the calculation on the simple relation indicated in equation (1), we use the first Born approximation (see e.g. Byron and Joachain 1989 and references therein), in which the projectile states are taken to be plane waves, while the target bound state and ejected electron wavefunctions are determined as solutions of the Schrödinger equation with a suitable effective potential. The effective potentials used for the present investigation of sodium clusters are obtained via the Kohn–Sham approach (see Dreizler and Gross 1990 and references therein) on the basis of the standard (spherical) jellium model of the valence electrons (for a review, see e.g. Brack 1993, Alonso and Balbás 1996). Exchange effects are

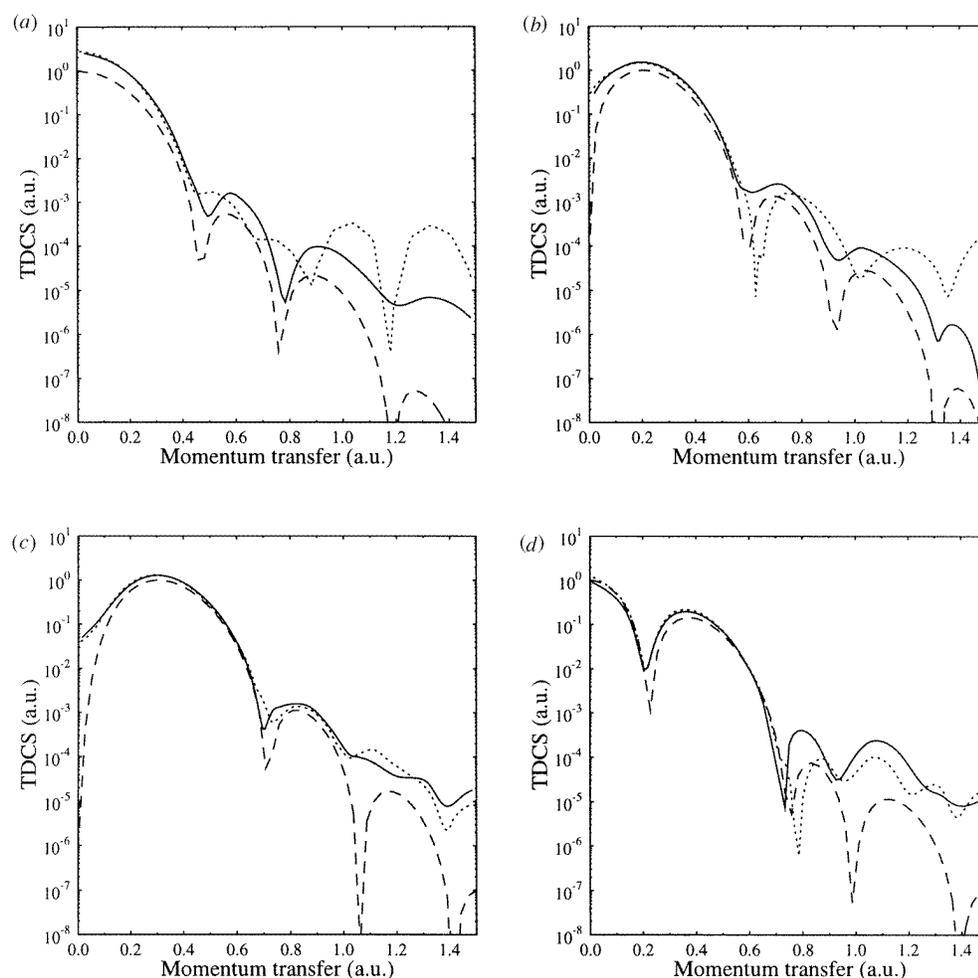


Figure 1. Triply differential cross sections (TDCS) for ionization of jellium sphere states corresponding to Na_{21}^+ , as a function of recoil ion momentum (au). Impact energy 1250 eV, fast outgoing electron energy 1000 eV, fast outgoing electron observation angle -26.24° . Full curve, calculated TDCS (au) for Na_{21}^+ ; dotted curve, calculated TDCS (au) for Na_{20} ; broken curve, momentum density of corresponding bound state (normalized). (a) 1s orbital; (b) 1p orbital; (c) 1d orbital; (d) 2s orbital.

treated exactly via the optimized potential method (OPM) (Engel and Vosko 1994), while correlation effects are accounted for in the local density approximation. We have chosen the closed-shell cation Na_{21}^+ as a test case because recent experimental results (Ellert *et al* 1997) indicate that this system is the smallest sodium cluster whose electronic response can reasonably be described in terms of the jellium model. Results for the isoelectronic neutral cluster Na_{20} are also presented.

