Collective and single-particle aspects in the optical response of metal microclusters

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(Received 15 April 1991; revised manuscript received 28 May 1991)

The photoabsorption response of the spherical, neutral Na₄₈, Na₂₀, and Na₄₀ clusters is studied in the random-phase approximation built upon a jellium background. Special attention is given to Na₄₀, which displays a particularly broad line shape. The theory provides an overall account of the observation in terms of the interplay between collective and individual electronic motion, and thus evidence for the importance of Landau damping in small metal clusters. The physics of this relaxation phenomenon as a quantum-size signature of the Coulomb interaction is analysed through simple models.

PACS numbers: 36.40.+d, 31.50.+w, 33.20.Kf

I. INTRODUCTION

There is strong experimental evidence (cf., e.g., Ref. [1], and references therein) that the valence electrons in a metal cluster—like sodium—are delocalized and able to explore the total volume of the cluster without being substantially scattered by the ionic cores. Then in an approximation known as the jellium approximation [2], the ionic lattice can be replaced by a uniform, positively charged background. As a result, it contributes only an electrostatic attraction to the delocalized valence electrons. On the contrary, the valence electrons are treated as a quantum system exhibiting exchange and correlation (xc) effects beyond their electrostatic repulsion. Treating the Coulomb interaction between the electrons in the local-density approximation, a central average (wine bottle [5, 6, 3]) potential U(r) can be determined that reproduces fairly well the observed ground-state properties (cf. Refs. [3, 5], and references therein).

Recently, excited-state properties of metal clusters have been measured. In particular, the absolute optical response of neutral sodium clusters Naₓ with 3 \leq x \leq 42 has been observed [7, 8] in the wavelength range 452–635 nm. At present, these measurements by Knight and co-workers represent the most systematic set of data available for excited states on a sequence of small metal clusters under identical experimental conditions, providing therefore a unique testing ground for the current theoretical models of metal clusters. Of this sequence, we have selected those with an even number of atoms that are expected to be spherical, namely, Na₄₀, Na₂₀, and Na₈ [7]. This choice makes the comparison between theory and experiment particularly straightforward. In fact, since a permanent deformation of the surface can be excluded as a source of fragmentation in the optical spectra [7], the profile of the photoabsorption cross section is expected to be particularly sensitive to quantal Landau damping (cf. Refs. [4, 9, 10]).

As will be shown below, the case of Na₄₀, considered together with the cases of Na₂₀ and Na₈ (cf. Ref. [4]), offers an ideal example for the workings of this process in metal clusters. As was the case with Ref. [4], we will employ here the discrete-matrix random-phase approximation (RPA) based on a uniform jellium background. It is the purpose of this paper to offer extensive results of this approach, and to provide an in-depth study of the process of Landau damping. Thus the present paper will explain how Landau damping can be understood as a manifestation of the long-range character of the Coulomb force, and will clarify the underlying microscopic processes by extracting from the full RPA some simple quantal models.

Concerning the calculations for Na₄₀, which will be presented below, the results are not only quantitatively, but also qualitatively different from those obtained earlier for Na₈ and Na₂₀. Indeed, we are dealing with the transition from a regime in which the surface plasmon exhibits one (Na₈) or two (Na₂₀) dominant peaks broadened by thermal surface fluctuations to a regime where Landau damping dominates and thus determines the full width at half maximum. Such a transition is clearly reflected in the presently available experimental data [7], which in the case of Na₈ and Na₂₀ (cf. also Refs. [11, 12]) reveal well-formed peaks, while in the case of Na₄₀ suggest a flat, almost structureless profile. This situation provides therefore a stringent test to check the validity of the different approaches.

II. OUTLINE OF RPA FORMALISM

For closed-shell, spherical clusters, the optical response of the system can be obtained by diagonalizing the Hamiltonian...
\[ H = H_0 + V, \]  
sum of the static self-consistent, single-particle Hamiltonian

\[ H_0 = T + U \]  
\[ (T \text{ being the single-particle kinetic energy, and of the two-body residual Coulomb interaction } V, \text{ in a discrete basis of } N \text{ particle-hole transitions coupled to a singlet spin state with angular momentum } I \text{ and negative parity.} \]

In particular, the total Hamiltonian \( H \) is diagonalized using the RPA. In what follows, we shall specify the single-particle potentials \( U(r) \) self-consistently in the spherical jellium-background model [3] using the density variational formalism in a semiclassical approximation [5]. These potentials are displayed in Fig. 1.

