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Collective spin excitations of alkali-metal clusters

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The response function of alkali-metal clusters, modeled as jellium spheres, to dipole ($L=1$) and quadrupole ($L=2$) spin-dependent fields is obtained within the time-dependent local-spin-density approximation of density-functional theory. We predict the existence of low-energy spin modes of surface type, which are identified from the strength function. Their collectivity and evolution with size are discussed.

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There is a large class of many-body systems that respond elastically to a sudden perturbation and plastically over long periods of time. Among them, one can mention the atomic nucleus. It displays giant resonances lying at energies considerably higher than the original particle-hole (p-h) excitations, and low-lying modes at energies much below the corresponding unperturbed p-h energies.

During the past years the study of simple metal clusters has received much attention. In particular, much effort has been devoted to their optical response properties. The existence of a giant dipole resonance (surface plasmon) in these systems, lying about 2–3 eV higher in energy than the original p-h excitations and carrying a large fraction of the energy-weighted sum rule (EWSR), has been clearly established [1–4]. A central subject in the systematic exploration of the collective properties of simple metal clusters is the search for low-energy vibrations, lying below the unperturbed p-h excitations. At variance with the plasmon, these vibrations are not expected to be directly observed in the infinite system. This is because they are expected to have, for all values of the linear momentum, excitation energies lying within the continuum of p-h excitations and thus be strongly Landau damped.

In the present paper we study the spin excitations of metal clusters, for which the residual interaction acting among the p-h excitations is attractive. It will be concluded that these modes are, for closed-shell clusters, likely to be the lowest collective modes of the system, appearing at energies well below 1.5 eV.

A rather detailed theoretical description of plasmon states in metal clusters can be obtained from the density-density response function within the framework of the time-dependent local-density approximation. The corresponding solutions can be worked out either in coordinate space [1], as well as in configuration space [2]. In both cases this is done in a basis that is built up of p-h excitations involving the single-particle orbitals where the electrons move. Below we shall follow a similar approach in dealing with the spin excitations of closed-shell clusters. In fact, we shall calculate, in coordinate space and within the time-dependent local-spin-density approximation (TDLSDA), the response of the system to an external multipole field that depends on the z component of the electron spin,

$$Q_\sigma \equiv Q\,\sigma^z = r^L\,Y_{L0}(\theta,\phi)\,\sigma^z\ . \tag{1}$$

This field simulates the effect on the electronic spins of an appropriate external probe, as could be a photon or electron beam. The coupling of this external probe with the orbital angular momentum of the electrons, leading to orbital magnetism [5], is not considered in the present formulation.

The linear-response theory of a field with a uniform direction of magnetization has been derived by Williams and Von Barth [6]. In the following, we will briefly recall the main points of the theory.

The variation in the electron spin density n_σ induced by a spin-dependent field Q_σ, with a time variation frequency ω, is expressed in terms of the field by means of the spin-density correlation function $\chi_{\sigma,\sigma'}$ as

$$\delta n_\sigma = \sum_{\sigma'} \int d^3r'\,\chi_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}';\omega)\,Q_{\sigma'}(\mathbf{r}')\ . \tag{2}$$

In the case of noninteracting particles, the correlation function is obtained from first-order perturbation theory as

$$\chi^0_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}';\omega) = -\delta_{\sigma,\sigma'} \sum_{p,h} \phi^*_h(\mathbf{r})\,\phi_p(\mathbf{r}) \left(\frac{1}{\varepsilon_p - \varepsilon_h - \omega - i\eta} + \frac{1}{\varepsilon_p - \varepsilon_h + \omega - i\eta} \right) \phi^*_p(\mathbf{r}')\,\phi_h(\mathbf{r}') \,, \tag{3}$$

where the ϕ's and ε's are the single-particle wave functions and energies, respectively, and the label $p\,(h)$ refers to unoccupied (occupied) single-particle levels.

