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Towards spectral pattern of spin polarized sodium clusters: The example of Na_{12}

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Abstract. We investigate spin modes in the ground state and the polarized first isomer of the Na_{12} cluster describing the valence electrons in time-dependent local-spin-density approximation (TDLSDA) and the detailed ionic background using local pseudopotentials. The spin modes show a collective redshift compared to the unperturbed particle-hole excitations. They are strongly fragmented and the average energy of the modes along the principal axes are related to the underlying geometry (triaxial or axially symmetric). For the polarized isomer, we find significant cross talk between the spin modes and the dipole plasmon, which hints at a possible spectroscopic identification.

PACS. 36.20.Kd Electronic structure and spectra – 36.40.Gk Plasma and collective effects in clusters – 36.40.Vz Optical properties of clusters

The optical response of metal clusters has been intensively studied in the past and there exists a widespread literature on that, for reviews see [1–4]. By far most of this work is concerned with the dipole response, the Mie plasmon. Other excitation channels are much less studied, mainly because they are much harder to access experimentally. Nonetheless, their physical aspects may be interesting and it is worthwhile to explore them at least from a theoretical side. There are, for example, the spin modes, which play a role in bulk matter [5,6] and whose corollaries in finite systems deserve closer inspection. In fact, spin modes in metal clusters have been studied previously [7,8], however, using the jellium model for the ionic background. While the jellium model is presumably sufficient for exhibiting qualitative trends, access to details at spectroscopic accuracy requires an explicit (full) account of ionic structure. It is the aim of this manuscript to investigate spin modes employing fully detailed ionic background. The test case is the cluster Na_{12} which is particularly interesting because it has a triaxially deformed ground state and an energetically very close axially symmetric but polarized isomer [9].

The technical details of our treatment are well documented in previous publications. We repeat here quickly the crucial ingredients. The electronic wavefunctions are computed in time-dependent local-spin-density approximation (TDLSDA), formulated at Kohn Sham level. We furthermore use a representation of single particle electronic wavefunctions $|\varphi_\alpha\rangle$ on an equidistant 3D grid as in [10] (mesh size $0.8a_0$ on a $48 \times 48 \times 48$ grid). Only the valence electrons are treated explicitly. The nuclei with core electrons are kept frozen and their interaction with the valence electrons is described by a local pseudopotential for which we take a smooth form in terms of error functions. The relevant parameters of the pseudopotential are given in [9,11] together with a more detailed description of its derivation and the computation of the ionic structure *via* simulated annealing. This error function approach gives a slightly too large plasmon frequency. But the principle features studied here will not be affected by this.

The spectral features are deduced from time-dependent analysis as outlined in [12]. To explore the dipole mode in z direction, the system is excited instantaneously by a dipole shift of the electron cloud and the time-evolution of the dipole moment, $D_z(t) = \sum_\alpha \langle\varphi_\alpha|z|\varphi_\alpha\rangle$, is recorded. The dipole strength distribution is then obtained from the Fourier transformed signal as $\tilde{D}_z(\omega)$, and similarly for the x- and y-modes. The spin mode is analyzed in an analogous manner by tracking the spin-dipole moment $S_z(t) = 1/N_\uparrow \sum_{\alpha\in\uparrow}\langle\varphi_\alpha|z|\varphi_\alpha\rangle - 1/N_\downarrow \sum_{\alpha\in\downarrow}\langle\varphi_\alpha|z|\varphi_\alpha\rangle$ after a corresponding initial shift of the different spin-densities in opposite directions to start from a finite value of $S_z(t=0)$. The initial amplitude $D(0)$ or $S(0)$ can be tuned arbitrarily which allows to switch from the linear regime of small amplitudes high into the nonlinear regime, although we will be concerned here mostly with the linear response. Finally, we can check the cross talk between the modes by tracking D after spin excitation and S after dipole excitation. In that case, we draw $|\tilde{D}|(\omega)$, or $|\tilde{S}|(\omega)$ respectively, as a more robust quantity.

