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REINTRODUCING THE IONIC STRUCTURE IN THE JELLIUM MODEL FOR METAL CLUSTERS: PSEUDOPOTENTIAL PERTURBATION THEORY

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Ionic structure effects in small sodium clusters are studied via second-order pseudopotential perturbation theory. It is found that this formulation not only leads to the same ionic structures found via *ab-initio* Car–Parrinello structure optimization, but also to a substantial improvement in the overall description of the optical response of the clusters.

1. Introduction

For bulk forms of simple metals, the jellium model constitutes a first step towards realistic description of the dynamical behavior of electrons. Starting from the jellium model, it is well known[1] that the ionic structure, though providing a weak correction, is essential in order to achieve a quantitative prediction of physical properties. Because for the simple alkaline metals the associated pseudopotentials are very weak, one can attempt to introduce the ionic structure by means of perturbation theory. Indeed, pseudopotential perturbation theory has proved very successful in connection with lattice relaxation at metal surfaces.[2]

Since its proposal as a physical model for metal clusters,[3] the jellium model has become the most used in this field. Because the ions are replaced by a uniform charge distribution, this model can be considered as a purely electronic model of metal clusters. In spite of its simplicity, it has registered a remarkable success, not only in the overall description of ground-state properties of clusters, but also in predicting detailed features of the optical response of these systems. It is therefore natural to include ionic structure effects in this model via pseudopotential perturbation theory. In this work we shall illustrate the use of pseudopotential perturbation theory to study structural ground-state properties, as well as the optical response[4] of two small neutral sodium clusters, Na_6 and Na_8. By comparing with the corresponding results obtained with the jellium model, one will be able to put into evidence the role played by the ions in some of the clusters properties. It will be found that by reintroducing the ionic structure one obtains a better definition of the cluster volume in which the delocalized valence electrons move. Furthermore, one finds that the volume of delocalization together with the global shape of the cluster are the basic ingredients characterizing the optical response of these systems. For the small clusters treated here, surface quantization determines the main features of the optical spectra. For magic clusters, we find the spherical approximation to be adequate for the computation of the optical response, whereas for open-shell clusters one has to include the effects of nonspherical ionic perturbations in the optical response.

2. Theory

The underlying assumption for using pseudopotential perturbation theory is that the loosely bound valence electrons are responsible for binding the atoms into a cluster. On the other hand, the tightly bound core electrons are considered to be frozen in their core orbitals, so that the valence electrons interact with the ions via weak pseudopotentials, $v_{\rm ps}$. The electron–ion interaction can then be written in the form

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

where $\mathbf{R}$ represents the set of ionic positions $\mathbf{R}_i$, which is to be determined by minimizing the total energy of the system.

With respect to any chosen center of the cluster, the sum of the pseudopotentials can be expanded as follows (we carried out the expansion with respect to the center of mass of the clusters):

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

The first term is just the monopole, spherical part of the total ionic contribution, which is taken into account exactly by solving the set of Kohn–Sham equations for the N valence electrons moving self-consistently in this external potential. The second term in the pseudopotential multipole expansion is included perturbatively up to second order, which leads to the following contribution to the total energy:

$$\begin{aligned} \Delta E_{\mathrm{ps}} &= \frac{1}{2}\int d\mathbf{r}\,\delta n_2(\mathbf{r},\,\mathbf{R})v_{2,\mathrm{ex}}(\mathbf{r},\,\mathbf{R}) \\ &= \frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,v_{2,\mathrm{ex}}(\mathbf{r},\,\mathbf{R}) \\ &\quad \times \chi_0(\mathbf{r},\,\mathbf{r}',\,\mathbf{R})v_{2,\mathrm{ex}}(\mathbf{r}',\,\mathbf{R})\,. \qquad (3) \end{aligned}$$

In the above equation, $\delta n_2(\mathbf{r},\,\mathbf{R})$ is the induced screened density change caused by the external potential $v_{2,\mathrm{ex}}(\mathbf{r},\,\mathbf{R})$. In order to calculate the second-order correction, we have to calculate the static electronic susceptibility χ_0 using the one-electron states of the spherical potential $v(r,\,\mathbf{R})$,[6] which can be readily carried out in a numerically exact way via Green's function methods.[7,8]

