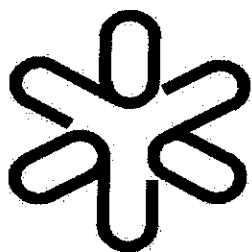


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**Long-Range Excitation of Collective Modes in
Mesoscopic Metal Clusters**

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LONG-RANGE EXCITATION OF COLLECTIVE MODES IN MESOSCOPIC METAL CLUSTERS

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Abstract

We develop a semiclassical theory for the long range excitation of plasmon resonances in atomic clusters, based on the doorway hypothesis. The effect of the width of the plasmon resonance is fully taken into account. As an application we study plasmon excitation in small Sodium clusters, in collisions with electrons and protons.

I. INTRODUCTION

Metal atomic clusters have been studied intensively for many years to explore the difference between atomic-like and bulk material behavior of the nano-meter metal particles [1].

Intermediate size clusters, being between molecules and bulk materials, have shown very complex energy spectra and relaxation dynamics. This complexity results from chaotic behavior of multi electron energy levels and their interaction with multiple vibrational modes of the cluster atoms. Experimental data about photo-absorption and photo-ionization spectra of mesoscopic clusters have exhibited pronounced structure related to the collective excitation of cluster electrons [1,2]. To explain the manifestation of plasmon-like modes in small size atomic clusters, "ab initio" calculations have been done in the framework of the Functional Density Method (FDM) and the Random Phase Approximation (RPA) [2]- [4]. Later, a better agreement between theory and experiment has been reached using Hartree-Fock and RPA evaluations for detailed treatment of electronic collective modes [5,6]. At the same time, semi-empirical models have been developed for simple explanations of the experimentally observed collective phenomena on the base of the surface and volume plasmon effects [1,7].

An alternative way to investigate the dynamics of excited cluster states is through cluster excitation by charged particles: protons, ions, fast electrons or charged clusters. The involvement of a large number of internal degrees of freedom influences strongly the cluster response to the external field. For example, electronic excitation may relax so rapidly among numerous vibrational modes, that it can change the character of a collective wave function during an excitation process. We will show, that the dynamics of cluster excitation can be described as the excitation of some envelope state of cluster eigenfunctions, even under conditions when the cluster spectra display a strong chaotic behavior. The scale alteration of the time and intensity of the cluster excitation by variation of velocity v , impact parameter b and charge Z of projectile particles may be used for investigations of the dynamics of the cluster excitation and its energy relaxation. Analysis of the energy for different (v, Z) in conjunction with a description of the structure of the chaotic part of clusters' spectra can provide the basis for a theoretical description of excitation and decay of the collective excitations in mesoscopic clusters.

In the present article we have developed a semi-classical method for the description of the

long-range cluster excitation in collisions with charged particles. Our theoretical approach takes fully into account the finite lifetime of the excited modes and their reconstruction into chaotic states of excited clusters. The dynamical description presented in this article may be considered as concrete realization of the doorway phenomena [8,9]. Excitation of the doorway mode is well known for inelastic collisions of nuclear particles as well as for electronic transport through mesoscopic quantum dots [10].

The paper is organized as follows: The basic semiclassical reaction theory is presented in Section II. In Section III we give a full account of the doorway model of plasmon resonance excitations. This model is then incorporated, in Section IV, into the reaction theory of Section II, and application of the theory to several cases are then presented in Section V. Finally, in Section VI, concluding remarks are made.

II. PLASMON OSCILLATIONS AS SEMICLASSICAL COULOMB EXCITATION OF ATOMIC CLUSTERS

We consider in this section the excitation of collective plasmon resonances in metal clusters. The probe could be any charged particle (electron, positron, proton, nucleus, cluster etc.). The theoretical framework of our development is a time-dependent semiclassical collision theory [11]. The collective modes excited in the atomic clusters are treated as damped vibrations specified by an energy and a decay width. The novel feature of our theory is the treatment of the life-time of the resonances and reconstruction of the chaotic part of the cluster in a dynamical way.

We show in figure 1 a schematic representation of our scattering system. The interaction between the projectile, with charge Ze , and the cluster's free electrons is given by

$$V(\mathbf{r}_i, \mathbf{R}) = - \sum_{i=1}^N \frac{Ze^2}{|\mathbf{R}(t) + \mathbf{r}_i|} + \frac{Ze^2}{R(t)} \approx \frac{Ze^2}{R^2(t)} \sum_{i=1}^N \hat{\mathbf{R}}(t) \cdot \mathbf{r}_i, \quad (1)$$

where N is the number of free electrons in the cluster, $\hat{\mathbf{R}}(t)$ is the unit vector parallel to the projectile's position vector, $\mathbf{R}(t)$, and \mathbf{r}_i gives the position of the i -th free electron inside

the cluster. Above, the dipole approximation has been introduced. The projectile motion is described classically and, therefore, once the over-all mean field potential describing the projectile-cluster interaction is given, $\mathbf{R}(t)$ is considered to be known. The interaction, Eq. (1), can be rewritten as

$$V(\mathbf{r}_i, \mathbf{R}) = -\mathbf{D} \cdot \mathbf{E}(t), \quad (2)$$

where $\mathbf{E}(t)$ is the classical time-dependent electric field vector,

$$\mathbf{E}(t) = \frac{Ze}{R^2(t)} \hat{\mathbf{R}}(t) \quad (3)$$

and $\mathbf{D} = e \sum_{i=1}^N \mathbf{r}_i$ is the quantum mechanical dipole operator.

Having specified the degrees of freedom of the system, we turn now to the description of the collision process. The time-dependent Schrödinger equation that describes the evolution of the atomic cluster is

$$[H_0 + V] \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) = i\hbar \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)}{\partial t}, \quad (4)$$

where H_0 is the intrinsic Hamiltonian of the cluster whose spectrum is given by

$$H_0 |\varphi_n\rangle = \varepsilon_n |\varphi_n\rangle. \quad (5)$$

Making the expansion

$$|\Psi\rangle = \sum_n a_n(t) e^{-i\varepsilon_n t/\hbar} |\varphi_n\rangle, \quad (6)$$

we derive the following familiar set of coupled equations (we are taking $\varepsilon_0 = 0$)

$$i\hbar \frac{da_0(t)}{dt} = \sum_n e^{-i\varepsilon_n t/\hbar} V_{0n}(t) a_n(t) \quad (7)$$

$$i\hbar \frac{da_n(t)}{dt} = e^{i\varepsilon_n t/\hbar} V_{n0}(t) a_0(t) + \sum_{m \neq 0} e^{i(\varepsilon_n - \varepsilon_m)t/\hbar} V_{nm}(t) a_m(t), \quad (8)$$

These equations are solved with the usual initial conditions

$$a_n(t \rightarrow -\infty) = \delta_{n0}, \quad (9)$$

and the excitation probabilities are

$$P_n = |a_n(t \rightarrow +\infty)|^2. \quad (10)$$

The expansion in Eqs. (7,8) is overwhelmingly complicated in the case of mesoscopic clusters, especially in the region of dynamic excitation. A convenient way to describe the average behavior of the dynamics is through the introduction of doorway states, a well known concept in the theory of nuclear reactions [8]. In the following, we give an account of this approach.

III. DOORWAY STATE DESCRIPTION OF DYNAMICAL COLLECTIVE EXCITATION OF ATOMIC CLUSTERS

It is well known that quantal many-body systems exhibit both collective and statistical, chaotic, behaviors. The interplay between these modes is clearly exhibited in the response of these systems to external probes. One sees usually in the spectrum a concentration of dipole oscillation strength at a given excitation energy which is spread over a rather large interval. The spread defines the width of the so-called collective excitation which is connected to the coupling to the more complex, chaotic degrees of freedom.