The residual two-body interaction \( V \) is given in the local-density approximation by

\[ V(r_1 - r_2) = \frac{e^2}{|r_1 - r_2|} + \frac{dE_{xc}[\rho]}{d\rho} \delta(r_1 - r_2). \]  

Here \( E_{xc}[\rho] = \frac{dE_{xc}[\rho]}{d\rho} \) is the exchange-correlation potential in the ground state. As in Refs. [3, 5], we use the exchange-correlation energy density \( E_{xc}[\rho] \) of Gunnarsson and Lundqvist [13]. As a result, the exchange-correlation potential \( V_{xc} \) is given in atomic units by the expression

\[ V_{xc}(r) = -1.222/r_s(r) - 0.0666 \ln \left( 1 + \frac{11.4}{r_s(r)} \right), \]

where \( r_s(r) = \left[ \frac{3}{4\pi \rho(r)} \right]^{1/3} \) is the local value of the Wigner-Seitz radius.

The RPA equations (see, e.g., Refs. [14, 15]) have the matrix form

\[ \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X_n \\ Y_n \end{pmatrix} = E_n \begin{pmatrix} X_n \\ -Y_n \end{pmatrix}. \]

The submatrices \( A \) and \( B \) are specified in terms of the angular momentum coupled matrix elements of the interaction (3), i.e.,

\[ A(p, p'; \gamma') = (\epsilon_{n_p, l_p} - \epsilon_{n_{p'}, l_{p'}}) \delta_{\gamma', \gamma} \delta_{l_p, l_{p'}} \delta_{l_\gamma, l'_\gamma} \delta_{n_p, n_{p'}} \delta_{n_{\gamma}, n_{\gamma'}}. \]

\[ = 2 R(p, p'; \gamma') (-1)^{l_p + l_{p'}} \left[ \frac{(2l_p + 1)(2l_{p'} + 1)(2l_\gamma + 1)(2l_{\gamma'} + 1)}{(2\lambda + 1)} \right]^{1/2} \begin{pmatrix} \lambda_l \lambda_{l'} \\ 0 \ 0 \end{pmatrix} \begin{pmatrix} 0 \ 0 \ 0 \ 0 \end{pmatrix}, \]

where

\[ R(p, p'; \gamma') = \int r_1^2 dr_1 r_2^2 dr_2 \mathcal{R}_{n_p, l_p}(r_1) \mathcal{R}_{n_{p'}, l_{p'}}(r_2) V(r_1, r_2; \gamma) \mathcal{R}_{n_{\gamma}, l_{\gamma}}(r_1) \mathcal{R}_{n_{\gamma'}, l_{\gamma'}}(r_2). \]
and where \( R_{n,i}(r) \) is the radial part of single-particle wave functions. In multipole order \( \lambda \), the radial contribution of the two-body function (3) is given by

\[
V(r_1, r_2; \lambda) = \varepsilon^2 \frac{r_2^3}{r_2^{\lambda+1}} \frac{dV_{\text{ec}}[\rho]}{d\rho} \left( \frac{\rho}{r_1^2} \right)^{2\lambda + 1} \frac{2\lambda + 1}{4\pi},
\]

(8)

where \( r_2 = \min(r_1, r_2) \) and \( r_2 = \max(r_1, r_2) \).

The indices \( n_i \) appearing in Eqs. (6) and (7) denote the number of nodes for the corresponding single-particle states. The orbital angular momenta of the particles and holes participating in the excitations are denoted by \( l_i \), the total angular momentum of the excitation being \( \lambda \), which in the present calculation is set equal to 1 (dipole vibration). The \( 3j \) symbols appearing in (6) take proper care of the angular momentum coupling, as well as of the parity-conservation conditions. The factor 2 accounts for the spin degeneracy.

The radial wave functions \( R_{n,i} \), are calculated by diagonalizing the single-particle Hamiltonian \( H_0 \) in a basis including \( N = 25 \) harmonic-oscillator major shells. (The optimal oscillator parameter of this basis varies with the size of the cluster between 1.1 to 0.8 eV; the results, however, are independent of this choice.)

The RPA eigenstates are formed as a linear superposition of particle-hole excitations in terms of the forward-going and backward-going amplitudes \( X_n(\rho) \) and \( Y_n(\rho) \), respectively, according to

\[
|n\rangle = \sum_{p,h} \left[ X_n(\rho)(\rho^{-1})_{\lambda\mu} \rho_{n,h}(\rho^{-1})_{\lambda,-\mu} \right],
\]

(9)

where a singlet spin configuration is implied. Examples of the unperturbed single-particle excitations entering into Eq. (9) are displayed in Fig. 1.