In figure 1, we show the calculated triply differential cross sections for a typical coplanar asymmetric geometry suitable for (e, 2e) spectroscopy for the 1s, 1p, 1d and 2s manifolds, respectively, along with the momentum densities $\rho(q)$ of the corresponding effective one-particle orbitals. The scattering angle has been chosen such that the Bethe ridge condition $q = 0$ can be satisfied for the calculated OPM binding energy of the sodium atom valence electron (0.2012 Hartree). Figure 1 demonstrates clearly the principle of (e, 2e) spectroscopy discussed above. The prominent oscillatory structures are readily understood in terms of the fact that the orbitals are essentially localized on the jellium background, so that their

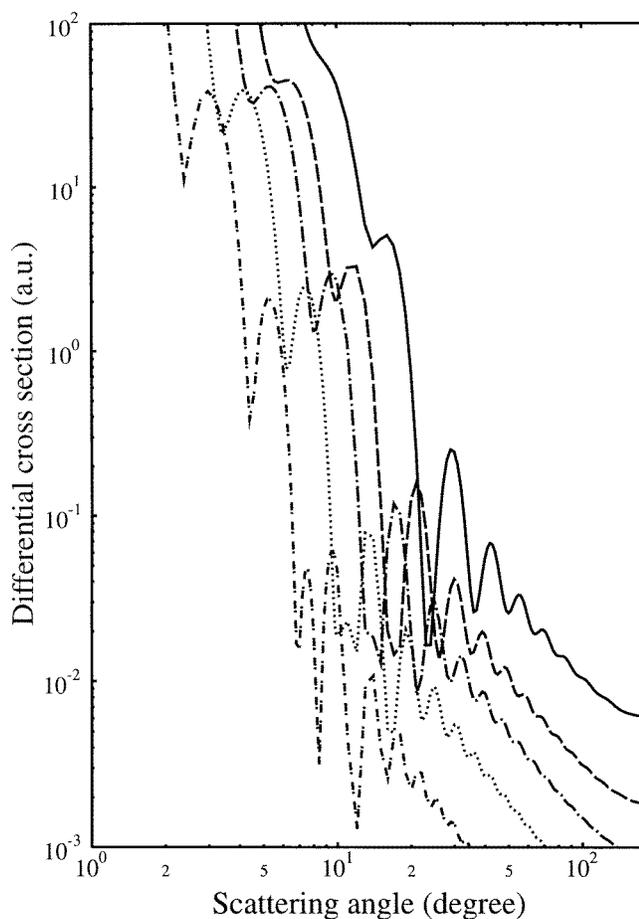


Figure 2. Differential cross section (in au) for elastic electron scattering from a Na_{20} jellium sphere, as a function of scattering angle. Full curve, 100 eV; long-broken curve, 200 eV; long-chain curve, 300 eV; dotted curve, 500 eV; short-chain curve, 1000 eV.

Fourier transforms are characterized by the scale parameter π/R , where R is the jellium sphere radius. Similar structures are known from the (e, ep) nuclear reaction (Leuschner *et al* 1994 and references therein). Indeed, the striking similarity between atomic clusters and nuclear systems with respect to the effective one-particle potential which is characterized by an intrinsic length scale, has stimulated numerous investigations (Schmidt *et al* 1992). The results in figure 1 indicate that (e, 2e) spectroscopy of clusters is a possible means of studying the cluster–nucleus analogy in detail by comparing the effective single-particle orbitals. Moreover, observation of the diffractory oscillations would obviously allow us to determine the effective cluster radii experimentally. In fact, there are numerous possible ways of measuring cluster radii via oscillations in Fourier space, e.g. in the differential elastic scattering cross section at high energies (Connerade and Solov'yov 1995), as is well known from nuclear physics (Hofstadter 1957) and exemplified by figure 2, or the total photoionization cross section (Frank and Rost 1996, 1997).