For a nonpolarized ground state, the theory is more easily formulated in terms of the magnetization density $m = n_\uparrow - n_\downarrow$ and the corresponding spin-spin correlation function

$$\chi_{m,m} = \chi_{\uparrow\uparrow} + \chi_{\downarrow\downarrow} - \chi_{\uparrow\downarrow} - \chi_{\downarrow\uparrow} \,, \tag{4}$$

in terms of which the variation of the magnetization density is written as

$$\delta m(\mathbf{r}) = \int d^3r'\, \chi_{m,m}(\mathbf{r},\mathbf{r}';\omega)\, Q(\mathbf{r}') \,. \tag{5}$$

It can be easily verified that for free particles the correlation function in both spin-spin and density-density responses coincide ($\chi^0_{m,m} = \chi^0_{n,n} \equiv \chi^0$) and thus one can use well-known methods to obtain it. In particular, we choose to obtain χ^0 by means of the single-particle Green's function calculated in coordinate space, and the set of Kohn-Sham ground-state orbits

$$\chi^0(\mathbf{r},\mathbf{r}') = -\sum_h \phi^*_h(\mathbf{r})\,\phi_h(\mathbf{r}')\,[\,G(\mathbf{r},\mathbf{r}';\varepsilon_h + \omega) + G(\mathbf{r},\mathbf{r}';\varepsilon_h - \omega)] \,, \tag{6}$$

where the Green's function is defined as

$$G(\mathbf{r},\mathbf{r}';\omega) = \left\langle \mathbf{r} \left| \frac{1}{H-\omega} \right| \mathbf{r}' \right\rangle \,. \tag{7}$$

Within the TDLSDA theory, we assume that the electrons respond as free particles to the perturbing effective field, which consists of the external one plus the induced variation of the ground-state effective field. This condition defines a new $\chi_{m,m}$ in terms of the noninteracting one by means of the Dyson-type integral equation

$$\chi_{m,m}(\mathbf{r},\mathbf{r}';\omega) = \chi^0_{m,m}(\mathbf{r},\mathbf{r}';\omega) + \int d^3r_1\, d^3r_2\, \chi^0_{m,m}(\mathbf{r},\mathbf{r}_1;\omega) \times K(\mathbf{r}_1,\mathbf{r}_2)\, \chi_{m,m}(\mathbf{r}_2,\mathbf{r}';\omega) \,, \tag{8}$$

which is solved as a matrix equation in coordinate space, after performing an angular decomposition. The kernel $K(\mathbf{r},\mathbf{r}')$ is the residual two-body interaction, which in our case is exactly given by

$$K(\mathbf{r},\mathbf{r}') = \left(\frac{\delta^2 E_{\rm xc}[n,m]}{\delta m(\mathbf{r})\,\delta m(\mathbf{r}')} \right)_{n_0,m_0} \,, \tag{9}$$

where $E_{\rm xc}[n,m]$ is the exchange and correlation energy functional for arbitrary density and magnetization, n_0 and m_0 being the ground-state ones. In the present case we assume $m_0 = 0$.

We approximate $E_{\rm xc}$ within the local-spin-density approximation (LSDA), i.e.,

$$E_{\rm xc}[n,m] = \int d^3r\, n(\mathbf{r})\, \varepsilon_{\rm xc}(n,m) \,, \tag{10}$$

where $\varepsilon_{\rm xc}$ is the exchange-correlation energy density of the homogeneous system. For the correlation energy, we use the parametrization of Vosko, Wilk, and Nusair [7]. Thus, we have

$$K(\mathbf{r},\mathbf{r}') = \left(-\frac{1}{3} \left(\frac{3}{\pi} \right)^{1/3} n^{-2/3} + \frac{\alpha_c(r_s)}{n} \right) \delta(\mathbf{r} - \mathbf{r}') \,, \tag{11}$$

where $\alpha_c(r_s)$ is the correlation contribution named α_c fit in Ref. [7].