Both in the theory of nuclear reactions and in the many body theory of atoms [4]-[6], it has been common to give explicit reference to the collective state, although it is not an eigenstate of the isolated quantal system. The term 'doorway state' is used to label the collective state usually called Giant Resonance in the nuclear physics context. The only eigenstates of the systems are the complicated configurations mentioned in the introduction. However, due to the usually very large number of these states, it has been proven useful the use of the doorway state to describe the average excitation of the system. In the following, we develop a theoretical framework that allows the treatment of the excitation of the doorway state (collective state) in the collision process. Implicit reference to the statistical degrees of freedom is allowed through explicit consideration of the damping width of the doorway.

The starting point of our consideration is Eq. (5), which describes the spectrum of the atomic cluster. In a collision process, the cluster is originally in the ground state, $|\varphi_0\rangle$, and transitions to excited states take place through the external-coupling, V . We shall assume that these excited states are modulated by a doorway, which could be a plasmon resonance. Further, to reach these 'fine structure' states, we assume that the systems has to go through the doorway(s) $|d\rangle$ [8,9]. We formally accomplish this by expressing $|\varphi_n\rangle$ as

$$|\varphi_n\rangle = \alpha_n |d\rangle + \sum_m \beta_n^m |m\rangle, \quad (11)$$

where the states $|m\rangle$ form an orthonormal set which spans the intrinsic subspace orthogonal to $|d\rangle$. Notice that neither $|d\rangle$ nor $|m\rangle$ are eigenstates of the system. The doorway nature of $|d\rangle$ is accomplished by requiring that $\langle\varphi_0|V|m\rangle = 0$, so that the ground state is coupled to the excited states through

$$\langle\varphi_0|V|\varphi_n\rangle \equiv V_{0n} = \alpha_n \langle\varphi_0|V|d\rangle = \alpha_n V_{0d} \quad (12)$$

Above, we assume that $\alpha_n \equiv \langle d|\varphi_n\rangle$ depends exclusively on the energy of the state $|\varphi_n\rangle$, namely, $\alpha_n \equiv \alpha(\varepsilon_n)$.

It is convenient to represent the intrinsic Hamiltonian in the space spanned by the doorway and the subspace orthogonal to it, in the following way:

$$H_0 = |\varphi_0\rangle \varepsilon_0 \langle\varphi_0| + \sum_m |m\rangle \Lambda_m \langle m| + |d\rangle \varepsilon_d \langle d| + \sum_m \{ |m\rangle \Delta_m \langle d| + |d\rangle \Delta_m^* \langle m| \}. \quad (13)$$

The last term in the above equation represents the spreading of $|d\rangle$. We emphasize that, although $\langle m|d\rangle = 0$, neither $|d\rangle$ nor $|m\rangle$ are eigenstates of the system. We have also ignored coupling among different $|m\rangle$ in H_0 .

It is now a simple matter to derive an expression for $\alpha(\varepsilon_n)$ and Λ_m . Inserting Eq. (13) into Eq. (5), and using that $\langle\varphi_{n'}|\varphi_n\rangle = \delta_{n'n}$, we obtain

$$|\alpha(\varepsilon_n)|^2 = \frac{1}{1 + \sum_m \frac{|\Delta_m|^2}{(\varepsilon_n - \Lambda_m)^2}} \quad (14)$$

and

$$\varepsilon_n = \varepsilon_d + \sum_m \frac{|\Delta_m|^2}{\varepsilon_n - \Lambda_m} \quad (15)$$

It is convenient for our purposes to obtain an expression for $|\alpha(\varepsilon_n)|^2$ which contains explicit reference to the difference $\varepsilon_n - \varepsilon_d$. For this purpose one must eliminate Λ_m from Eqs. (14) and (15). This is analytically possible only for a restricted set of cases. If one uses the model of ref. [12], namely a constant $\Delta_m = \Delta$, and a uniform spectrum $[\Lambda_m]$ in the sense $\Lambda_m = m s$, where s is the constant spacing between adjacent levels and $m = 0, \pm 1, \pm 2, \dots$, exact expressions for ε_n and $|\alpha(\varepsilon_n)|^2$ can be derived:

$$\varepsilon_n = \varepsilon_d + \frac{\pi \Delta^2}{s} \cot\left(\frac{\pi \varepsilon_n}{s}\right) \quad (16)$$

and

$$|\alpha(\varepsilon_n)|^2 = \frac{1}{1 + (\pi \Delta/s)^2 \csc^2(\pi \varepsilon_n/s)} = \frac{1}{1 + (\pi \Delta/s)^2 + \frac{(\varepsilon_d - \varepsilon_n)^2}{\Delta^2}}. \quad (17)$$

Defining the damping width of the doorway state $\Gamma_d^\downarrow = 2\pi \Delta^2/s \equiv 2\pi \Delta^2 \rho$, where $\rho = 1/s$ is the constant density of the $|m\rangle$ states, we may finally write

$$|\alpha(\varepsilon_n)|^2 = \frac{1}{2\pi \rho} \left[\frac{\Gamma_d^\downarrow}{(\varepsilon_n - \varepsilon_d)^2 + \frac{\Gamma_d^{\downarrow 2}}{4} + \Delta^2} \right] \quad (18)$$

The term Δ^2 in the denominator is usually absorbed in the definition of the doorway energy: $\varepsilon'_d = \varepsilon_d + \Delta^2$. This then results in the celebrated Breit-Wigner formula for $|\alpha(\varepsilon_n)|^2$,

$$|\alpha(\varepsilon_n)|^2 = \frac{1}{2\pi \rho} \left[\frac{\Gamma_d^\downarrow}{(\varepsilon_n - \varepsilon_d - \Delta \varepsilon_d)^2 + \frac{\Gamma_d^{\downarrow 2}}{4}} \right] \quad (19)$$

We may now normalize $\alpha(\varepsilon_n)$,

$$\sum_n |\alpha(\varepsilon_n)|^2 \approx \int |\alpha(\varepsilon_n)|^2 \rho(\varepsilon_n) d\varepsilon_n = 1 \quad (20)$$

The normalization above may be easily performed if we make the assumption that the density of the eigenstates of the system, $\rho(\varepsilon_n)$, equals that of the states orthogonal to the doorway, $\rho = 1/s$.

Since the doorway decays into the open channels, one should add to Γ_d^\downarrow in Eq. (18) the escape width, Γ_d^\uparrow . This can be formally done using reaction theory techniques [8]. Therefore, the coupling matrix elements will be calculated according to Eq. (12) with $|\alpha(\varepsilon_n)|^2$ given by

$$|\alpha(\varepsilon_n)|^2 = \frac{1}{2\pi\rho} \left[\frac{\Gamma_d}{(\varepsilon_n - \varepsilon_d - \Delta\varepsilon_d)^2 + \Gamma_d^2/4} \right] \quad (21)$$

where

$$\Gamma_d = \Gamma_d^\downarrow + \Gamma_d^\uparrow \quad (22)$$

is the total width of the doorway state.

The doorway approach described above depends on the incident energy. The faster the colliding probe is, the less details will be exhibited by the collision spectrum. If the energy is lowered, one expects that more details of the cluster structure will be revealed. Namely, the doorway state described above will fragment, at lower energies, owing to the coupling to some particular $|m\rangle$ states.