Figure 1 also shows that at larger momentum transfers, the calculated TDCS fall off more slowly than the bound-state momentum profile, and that the oscillations tend to be washed out. The apparent breakdown of the simple argument given above is due to the long-range Coulomb asymptotics of the effective potentials. These observations illustrate that (e, 2e) spectroscopy is particularly suited to studying the small- q behaviour of wavefunctions. Notwithstanding the different physical situations modelled, the results for Na_{20} and Na_{21}^+ are in remarkably close agreement in the region of the binary maximum. One may thus conclude that the results of model calculations for neutral systems may be transferred to the experimentally relevant charged cluster case. It should be noted that the Na_{20} potential used here has the correct asymptotic $-1/r$ behaviour. The question of whether the short-range

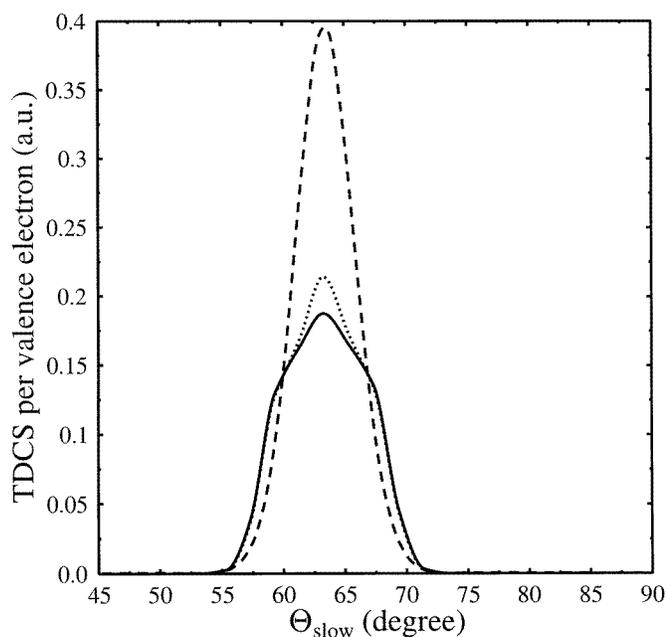


Figure 3. Triply differential cross section (in au) per valence electron for electron impact ionization of a Na_{21}^+ jellium sphere (full curve), a Na atom (broken curve) and a Na_{20} jellium sphere (dotted curve), as a function of slow electron observation angle. Kinematics are as in figure 1.

LDA potential (without the latter correction), conventionally used in jellium model studies of electron cluster scattering processes, is adequate, will be discussed elsewhere.

The eigenvalues of a jellium sphere typically differ by 0.5 eV. While it is certainly possible to resolve such energy splittings in (e, 2e) coincidence experiments (see, for example, Guo *et al* 1996), the demand for high-energy resolution will be inconvenient in first-generation cluster (e, 2e) experiments due to the associated lower count rates. It is therefore of interest to consider the triply differential cross section for the summed ionization probability due to all valence electrons. In figure 3, we compare the sum of the cross sections of figure 1, scaled to the total number of valence electrons, with the result obtained for the 3s state of atomic sodium. The results show that the maximum jellium sphere TDCS are significantly smaller than the atomic ones, and that the cross section function is broader than in the atomic case. While it is clearly inappropriate to make any more general statement on the basis of these data, it is evident that significant discrepancies between atomic and jellium sphere TDCS are to be expected even if the individual valence electron levels of the cluster are not energetically resolved. It is also worth noticing that the calculated TDCS are of the same order of magnitude, and thus not prohibitively small for the cluster case.

To date, electron scattering is used mainly to prepare excited or ionized clusters with the aim of analysing the subsequent decay processes, though a number of total ionization cross section and electron energy loss measurements have also been carried out for van der Waals clusters (Lezius and Märk 1989, Burose *et al* 1991) and fullerenes (Dünser *et al* 1995, Burose *et al* 1993). The strong interaction between electron and cluster (in comparison to photon and cluster) has generally been considered to render electrons unsuitable as a spectroscopic probe. However, our present considerations show that by using sufficiently fast electrons and applying coincidence techniques, this handicap could be overcome. This would make the study of differential cross sections for fast electron elastic and inelastic scattering from clusters a very challenging, but also potentially very rewarding new subfield of cluster physics.

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