# Surface- and volume-plasmon excitations in electron inelastic scattering on metal clusters

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In this work we treat inelastic scattering of fast electrons on metal clusters in the range of transferred energies above the ionization threshold. We demonstrate that in this energy range many-electron collective excitations, namely, the volume plasmons, provide dominating contribution to the differential cross section resulting in its resonance behavior. The volume-plasmon resonances excited in the cluster during the collision decay via the ionization process. We determine the resonance frequency and the autoionization width of the volume plasmon excitations. In order to elucidate the role of plasmon excitations, we calculate the differential cross section of the process using two different approaches. We calculate the cross section in the random-phase approximation using the Hartree-Fock wave functions as a basis and accounting simultaneously for all single-particle and collective excitations in the cluster. We compare the results of this approach with those obtained in the plasmon resonance approximation.

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## I. INTRODUCTION

In this paper, we study the role of collective electron excitations in the formation of inelastic scattering cross sections of fast electrons on metallic clusters in the range of transferred energies above the ionization threshold. There are two types of collective electron excitations in metal clusters known as the surface and volume plasmons. Resonance frequencies of surface plasmons are typically lower than the ionization potential of a cluster, while the resonance frequencies of volume plasmon modes are above the ionization threshold. In the present paper, our attention is devoted mainly to volume plasmon excitations, because they are essential for the formation of the electron impact ionization cross section of metal clusters.

Surface plasmon excitations are well-known in atomic cluster physics. The dipole surface plasmons are responsible for the formation of giant resonances in photoabsorption spectra of metal clusters, see, e.g., [1–8]. They also play an important role when considering inelastic collisions of charged particles with metal clusters [9–13]. In the inelastic scattering process the plasmon excitations with higher angular momenta $l>1$ become essential. The role of surface plasmon excitations in inelastic electron-cluster scattering was thoroughly studied in our previous papers [11–13]. It was demonstrated that collective excitations provide significant contribution to the electron energy loss spectrum (EELS) in the region of the surface plasmon resonance. With increase of the scattering angle, the plasmon excitations with higher angular momenta become more probable. The main contribution to the partial cross section corresponding to the angular momentum $l$ arises from impact parameters about $R/l$, where $R$ is the cluster radius. This condition reflects the trivial fact that the probability of excitation of a surface plasmon mode is maximal when the characteristic collision distance is about the wavelength of surface plasmon. At higher scattering angles, the broad maximum arises in the EELS in the region of transferred energies well above the ionization potential. This was noticed first by [10], when calculating the cross sections of electron inelastic scattering on metal clusters in the time-dependent local density approximation (TDLDA), and was ascribed to the volume plasmon excitation.

The first calculation of the electron impact ionization of metal clusters has been performed by [14] in the local density approximation (LDA). This work was devoted to the investigation of the diffraction behavior of the differential ionization cross section. Independently, the similar diffraction phenomena have been described in [11,13] both for elastic and inelastic collisions of electrons with metal clusters. In [14] the ionization process has been considered at energies of the projectile and ionized electrons much larger than the energy of cluster electrons. In this energy region one can neglect the many-electron interaction responsible for the formation of the plasmon oscillations. In the present paper we investigate collisions at lower energies and demonstrate that in this case the plasmon oscillations play an essential role in the ionization process. Therefore, the correct description of the process implies the proper treatment of the many-electron correlations in a cluster.

Calculation of the EELS based on the random-phase approximation with exchange (RPAE) simultaneously takes into account all collective and single-particle excitations in the cluster. In order to elucidate the role of collective excitations in the formation of the EELS we compare the EELS calculated using two different methods. We calculate the inelastic differential cross section in the RPAE with the jellium

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model Hartree-Fock wave functions used as a basis. We perform also the calculations in the plasmon resonance approximation, accounting for collective electron excitations only.

We have applied the similar approach studying the role of surface plasmon excitations in the formation of the EELS on metal clusters [12,13]. Comparison of the RPAE results with those obtained from the plasmon resonance approximation demonstrated that the excitation of surface plasmons in a cluster provides dominating contribution to the differential inelastic scattering cross section in the vicinity of the plasmon resonance. However, in the energy region above the ionization potential, the RPAE cross sections systematically surpassed those derived from the plasmon resonance approximation. In this region of transferred energy, the discrepancy between two approaches arose in each partial contribution of the EELS. These numerical results allowed us to assume that the discrepancy is connected with the ionization process that occurs via the volume plasmon excitations. In this process the projectile electron excites volume plasmon oscillations in the target cluster, which afterward decay via the ionization.

The main goal of the present paper is to prove this assumption and to clarify the role of the volume plasmon excitations in the electron impact ionization of metal clusters. For this purpose we have performed the RPAE calculations of the differential EELS and alternatively calculated the ionization cross section in the plasmon resonance approximation. This approximation leads to a simple analytic description of the cluster collective dynamic response, which for example reproduces well enough the main features of the electron inelastic scattering process on clusters in the vicinity of the surface plasmon resonance [12,13]. The advantage of this approach compared to the pure numerical RPAE calculation consists of the posibility to separate the contributions of collective and single-particle excitations. Analogously, the comparison of the EELS derived from the RPAE calculation with the ionization cross section obtained in the plasmon resonance approximation demonstrates which part of the EELS is formed via the ionization channel of the electron inelastic scattering process. Such a comparison performed in this work shows that in collisions taking place via the volume plasmon excitation, the ionization process provides the main contribution to the EELS. This fact leads us to the conclusion that the ionization of the cluster is the main mechanism of damping for the volume plasmons.

