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Microscopic description of the plasmon resonance in small deformed metal clusters

M. Bernath and M. E. Spina
Departamento de Física, Comisión Nacional de Energía Atómica, Avenida del Libertador 8250, 1429 Buenos Aires, Argentina

J. M. Pacheco
Departamento de Fisica da Universidade, 3000 Coimbra, Portugal

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A full matrix random-phase-approximation calculation is performed to analyze surface plasmon excitations in spheroidal alkali-metal clusters, described in the jellium model. The single-particle levels are obtained in the local-density approximation to density-functional theory by solving the Kohn-Sham equations for deformed systems, making use of a one-center expansion method for the different potential terms. Numerical results are shown for the prolate Na_{10} and the oblate Na_6 clusters.

It is well established that quantum size effects play a crucial role in the study of surface plasmon excitations in jelliumlike spherical metal clusters. To reach a satisfactory description of these excitations a quantum mechanical calculation, based on the theory of linear response or on the random-phase approximation (RPA) is in order.[1-3] Indeed, these microscopic descriptions have provided a simple understanding of many detailed features of the optical response of small alkali clusters, in particular, one of the main broadening mechanisms of the surface plasmon due to its coupling to long-lived single-particle excitations.[1-5]

In the case of nonspherical metal clusters one expects, even at a classical level, an extra fragmentation of the surface plasmon mode, due to oscillations along the different principal axis of the cluster. Attempts to describe microscopically the dipole mode in jelliumlike, deformed metal clusters were published in Refs. 7 and 8. The calculation performed in Ref. 7 is based on the self-consistent spheroidal jellium model plus a time-dependent local-density approximation linear-response formalism. This model was applied to Na_{10} which has a spheroidal prolate ground state and the results compare well with available experimental data. In Ref. 8 a matrix-RPA calculation was performed to compute the surface plasmon excitation in the spheroidal clusters Na_6 and Na_{10} and the ellipsoidal Na_{12}. It was based on single-particle states of a triaxially deformed harmonic oscillator potential plus an l^2 term.[9] The results reproduce reasonably well the measured deformation splitting,[10] although they fail to explain the absolute value of the cross sections. This is partly due to the simplified single-particle levels used in the calculation and also to the lack of self-consistency between the ground state (GS) calculation and the RPA residual interaction, which was taken to be of a separable form.

In the present paper we perform a full matrix-RPA calculation in order to describe collective excitations in deformed alkali-metal clusters. We consider the sodium clusters Na_6 and Na_{10}, which have been calculated to display an oblate and prolate spheroidal deformation in their GS (Ref. 11), respectively. The present formulation has the same matrix form used in Refs. 3 and 8 but is now carried out fully self-consistently. Namely, both the (deformed) GS potential and the RPA residual interaction are computed self-consistently. This brings it to the standards of Ref. 7, with which our results for Na_{10} can be compared directly. However, and in contrast with Ref. 7, our formulation is more general and not restricted to spheroidal deformations. This, together with a smoother growth in computer demand as a function of cluster size, makes this method feasible to be applied to more complex finite systems such as the fullerene family.

The single-particle spectrum necessary to construct the RPA matrix is obtained by means of a self-consistent calculation for the deformed cluster. This is carried out in the local-density approximation (LDA) to density-functional theory, via the solution of the (deformed) Kohn-Sham equations.[6] For the exchange-correlation potential V_{XC} we use the parametrization of Gunnarsson and Lundqvist.[12] To construct the eigenfunctions corresponding to occupied and to unoccupied single-particle orbitals we use the following strategy. At each iteration of the self-consistent cycle, we perform a one-center multipole expansion of the density of valence electrons ρ and of the mean field potential V_{MF}, that is, we write $\rho(\vec{r}) = \sum_L \rho_L(r) Y_{L,0}(\theta)$ and $V_{MF}(\vec{r}) = \sum_L V_{MF,L}(r) Y_{L,0}(\theta)$.

Since we limit ourselves to external potentials which display axial symmetry, both parity and the azimuthal quantum number m are conserved. Making explicit use of these conserved quantum numbers, we write the solutions of the Kohn-Sham equations as $\Psi_{i,m,\pi}(\vec{r})$, where $\pi = (-)^l$ is the parity of the state and i labels the solutions. We then expand these wave functions in a complete basis set, $\Psi_{i,m,\pi}(\vec{r}) = \sum_{n,l} c^{n,l}_{i,m,\pi} \Phi^{n,l}_{\omega_0}(\vec{r})$. For basis functions we selected the complete set formed by the eigenfunctions of the spherically symmetric three-dimensional harmonic oscillator in spherical coordinates, with ω_0 as its fundamental frequency. These are completely specified by the quantum numbers n, l, m and can be written as $\Phi^{n,l}_{\omega_0}(\vec{r}) = R^{n,l}(r) Y_{l,m}(\theta,\phi)$, being eigenstates of the harmonic oscillator potential with energies $\hbar\omega_0(N_{sh} + 3/2)$ with $N_{sh} = 2n + l$.