The method proposed here should be particularly useful in the collisional determination of the complicated spectrum of large atomic clusters. This is because a detailed description of such large many-body system is, in general, prohibitively complicated.

IV. PLASMON OSCILLATIONS AS DOORWAY CHANNEL FOR COULOMB EXCITATION OF METALLIC CLUSTERS

Let us now consider the specific case of an electric dipole resonance. If φ_0 has angular momentum $j = 0$ and the coupling V is not too strong, only excited states with $j = 1$ (in \hbar units) are significantly populated. In this case, such states can be labeled by their energies (in principle a continuous label) and the z -component of j , $\mu = 0, \pm 1$; namely: $n \equiv \varepsilon, \mu$. Thus, we get the coupled channels equations

$$\frac{da_0(t)}{dt} = \frac{1}{i\hbar} \sum_{\mu} \int d\varepsilon e^{-i\varepsilon t/\hbar} V_{0,\varepsilon\mu} a_{\varepsilon\mu}(t) \quad (23)$$

$$\frac{da_{\varepsilon\mu}(t)}{dt} = \frac{1}{i\hbar} e^{i\varepsilon t/\hbar} V_{\varepsilon\mu,0} a_0(t), \quad (24)$$

with the initial condition $a_n(t \rightarrow -\infty) = \delta_{n,0}$. Above, we have used the fact that the dipole coupling does not mix the excited states. This is so because the dipole operator is a spherical tensor of rank 1 and all these states have $j = 1$. In this case the excitation occurs through the three degenerate doorways $|d_{\mu=0,\pm 1}\rangle$, with energy ε_d and angular momentum $j = 1$. These doorways differ only in the z -component of the angular momentum, $\mu = 0, \pm 1$. We assume that the expansion coefficients $\alpha(\varepsilon)$ are the same for the three doorways, independently of μ . The coupling matrix elements are then written

$$V_{\varepsilon\mu,0} = \alpha(\varepsilon) \langle d_\mu | V(t) | \varphi_0 \rangle \equiv \alpha(\varepsilon) V_\mu(t). \quad (25)$$

Integrating Eq. (24) over time, substituting the result in Eq. (23) and using Eq. (25), we obtain

$$\frac{da_0(t)}{dt} = \frac{1}{\hbar^2} \sum_\mu V_\mu(t) \int d\varepsilon |\alpha(\varepsilon)|^2 \int_{-\infty}^t dt' e^{-i\varepsilon(t-t')/\hbar} [V_\mu(t')]^* a_0(t'). \quad (26)$$

Assuming the Breit-Wigner shape for $|\alpha(\varepsilon)|^2$, the integration over ε can be carried out in the complex plane. We find,

$$\frac{da_0(t)}{dt} = \frac{1}{\hbar^2} \sum_\mu V_\mu(t) \int_{-\infty}^t dt' e^{-i(\varepsilon_d - i\Gamma_d/2)(t-t')/\hbar} [V_\mu(t')]^* a_0(t'). \quad (27)$$

This equation can be solved by introducing the auxiliary amplitudes $A_\mu(t)$, such that $a_0(t) = 1 + \sum_\mu A_\mu(t)$. Eq. (27) then reduces to the set of three coupled differential equations

$$\ddot{A}_\mu(t) + \left[\frac{\dot{V}_\mu(t)}{V_\mu(t)} - \frac{i}{\hbar} \left(\varepsilon_d - \frac{i}{2}\Gamma_d \right) \right] \dot{A}_\mu(t) + \frac{|V_\mu(t)|^2}{\hbar^2} \left(1 + \sum_\mu A_\mu(t) \right) = 0, \quad (28)$$

with initial conditions $A_\mu(t \rightarrow -\infty) = 0$. Eq. (28) can be handled by standard numerical procedures. Once the asymptotic amplitude $a_0(t \rightarrow \infty)$ is calculated, the excitation probabilities are easily obtained from Eqs. (10) and (24) (integrated over time)

$$P_{\varepsilon,\mu} \equiv |a_{\varepsilon\mu}(t \rightarrow \infty)|^2 = \frac{1}{2\pi} \left[\frac{\Gamma_d}{(\varepsilon_n - \varepsilon_d)^2 + \frac{\Gamma_d^2}{4}} \right] \left| \int_{-\infty}^{\infty} dt e^{i\varepsilon t/\hbar} [V_\mu(t)]^* a_0(t) \right|^2. \quad (29)$$

Integrating over the impact parameter (implicit in the dependence of $V(t)$ on the trajectory), we obtain the excitation cross sections

$$\frac{d\sigma_\mu}{d\varepsilon} = 2\pi \sum_\mu \int_{b_{min}} b db P_{\varepsilon,\mu}(b) \quad (30)$$

In Eq. (30), σ_μ stands for the cross section for population of states with quantum number μ , and b_{min} represents the value of b below which trajectories suffer strong inelastic transitions. We take b_{min} to be an effective radius of the cluster core $\approx l \mathcal{N}^{1/3}$ where l is the mean interatomic distance in the cluster and \mathcal{N} is the number of atoms.

V. APPLICATIONS

Now we apply the formalism of the previous sections to the plasmon resonance in Sodium clusters, identified here as the doorway state. The resonance is excited in collisions with electron and proton projectiles. We consider the excitation in both neutral and ionized clusters. In the former case, one can use straight line trajectories for $\mathbf{R}(t)$ while in the latter one should use Coulomb trajectories.

First we write the explicit expression for the coupling, V_μ . Using the dipole approximation and writing Eq. (2) in terms of the spherical components of the dipole field $E_\mu(t)$ and of the dipole operator D_μ , we get

$$V = - \sum_\mu E_\mu(t) \cdot D_\mu, \quad (31)$$

with

$$E_\mu(t) = E(t) \sqrt{\frac{4\pi}{3}} Y_{1\mu}^*(\hat{\mathbf{R}}(t)), \quad (32)$$

where $E(t)$ is the electric field strength

$$E(t) = \frac{Ze^2}{R^2(t)}. \quad (33)$$

If we use the reference frame of figure 1, where the z-axis is orthogonal to the collision plane, the x-axis is along the apex-line towards the projectile and the initial velocity has

positive y-component, the matrix element $V_{\mu=0}$ vanishes identically [11]. Using Wigner-Eckart's theorem and representing the other two components with the shorthand notation $V_{\mu=\pm 1} \equiv V_{\pm}$, we obtain

$$V_{+} = \frac{|\langle \varphi_0 || D || d \rangle|}{\sqrt{2}} E(t) e^{-i\phi(t)}, \quad (34)$$

$$V_{-} = V_{+1}^*. \quad (35)$$

The phase $\phi(t)$ is given by

$$\phi(t) = -\frac{\pi - \Theta}{2} + bv \int_{-\infty}^t \frac{dt'}{R^2(t')}, \quad (36)$$

where Z_c is the charge of the projectile and Θ is the scattering angle.

The reduced matrix-element $\langle \varphi_0 || D || d \rangle$ can be estimated from the energy weighted sum rule, applied to collective oscillations in the small sodium clusters [4]- [6]. It leads to

$$\langle \varphi_0 || D || d \rangle = e \sqrt{\frac{\hbar^2 \mathcal{N} K}{2m \varepsilon_d}}, \quad (37)$$

where K is the fraction of the total oscillator strength exhausted by the plasmon mode, \mathcal{N} is the number of atoms in the clusters, and m is the electron mass. As an illustration, we consider a small Sodium cluster with $\mathcal{N} = 8$ atoms. In this case, we have the typical values: $\varepsilon_d \approx 2.5$ eV = 0.093 a.u., $\Gamma_d = 0.1 \varepsilon_d$, $K \approx 0.7$, and the interatomic distance $l \approx 3$ Å. Since we are dealing with a peripheral process, we use as the lower limit for the impact parameter integration of Eq. (30) the radius of the cluster. In the present case, $b_{min} = R_{cluster} \approx 7.5$ a.u..

