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Anisotropic effects in the optical spectra of magic metal clusters: the role of ionic structure

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Abstract. The effect of the ionic positions on the optical spectra of magic metal clusters is studied via pseudopotential perturbation theory. Electronic many-body effects are considered within perturbed time-dependent local-density-approximation. Quantitative agreement with recent experiments by Reiners et al. is obtained. In this way a natural explanation is obtained for the temperature dependence of the optical absorption of magic metal clusters.

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Magic Metal clusters X_N (X preferentially one of the Ia, or Ib-group and $N = 8$, 20, 40, 58, 92, 138, 196, etc.) are normally considered to be ideal candidates for a natural realisation of the spherical jellium model (SJM) for metal clusters [1] (see also the review in [2]). Indeed both the pioneering experimental data of the Berkeley group [3] and first Density Functional Theory (DFT) based theoretical predictions by one of us [4, 5], making use of the Time Dependent Local Density Approximation (TDLDA), confirmed this simple picture. For this reason, it was rather spectacular that Reiners et al. [6] found for the photoabsorption of cold ($T \approx 130$ K) Na_9^+ clusters a double-peak structure, whereas for warm Na_9^+ clusters a single peak structure (quite broad) has been measured, in accord with the closed-shell SJM-based expectations. The difference in the warm/cold spectra can be understood by the very nature of the photoabsorption process, which is a very fast transition from the ground state to one of the excited states: at low T all ionic positions are nearly frozen, corresponding either to the ground state or to one of the low-energy isomeric states. At these experimental conditions, the ionic positions can be relevant in the absorption process (here tentatively understood as a vertical transition from the ground state ionic positions). At higher T, the ions oscillate with sizeable amplitude around their equilibrium positions. For this reason, it is normally assumed that a jellium type of picture applies, because all ions are "smeared" out to produce one homogenously charged background. However, this picture is oversimplifying, as can be seen, e.g., from the fact that the resulting line width is much too narrow [7]. Indeed, it is clear from [8] that the following picture is more appropriate (cf. also [9]): The measured photoabsorption cross section σ is the ensemble average of the instantaneous photoabsorption cross sections computed for all accessible (at a given temperature) ionic configurations. If the motion is ergodic, this shows that the observed width of the plasmon at finite temperature is NOT to be confused with the lifetime of this collective excitation [9]. Furthermore, it will be shown in this work that the ionic structure can lead to subtle microscopic structural effects in the absorption profile which cannot be accounted for in plasmon-pole type descriptions such as those underlying [8].

In what follows we apply the above considerations to study the ionic position effects in the spectra of cold magic clusters. We adopt the pseudopotential perturbed TDLDA formulation developed in [10], in the spirit of Pseudopotential Perturbation Theory (PSP-PT). To be self-contained, we give a short summary of the formalism below. This, as we shall show, results in a quantitative interpretation of the experimental absorption spectra of various charged and neutral magic metal clusters (for details of the theoretical formulation cf. [10]).

The delocalized electrons, whose optical response we are going to investigate, interact with the ensemble of ions (located at sites $\mathbf{R}_i$) via (weak) pseudopotentials:

$$v_{\mathrm{ex}}(\mathbf{r}, \mathbf{R}) = \sum_{i=1}^{N} v_{ps}(\mathbf{r} - \mathbf{R}_i), \quad \mathbf{R} = \{\mathbf{R}_i\}. \tag{1}$$

Here, $\mathbf{R}$ is to be determined by an appropriate structural minimization technique [10–12]. For reasons given in [10] we make use of the Heine-Abarenkov pseudopotential with the parameters given by Barnett et al. [13]. The external potential can be represented by its multipole-expansion around the "cluster-center", which can be any of the various possibilities discussed by Manninen [14].

We chose, as in [10], the center of mass of the cluster, writing

$$v_{\mathrm{ex}}(\mathbf{r},\mathbf{R}) = v(\mathbf{r},\mathbf{R}) + v_{2,\mathrm{ex}}(\mathbf{r},\mathbf{R}) = v_0(\mathrm{r},\mathbf{R})\,Y_{0,0}(\hat{r}) + \sum_{l=1}^{\infty}\sum_{m=-\ell}^{l} v_{l,m}(\mathrm{r},\mathbf{R})\,Y_{l,m}(\hat{r}). \qquad (2)$$

The optical absorption is now calculated via the following steps:

1. The electronic orbitals are calculated by solving the LDA Kohn-Sham-equations with the monopole term, v_0, as the external potential. At this level the response is isotropic, and the computation of the Greens function G proceeds as usual [5];
2. The "geometric part" of the external potential $v_{2,\mathrm{ex}}$ is taken into account by stationary perturbation theory, both for the (degenerate) set of eigenstates of the "monopole-problem", as well as for the correction of the Greens-function G of the monopole-problem. The expansion of the external potential (2) is cut at the maximum angular momentum which contributes (in first order stationary perturbation theory) to the splitting of the eigenvalues of the unperturbed system.
3. The optical absorption is calculated by solving the TDLDA-integral equation, where the free-particle correlation function χ_0 is calculated by means of the electronic orbitals and Greens functions, according to the perturbative expansion,

$$\chi_0(\mathbf{r},\mathbf{r}_1;\omega) = \chi_0^{(0)}(\mathbf{r},\mathbf{r}_1;\omega) + \chi_0^{(1)}(\mathbf{r},\mathbf{r}_1;\omega) + \cdots . \qquad (3)$$

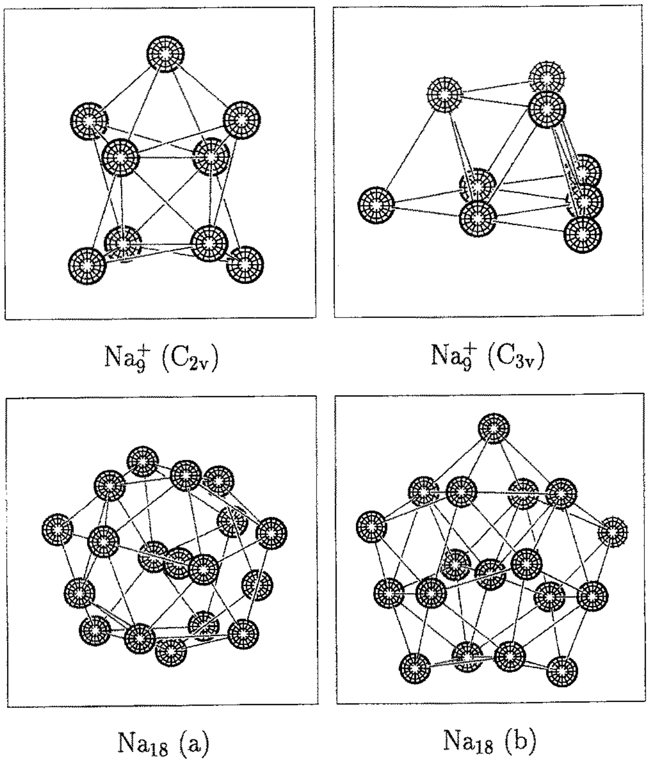
From χ_0, one obtains the TDLDA screened induced density

$$\delta n_1(\mathbf{r};\omega) = \int d\mathbf{r}_1 \chi_0(\mathbf{r},\mathbf{r}_1;\omega) v_{1,\mathrm{eff}}(\mathbf{r}_1;\omega), \qquad (4)$$

from which the photoabsorption cross section can be readily computed [5, 10]. In practice, the quantities in (4) are expanded into spherical harmonics which leads to a set of one dimensional integral equations which in turn are solved on an equally spaced mesh with a practical infinity chosen to be three times the "cluster radius" in the SJM. The expansion of $\delta n_1(\mathbf{r};\omega)$ gives rise to another cut-off parameter. Contrary to the case of the external potential there is no natural way to define a maximum angular momentum. In this work we terminate the expansion at $l = 1$. The example of Na_{18} shows that the differences in the absorption spectrum are negligible and do not justify the increase in computer time [15]. The smallness in the changes of the spectrum stems form the fact that we are considering perturbations of a spherical system, in which the only non-zero component of the density change (in the dipole approximation) is the dipole component.

In the following we apply the formalism above to Na_9^+ in order to compare our results with the cold spectra obtained in [6]. We start from the geometries determined in [11] (displayed in the upper panel of Fig. 1), which were obtained via a SCF-CI structural minimization (cf. [11] for details). Since we work with a DFT-based PSP-PT, we rescaled the bond-lengths and searched for the ionic coordinates which, within the same geometry, minimize the total energy, computed now in second order PSP-PT. The two structures, which are nearly degenerate in the SCF-CI quantum-chemical calculation, show a similar behaviour in PSP-PT. Since the experiment points to an oblate structure we apply the formalism above to the C_{3v} geometry, whose moments of inertia clearly reflect its oblate character [17]. The absorption spectrum is given in the top panel of Fig. 2: The vertical bars correspond to the experimental peak-positions of [6]. As can clearly be seen, we obtain quantitative agreement between theory and experiment, which indicates that the perturbative effect of the ions is capable of producing a multiple peak structure for Na_9^+. We would like to point out that, if we would have obtained a single peak structure, as with the SJM. Therefore, one can expect the SJM to be adequate to establish predictions for hot clusters, but it is likely to fail for cold ones. Furthermore, the photoabsorption cross section seems to be a good candidate to distinguish between different isomeric structures in a cluster.