The dipole transition probabilities associated with the state (9) can be written as

\[
B(E1, 0 \rightarrow n) = \frac{2}{3} \langle n\rangle |\mathcal{M}(E1)|\langle 0\rangle |^2,
\]

(10)

where

\[
\langle n\rangle |\mathcal{M}(E1)|\langle 0\rangle | = \sum_{p,h} \left[ X_n^*(\rho; 1) + (-1)^\lambda Y_n^*(\rho; 1) \right] \rho_{n,h}(\rho^{-1})_{\lambda,-\mu} \mathcal{M}(E1)|h\rangle
\]

are reduced matrix elements \( \langle 16 \rangle \) of the dipole operator \( \mathcal{M}(E1; \mu) = \sqrt{4\pi/3} \varepsilon \mathcal{V}_{\mu}(r) \).

Since the RPA preserves the energy-weighted (Thomas-Reiche-Kuhn) sum rule \( S(E1) = N R^2 e^2 / 2m \), the dipole transition probabilities (10) and associated eigenvalues \( E_n \) obey the relation

\[
\sum_n f_n = 1,
\]

(12)

where the oscillator strengths \( f_n \) per atom are defined as

\[
f_n = \frac{E_n B(E1, 0 \rightarrow n)}{S(E1)}.
\]

(13)

This result is also valid for the unperturbed particle-hole excitations, that is,

\[
\sum_{p,h} (\varepsilon_{n_p,i_p} - \varepsilon_{n_h,i_h}) |\sqrt{2/3} (p||\mathcal{M}(E1)||h)|^2 = S(E1),
\]

(14)

where \( \varepsilon_{n_i,i_i} \) are the single-particle energies.

To calculate the photoabsorption cross section per atom, \( \sigma \), one folds the oscillator strengths with Lorentzian shapes normalized to unity as follows:

\[
\sigma(E) = C \sum_n f_n L(E; E_n, \Gamma_n),
\]

(15)

where \( \Gamma_n \) denotes the width of the Lorentzian profiles, and the constant \( C \) is given by

\[
C = \frac{2\pi^2 e^2 \hbar}{mc} = 1.0975 \text{ (eV A}^2).\]

(16)

### III. ANALYSIS OF RPA RESULTS

**A. Landau damping in full RPA**

In Figs. 2(c), 3(d), and 3(b), we display the oscillator-strength functions versus excitation energy for the case of neutral Na\(_{40} \), Na\(_{20} \), and Na\(_{8} \). A conspicuous feature of the RPA results is the extent of fragmentation (Landau damping) exhibited by both Na\(_{40} \) and Na\(_{20} \).

In particular, the optical response for Na\(_{40} \) [cf. Fig. 2(c)] is dominated by several lines within an energy range of 1 eV. The oscillator strengths are plotted in Fig. 2(c) for the Na\(_{40} \) subspace with \( \Delta N = 1 \) and total (c) subspaces for Na\(_{40} \). (The text for a full description.) Particle-hole transitions within parentheses have been removed from the full space (the full space includes all the transitions up to \( \Delta N = 7 \)). The symbol \( \times 10 \) implies multiplication by 10 for the line to the left of it.

![FIG. 2. RPA oscillator strengths in restricted [(a) and (b)] and total (c) subspaces for Na\(_{40} \) (cf. the text for a full description). Particle-hole transitions within parentheses have been removed from the full space (the full space includes all the transitions up to \( \Delta N = 7 \)). The symbol \( \times 10 \) indicates those transitions that have been included in the restricted subspace. The symbol \( \times 10 \) implies multiplication by 10 for the line to the left of it.](image)
From an inspection of these results, one can conclude that the observed particle-hole fragmentation (Landau damping of the RPA damping) is the manifestation of a strong coupling supplied by the Coulomb force between the $\Delta N = 1$ and the $\Delta N = 3, 5, 7$ unperturbed particle-hole transitions. An estimate of the relative importance of these couplings with respect to the couplings inside the $\Delta N = 1$ subspace can be obtained most simply by first replacing the average potential $U(r)$ by an isotropic harmonic oscillator and then comparing typical elements of the RPA $B$ matrix [cf. Eq. (5)]. In the harmonic-oscillator basis, the calculations involving the bare Coulomb force [17] can be carried out analytically. One finds, for example, that the diagonal matrix elements associated with the $\Delta N = 1$, $1f \rightarrow 1g$ transition, as well as the matrix elements connecting this configuration with the $\Delta N = 3$, $2p \rightarrow 4s$ transition can be written as

$$B(1g, 1f; 1g, 1f) = \frac{589}{280\sqrt{2\pi}} \frac{\sqrt{m \omega_e^4}}{\hbar},$$

$$(17)$$

$$B(1g, 1f; 4s, 2p) = \frac{1071}{1280\sqrt{2\pi}} \frac{\sqrt{m \omega_e^4}}{\hbar},$$

where $m$ is the electron mass and $\omega$ the oscillator frequency specifying $U(r)$ in the harmonic approximation. The ratio of these two matrix elements is rather large, namely $\sim \frac{1}{3}$.