A. Excitation of a neutral atomic metal cluster

Let us consider the excitation of the plasmon resonance in a metal cluster with net charge equal to zero. In this case it is reasonable to use a straight line trajectory for the projectile motion. In the reference frame of figure 1, the trajectory reduces to a straight line parallel to the y-axis, so that

$$\mathbf{R}(t) = b \hat{\mathbf{x}} + vt \hat{\mathbf{y}}. \quad (38)$$

The electric field strength (Eq. (33)) and the phase $\phi(t)$ (Eq. (36)) are then given by

$$E(t) = \frac{Ze^2}{b^2 + v^2 t^2} \quad (39)$$

and

$$\phi(t) = \arctan\left(\frac{vt}{b}\right). \quad (40)$$

We have solved numerically Eq. (28) taking as projectiles electrons with incident energy $E = 100$ eV and protons with $E = 100$ keV. In figures 2a and 2b, we show the time evolution of the probabilities for the cluster to remain in the ground state, P_0 , and to be excited to a state with each of the possible values of μ , P_1 and P_{-1} . The latter were obtained by summation over the excitation energy. The results were obtained for the impact parameter $b = 7.5$ a.u. It is interesting to notice that the population probability for $\mu = -1$ is much larger than that for $\mu = 1$.

In figures 3a and 3b, we give the calculated excitation spectra for the same projectiles and energies. We notice that the results are rather similar, despite of the different sign of the projectile charge in each case. The reason is that the cross section depends basically on the projectile velocity, which is of the same order of magnitude in the two cases. We have found that effect of the width Γ_d (taken here as $\Gamma_d = 0.1 \hbar\omega_d$ [2,4,7]) on the cross sections is very small. For all practical purposes one may set $\Gamma_d = 0$ in the coupled channel calculation, using the doorways as eigenstates of H_0 , and then use Eq. (29) for the probabilities $P_{\epsilon\mu}$.

Consistently with the probabilities of figures 2a and 2b, we find that the contribution of the state with $\mu = -1$ completely dominates the cross section. This can be understood if one neglects the width Γ_d and use first order perturbation theory to calculate the excitation amplitudes. In this case the amplitudes $a_{\pm}(t) \equiv a_{\mu=\pm 1}$ are obtained by integrating Eq. (8) with $a_0(t) = 1$. Using the explicit form of the matrix elements (Eqs. (33) and (34)), we get

$$a_{\pm}(t) = -\frac{i}{\hbar} \frac{\langle \varphi_0 || D || d \rangle}{\sqrt{2}} \int_{-\infty}^t dt' E(t') \exp\left[\frac{i}{\hbar} (\epsilon_d t' \pm \hbar\phi(t'))\right]. \quad (41)$$

Using Eq. (39) and (40) we find that the stationary phase points of the integrand are given by the condition

$$\varepsilon_d = \mp \frac{\hbar v}{b} \left[\frac{b^2}{b^2 + v^2 t_{\pm}^2} \right], \quad (42)$$

where t_{\pm} stands for the stationary point in the integrand giving the amplitude a_{\pm} . Since the energy ε_d is positive, a_+ has no stationary point. For a_- , the stationary point is

$$t_- = \sqrt{\frac{\hbar b}{v \varepsilon_d} - \frac{b^2}{v^2}}. \quad (43)$$

Within the stationary phase approximation, the amplitude a_+ vanishes, consistently with the low probability and cross section for $\mu = +1$ in figures 2a, 2b, 3a and 3b.

It is important to point out that the validity of the stationary phase approximation requires that the phase in Eq. (41) varies rapidly within the collision time, τ_c . The opposite situation would be the sudden limit where the doorway energy is negligible, i.e. $\varepsilon_d \ll \hbar/\tau_c$. In this case, it can be easily seen that $a_- \simeq a_+$ and $\sigma_- \simeq \sigma_+$.

B. Excitation of a charged metal cluster

We now consider the excitation of the plasmon mode in a ionized metal cluster with net charge $Z_c e$, in collisions with the same projectiles of the previous section. All the parameters of the metal cluster are the same as in the previous subsection. In this case, $\mathbf{R}(t)$ is a Rutherford trajectory. We first consider the case where the Coulomb field is repulsive (Z and Z_c have the same sign). We introduce the Sommerfeld parameter

$$\eta = \frac{Z Z_c e^2}{\hbar v}, \quad (44)$$

the half-distance of closest approach in a head-on collision,

$$a = \frac{Z Z_c e^2}{2 E} \quad (45)$$

and the excentricity,

$$\epsilon = \sqrt{1 + \frac{b^2}{a^2}}. \quad (46)$$

It is convenient to introduce a new variable w , defined by its relation with the time,

$$t = \frac{a}{v} [\epsilon \sinh w + w]. \quad (47)$$

From the equations of motion under the action of the Coulomb field, it is easy to show that the trajectory on the xy -plane, specified by the coordinates R and ϕ (see figure 1), is given in terms of w as

$$\begin{aligned} R(w) &= a [\epsilon \cosh w + 1] \\ \phi(w) &= \arcsin \left(\frac{a \sqrt{1 - \epsilon^2} \sinh w}{R(w)} \right). \end{aligned} \quad (48)$$

Using the variable w in Eq. (28) we get

$$A''_{\mu}(w) + \frac{1}{f(w)} \left[\frac{\dot{V}_{\mu}(t(w))}{V_{\mu}(t(w))} - \frac{i}{\hbar} \left(\epsilon_d - \frac{i}{2} \Gamma_d \right) \right] A'_{\mu}(w) + \left| \frac{V_{\mu}(t(w))}{\hbar f(w)} \right|^2 \left(1 + \sum_{\mu} A_{\mu}(w) \right) = 0, \quad (49)$$

where primes stand for derivation with respect to w and

$$f(w) = \frac{dw}{dt} = \frac{v}{R(w)}. \quad (50)$$

From the amplitudes $A_{\mu}(w)$, we obtain

$$a_0(w) = 1 + \sum_{\mu} A_{\mu}(w) \quad (51)$$

and

$$a_{\epsilon\mu}(w) = \frac{1}{i\hbar} [\alpha(\epsilon)]^* \int_{-\infty}^w e^{i\epsilon t(w')/\hbar} [V_{\mu}(w')]^* a_0(w') \frac{dw'}{f(w')}. \quad (52)$$

For attractive Coulomb interactions, it is necessary to make the changes:

$$\begin{aligned} t &= \frac{a}{v} [\epsilon \sinh w - w] \\ R(w) &= a [\epsilon \cosh w - 1], \end{aligned} \quad (53)$$

the other equations remaining the same as for the repulsive Coulomb field.

We have performed calculations for the excitation of the plasmon mode in the same cluster and for the same projectiles as in the previous sub-section. However, here we consider an ionized Sodium cluster. In this case, the projectile's trajectory is no longer a straight line but a hyperbola. To assess the importance of this effect we have calculated the total plasmon excitation cross sections (integrated over excitation energy and summed over μ) as a function of the collision energy and of the cluster's net charge. In this simple example, we have disregarded the effects that the cluster charge might have on its structure.