Once the ionic structure which minimizes the total energy (including the perturbation correction) has been determined, we can compute the frequency-dependent susceptibility, in order to study the optical response of the metal clusters. This will be carried out at two different levels. First, and for closed-shell systems, we shall compute the optical response in the spherical approximation, i.e., neglecting the effect of the high multipole ionic contribution — this will be referred to as the isotropic response. Second, we shall include the effect of the ionic anisotropy by computing the optical response of a cluster, not only in the presence of an external frequency-dependent electromagnetic field, but also in the presence of a perturbing static field due to the anisotropic contribution of the ionic pseudopotential — this will be referred to as the anisotropic response. All calculations will be carried out using the same methods employed in the standard jellium model for metal clusters,[3,8] namely, density-functional theory in the local-density approximation. The response calculations (also the computation of the static susceptibilities) have been carried out at the level of time-dependent local-density approximation. Details of these methods as applied to spherical many-electron systems can be found, for instance, in Ref. 8.

3. Results and Discussion

Our calculations take, as a starting point, the global minimum-energy structure and low-lying isomers found in Ref. 9, in which geometry optimization was carried out in a fully relaxed way, using the Car–Parrinello method. Two close-lying isomers were found for Na_6 and three were found for Na_8, which are shown in Fig. 1. We put emphasis on two basic features of the ionic structure: its symmetry and, for each symmetry, the bond lengths, which define the cluster volume. Therefore, and starting from the geometries shown in Fig. 1, we calculate the total energy in the second-order pseudopotential perturbation theory, scaling the coordinates $\mathbf{R}$ so as to keep the symmetry of each ionic arrangement, but change the magnitude of the bond lengths, in order to see for which value of this scaling parameter the minimum is obtained.

For both clusters, and for each structure, we varied the scaling parameter from 0.90 to 1.10, corresponding to volume changes up to 30%. The pseudopotential used is of the Heine–Abarenkov form, with the parametrization of Ref. 2. For both clusters we obtain an excellent agreement with the results of Ref. 9. Not only do we reproduce the energy

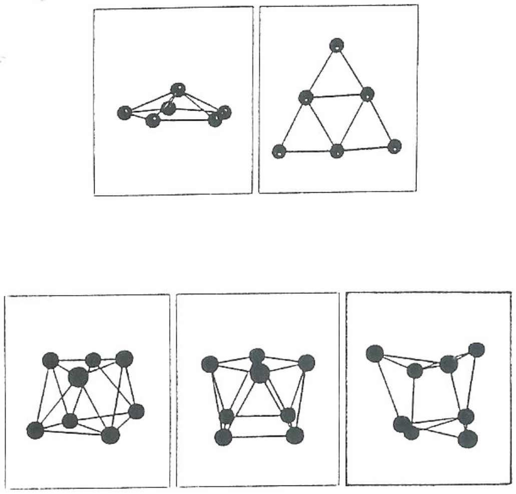

Fig. 1. The two different geometries obtained in Ref. 9 for Na_6, together with the three structures obtained for Na_8, corresponding to the ground-state and two lowest isomers (energy is increasing from left to right), and used as our starting geometries which we minimize as a function of a dimensionless scaling parameter (see main text for details).

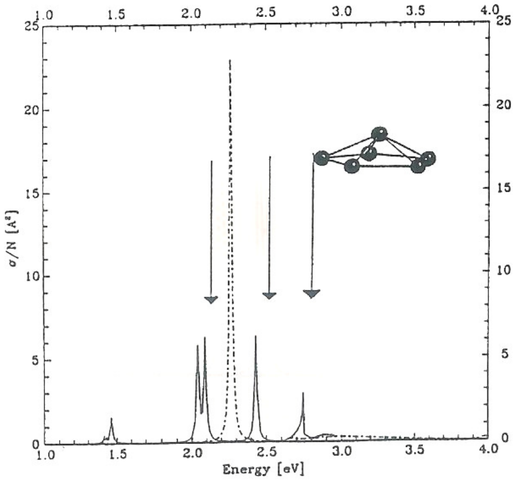

Fig. 2. Optical response of Na_6, obtained by making use of the isotropic response (dashed line) and the anisotropic perturbed response (full line). The vertical arrows indicate the energy position of the three main peaks found experimentally for this cluster in Ref. 11.