The next example we study is Na_{18}, which is closed-shell cluster within the SJM [1], but is predicted to be an oblate spheroid within the spheroidal jellium model [18]. Here, we start from ionic positions obtained with the Car-Parrinello method [12], which leads to two close-lying isomers, displayed in the lower panel of Fig. 1. According to [12], the two isomers are nearly degenerate. Calculating the moments of inertia, one of the structures (B) can easily be identified as oblate-like, which also corresponds to the deformation of the experimental data of


Na_9^+ ($\mathrm{C_{2v}}$) Na_9^+ ($\mathrm{C_{3v}}$)

Na_{18} (a) Na_{18} (b)

Fig. 1a, b. Geometries of low-energy isomers of Na-clusters considered in this work: Na_9^+ is obtained by all-electron-CI calculations [11], whereas the geometries and coordinates for Na_{18} are from Car-Parinello-MD calculations of Röthlisberger and Andreoni [12]. For further explanation see main text

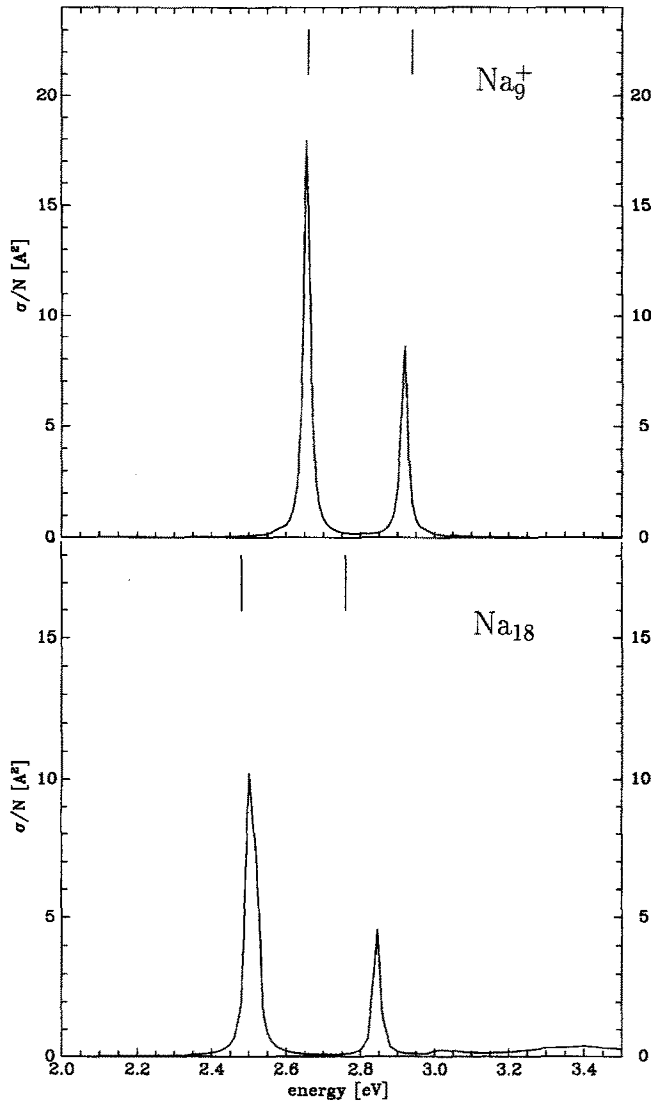


Fig. 2. Optical absorption of Na_9^+ and Na_{18} as obtained by pseudopotential perturbation theory (*continuous line*). The peak positions of the experimental results as obtained by Reiners et al. [6] for Na_9^+ and for Na_{18} by Selby et al. [19] are given by *vertical bars*

the Berkeley group [19]. Applying the formalism above produces the absorption spectrum shown in the lower panel of Fig. 2. The pattern of the peak structure reproduces very well the experimental data (vertical bars), apart from self-interaction effects [16] typical for TDLDA, which lead to the standard blue-shift of the theoretical results as compared to the experimental data. To summarize, the results obtained in the present work, together with the results of [10], indicate that PSP-PT is able to provide accurate predictions of several properties of metal clusters. Since the present method, in contrast with full-fledged ab initio alternatives, can be extended to very large clusters [20], one may aim at studying quantal effects in large, mesoscopic clusters. Finally, a natural interpretation of the temperature dependence of the photoabsorption spectra has been achieved, pointing out to the possibility of identifying, together with detailed experimental measurements, which isomers are predominantly formed in cold cluster beams, shining light into the process of formation of clusters in a beam.

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