In this paper we determine also the autoionization width of the volume plasmon resonance. Let us note that the evaluation of widths of plasmon resonances is one of the fundamental problems in atomic cluster physics. This problem had been solved for surface plasmons [15–17]. For volume plasmon excitations we solve the problem. In general, the width of plasmon resonance is formed via the Landau damping mechanism, i.e., via the decay of the collective excitations to the single-particle ones. However, there is an important difference between damping of the surface plasmons in metal clusters and the Landau damping well-known in plasma physics, because the resonance frequencies of surface plasmons are smaller than the ionization potential of the cluster. Single-particle excitations in the region of surface plasmon resonances have the discrete spectrum. In this case the plasmon resonance width determines the energy region where the collective excitation spreads over the single-particle ones. The cluster excitation spectrum remains discrete if one does not take into account coupling of the electron and the ion motion [18–24]. According to these papers the electron excitation linewidth in the vicinity of the surface plasmon resonance originating from the electron-ion coupling is about $\Gamma \sim 0.2$ eV.

Contrary to surface plasmons, the resonance frequency of volume plasmons in metal clusters is higher than the ionization potential. Therefore, volume plasmons can decay via the ionization process. It will be shown that volume plasmon width connected with the ionization process is considerably larger than the width originating from the electron-ion coupling. Also, it is worth noting that the number of the volume plasmon modes in a cluster is larger than the number of the surface ones and that all the volume plasmons have the same resonance frequency. These facts result in the strong dependence of the effective electric potential created by volume plasmons upon the kinematics of the collision. In such circumstances, methods of the plasmon width evaluation used in the earlier papers for the surface plasmons are inapplicable. In this paper we suggest an approach for the plasmon width determination. This approach allowed us to determine the volume plasmon resonance width and also to reproduce the expression for the width of the surface plasmon resonance, which was obtained in the earlier papers by other methods.

The paper is organized as follows. In Sec. II, we briefly outline our approach for the description of the fast electron-cluster collision, which is based on the Hartree-Fock jellium model and the RPAE. A more detailed description of this method was given in our previous works [12,13]. In Sec. III, the plasmon resonance approximation is outlined and the expression for the plasmon resonance width is derived. In Sec. IV, we compare the results obtained by the two methods in the case of a 50 eV electron collision with the $Na_{40}$ cluster. The atomic system of units $m_e = |e| = \hbar = 1$ is used throughout the paper.

## II. RANDOM PHASE APPROXIMATION WITH EXCHANGE

The differential cross section for the electron inelastic scattering on a metal cluster is equal to

$$d^4\sigma = \frac{2\pi}{v}\left|\frac{4\pi}{q^2}\left\langle \Psi_f \left| \sum_a e^{i\mathbf{q}\cdot\mathbf{r}_a} \right| \Psi_i \right\rangle\right|^2 \times \delta\left(\frac{\mathbf{p}'^2}{2} + \varepsilon_f - \frac{\mathbf{p}^2}{2} - \varepsilon_i\right) df \frac{d\mathbf{p}'}{(2\pi)^3}. \quad (1)$$

Here $\mathbf{p}$ and $\mathbf{p}'$ are the initial and the final momenta of the projectile electron, indexes $i$ and $f$ denote the initial and the final states of the cluster, $\varepsilon_i$ and $\varepsilon_f$ are their energies respectively, $\mathbf{r}_a$ are the coordinates of the delocalized electrons in the cluster, $\mathbf{q} = \mathbf{p}' - \mathbf{p}$ is the transferred momentum, the wave functions $\Psi_i$, $\Psi_f$ are the many-electron wave functions of

the initial and final states of the cluster, respectively. The cross section (1) has been obtained in the Born approximation, which is valid for projectile electrons with energies much larger than the cluster ionization potential.

Performing multipole expansion of matrix elements in Eq. (1), we derive the following expression for the differential cross section:

$$\frac{d^2\sigma}{d\varepsilon' d\Omega} = \frac{p'}{\pi p} \sum_{lm} \int \left| \left\langle \Psi_f \left| \sum_a V_{lm}(\mathbf{r_a}) \right| \Psi_i \right\rangle \right|^2 \times \delta\left( \frac{\mathbf{p}^2}{2} - \frac{\mathbf{p'}^2}{2} - \omega_{fi} \right) df. \quad (2)$$

Here $\varepsilon' = \mathbf{p'}^2/2$ is the excitation energy, $\omega_{fi} = \varepsilon_f - \varepsilon_i$, and integration over $df$ implies the summation over the discrete spectrum and the integration over the continuous spectrum of the final states of the cluster.