The results are shown in figures 4a, for electrons, and in 4b, for protons. In collisions with electrons, we notice that the cross section decreases with the collision energy in the energy range considered. Although the deviations from results using a straight line trajectory (curve with $Z_c = 0$) are very small for high energies, Coulomb effects on the trajectory play an increasingly important role as the collision energy decreases. The situation for proton projectiles is somewhat different for the collision energies considered in figure 4b. First, we notice that the cross section reaches a maximum at $E \approx 25$ keV. The second difference is that the cross section is not affected by the cluster's net charge. In this case the curves for 0, 1, ..., 8 units of charge cannot be distinguished in the figure. This result is not surprising. If we estimate the maximal deflection angle Θ involved in the graph: for maximal charge ($Z_c = 8$), minimal impact parameter ($b = b_{min} = 7.5$ a.u.) and minimal energy ($E = 20$ keV), we find $\Theta_{max} = 0.04$ deg. Therefore, the Coulomb trajectory is very closely a straight line.

VI. CONCLUSIONS

We have developed a general theoretical framework through which the collisional excitations of collective plasmon resonances in metallic clusters can be quantitatively described. The idea of a doorway state representing the resonance, which is coupled to both the open decay channels and the chaotic degrees of freedom of the cluster, is used for this purpose.

Application of the semiclassical scattering theory in conjunction with the "exit" doorway model is made to light Na-clusters using electrons and protons as projectiles. Although Pauli exchange effects in the electron scattering are important and they result in non-local potentials, we have ignored these effects here for simplicity. The formalism can be applied easily to cluster-cluster collisions. Furthermore, it can be generalized to cases involving the excitation of multiplasmon states in both spherical and deformed clusters. In the deformed cluster case one sees a two-peaked one plasmon resonance [1] and should see a three-peaked two-plasmon resonance, a four-peaked three-plasmon resonance etc. [12]. These resonances can be reached in multistep processes (ground state \rightarrow one plasmon \rightarrow two plasmon \rightarrow etc.).

In our theory only the average cross-section corresponding to the excitation of the doorway state was calculated. There should be fluctuation contributions, not considered here. Such contributions will be discussed in future work.

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Figure Captions.

- Figure 1: Collision of a charged projectile (open circle) with metal cluster (solid circle). In this illustration, the charge of the cluster has the same sign as that of the projectile. In this reference frame, the trajectory lies on the xy -plane and the z -axis points upwards, away from the paper sheet. The coordinates R and ϕ , and the distance of closest approach, $2a$ are indicated.
- Figure 2a: Time evolution of the elastic and inelastic probabilities in collisions of 100 eV electrons with a Na-cluster. The time is indicated in atomic units (a.u.), defined as the ratio of the radius of the ground state Bohr orbit in the Hydrogen atom to the electron speed in this state.
- Figure 2b: Same as figure 2a for 100 keV protons.
- Figure 3a: The differential cross section as a function of the cluster excitation energy in the plasmon region. The projectile is a 100 eV electron. For details see the text. The cross section is given in atomic units, which in this case are defined as the radius square of the ground state Bohr orbit in Hydrogen.
- Figure 3b: Same as figure 3a for 100 keV protons.
- Figure 4a: Cross sections for the excitation of the plasmon resonance in ionized Sodium clusters. The results are given as functions of the collision energy, for a few different values of the cluster's net charge. For details see the text.
- Figure 4b: Same as Figure 4a for protons. Here the curves for different cluster charges cannot be distinguished.