This is to be contrasted with the case of the giant dipole resonance in nuclei [18], where the short-range nuclear force can be approximated by a dipole-dipole separable interaction. Since the dipole transition moments for $\Delta N \neq 1$ are zero in the case of a harmonic oscillator, and extremely small in the case of a realistic average potential, this separable force effectively supplies no couplings outside the $\Delta N = 1$ subspace and the resulting photoabsorption response will be a structure of two largely unequal peaks similar to that shown in Fig. 2(a) [19].

### C. Two-stage fragmentation

From the numerical results displayed in Figs. 2 and 3 (restricted subspaces versus the total space), one can conclude that the Landau fragmentation may act in two stages. In the first stage, the couplings from the $\Delta N = 1$ to all the other higher transitions are coherent and lower the energy of the strongest line (surface plasmon), while an appreciable amount (25–50%) of the oscillator strength is shifted upwards producing a high-energy tail (the first stage is the only one manifested in the case of $\mathrm{Na}_8$, since this cluster exhibits a narrower average potential and has a simple closed-shell structure). In the second stage, some special $\Delta N = 3$ transitions with almost zero strength might be degenerate with the renormalized surface plasmon, breaking it up into two (case of $\mathrm{Na}_{20}$ [21]) or three (case of $\mathrm{Na}_{80}$) peaks, which retain, however, among themselves the original oscillator strength (before the second-stage breakup).

To understand in detail how the second-stage fragmentation comes about, we display in Fig. 4 the unperturbed
particle-hole oscillator strengths for Na40. The arrow marks the position of the unbroken surface plasmon at 2.83 eV [cf. Fig. 2(b)], while the two lines immediately to the left of it are the special T1 and T2 transitions that are responsible for the additional fragmentation typical of this second stage. These two transitions are lower than the rest of the $\Delta N \neq 1$ excitations, since in the potential for Na40 [cf. Fig. 1(b)] the 2p one-particle state lies higher in energy than the 1f state, even though both belong to the highest closed shell having the same principal quantum number, $N = 3$. Important factors in the interaction of the $\Delta N \neq 1$ excitations with the surface plasmon are the effective particle-hole energies that are defined by the diagonal elements of the RPA A matrix [cf. Eq. (5)]. Since the Coulomb force is repulsive, these effective particle-hole energies are slightly larger than the unperturbed particle-hole energies shown in Fig. 4. As a result, the rest of the $\Delta N \neq 1$ transitions are pushed to higher energies, away from the surface plasmon, while the two special T1 and T2 transitions are brought even closer to it, allowing for a redshifted, sizeable redistribution of the strength at energies below 3 eV, as exhibited in Fig. 2(c) [22]. This redshift of the oscillator strength of Na40 with respect to the case of Na20 conforms to the observation [7], and contrasts with the blueshift expected from one-pole approaches (ellipsoidal model, cf. Refs. [7, 8]) as a result of the decreasing values of the corresponding static polarizabilities.

Figure 4 also displays the unperturbed particle-hole strengths for Na20 and Na8. The arrow marks again the position of the surface plasmon before the second-stage breakup. In the case of Na8, the surface plasmon falls well within the gap between the $\Delta N = 1$ and the rest of the particle-hole excitations; no particle-hole excitation lies sufficiently close to it, and thus the second-stage fragmentation does not materialize.