The partial contribution of the potential of the projectile electron is

$$V_{lm}(\mathbf{r}) = 4\pi/q^2 j_l(qr) Y_{lm}(\mathbf{n}), \quad (3)$$

where $l$ and $m$ are the angular momentum and its projection respectively, $j_l$ is the spherical Bessel function. In the present paper, we only consider the spherical clusters having all electron shells closed and also the zero total angular momentum of the ground state $\Psi_i$. In this case, contributions of different multipolarity do not interfere in the cross section (2).

Calculation of the inelastic cross section (2) has been performed in the RPAE, using the Hartree-Fock jellium model wave functions as the basis functions [25,26,11]. Transition amplitude between the ground state $\Psi_i$ and the excited state $\Psi_f$, can be expressed in the RPAE as a linear combination of the single-particle matrix elements

$$\langle \Psi_f | \sum_a V_{lm}(\mathbf{r_a}) | \Psi_i \rangle = \sum_{\nu\mu} [X^{fi}_{\nu\mu} \langle \psi_\nu | V_{lm}(\mathbf{r}) | \psi_\mu \rangle + Y^{fi}_{\nu\mu} \langle \psi_\mu | V_{lm}(\mathbf{r}) | \psi_\nu \rangle]. \quad (4)$$

The single-particle wave functions $\psi_\nu$ in Eq. (4) are the solutions of the system of coupled nonlinear integrodifferential Hartree-Fock equations [25–27]

$$\left( \frac{\hat{p}^2}{2} + U + V_{HF} \right) \psi_\nu = \varepsilon_\nu \psi_\nu, \quad (5)$$

where $U$ is the potential of the positively charged ionic background and $V_{HF}$ is the nonlocal potential of the HartreeFock inter-electron interaction.

The forward-going, $X^{fi}_{\nu\mu}$, and the backward-going, $Y^{fi}_{\nu\mu}$ amplitudes in Eq. (4) are the solutions of the RPAE equation

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X^{fi} \\ Y^{fi} \end{pmatrix} = \omega_{fi} \begin{pmatrix} X^{fi} \\ -Y^{fi} \end{pmatrix}, \quad (6)$$

where the matrixes $A$ and $B$ are defined as follows:

$$A_{\nu\rho,\sigma\mu} = (\varepsilon_\nu - \varepsilon_\rho)\delta_{\rho\mu}\delta_{\nu\sigma} + \left\langle \psi_\nu \psi_\mu \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \psi_\rho \psi_\sigma \right\rangle,$$

$$B_{\nu\rho,\sigma\mu} = \left\langle \psi_\nu \psi_\sigma \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \psi_\rho \psi_\mu \right\rangle.$$

Here $\langle \psi_\nu \psi_\mu | 1/|\mathbf{r}-\mathbf{r}'| | \psi_\rho \psi_\sigma \rangle$ is the matrix element of the residual interelectron interaction, which contains the direct and the exchange terms.

The more detailed description of the RPAE method employed for the calculation of the inelastic scattering cross section in collisions of electrons with metal clusters is given in our previous papers [12,13].

## III. PLASMON RESONANCE APPROXIMATION

The RPAE calculation of the inelastic scattering cross section simultaneously takes into account all single-particle and collective electron excitations in the cluster. In order to perform the analyses of the role of collective electron excitations in the formation of inelastic scattering cross sections, we have described the electron impact ionization process in the plasmon resonance approximation [15,11]. In this approximation, the dynamic response of the cluster on the electric field of the projectile is described analytically in an approach relying on the smallness of interatomic distances in comparison with the cluster radius $R$.

The cross section (2) can be expressed via the variation of the electron density of the cluster $\delta\rho(\mathbf{r})$ under the action of the external electric field $V_{lm}(\mathbf{r})$:

$$\frac{d^2\sigma}{d\varepsilon' d\Omega} = \frac{1}{\pi^2} \frac{p'}{p} \sum_{lm} \int V_{lm}(\mathbf{r}) \, \mathrm{Im}\{\delta\rho_{lm}(\mathbf{r})\} d\mathbf{r} \quad (7)$$

using the relationship

$$\mathrm{Im}\{\delta\rho_{lm}(\Delta\varepsilon, \mathbf{r})\} = \pi \int \langle \Psi_i | \sum_a \delta(\mathbf{r}-\mathbf{r_a}) | \Psi_f \rangle \langle \Psi_f | \sum_a V_{lm}(\mathbf{r_a}) | \Psi_i \rangle \times \delta(\Delta\varepsilon - \omega_{fi}) df, \quad (8)$$

where $\Delta\varepsilon = \mathbf{p}^2/2 - \mathbf{p'}^2/2$ is the transferred energy. In the plasmon approximation $\delta\rho_{lm}(\Delta\varepsilon, \mathbf{r})$ can be calculated as a response of a dielectric sphere, having the dielectric permeability $\epsilon = 1 - \theta(R-r)\omega_p^2/\omega^2$ [15]:

$$\delta\rho_{lm}(\Delta\varepsilon, \mathbf{r}) = \frac{\omega_p^2}{\Delta\varepsilon^2 - \omega_p^2 + i\Delta\varepsilon\Gamma_{vl}} j_l(qr)\theta(R-r)Y_{lm}(\mathbf{n}) + \left( (2l+1) \frac{\omega_l^2}{\Delta\varepsilon^2 - \omega_l^2 + i\Delta\varepsilon\Gamma_{sl}} \frac{j_l(qR)}{q^2 R} - \frac{\omega_p^2}{\Delta\varepsilon^2 - \omega_p^2 + i\Delta\varepsilon\Gamma_{vl}} \frac{j_{l+1}(qR)}{q} \right) \times \delta(r-R) Y_{lm}(\mathbf{n}) \quad (9)$$

where $\omega_p=\sqrt{3N_e/\alpha}$ is the volume plasmon resonance frequency, $\omega_l=\sqrt{l/(2l+1)}\omega_p$ is the frequency of surface plasmon excitation with the angular momentum $l$, $N_e$ is the number of delocalized electrons, $\alpha$ is the static polarizability of the cluster, and $\Gamma_{vl}$ and $\Gamma_{sl}$ are the widths of the volume and surface plasmon resonances, which are defined below. Note that volume plasmon excitations with different angular momenta have the equal resonance frequency $\omega_p$.

Substituting Eq. (9) to Eq. (7), we obtain the inelastic scattering cross section in the plasmon resonance approximation:

$$\frac{d^2\sigma}{d\varepsilon' d\Omega}=\frac{4p'R}{\pi pq^4}\sum_l (2l+1)^2 j_l^2(qR)\frac{\omega_l^2\Delta\varepsilon\Gamma_{sl}}{(\Delta\varepsilon^2-\omega_l^2)^2+\Delta\varepsilon^2\Gamma_{sl}^2}$$
$$+\frac{2p'R^3}{\pi pq^2}\sum_l (2l+1)\frac{\omega_p^2\Delta\varepsilon\Gamma_{vl}}{(\Delta\varepsilon^2-\omega_p^2)^2+\Delta\varepsilon^2\Gamma_{vl}^2}$$
$$\times\left(j_l^2(qR)-j_{l+1}(qR)j_{l-1}(qR)\right.$$
$$\left.-\frac{2}{qR}j_{l+1}(qR)j_l(qR)\right). \quad (10)$$

This cross section is totally determined by collective electron excitations in the cluster. The first and the second terms in Eq. (10) describe contributions of the surface and the volume plasmon excitations, respectively.

Now let us determine the widths of plasmon resonances. Damping of the plasmon oscillations is connected with the decay of the collective electron excitations to the single-particle ones similar to the mechanism of Landau damping in infinite electron gas. Frequencies of the surface plasmon excitations usually lie below the ionization threshold. Therefore single-particle excitations in the vicinity of the surface plasmon resonance have the discrete spectrum. In this case the width of a surface plasmon excitation caused by the Landau damping should be treated as the width of the distribution of the oscillator strengths in the vicinity of the resonance. The problem of the formation of the surface plasmon resonance width has been intensively studied during past years [15–17]. Thus in the present paper we pay the most attention to the width formation of volume plasmons. The resonance frequencies of volume plasmons are above the ionization threshold. This means that the volume plasmon excitations are quasistable. They have the real channel of the Landau damping leading to the ionization of the cluster. The process of inelastic scattering in the region of transferred energies above the ionization threshold can be described as follows. The projectile particle induces the oscillations of the electron density in the cluster. Oscillations of the electric field caused by the electron motion result in the ionization of the cluster. Coupling with the ionic motion leads also to the damping of the plasmon oscillations. However, the corresponding linewidth, which we assume to be the same order of magnitude as in the region of the surface plasmon resonance, is about ($\Gamma\sim 0.2$ eV). This value is considerably smaller than the autoionization width determined below and therefore it can be neglected.

In order to describe the Landau damping of plasmon excitations, let us rewrite the inelastic scattering cross section via the amplitudes of single-particle transitions accounting for many-electron correlations in the cluster by means of the plasmon resonance approximation instead of the RPAE. In the region of the excitation energies above the ionization threshold, where single-particle electron excitations have continuous spectrum, the inelastic scattering cross section reduces to the ionization cross section. The many-electron interaction in the cluster results in plasmon oscillations of the electron density induced by the electric field of the projectile. This means that the single-particle transitions in the cluster leading to the ionization occur in the effective electric field created both by the projectile, $V_{lm}(\mathbf{r})$, and by the variation of the electron density in the cluster during the excitation process $\tilde{V}_{lm}(\mathbf{r})$. Indeed, the consistent many-body description of the ionization process leads to the replacement of the projectile electron potential by the effective potential, which takes into account many-electron correlations in the target [28]. In general, this result is applicable to single-particle transitions in an arbitrary fermion system under the action of an external field [29]. Many-electron correlations in the target atom can be taken into account for example in the RPAE approach [28]. According to this approximation, the cross section can be expressed via the single-electron wave functions and the total effective potential of the whole system: $V_{lm}+\tilde{V}_{lm}$. In the present paper, we describe this potential in plasmon resonance approximation:

$$\frac{d^2\sigma}{d\omega\, d\Omega}=\frac{p'}{\pi p}\sum_{lm}\sum_{\nu}$$
$$\times\int |\langle\psi_\mu|V_{lm}(\mathbf{r})+\tilde{V}_{lm}(\mathbf{r})|\psi_\nu\rangle|^2$$
$$\times\delta(\Delta\varepsilon-\varepsilon_\mu+\varepsilon_\nu)d\mu, \quad (11)$$

where summation is performed over all occupied single-electron Hartree-Fock states $\nu$ and over all vacant states $\mu$ including the integration over the continuum. In the region of $\Delta\varepsilon$ larger than the cluster ionization potential, expression (11) describes the differential cross section of electron impact ionization of the cluster. Potential $\tilde{V}_{lm}(\mathbf{r})$ created by the electron excitation is connected with the variation of the electron density in the field of the projectile particle:

$$\tilde{V}_{lm}(\mathbf{r})=\frac{4\pi}{q^2}\frac{\omega_p^2}{\Delta\varepsilon^2-\omega_p^2+i\Delta\varepsilon\Gamma_{vl}}$$
$$\times[j_l(qr)-j_l(qR)(r/R)^l]\theta(R-r)Y_{lm}(\mathbf{n})$$
$$+\frac{4\pi}{q^2}\frac{\omega_l^2}{\Delta\varepsilon^2-\omega_l^2+i\Delta\varepsilon\Gamma_{sl}}j_l(qR)$$
$$\times[(r/R)^l\theta(R-r)+(R/r)^{(l+1)}\theta(r-R)]Y_{lm}(\mathbf{n}). \quad (12)$$

The first and the second term in Eq. (12) describe the potential of the volume and the surface plasmons, respectively.

The resonance width of the particular plasmon mode can be derived from the comparison of the EELS (10) with the one following from Eqs. (11) and (12).

Let us consider the partial contribution to the EELS corresponding to the angular momentum $l$ in the vicinity of the plasmon resonance. This means $\Delta\varepsilon \approx \omega_l$ and $\Delta\varepsilon \approx \omega_p$ in the case of the surface and the volume plasmon, respectively. Both expressions (10) and (11) contain the resonance terms describing various plasmon modes. Comparing the corresponding resonance terms in Eqs. (10) and (11), one can determine the plasmon resonance width. For example, comparing the surface plasmon contributions [see the second term in Eq. (12) and the first term in Eq. (10)], we determine the width of the surface plasmon resonance:

$$\Gamma_{sl}=\frac{4\pi\omega_l}{(2l+1)R}\sum_{\nu\mu}|\langle\psi_\mu|\varphi_{sl}(\mathbf{r})|\psi_\nu\rangle|^2\delta(\omega_l-\varepsilon_\mu+\varepsilon_\nu), \tag{13}$$

where

$$\varphi_{sl}(\mathbf{r})=[(r/R)^l\theta(R-r)+(R/r)^{(l+1)}\theta(r-R)]Y_{lm}(\mathbf{n}).$$

Note that the same expression was obtained earlier in [15,16] using other methods. Thus result (13) obtained in the case of surface plasmons confirms the validity of our method of calculations of resonance width. Evaluation of the expression (13) for sufficiently large clusters leads [16] to the well-known result for the Landau damping of the surface plasmon oscillations $\Gamma_{sl}=3lv_F/R$, where $v_F$ is the velocity of the cluster electron on the Fermi surface.

Performing similar calculations for the autoionization width of the volume plasmon resonance, one derives

$$\Gamma_{vl}=\frac{8\pi^2\omega_p}{q^2R^3}\frac{\sum_\nu\int|\langle\psi_\mu|\varphi_{vl}(\mathbf{r})|\psi_\nu\rangle|^2\delta(\omega_p-\varepsilon_\mu+\varepsilon_\nu)d\mu}{j_l^2(qR)-j_{l+1}(qR)j_{l-1}(qR)-\frac{2}{qR}j_{l+1}(qR)j_l(qR)}, \tag{14}$$

where $\varphi_{vl}(\mathbf{r})=[j_l(qr)-j_l(qR)(r/R)^l]\theta(R-r)Y_{lm}(\mathbf{n})$. Here the summation is performed over the occupied single-electron states $\nu$ and the integration is performed over the electronic states $\mu$ of the continuous spectrum.