The LSDA amounts to approximating the residual interaction by a contact one. This does not seem unreasonable, in view of the short range of the exchange and correlation interactions and, in fact, the LSDA has proved to be successful in the calculation of spin susceptibilities in bulk alkali metals [8]. Thus, one may be confident that it will provide a reasonable description of the spin states in metal clusters, in the same way as the LDA has given a good description of the plasmon states [1, 2].

The response function $\mathcal{R}$ to the multipole field (1) can be easily obtained from the L component of the spin-spin correlation function χ_L as

$$\mathcal{R}(\omega) = \int dr_1 dr_2\, r_1^2 r_2^2\, r_1^L\, \chi_L(r_1,r_2;\omega)\, r_2^L \,. \tag{12}$$

Its imaginary part is related to the strength function $S(\omega) = \frac{1}{\pi}\mathrm{Im}\,[\mathcal{R}(\omega)]$. In the actual calculation we have added a small imaginary part ($\delta = 8$ meV) to the energy ω. This makes an average of the strength function by transforming the delta peaks in Lorentzians of width 2δ and thus simplifies the analysis of the results.

As a test on the numerical accuracy of our calculations, we have checked that the EWSR, which can be independently calculated by sum-rule methods [9], is satisfied with less than a 3% error in all the cases. Another test is provided by the Kramers-Kronig relation

$$2 \int d\omega\, \frac{1}{\omega}\, S(\omega) = \mathrm{Re}\,[\mathcal{R}(\omega = 0)] \,. \tag{13}$$

This is satisfied by our calculations within, typically a 2% error.

In the unpolarized ground state the spin-up and -down densities cancel exactly, and the effect of a small external perturbation Q_σ is to change them, creating a local magnetization. However, it does not induce a net magnetic moment in the whole cluster. The induced magnetization is a spin wave, which, when spatially integrated, vanishes. Figure 1 shows the radial part of the induced magnetization for the static case ($\omega = 0$) in the Na_{20} cluster for $L = 1$ and 2 (the angular part in each L mode is Y_{L0}). One can observe that the magnetization is peaked at the surface and this allows us to identify the modes as surface spin excitations, which, by analogy with the spin-wave excitations in the bulk system, we call surface paramagnons.

Figure 2 displays the dipole strength function of the magic Na_N clusters with $N = 8$, 20, 40, and 92. Solid and dashed lines correspond to the TDLSDA and non-

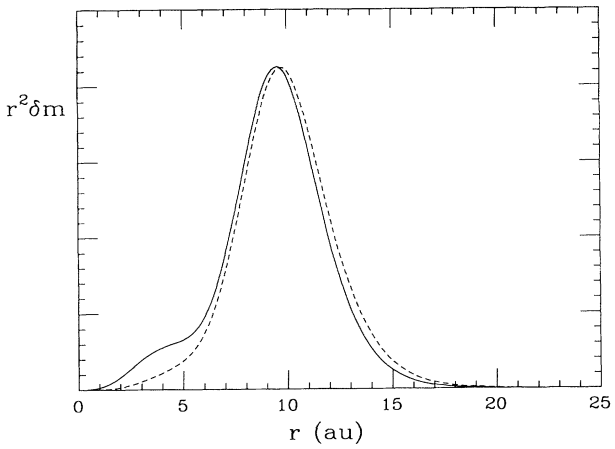

FIG. 1. Induced magnetization densities, in the static response, for the $L = 1$ (solid) and $L = 2$ (dashed) spin modes in the $N = 20$ Na cluster. We have used $r_s = 4$ for this metal. The radius of the jellium sphere, for this cluster, is $R = 10.86$ a.u.