D. Two-level model for Na20

Figure 3 also displays the RPA result for Na20, both in the full subspace [Fig. 3(d)] and in the restricted subspace, which is constructed by excluding the special $2s \rightarrow 3p$ ($\Delta N = 3$) transition [Fig. 3(c)]. Since only one unperturbed particle-hole transition is involved in this case, the physical content of Landau damping in the second stage of coupling can be easily modeled [24]. Indeed, if one labels with the index $c$ the RPA amplitudes ($x_{ph}^c$'s and $y_{ph}^c$'s in Table I) and the energy $\varepsilon_c$ of the surface plasmon defined in the restricted subspace, one can extract [26] from the RPA equations a dispersion relation that describes the interaction between the surface plasmon and the $2s \rightarrow 3p$ transition, that is,

$$E - \varepsilon_c = \frac{v^2}{E - \varepsilon_{2p2s}} - \frac{w^2}{E + \varepsilon_{2p2s}},$$  \hspace{1cm} (18)

where the effective coupling matrix elements $v$ and $w$ are given by the expressions

$$v = \sum_{p,h} (A_{2p2s,p,h} x_{ph}^c + B_{2p2s,p,h} y_{ph}^c)$$

$$= \sum_{p,h} A_{2p2s,p,h} (x_{ph}^c - y_{ph}^c) = -w. \hspace{1cm} (19)$$

Here, $\varepsilon_{2p2s}$ denotes the effective energy of the $2s \rightarrow 3p$ transition and $E$ denotes the energies of the final states in the full space.

Because of the large energy denominator, the second term in the right-hand side (rhs) of Eq. (18) can be neglected. As a result, the dispersion relation (18) becomes a second-order equation, and the RPA equations have been reduced to a simple, Hermitian two-level problem, namely,

$$\begin{pmatrix} \varepsilon_c & v \\ v & \varepsilon_{2p2s} \end{pmatrix} \begin{pmatrix} s \\ t \end{pmatrix} = E \begin{pmatrix} s \\ t \end{pmatrix}. \hspace{1cm} (20)$$

Equation (20) then yields two eigenvalues $E_+,$ $E_-$ with $E_+ \geq E_-$. If $|\xi| = (\varepsilon_{2p2s} - \varepsilon_c)/2v$, the distance between them is specified by the expression

$$\Delta E = 2v \sqrt{1 + \xi^2}, \hspace{1cm} (21)$$

while the fraction $f$ of the original oscillator strength shared between them is given as follows:

$$f_+ = \left| s_+ \right|^2 = 1 - f_- = \frac{1}{2} \left( 1 - \frac{\xi}{\sqrt{1 + \xi^2}} \right). \hspace{1cm} (22)$$

The quantities of Table I yield the value $v = 0.149$ eV for the effective coupling matrix element. Thus, since $\varepsilon_c = 2.81$ eV and $\varepsilon_{2p2s} = A_{2p2s,3p2s} = 2.84$ eV, the distance between the two peaks is found to be $\Delta E \approx 0.3$ eV, while the original oscillator strength is shared approximately equal to 55–45% between the two lines, in
good agreement with the full calculation and the available experimental data. In Table I, we further collect the RPA wave function in the full space \( (X's \text{ and } Y's) \) associated with the lower of the two most prominent lines in the optical response of Na_{20}. It can be seen that the collective surface plasmon (whose wave function is also specified in Table I through the \( x^c \)'s and \( y^c \)'s) and the single-particle transition \( 2s \rightarrow 3p \) are now well mixed, the surface plasmon having been depleted of a considerable amount of strength.

## IV. COMPARISON WITH EXPERIMENT

In order to compare the present RPA calculation with the experimental results for the photoabsorption cross sections, one has to take into consideration the coupling of the electronic dipole oscillations to the thermal fluctuations of the cluster surface [27, 28]. In keeping with the findings of Ref. [28], this can be simulated approximately by folding the lines predicted by the RPA spectrum with Lorentzian functions displaying a damping factor \( \Gamma/E_0 \approx 0.1 \) appropriate for room temperature (cf. Refs. [28, 9]), where \( E_0 \) is the energy of the peak of the Lorentzian function and \( \Gamma \) its full width at half maximum.

The theoretical cross sections for the three clusters are displayed in Fig. 5. Compared to the single-peak, displaced Mie resonance predicted by the ellipsoidal model [7, 8] for all spherical clusters, the RPA on a uniform jellium background offers a nontrivial prediction for the line profile in the visible range, where most of the strength is expected to lie. Apart from a moderate blueshift in energy [29], the present RPA theory provides an overall account of the experimental findings. In particular, going from Na_{28} to Na_{40}, the two most prominent trends inside the experimentally probed energy range are reproduced, namely, (1) the gradual decrease in the strength, and (2) the relative redshift of the photoabsorption strength. It should be noticed that the blueshift between the RPA results and the observation decreases with increasing size. In particular, for Na_{28}, Na_{20}, and Na_{40}, it is found to be 10%, 7%, and 5%, respectively.