Let us stress the significant difference between the surface (13) and the volume (14) resonance widths. Expression (13) does not depend on the transferred momentum and thus it characterizes purely the surface plasmon oscillations. On the contrary, expression (14) depends upon the transferred momentum $q$, i.e., the volume plasmon resonance width depends on the kinematics of the excitation process. This difference can be easily explained. Indeed, the surface plasmon excitation is determined completely by the angular momentum $l$ and its projection $m$. This is clear from the form of the surface plasmon potential $\varphi_{sl}(\mathbf{r})$ [see also Eq. (12)], which coordinate dependence for the given $l$ and $m$ does not depend on the kinematics of the collision. For the volume plasmon, the angular momentum $l$ and its projection $m$ do not define completely the radial dependence of the plasmon potential. Note that neglecting the spatial dispersion of possible volume plasmon modes leads to the same resonance frequency $\omega_p$ of these modes, which means the infinite degeneracy of the volume plasmon excitations. Treating the volume plasmon oscillations in the dielectric sphere as the problem on the eigenvalues, one can derive the potentials for the normal modes of the volume plasmon $\varphi_{vln}(\mathbf{r})=[j_l(q_{ln}r)-j_l(q_{ln}R)(r/R)^l]\theta(R-r)Y_{lm}(\mathbf{n})$, where the wave vector of $n$th normal mode, $q_{ln}$, satisfies the equation $j_l(q_{ln}R)=0$. The projectile particle excites simultaneously numerous modes of the volume plasmon. The sum of the potentials of all the modes gives the resulting potential $\varphi_{vl}(\mathbf{r})$. It is essential that all normal modes of the volume plasmon have the same resonance frequency $\omega_p$, but the excitation probability for these modes depends on the kinematics of collision. This leads to the dependence of the volume plasmon potential $\varphi_{vl}(\mathbf{r})$ upon the transferred momentum. The oscillations of the volume plasmon potential result in the ionization of the cluster, whose probability and the volume plasmon resonance width depend on transferred momentum $q$. However, the numerical analysis performed in the next section show that the dependence of $\Gamma_{vl}$ on $q$ is rather weak in the region of $q \ll 1$, where collective electron oscillations mainly take place. Therefore, the volume plasmon resonance width with the given $l$ can be approximated by the limiting value following from Eq. (14) at $q=0$:

$$\Gamma_{vl}=(2l+5)\frac{\pi^2\omega_p}{R}\sum_\nu\int|\langle\psi_\mu|\varphi_{vl}^0(\mathbf{r})|\psi_\nu\rangle|^2 \times\delta(\omega_p-\varepsilon_\mu+\varepsilon_\nu)d\mu, \tag{15}$$

where $\varphi_{vl}^0(\mathbf{r})=(r/R)^l[1-(r/R)^2]\theta(R-r)Y_{lm}(\mathbf{n})$.

## IV. NUMERICAL RESULTS AND DISCUSSION

Let us now apply the approaches developed in the previous section to the description of the collision of 50 eV electrons with the $Na_{40}$ cluster. The number of plasmon modes with different angular momenta excited in a cluster depends on the cluster size [12,13]. Indeed, the wavelength of a collective excitation should be larger than the characteristic wavelength of the delocalized cluster electrons. Thus the angular momentum of plasmon excitations should be smaller

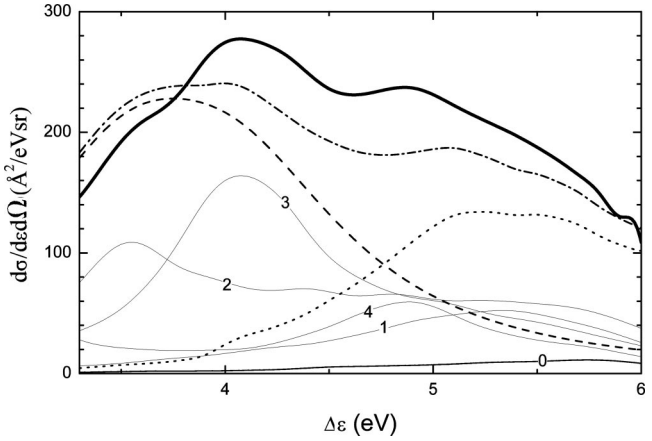


FIG. 1. Differential cross section, $d\sigma/d\varepsilon' d\Omega$ as a function of the transferred energy $\Delta\varepsilon$ calculated for the collision of 50 eV electron with the $Na_{40}$ clusters. The electron scattering angle is $\theta = 9°$. Solid lines represent the results derived from the RPAE approach (4)–(7) with the Hartree-Fock jellium model basis wave functions. Thick solid line is the total energy-loss spectrum. Thin solid lines marked by the corresponding angular momentum number represent various partial contributions to the energy-loss spectrum. Contributions of the surface and the volume plasmons calculated in the plasmon resonance approximation (11) are shown by dashed and dotted lines, respectively. Dashed-dotted line represents the sum of the surface and volume plasmon contributions to the EELS.

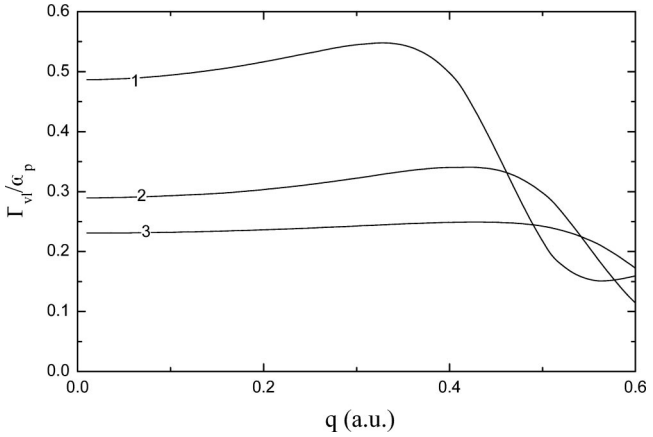


FIG. 2. Autoionization width $\Gamma_{vl}$ of the dipole (1), the quadrupole (2), and the octupole (3) volume plasmon excitations as a function of transferred momentum $q$.

than the maximum angular momentum of the cluster electrons in the ground state. The electron excitations with larger angular momenta have a single-particle character rather than collective one. Therefore analyzing the contribution to the cross section of those partial modes, which have strong resonance behavior, we have to consider relatively small angular momenta only. For example, according to the jellium model, the maximum angular momentum of delocalized electrons in the $Na_{40}$ cluster is equal to 4. Therefore, only the dipole, the quadrupole, and the octupole collective modes can be expected in this case [12,13].