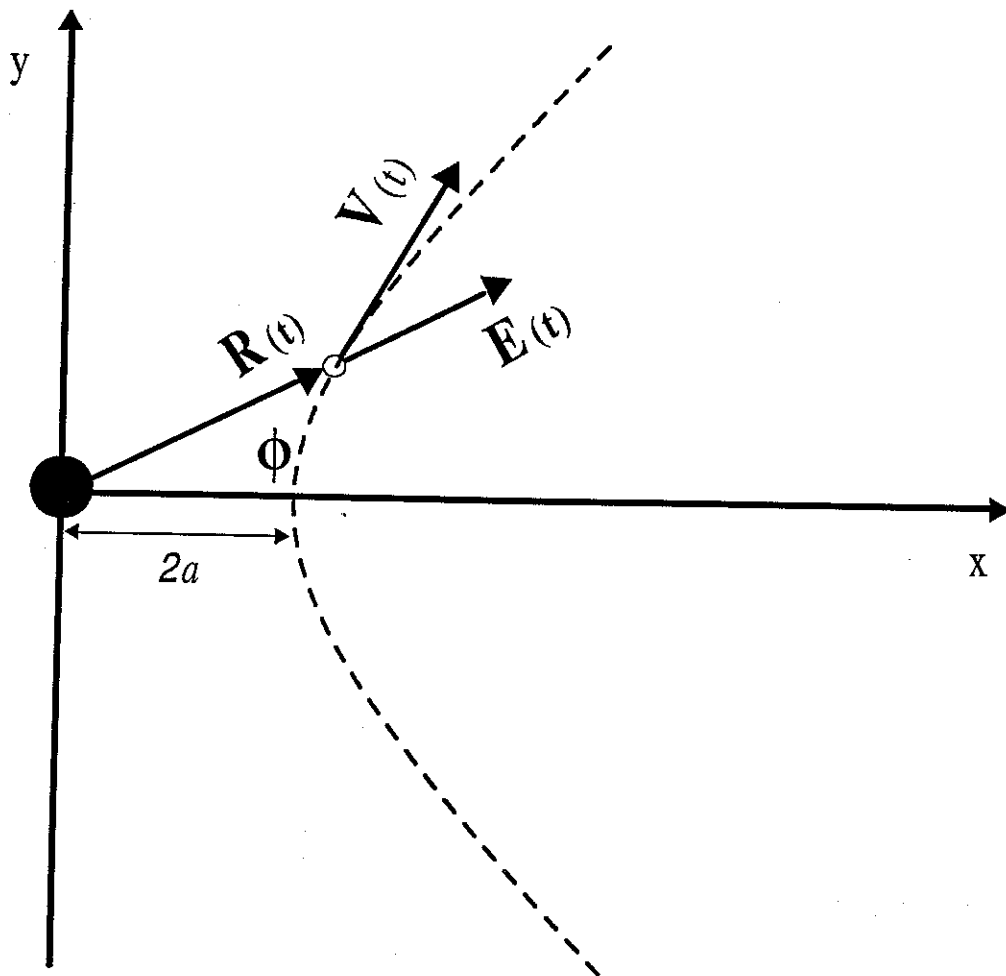


Figure 1

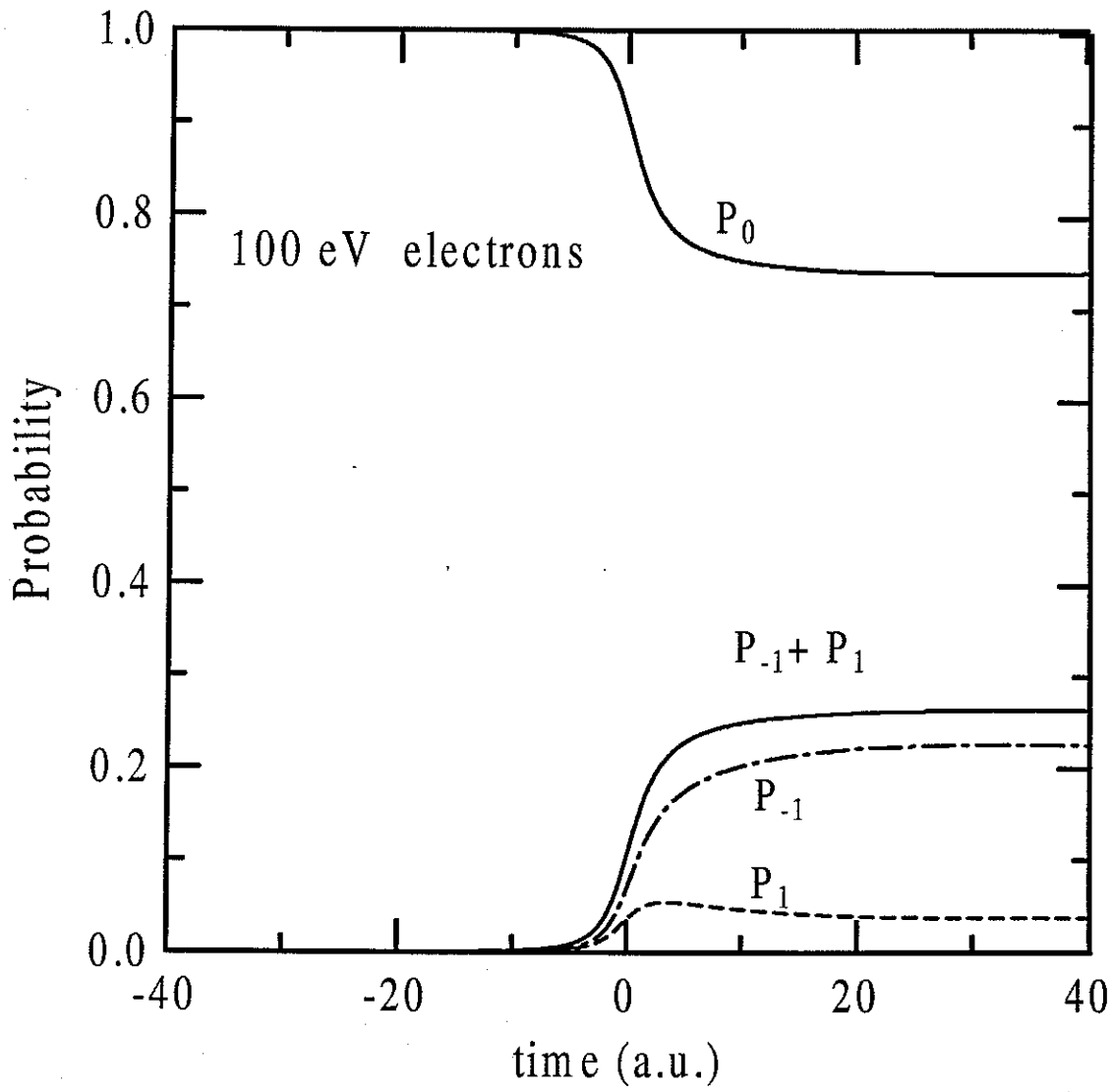


Figure 2a