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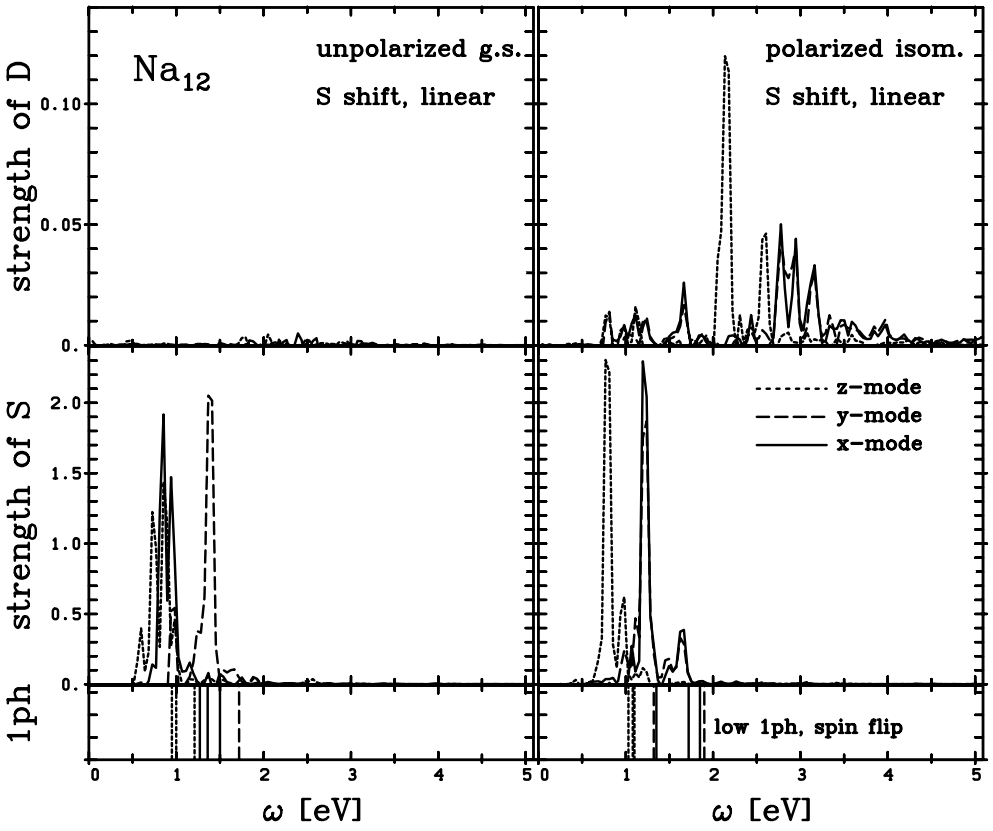

Fig. 1. Spectral strength distributions for the dipole signal (upper panel) and the spin-dipole signal (middle panel) after initialization of the spin-dipole. The left part shows results from the triaxial ground state of Na_{12} and the right part from the polarized isomer. In the lowest panel the energies of the corresponding $1ph$ transitions between levels with opposite spins are plotted. The assignment of line types is: x-mode (full line), y-mode (dotted), and z-mode (dashed).

The test case is the cluster Na_{12}. Its electron cloud is unstable at symmetric configurations and tries to escape by symmetry breaking. In the jellium model, it was found that the ground state becomes spontaneously polarized with net spin 2 [13]. With detailed ionic background, the symmetry breaking to a triaxial ground state was preferable, but spin polarization remains competitive and yields the first isomer with an energy difference of 100 meV relative to the ground state. The triaxial ground state has an overall deformation of $\beta_2 = 0.55$ and triaxiality $\gamma = 17°$ with small octupole moments ≤ 0.1. (for a definition of these dimensionless deformations, see *e.g.* [13]). The polarized isomer is axially symmetric with about the same deformation $\beta_2 = 0.58$ but $\gamma = 0$, and the spin polarization is 2. In fact, these two states have basically the same electronic wavefunctions except for the occupation of the last state [9].