The parameters of the surface plasmon excitations, $\omega_l$ and $\Gamma_{sl}$, in the $Na_{40}$ cluster have been determined in our previous works [12,13], where the role of surface plasmons in the formation of an inelastic scattering cross section has been studied. In this paper, we determine parameters of the volume plasmon modes. Figure 1 shows the EELS in the region above the ionization threshold $\Delta\varepsilon > 3.3$ eV calculated using the RPAE [see Eqs. (2)–(6)]. The energy of the collision is equal to $\varepsilon = 50$ eV and the scattering angle $\theta = 9°$. The thick line corresponds to the total energy-loss spectrum, while thin lines show various partial contributions. The angular momenta corresponding to these lines are marked by numbers from 0 to 4. The partial contributions to the EELS with $l < 3$ have the broad maximum in the vicinity of $\Delta\varepsilon \simeq 5.1$ eV. Note that the position of the maximum does not depend much on the angular momentum. This fact allows us to ascribe this peak to the volume plasmon excitation having the resonance frequency $\omega_p = 5.1$ eV, which is quite close to $\sqrt{3N_e/\alpha}$.

Figure 2 shows the dependence of the autoionization width on the transferred momentum $q$ for the volume plasmon modes, which provide a significant contribution to the EELS. The width of the dipole, the quadrupole, and the octupole volume plasmon resonances has been calculated according to Eq. (14). The transferred momentum $q$ plays the role of the wave vector for the volume plasmon excitations. All three plasmon modes have the similar dependence of $\Gamma_{vl}$ upon $q$. The width grows slowly in the region of small $q$ and it decreases rapidly at larger $q$. In the latter region, the probability of volume plasmon excitation by the incoming electron is correspondingly reduced. Note that the wavelength of a collective electron oscillation should be larger than the interelectronic distance in the cluster, i.e., the plasmon wave vector should be smaller than the Fermi momentum of cluster electrons $q < 0.5$. In the region $q < 0.5$, where the latter condition is fulfilled, the dependence of $\Gamma_{vl}$ upon $q$ is rather weak. We can approximate the resonance width by following values $\Gamma_{v1} \simeq 0.5\omega_p$, $\Gamma_{v2} \simeq 0.3\omega_p$, and $\Gamma_{v3} \simeq 0.23\omega_p$. Contrary to surface plasmons, the autoionization width of a volume plasmon decreases with the growth of the angular momentum.

In order to elucidate the role of collective excitations in the formation of the EELS, we have calculated the inelastic scattering cross section in the plasmon resonance approximation. In Fig. 1 we plot the sum of the dipole, the quadrupole, and the octupole partial differential cross sections calculated according to Eq. (10). Contributions of the surface and the volume plasmons are shown by dashed and dotted lines, respectively. The dashed-dotted line represents the sum of the surface and volume plasmon contributions to the EELS. Comparison of the EELS calculated in the two different approaches proves our assumption that the peculiarity in the EELS in the vicinity of $\Delta\varepsilon \sim 5$ eV is connected with the volume plasmon excitation. Figure 1 demonstrates that collective excitations provide a dominating contribution to the total EELS determining its pattern.

The more detailed analyses of partial contributions to the EELS is performed in Fig. 3. The solid line corresponds to