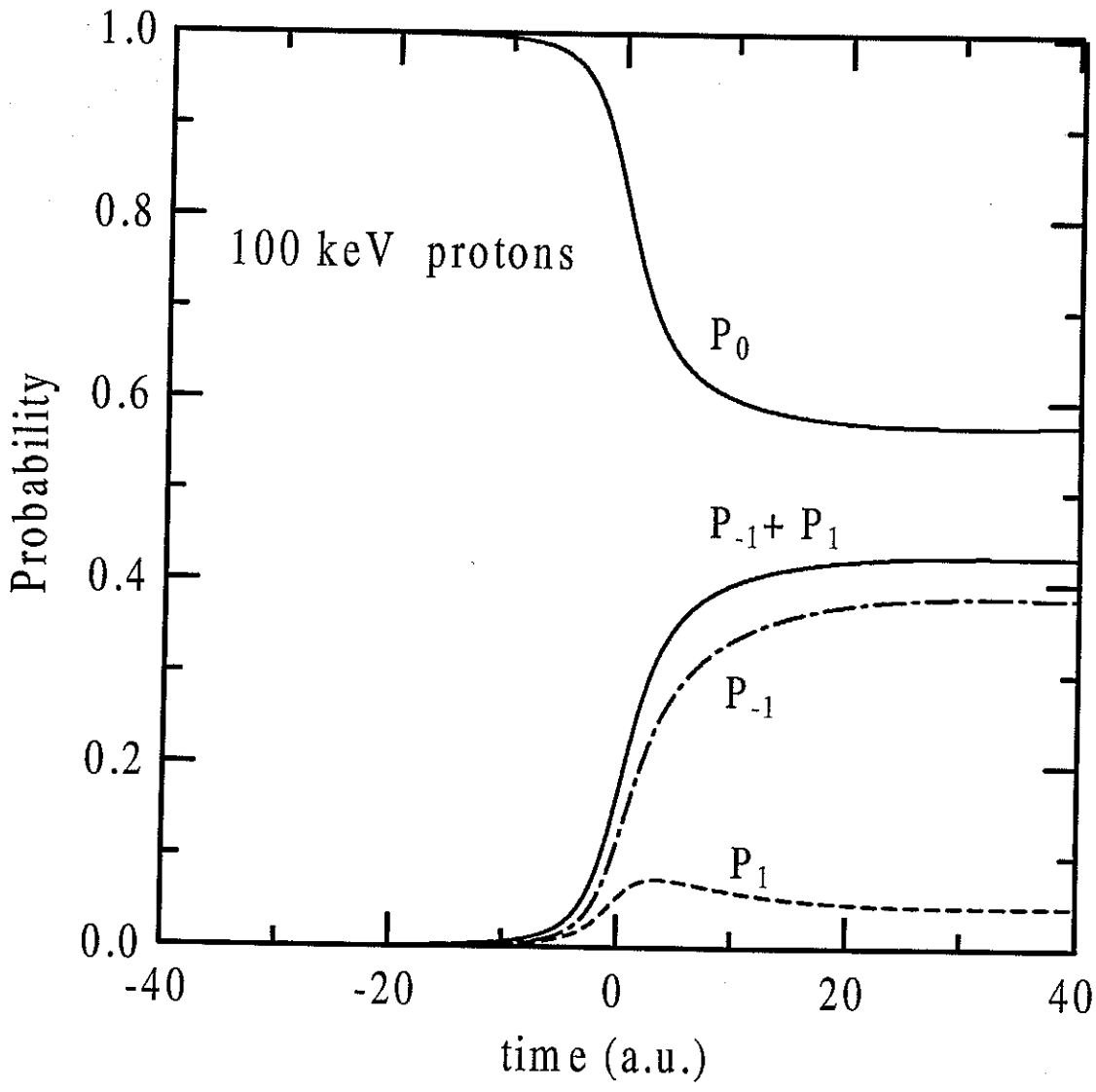


Figure 2b

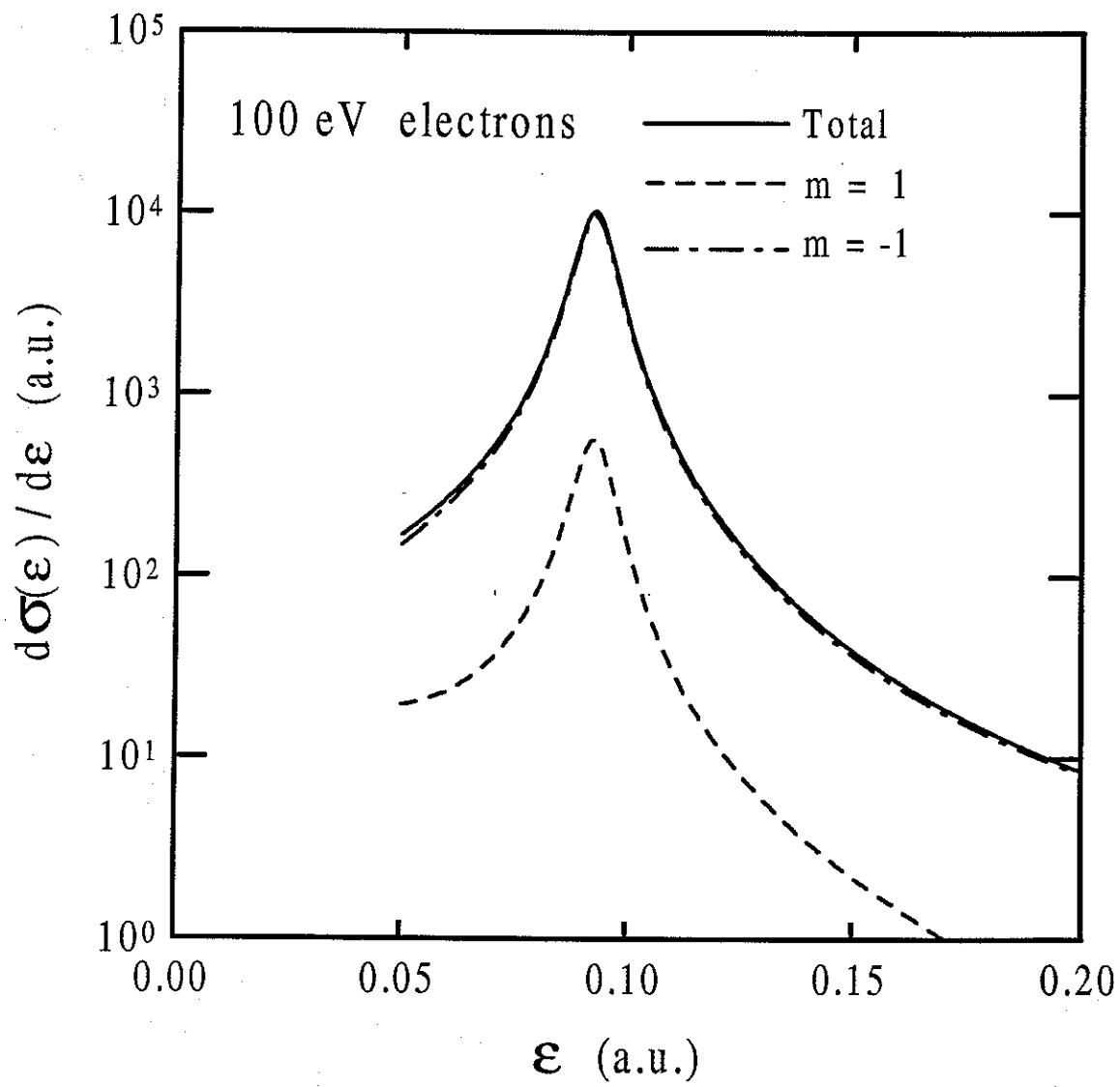


Figure 3a

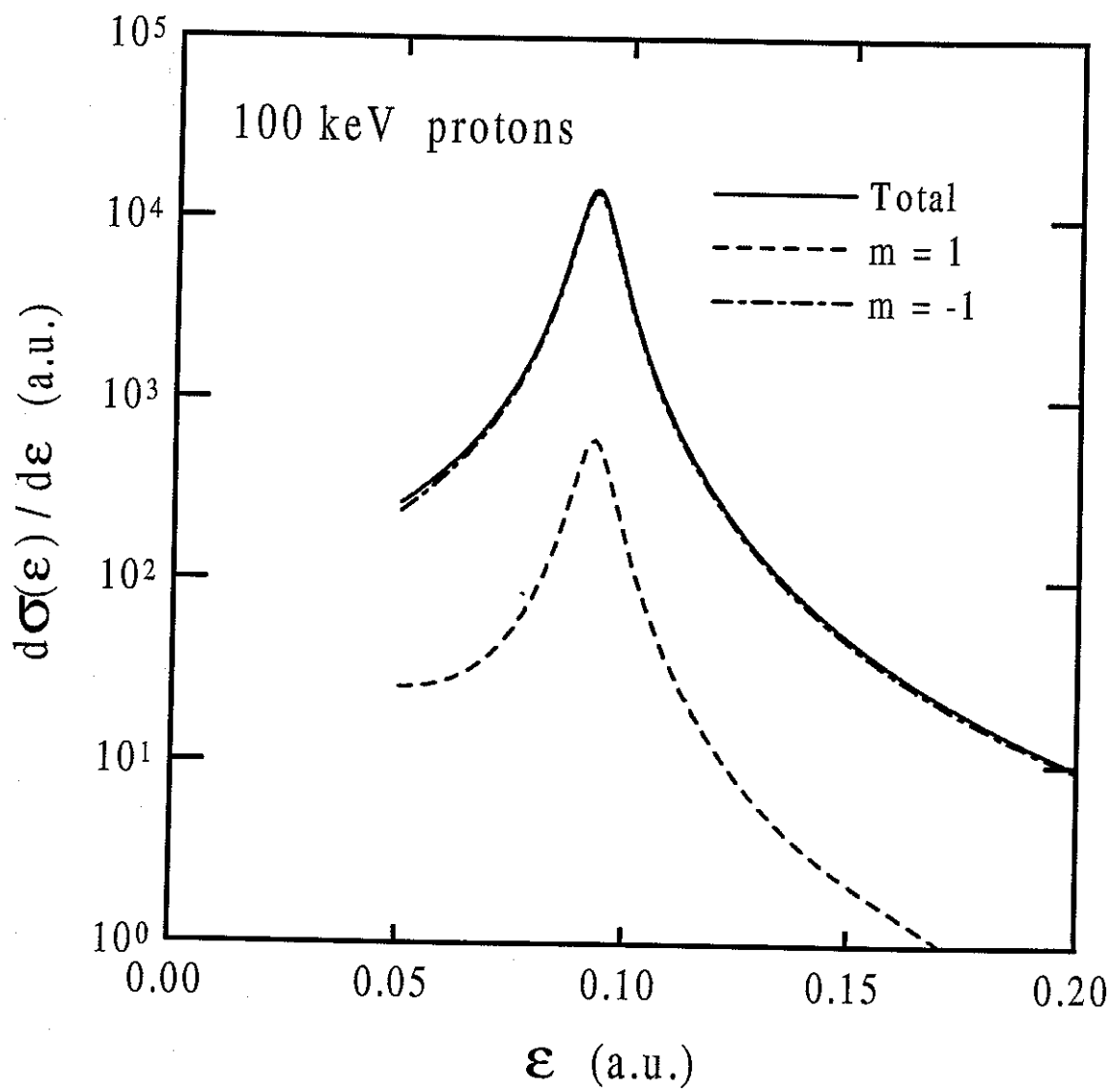