Figure 1 shows the strength functions as they result from a spin-dipole excitation in the linear regime with an excitation energy of ≈ 40 meV coming from a diagonal shift of the spin-densities by $\pm\sqrt{3}\ 0.15a_o$. The lower panels provide the strengths of the spin-dipole $S_{x,y,z}$. The modes are concentrated in a region around 1 eV. This value complies with the spin modes previously found for systems of this size within the jellium model [7,8]. But now the spectra carry a much richer fine structure which is related to the larger fragmentation of the particle-hole ($1ph$) states in case of detailed ionic background. The $1ph$ spectra for the x-, y-, and z-excitations are indicated in the small band below. The number of states complies with the amount of fragmentation seen in the spin-dipole strength. But it is also visible that the actual strength are redshifted with respect to the mere $1ph$ states. This is the effect of the residual interaction which is attractive in the spin channel [5] (opposite to the strong repulsive interaction in the dipole channel). One sees also that the average frequencies of the x-, y-, and z-modes differ and that they are closely related to the underlying geometry. The longest spatial extension in z-direction yields the lowest frequencies, and the smallest extension in y direction for the triaxial case the highest. The axial symmetry of the polarized isomer yields degenerate spectra in x- and y-direction. All that is similarly known from the dipole mode and it is here related to the same energetic situation already preformed in the mere $1ph$ spectrum. The redshift is small and about the same in each mode such that the energetic ordering of the $1ph$ spectrum remains unmodified. There is another consequence of the fact that the residual interaction is small: the energetic position of the spin modes follows the trend $\propto N^{-1/3}$ similar as the $1ph$ modes. This trend is related to the momentum dependence $\omega \propto q$ of the spin modes in the bulk. That means that the frequency of about 1 eV,

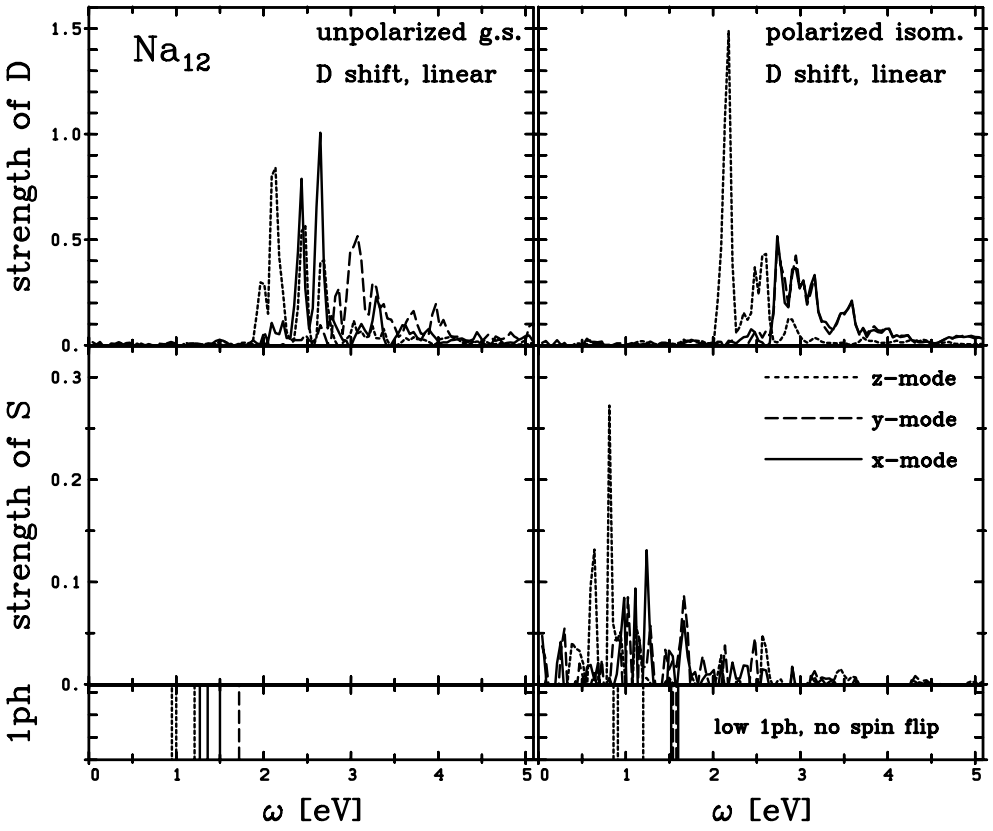

Fig. 2. Spectral strength distributions for the dipole signal (upper panel) and the spin-dipole signal (middle panel) after initialization of the dipole. The left part shows results from the triaxial ground state of Na_{12} and the right part from the polarized isomer. In the lowest panel the energies of the corresponding $1ph$ transitions between levels with equal spins are plotted. The assignment of line types is: x-mode (full line), y-mode (dotted), and z-mode (dashed).

observed here, is typical for Na_{12} and that lower frequencies are to be expected for larger clusters.