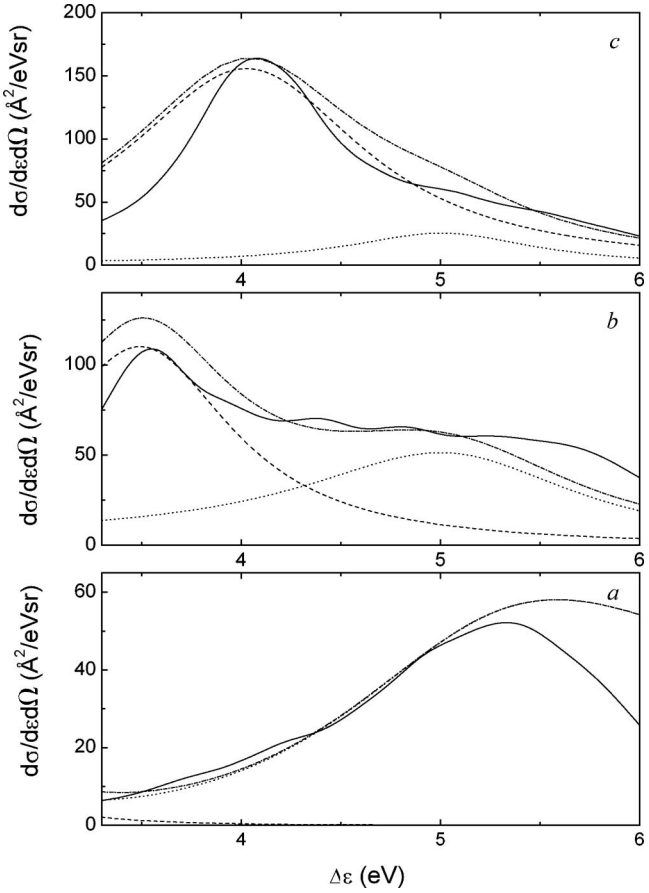


FIG. 3. The dipole (a), the quadrupole (b), and the octupole (c) partial cross sections of inelastic scattering of 50 eV electron on the $Na_{40}$ cluster as a function of transferred energy. The electron scattering angle is $\theta = 9°$. Solid lines show results of the RPAE calculation [see Eqs. (4)–(7)]. Dashed and dotted lines represent contributions of the surface and the volume plasmon excitations calculated in plasmon resonance approximation (11). Dashed-dotted line corresponds to the partial contribution to the ionization cross section (12), which takes into account the interference of the surface and the volume plasmon modes with the single-particle excitations.

the partial differential cross section calculated in the RPAE. Dashed and dotted lines show the contributions of the surface and the volume plasmon excitations calculated in plasmon resonance approximation (10). To check our assumption that the main contribution to the EESL above the ionization energy is given by the ionization process, we have calculated the partial ionization cross sections (11) accounting for the interference of the surface, the volume plasmon modes and the single-particle excitations. The results of this calculation are shown by dashed-dotted lines. Figure 3 demonstrates rather good agreement between the EELS calculated in the RPAE and in the ionization cross section calcuated in plasmon resonance approximation. It is seen that collective electron excitations provide the dominating contribution to each partial EELS. Therefore, we can conclude that the electron-impact ionization of metal clusters in the energy

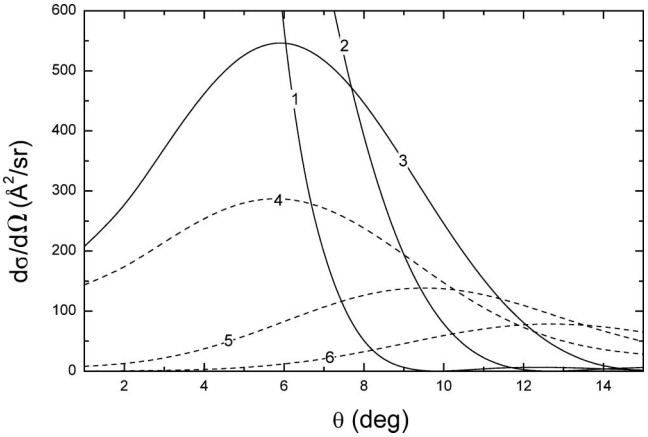


FIG. 4. Partial cross sections of excitations $d\sigma_l/d\Omega$ for the different plasmon modes as a function of scattering angle. Solid and dashed lines correspond to the surface and the volume plasmons, respectively. Value of the angular momentum corresponding to the plasmon mode is shown near each line.

range considered takes place via the intermediate excitation of plasmons.

Figure 3 shows that the volume plasmon excitation dominates in the dipole partial EELS, while the surface and the volume plasmon excitations provide comparable contributions to the quadrupole partial EELS. For the octupole contribution, the surface plasmon excitation becomes the most important.

As demonstrated in our previous work [13], the probability of excitation of various plasmon modes nonmonotonously depends upon the scattering angle. For the given plasmon mode, there is an interval of scattering angles in which this mode provides the maximum contribution to the EELS. In Fig. 4, in order to illustrate relative importance of various plasmon modes we have plotted the cross sections $d\sigma/d\Omega$ as a function of the scattering angle. These cross sections were obtained in the plasmon resonance approximation by integration of the partial differential inelastic scattering cross sections $d\sigma_l/d\varepsilon' d\Omega$ in Eq. (10) over the transferred energy. Figure 4 demonstrates that that the excitation of plasmon modes with higher angular momenta is more probable at larger scattering angles. It is also seen that at larger scattering angles, the volume plasmon oscillations are excited more effectively than the surface ones.

## V. CONCLUSION

Consistent many-body treatment of the EELS on metal clusters in the region of transferred energies above the ionization potential is performed. Our calculations have demonstrated that in this transferred energy range, collective electron excitations play the important role in the formation of the EELS. Comparison of the inelastic scattering differential cross section calculated in the RPAE with the ionization cross section calculated in the plasmon resonance approximation demonstrates that the ionization channel dominates in

the EELS in the vicinity of the volume plasmon resonance. Qualitatively, the process of electron-impact ionization of metal clusters can by described as follows. The projectile electron excites plasmon oscillation, which decays afterwards via the ionization process. In the present paper, the autoionization width for the volume plasmon resonance has been determined. The theory developed leads to the known expression for the surface plasmon resonance width.

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