Figure 3b

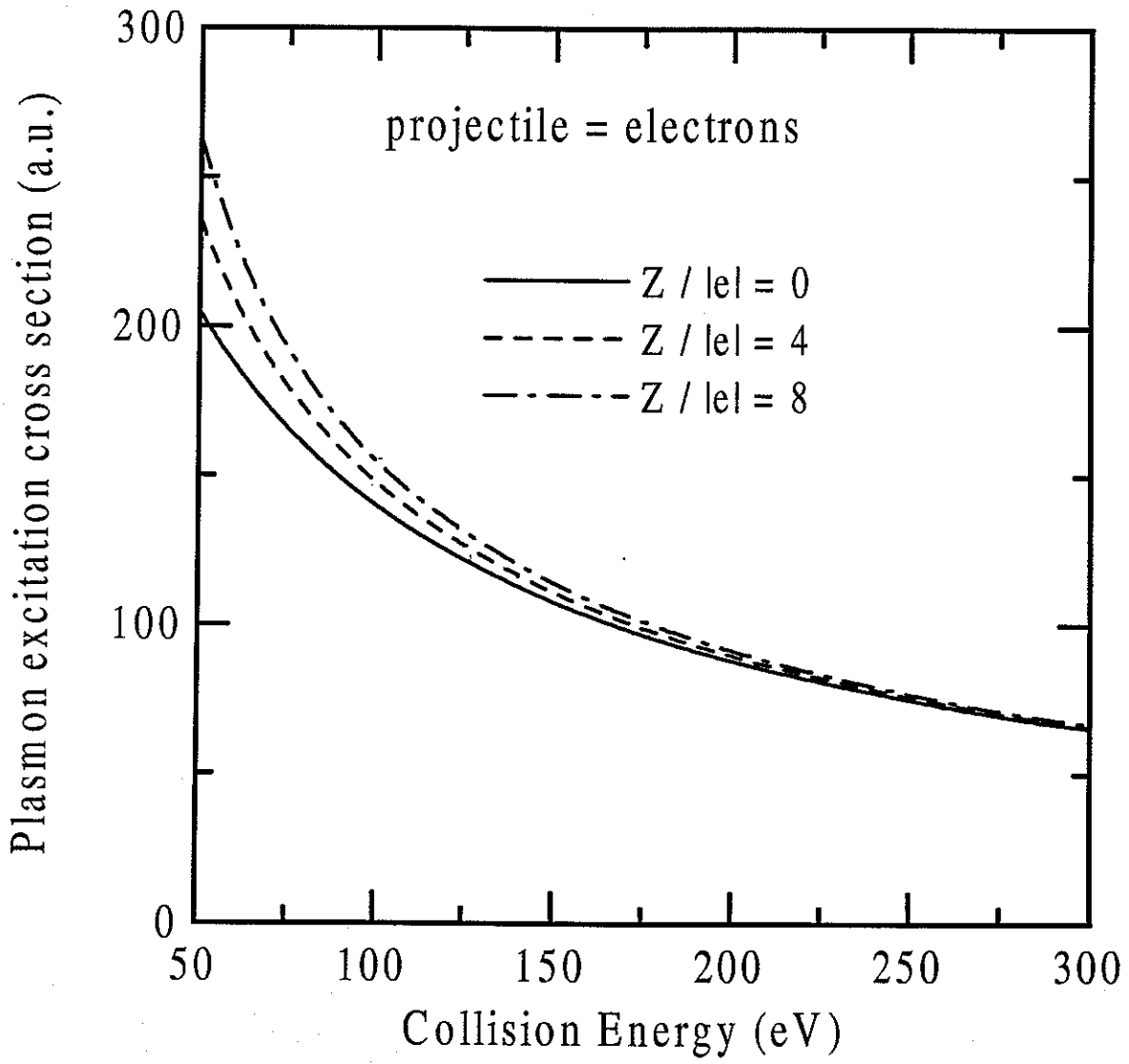


Figure 4a

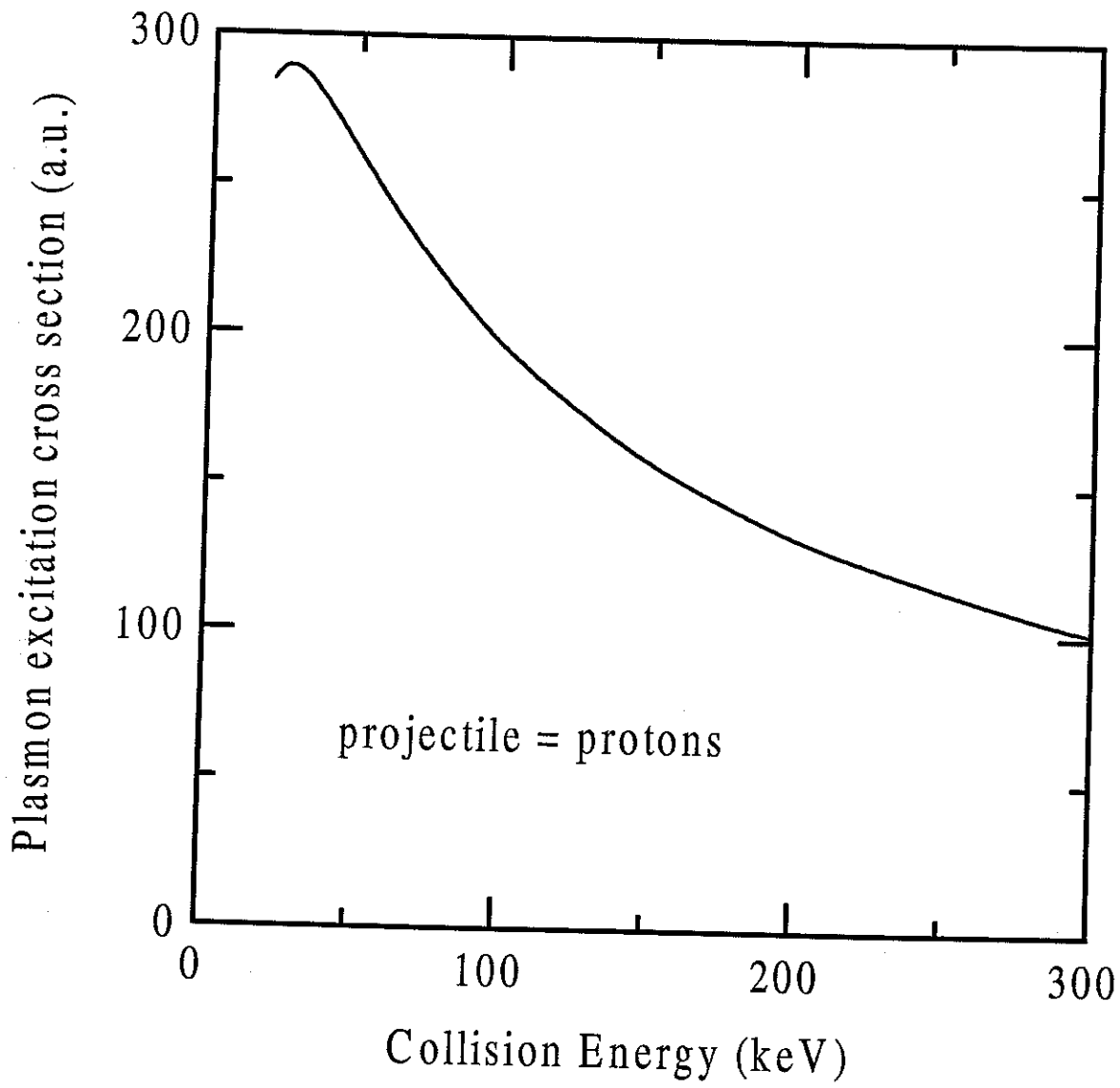


Figure 4b