The choice of the basis set is not arbitrary. In fact, har-

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monic oscillator potentials are able to account for some qualitative features of alkali-metal microclusters.[9,10] They also present the advantage that all angular integrations can be performed analytically. Furthermore, for axially symmetric systems, the Hamiltonian matrix is a real symmetric matrix, block diagonal in the quantum number m and states with different parity do not mix, which greatly speeds up the diagonalization process.

The harmonic oscillator wave functions depend parametrically on the choice of the fundamental frequency ω_0. We used $\hbar\omega_0 = 0.1$ Ry and eigenfunctions up to the energy $21.5\hbar\omega_0$, i.e., $N_{\rm sh} = 20$ major oscillator shells, were considered in the diagonalization.

A further truncation is necessary in the one-center multipole expansions. For symmetry reasons only even L components are present in the different multipole expansions and we checked that convergence was already achieved for $L = 8$, even though we kept the expansion up to $L = 10$.

For the external potential of the ions we make use of the jellium model approximation and, following Ref. 11 we keep the jellium density constant as a function of deformation, and equal to the bulk value for sodium, associated with $r_s = 4a_0$. We enclose the jellium charge density in a volume limited by a surface which, in spherical polar coordinates we define as $R(\theta) = \alpha^{-1}R_0\{1 + \sum_1^4 a_n P_n[\cos(\theta)]\}$. For the clusters we consider in the present paper, the a_3 parameter plays no role, and therefore we searched for the optimum shape of the clusters in the two parameter space defined by a_2 and a_4. We defined a grid in the a_2, a_4 "plane," and computed the total energy (LDA) associated with each shape, looking for the GS shape of the cluster which we define as the one to which corresponds the minimum energy. Once the GS is found, we compute the set of single-particle Kohn-Sham orbitals in an extended basis including eigenfunctions up to $N_{\rm sh} = 20$. This defines the model space to be used in the construction of the RPA matrix.

The residual interaction entering the RPA matrix (for a detailed description of the RPA formalism see, for instance, Refs. 3, 4, and 6) is a double variational derivative of the energy density functional

$$V_{\rm res}(\vec{r_1},\vec{r_2}) = \frac{e^2}{|\vec{r_1}-\vec{r_2}|} + \frac{dV_{\rm XC}}{d\rho}\delta(\vec{r_1}-\vec{r_2}). \qquad (1)$$

The main task is the evaluation of the matrix elements of the residual interaction. According to Eq. (1) we have to evaluate two contributions, one due to the direct part of the Coulomb potential and the other to the exchange-correlation term. The Coulomb contribution to the A matrix can be written

$$A^{\rm Coul}_{ph,p'h'} = \sum_{\lambda} \sum_{n_p,l_p,n_h,l_h,n_{p'},l_{p'},n_{h'},l_{h'}} c_p^{n_p,l_p} c_h^{n_h,l_h} c_{p'}^{n_{p'},l_{p'}} c_{h'}^{n_{h'},l_{h'}} \frac{4\pi}{2\lambda+1} R^{ph,p'h'}_{\rm Coul} \langle l_p, m_p|Y^*_{\lambda,\mu}|l_h, m_h\rangle\langle l_{h'}, m_{h'}|Y_{\lambda,\mu}|l_{p'}, m_{p'}\rangle, \qquad (2)$$

with

$$R^{ph,p'h'}_{\rm Coul} = \int R^{n_p,l_p}(r_1)R^{n_h,l_h}(r_1)\frac{r_<^{\lambda}}{r_>^{\lambda+1}}R^{n_{p'},l_{p'}}(r_2)R^{n_{h'},l_{h'}}(r_2)\; r_1^2\; r_2^2 dr_1 dr_2.$$