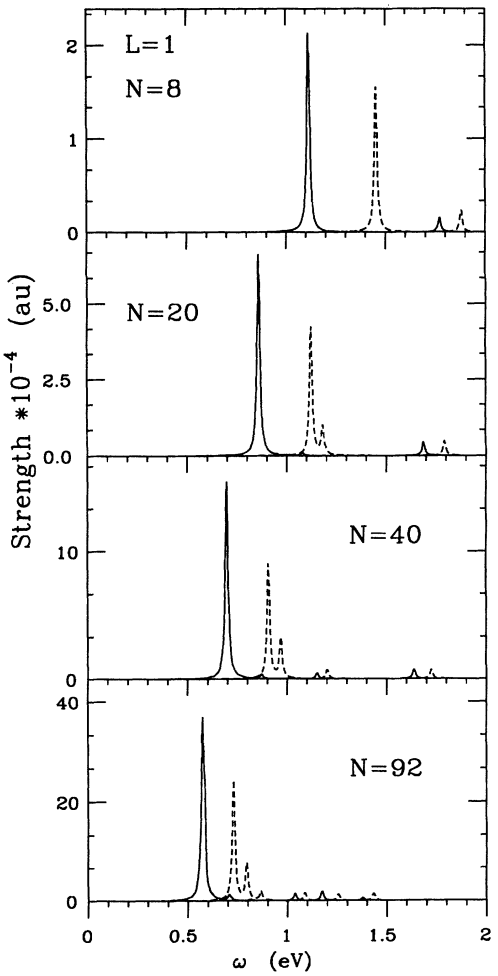

FIG. 2. Spin-dipole strength functions in magic Na clusters $N = 8$, 20, 40, and 92. Solid and dashed lines are the TDLSDA and noninteracting results, respectively.

interacting results, respectively. The noninteracting response has peaks at the energies of the allowed p-h excitations, whose strength in general decreases for increasing energy. In the case of Na_8 these p-h excitations are well separated. However, for bigger sizes there are several low-energy transitions that lie very close, two in the cases of Na_{20} and Na_{40} and three for Na_{92}.

The residual interaction has a conspicuous effect on the previous picture. It shifts the strength to lower energies and leads to essentially one peak, a collective spin excitation (paramagnon), which exhausts a large fraction of the EWSR (from approximately 90% in Na_8 to 80% in Na_{92}). This collective state washes out, almost completely, the low-energy p-h transitions (below 1.5 eV in Na_{20} and 1 eV in Na_{92}). The higher-lying ones are not so strongly affected by the interaction. They are only slightly shifted in energy, still keeping approximately their original strength.

Regarding the evolution with size, the short-range interaction causes the energy of the collective state to decrease with increasing size, in a way that resembles the behavior of the analogous nuclear collective excitations (in fact, a rough $N^{-1/3}$ behavior can be guessed) and that is opposite that exhibited by the surface plasmon

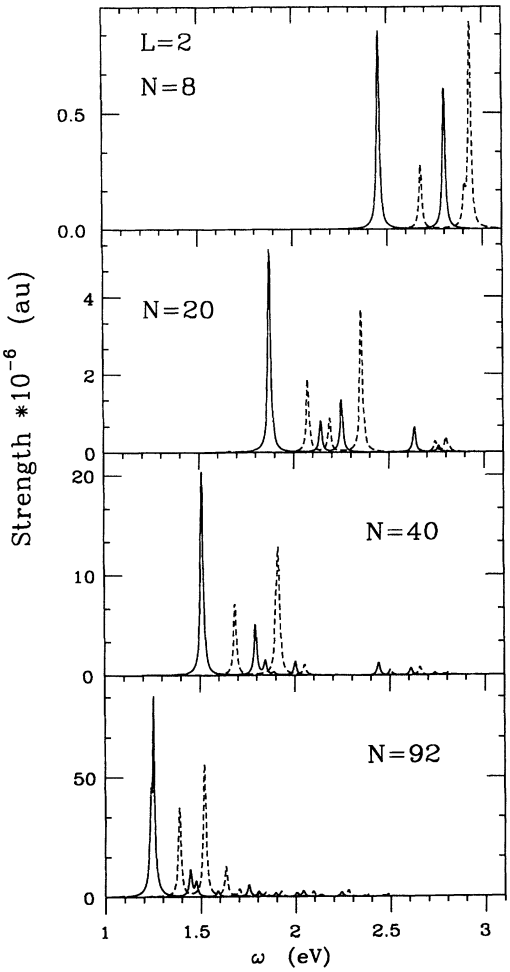

FIG. 3. Same as Fig. 2, but for the quadrupole ($L = 2$) spin mode.

in alkali-metal clusters. For increasing sizes, the residual interaction is less and less effective in separating the collective spin state from the p-h excitations. Thus, for large clusters, we expect to approach the bulk picture in which the spin-wave excitations are strongly damped by surrounding p-h excitations (Landau damping).