## V. DISCUSSION

The optical response of a jellium sphere has also been studied ([10],[30]–[35]) within the formalism of the integral equation for the polarization propagator in the coordinate space. This approach is usually known as the time-dependent local-density approximation (TDLDA), and, although a quite different mathematical formulation, it is in principle equivalent [32, 36] to the matrix, RPA formalism. In practice, the two approaches are com-

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**TABLE I.** RPA wave functions for Na_{20}. The lower case \( x^c \)'s and \( y^c \)'s specify the surface plasmon in the restricted subspace [before the second-stage breakup, Fig. 3(c)]. The upper case \( X's \) and \( Y's \) specify the lower member of the ensuing doublet in the full space [Fig. 3(d)]. The coupling matrix elements, \( A(3p2s, ph) \), between the special \( 2s \rightarrow 3p \) transition and the particle-hole components of the surface plasmon are also listed.

<table>
<thead>
<tr>
<th>( \Delta N )</th>
<th>( h \rightarrow p )</th>
<th>( x^c )</th>
<th>( y^c )</th>
<th>( A(3p2s, ph) )</th>
<th>( Y )</th>
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<tbody>
<tr>
<td>1</td>
<td>1d ( \rightarrow 1f )</td>
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</tbody>
</table>
In the case of small neutral and cationic alkali clusters, the spectra exhibit a high degree of discreteness. For the neutral species, the highest occupied orbital lies halfway in depth with regard to the bottom of the binding potential. As a result, the plasmon—fragmented or not—lies below or in the immediate vicinity of the ionization threshold. In addition, all the unoccupied orbitals that participate in the $\Delta N = 1$ particle-hole transitions are well bounded. Apart from a couple of slightly unbound orbitals, the same is true for the unoccupied orbitals that participate in the $\Delta N = 3$ particle-hole transitions. In particular, the important 5p orbital for the second-stage fragmentation in Na$_{20}$, as well as the corresponding 4s and 3d orbitals in the case of Na$_{40}$, lie at the rim of the potential having practically zero energy, and represent very narrow resonances (cf. also in Ref. [30] the phase-shift analysis for the potential of Li$_{20}$, especially Fig. 3).

This situation is quite different from the case of nuclei, where the neutron binding energy is only 20% of the potential depth and the giant dipole resonance is pushed far into the continuum, well above the edge of the potential. It should be noticed that many cases of collective vibrations in atoms also exhibit broad, structureless cross-section profiles, in close resemblance to the typical nuclear case of the tin isotopes [37].

With the exception of Ref. [32], the TRK sum rule has not been discussed in connection with the TDLDA. Instead of the oscillator strengths, this method calculates first the dynamic polarizability $\alpha(\omega)$ as a function of energy. Usually the imaginary part of the dynamic polarizability, which is proportional to the cross section, is plotted on a logarithmic scale, and its peaks provide information about the positions of the excitation spectra and, qualitatively, about the corresponding strengths. A small smoothing parameter must be used to treat numerically the divergencies of the polarizability at discrete excitations below the ionization threshold. The associated oscillator strengths are proportional to the area under these sharp peaks, a quantity that becomes the more difficult to be calculated than the sharper the peak. Use of a larger smoothing parameter tends to blur the discrete structure of the response.

In spite of these practical differences, studies using the polarization-propagator approach are in general agreement with the trends reported from matrix-RPA studies. Both methods, when using the local-density approximation, yield positions and centroids for the most prominent peaks that are systematically blueshifted by 5–15% with respect to the observation. Although qualitative in nature, a different analysis that looked at the frequency-dependent complex polarization density $\alpha(r,\omega)$ had suggested [10] a strong coupling between single-pair and collective surface mode in Na$_{20}$, an effect later expressed quantitatively by the matrix-RPA approach [4] through the detailed allocation of oscillator strengths. In analogy with the case of Na$_{20}$, two closely spaced prominent peaks were found for K$_{20}$ in Ref. [34]. The pronounced fragmentation of the photoabsorption response and the
importance of Landau damping in the case of Na_{40} have also been emphasized in Ref. [35].

Reference [35] has proposed an empirical modification of the TDLLDA, so that self-interaction corrections are incorporated in the time-dependent picture. In general, the proposed corrections in this direction produce a static potential that is deeper than the LDA potential. More importantly, the single-particle orbitals are shifted downwards almost as a block (cf., in particular, Fig. 1 of Ref. [38]), producing only small changes in the particle-hole energy differences that enter into the linear-response equations. For the case of Na_{8}, these small changes lowered the position of the plasmon by 0.3 eV and in this respect yielded a better agreement with the observation [35]. However, in the case of Na_{40}, the corresponding calculation yielded substantial strength at too low energies, namely at 2.0 eV, which is 0.4 eV lower than the experimentally observed first peak at 513 nm [7].