The exchange-correlation contribution is

$$A^{\rm XC}_{ph,p'h'} = \sum_{\lambda} \sum_{n_p,l_p,n_h,l_h,n_{p'},l_{p'},n_{h'},l_{h'}} c_p^{n_p,l_p} c_h^{n_h,l_h} c_{p'}^{n_{p'},l_{p'}} c_{h'}^{n_{h'},l_{h'}}$$
$$\times \sum_L R_L^{\rm XC} \sum_J \frac{\hat{\lambda}\hat{L}}{\hat{J}\sqrt{4\pi}}(\lambda 0 L 0|J0)(\lambda\mu L0|J\mu)\langle l_p, m_p|Y^*_{J,\mu}|l_h, m_h\rangle\langle l_{h'}, m_{h'}|Y_{\lambda,\mu}|l_{p'}, m_{p'}\rangle, \qquad (3)$$

where $\hat{\ell} = \sqrt{2\ell+1}$, $(l_1 m_1 l_2 m_2|LM)$ are the usual Clebsch-Gordan coefficients, and

$$R_L^{\rm XC} = \int R^{n_p,l_p}(r)R^{n_h,l_h}(r)R^{n_{p'},l_{p'}}(r) \times R^{n_{h'},l_{h'}}(r)V_L^{\rm XC}(r)r^2 dr.$$

$V_L^{\rm XC}$ is the L component of the multipole expansion of the $dV_{\rm XC}/d\rho$. We have to include a full summation over the quantum number $\lambda = 1, 3, 5, \ldots$ although for the deformations considered here it is enough to sum up to λ equal to 5 or 7. The exchange contribution has an additional difficulty due to the coupling of λ with L, which runs up to $L = 10$. We have checked that $V_L^{\rm XC}(r)$ is a slowly decreasing function of L and that even for large L values $V_L^{\rm XC}(r)$ goes to infinity in the limit of large r.

We now present results for the prolate $\rm Na_{10}$ and the oblate $\rm Na_6$ clusters. First, we carry out the energy minimization in the a_2, a_4 plane. We also map our deformation to the δ deformation used in Ref. 11, and we obtain as a result that our GS shapes for both $\rm Na_6$ and $\rm Na_{10}$ are in excellent agreement with the shapes listed in Ref. 11. In particular, we find $\rm Na_6$ to be oblate, with deformation parameter $\delta = -0.5$, that is, $a_2 = -0.34$ and $a_4 = 0.09$, whereas $\rm Na_{10}$ is prolate, with $\delta = 0.5$, that is, $a_2 = 0.33$ and $a_4 = 0.08$. Once the GS has been obtained we compute the RPA response. In Fig. 1 we display the photoabsorption cross section obtained for $\rm Na_{10}$ together with the experimental data of Ref. 10. We simulate the coupling of the dipole oscillations to the thermal vibrations of the surface[13] and to the ionic vibrations[5] by folding the RPA lines with Lorentzian functions. The

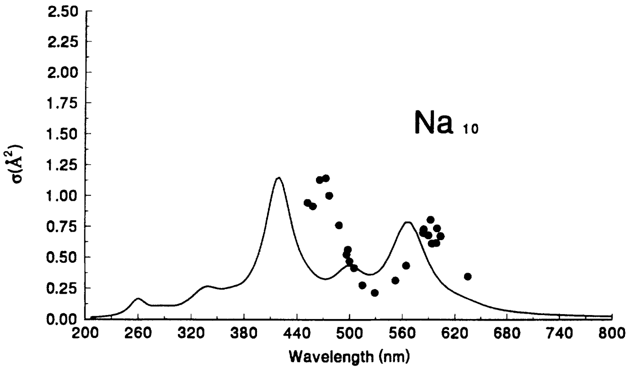

FIG. 1. Photoabsorption cross section for the Na_{10} cluster as a function of the wavelength of the incident photons. The experimental data were taken from Ref. 10.

damping factor $\gamma = E_0/\Gamma$, E_0 being the centroid of the resonance and Γ the width, is fixed at $\gamma = 0.09$. This is the only parameter in Fig. 1 and in that sense we remark on the good agreement obtained for the distance between the peaks, directly dependent on the deformation, and for their relative magnitude. An excellent agreement is also found between our results and those of Ref. 7. Apart from the deformation splitting which we just mentioned, the RPA cross section shows some structure at high excitation energies (in the ultraviolet region) which may eventually be enhanced in a more refined treatment which would remove the self-interaction errors inherent in the LDA, including naturally the Rydberg states which are missing at the level of the LDA.[5] The photoabsorption cross section for the oblate sodium cluster Na_6 is shown in Fig. 2. Both the splitting and the relative strength of the peaks are well reproduced by our calculation, which includes a damping factor $\gamma = 0.07$. For this cluster the third small peak present in the experimental optical response (at wavelength ~500 nm) is also predicted by our theoretical calculation as a yield of the $\Delta m = 1$ contribution. From this comparison one can conclude that apart from the systematic blueshift of the LDA response,[14] the theoretical cross sections are in good agreement with the experimental ones. In particular, their absolute value fits well the experimental data. This is an important improvement with respect to Ref. 8, and stresses the importance of self-consistency in the treatment of the optical response.