The surface paramagnons are below the unperturbed p-h excitations due to the fact that the residual interaction (11) is attractive. This, in turn, has its origin in the exchange part of the interaction. In fact, the correlation contribution is positive and, in the inner part of the cluster, is about half of the exchange one in absolute value. Towards the surface, the correlation becomes more important and cancels a much bigger part of the attractive exchange contribution.

The rapid development of the tunable laser sources (Ti:sapphire lasers, for example), operating in the wavelength of 1 μm (energy range $\approx$ 1 eV), makes possible the use of photodepletion techniques (cf., e.g., Ref. [3]) for the study of the low-energy part of the spectrum relevant to the predictions displayed in Fig. 2. Moreover, preliminary experimental investigations may already be performed using the 1056-nm ($\approx$1.16-eV) line of the Nd:Yag (neodymium doped yttrium aluminum garnet) laser. This is almost exactly the energy of the dipole spin excitation in Na_8.

In Fig. 3 we show the results corresponding to $L = 2$. In contrast to the dipole case, now the residual interaction is not strong enough to collect almost all the strength, in a single state, especially for the smaller clusters. There is a clear fragmentation of the TDLSDA strength, which is reminiscent of the p-h excitations. However, the changes induced by the interaction in the p-h spectrum go in the same direction as that for the dipole, the quadrupole strength being preferentially transferred to a low-energy excitation that carries a large part of the EWSR, ranging from 53% in Na_8 to 65% in Na_{92}. Thus, this quadrupole spin state is becoming more collective as the size increases.

In small clusters, the main source of damping of the plasmon can be traced back to its coupling to thermal fluctuations of the surface. The most important among these fluctuations are those of quadrupole character [10], which lead to a damping width $\Gamma = \sqrt{T/C}\,\hbar\omega$. In this expression T is the temperature of the cluster (and thus associated with the fluctuations of the ions). The quantity C is the restoring force associated with quadrupole distortions of the system and thus is controlled by the electrons. A simple estimate of this quantity is provided by the expression $C \approx \varepsilon_F N$, where ε_F is the Fermi energy of the metal cluster and N is the number of electrons. Finally, $\hbar\omega$ is the energy of the dipole mode. In the case of Na and for clusters at $T \approx 600$ K (≈ 0.052 eV) one can write $\Gamma = (0.67/\sqrt{N})\hbar\omega$. In the case of Na_{20} one thus expects $\Gamma \approx 0.4$ eV for the dipole plasmon ($\hbar\omega \approx 2.6$ eV) and $\Gamma \approx 0.1$ eV for the dipole paramagnon ($\hbar\omega \approx 0.8$ eV). Consequently, we expect the dipole surface paramagnons to show up as rather sharp peaks.

Summarizing, we have presented a detailed calculation of the dipole and quadrupole spin excitations in selected sodium clusters, modeled as jellium spheres. We found that the dipole spin response is almost entirely dominated by a single collective state that lies in the low-energy part of the spectrum (< 1.5 eV), below the p-h excitations, and that decreases for increasing sizes. This collective spin excitation may be regarded as the counterpart, in the spin channel, of the dipole surface plasmon and, by analogy with the bulk system, we call it the dipole surface paramagnon. However, because it lies at a considerably lower excitation energy, it is expected to display a much narrower width. We have also found that the quadrupole spin response is more fragmented than the dipole mode, because Landau damping is more important in that case.

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