Figure 1 shows also the dipole strength functions from the spin-dipole initialization. There is very small cross talk for the unpolarized ground state (left upper panel). The signal is, however, not perfectly zero because the ionic configuration is slightly reflection asymmetric such that the two spin clouds shifted in opposite directions explore slightly different mean fields which, in turn, leaves a net effect on the dipole moment as well. In any case, the cross talk signal is very small compared to what we detect for the polarized isomer (right upper panel). There one sees several small "copies" of the spin mode and large response in the region of the dipole plasmons, *i.e.* around 3 eV (with standard geometrical splitting of the response). As found previously in the jellium model [8], the polarization mixes dipole and spin modes very efficiently.

For completeness, we explore the cross talk also from the other side, starting out from an initial dipole shift. Figure 2 shows the strength functions obtained from dipole excitation in the linear regime by a diagonal shift of the electronic density by $\sqrt{3}\ 0.3a_o$ resulting in an excitation energy of 0.66 eV. The upper panels contain the dipole spectra and these display the usual pattern of the plasmon response. The residual (Coulomb) interaction is strong and repulsive such that the plasmon frequency is much blueshifted as compared to the basic $1ph$ modes which carry the large dipole strength (shown at the bottom of the figure). The frequencies are finally concentrated around 3 eV and they are strongly fragmented by interference with $1ph$ states. The fragmentation seems to be a bit large for a cluster of this size [14]. But the ionic structure breaks reflection symmetry (yielding non-zero octupole β_3) which, in turn, enhances the Landau fragmentation substantially by accessing $1ph$ modes with different parities [15]. The average peak positions are related, again, to the background geometry showing a splitting into three different frequencies for the triaxial ground state and a splitting in only two groups for the axially symmetric isomer. This collective splitting due to background quadrupole deformation is one of the basic features of the dipole plasmons which had been noted very early [16] and which has been exploited extensively to explore the cluster geometry from analyzing optical response.

This far, the upper part of Figure 2 confirms earlier findings from the jellium model. Cross talk between dipole and spin modes is to be read off from the lower panels. Here we see an exactly vanishing signal for the ground state. This state is perfectly spin symmetric and there is thus no way to couple to the spin channel. Significant cross talk is seen, however, for the polarized isomer and the dominant response comes in the region around 1 eV

where the spin-modes reside. The actual strength distribution differs, of course, from the distribution seen in the previous Figure 1 because the indirect excitation couples to the various modes in a different manner. Nonetheless, there is significant response in the region around 1 eV and this cross talk may give access to spin modes as well as delivering a probe for spin polarized isomers in the sample.

As in all our earlier studies of plasmon resonances and spin modes [8,10–12], we have also investigated the changes of the spectral pattern when going to large excitation energies up to about 10 eV (corresponding to a four-plasmon excitation). The plasmon modes show, of course, their enormous robustness as harmonic modes independent of the ionic background, whether on jellium [12], or on detailed ionic structure [10], or even strongly deformed on insulating surfaces [11]. For the spin modes, we had seen in the jellium model that they survive also as resonant modes at large amplitudes [8]. With ionic background, however, the spin modes show a substantial spectral fragmentation in the linear regime and so it remained to be checked how the spectra extend to large amplitudes: we find again that the spin modes survive as clearly visible resonances, of course with the fragmentation pattern somewhat washed out. We skip a grafical demonstration as this result is rather expected from our earlier experience.

We have investigated optical response for Na_{12} in the dipole as well as in the spin-dipole channel. The configuration of Na_{12} was optimized with full ionic structure yielding a triaxial, unpolarized ground state and an energetically close axially symmetric, polarized isomer. The spin modes appear around 1 eV being redshifted by about 0.3 eV from their corresponding $1ph$ states due to the attractive residual interaction in the spin channel. The average position of the spin modes shows a geometrical splitting similar as it was seen in the dipole plasmon modes. The spin modes are, however, strongly fragmented which is a consequence of the symmetry breaking due to the underlying ionic structure. We have, furthermore, analyzed the cross talk between dipole and spin modes. It is negligible for the unpolarized ground state, but large for the polarized isomer. This cross talk could give a chance to observe the spin modes by optical absorption, at least indirectly.

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