It is well known that the exchange-correlation potential plays an important role in metal clusters. For the deformed systems considered here we analyzed the importance of the different terms of the multipole expansion of the XC term to decide where to truncate the summation. To this end we evaluated some relevant radial integrands R_L^{XC} corresponding to the harmonic oscillator wave functions which are the main component of particle-hole states with high transition probability. We observed that the integrands vanish out of the cluster region as expected and that it is sufficient to perform the summation up to $L = 8$. This was also concluded by following the evolution of the peaks of the oscillator strength with the inclusion of the successive L terms (see Fig. 3). The final result is practically reached at $L = 6$. We observed that all the terms are necessary not only to reproduce the correct position of the peaks but also to adjust their magnitude. The effect of including high multipolarity contributions is to favor a concentration of strength in the main plasmon (the one of lowest energy).

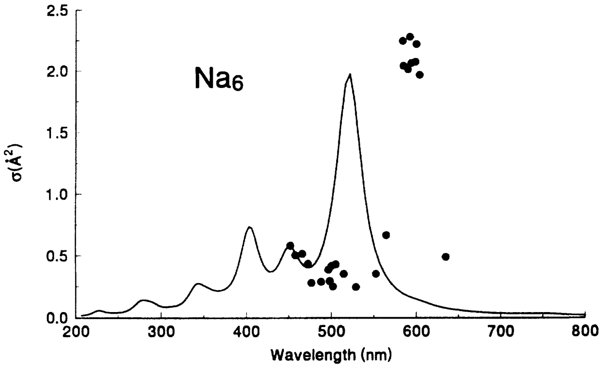

FIG. 2. Same as Fig. 1 but for the oblate Na_6 cluster.

Also arising from the deformed shape of the cluster is the sum over λ that has to be performed in Eqs. (2) and (3). By observing the convergence of the RPA results we have checked that truncation in $\lambda = 7$ is a very good approximation for the systems under study. Comparing the results for Na_{10} arising from the full calculation with a calculation performed considering only $\lambda = 1$, we noted that the inclusion of high multipolarity terms is essential to get the correct fragmentation (thus the absolute magnitude) although it is not very important in the determination of the position of the peak. The effect of including the multipolarities up to $\lambda = 7$ is a slight shift of the peaks to higher energies and a redistribution of the strength, displaying a more pronounced fragmentation. This can be explained as follows. As a consequence of the inclusion of $\lambda > 1$ terms in Eqs. (2) and (3), matrix elements $A_{ph,p'h'}$ that were negligible will take appreciable values. This leads to an extension of the effective particle-hole basis and thus a stronger coupling of the collective state with other particle holes that lie close in energy.

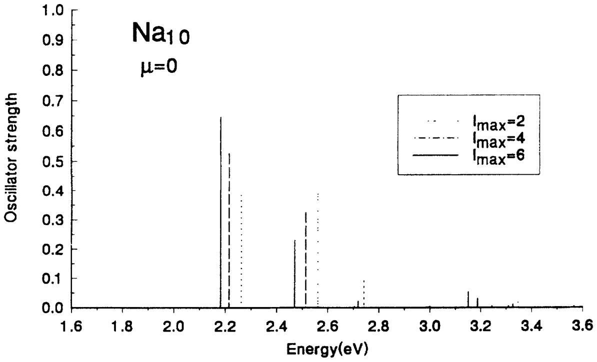

FIG. 3. Evolution of the oscillator strength for the z component of the dipole operator for the case of Na_{10} when different terms in the Legendre expansion of the XC part of the residual potential are included. l_{max} indicates the maximum L taken into account in the calculation.

We then conclude than the matrix-RPA formalism provides a satisfactory description of dipole plasmon resonances in deformed metal clusters. The one-center multipole expansion of the different potential terms and densities condense the solution into a repeated evaluation of radial integrals while angular terms are worked out in an analytical way. Besides the computational simplicity of the present method, another advantage of this kind of calculation is that further modifications in the single-particle spectrum (e.g., by inclusion of structural ionic effects via pseudopotentials) only involves a change in the coefficients of the expansion.

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