Reference [39] has calculated the allowed transitions for Na_{8} using a molecular \textit{ab initio} method (cf., also Ref. [40]). In this approach, a minimum of three ion-core configurations must be considered, namely the $T_{d}$, $D_{2h}$, and $D_{4h}$ structures. Because of the multiple configurations and the lowering of the symmetries with respect to the spherical symmetry, this approach predicts a larger number of optical transitions below 3 eV than the allowed two transitions of the present method. The positions of the strongest lines for two of these configurations ($T_{d}$, $D_{2h}$) are in good agreement with the experiment. It needs to be noticed, however, that the strongest transitions are accompanied by at least five smaller lines below 3 eV. Unlike the present RPA method, Ref. [39] does not provide photoabsorption cross sections, neither does it compare the \textit{ab initio} results with the absolute experimental cross sections of Ref. [8]. As a result, definite statements concerning the agreement between \textit{ab initio} and experimental profiles are difficult to make. In any case, the additional large width observed in the absorption cross section of Na_{8} will help in washing out this fivefold profile and in bringing the \textit{ab initio} results in gross agreement with the experimental profile. \textit{Ab initio} calculations for the optical response of clusters as large as Na_{20} are prohibitive, and for Na_{40} they appear to be impossible at the present time. It is thus encouraging that a simple approach, like the present RPA method, yields satisfactory results in comparison with the observation.

**TABLE II.** The variations of the TRK sum rule in RPA as shells of higher $\Delta N$ character are successively added to the particle-hole basis. A symbol like $\Delta N = 1 - 7$ denotes the minimum and maximum character, respectively, of the shells considered at each step.

<table>
<thead>
<tr>
<th>$\Delta N$</th>
<th>$Na_{8}$</th>
<th>$Na_{20}$</th>
<th>$Na_{40}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.904</td>
<td>19.532</td>
<td>38.667</td>
</tr>
<tr>
<td>1-3</td>
<td>7.933</td>
<td>19.770</td>
<td>39.580</td>
</tr>
<tr>
<td>1-5</td>
<td>7.946</td>
<td>19.823</td>
<td>39.668</td>
</tr>
<tr>
<td>1-7</td>
<td>7.958</td>
<td>19.895</td>
<td>39.840</td>
</tr>
</tbody>
</table>

the precise line shape of the strength fragments and to supply stringent experimental tests for the limits of validity of the jellium and local-density approximations.

**ACKNOWLEDGMENTS**

We wish to especially thank W.D. Knight and K. Selby for providing us with their data prior to publication. Stimulating discussions with B.R. Mottelson and S. Bjørnholm are gratefully acknowledged. One of us (C.Y.) wishes to acknowledge the kind hospitality extended to him by the Niels Bohr Institute, where part of this work was done, as well as the hospitality of the Joint Insti-

**VI. CONCLUSION**

We conclude that the study of the line shape of the optical response of neutral sodium microclusters allows for the identification of specific discrete particle-hole transitions that interact strongly with the surface plasmon, acquiring appreciable strength and thus strongly fragmenting the collective response. This quantal size effect is manifested in the RPA calculations and provides explicit microscopic information on the process of Landau damping as a signature of the long-range character of the Coulomb force. Since this process is temperature independent, a lowering of the temperature is likely to reveal

**FIG. 6.** Evolution of the RPA oscillator-strength distribution for Na_{8} as shells of higher $\Delta N$ character are successively added to the particle-hole basis. A symbol like $\Delta N = 1 - 9$ denotes the minimum and maximum character, respectively, of the shells considered at each step. A reliable basis is reached at the level of $\Delta N = 7$ particle-hole transitions.
tute for Heavy-Ion Research, Oak Ridge, TN, where the initial calculation for Na$_{40}$ was carried out.

APPENDIX

In this appendix, we elaborate on certain numerical points mentioned in the main text. The high accuracy of the present method concerning the energy-weighted sum rule is illustrated in Table II. The sum is expressed in units of $\hbar^2 e^2/2m$. In these units, its theoretical value coincides with the number of delocalized electrons. One can see that the discrepancy between numerical and theoretical values is of the order of 0.5% when the particle-hole basis includes transitions up to $\Delta N = 7$. This degree of accuracy is essential for recognizing the fine structure at low energies below the surface plasmon. An example is offered by the $\approx 2\%$ peak at around 2.0 eV of Na$_8$ that was recently seen experimentally [11, 7].

Figure 6 illustrates for Na$_8$ the convergence of the RPA oscillator-strength distribution as shells of higher $\Delta N$ are successively added to the particle-hole basis. Due to the parity selection rule, only transitions with odd $\Delta N$ participate. Taking into consideration Fig. 3(a), it is seen that the qualitative picture of a strong surface plasmon accompanied by a high-energy tail has already developed at the level of the $\Delta N = 3$ shell. Subsequently, the higher-$\Delta N$ shells act coherently to adjust the position and the strength of the surface plasmon. A reliable particle-hole basis is reached at the level of the $\Delta N = 7$ transition shell.

As seen from Table I, there are 6 $\Delta N = 3$ particle-hole excitations in the case of Na$_{20}$. The unoccupied orbitals that participate in these transitions are the following: $2p$, $3s$, $2d$, $3p$, and $2f$. An inspection of Fig. 1(a) shows that only two of these orbitals are slightly unbound, namely, the $3p$ and the $2f$. The $3p$ orbital for Na$_{20}$, as well as the $4s$ and $3d$ orbitals in Na$_{40}$, have practically zero energy; they stand apart from the other orbitals in that they participate in the special particle-hole transitions that produce the second-stage fragmentation of the surface plasmon. As an illustration of the accuracy with which they are specified, we list in Table III the expansion coefficients of the $3p$ orbital in Na$_{20}$ in the basis including up to 25 harmonic-oscillator major shells. For comparison, the corresponding expansion for the highest occupied $2s$ orbital is also listed. Due to the spherical symmetry, only states with the same angular momentum enter in the expansion. The good convergence in this basis is reflected in the rapidly diminishing coefficients for basis states with higher nodes. It should be noticed that the largest coefficients correspond to basis states that have the same number of nodes as the expanded states.

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
$(n,l)$ & $3p$ Coeff. & $(n,l)$ & $2s$ Coeff. \\
\hline
(1,1) & 0.071 & (1,0) & -0.123 \\
(2,1) & -0.196 & (2,0) & -0.956 \\
(3,1) & 0.765 & (3,0) & -0.249 \\
(4,1) & -0.285 & (4,0) & -0.009 \\
(5,1) & 0.374 & (5,0) & 0.066 \\
(6,1) & -0.272 & (6,0) & 0.053 \\
(7,1) & 0.191 & (7,0) & 0.026 \\
(8,1) & -0.165 & (8,0) & 0.004 \\
(9,1) & 0.090 & (9,0) & -0.007 \\
(10,1) & -0.059 & (10,0) & -0.010 \\
(11,1) & 0.019 & (11,0) & -0.009 \\
(12,1) & 0.005 & (12,0) & -0.006 \\
(13,1) & -0.007 & (13,0) & -0.002 \\
\hline
\end{tabular}
\caption{The expansion coefficients of the $3p$ and $2s$ orbitals for Na$_{20}$ in the basis of 25 harmonic-oscillator major shells. $n$ denotes the number of nodes plus 1; $l$ is the angular momentum.}
\end{table}


[14] G.E. Brown, Unified Theory of Nuclear Models and
Forces, 2nd ed. (North-Holland, Amsterdam, 1967).
[17] The exchange-correlation contribution to the total force is usually of the order 10% of the direct Coulomb contribution. It thus has no effect for the point developed here.
[19] The different behavior of the Coulomb force compared to the nuclear force can also be seen from the fact that the plasmon frequency increases with the size of the cluster and approaches the classical Mie value [20], while the energy of the nuclear giant dipole resonance decreases as $A^{-1/3}$, where $A$ is the total number of nucleons.
[21] Reference [12] has reported recently that the full profile of the double peak in Na$_{20}$ has been seen in measurements covering the wavelength band from 370 to 600 nm.
[22] In the case of larger clusters ($\geq 100$), the surface plasmon is expected to fall well inside the forest of unperturbed $\Delta N \neq 1$ transitions. The repulsion between the resulting multiple fragments, however, is controlled by the precise value of the effective coupling matrix elements $v$ and $w$ (see following discussion in text), whose behavior is of importance in light of the $1/R$ broadening [23], where $R$ is the radius of the cluster.
[24] Using the RPA method in the polarization-operator formalism, Ref. [25] has also treated the case of Na$_{20}$ as a two-level model similar in spirit to the present approach.
[29] That the RPA response is blue-shifted with respect to the observation is a reflection of the fact that the jellium model underestimates the static polarizabilities. (See also Ref. [1].) However, this discrepancy decreases with increasing size, indicating that the jellium approximation becomes better for larger clusters.