ordering of the different structures which was obtained in Ref. 9, but also the deviations in the average bond length, between our results and those of Ref. 9, do not exceed 2%. This is to be contrasted with the results obtained by neglecting the anisotropic contribution of the pseudopotential in the computation of the total energy (e.g., ΔE_{ps}), which corresponds to minimizing the total energy within the SAPS model developed by the Spanish group.[10] Not only the results obtained lead to minimum-energy geometries which correspond to excited isomeric states in both our formulation and Ref. 9, but also the volume of delocalization is markedly different, evidencing strong deviations from the present results. This reflects the necessity of incorporating ΔE_{ps} in performing structural minimization, indicating also the sufficiency of using such a total-energy expression as a control parameter. This is gratifying, since the present methodology of computing the total energy of the cluster is several orders of magnitude easier (and faster) to compute than that associated with the Car–Parinello method.

In the next step we calculate, with the monopole part of the external potential, the optical response of Na_6 and Na_8. This corresponds to computing the isotropic response for these clusters. Then, we repeat the calculation for both clusters, including the anisotropic pseudopotential contribution. The results are shown in Figs. 2 and 3, for Na_6 and Na_8, respectively. Specifically, the dashed line in Fig. 2 shows the isotropic response of Na_6, which is essentially dominated by a single peak. This is clearly insufficient to account for the experimental data of Ref. 11, as one would expect from the open-shell nature of this cluster. The full line shows the result of computing the anisotropic response for this cluster (for technical details, cf. Ref. 5), evidencing a good agreement with the experimental observations of Ref. 11, which reveal a multipeak structure for the optical response of this small open-shell cluster. Figure 3 shows the results for Na_8. The dashed line corresponds to the optical response computed with the jellium model, whereas the full line shows the results of both the isotropic- and anisotropic-response calculations, which cannot be distinguished by eye inspection. The vertical arrows show the position of the single peak observed experimentally for the excitation of the surface plasmon in Na_8. The present results indicate that, for the closed-shell cluster, the perturbation due to the anisotropic part of the pseudopotential contribution plays essentially no

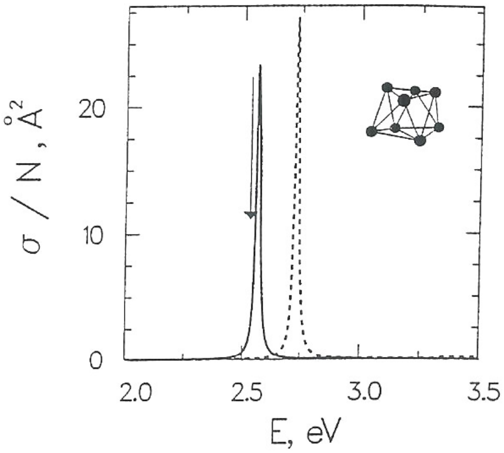

Fig. 3. Optical response of Na_8, computed at three different levels: the jellium calculation is shown with a dashed line, the isotropic response with a full line, and indistinguishable by eye inspection from this line is the result of computing the optical response with the anisotropic-response method. The vertical arrow indicates the energy position of the main peak found experimentally for this cluster.[12]

role, the isotropic response being a good approximation. This is to be contrasted with the open-shell case. On the other hand, the present response calculation clearly improves the agreement with the available experimental data, when compared with the jellium results. This reflects the fact that a global energy minimization with inclusion of the ionic structure leads to another volume of delocalization for the loosely bound electrons. This, in turn, seems to be the major effect provided by the ionic structure in correcting the physical properties obtained in a jellium description. Further evidence for this main effect is provided by the results obtained for Na_{10} and Na_{20},[5] which fully corroborate this picture.

4. Conclusions

Second-order pseudopotential perturbation theory seems to provide a simple and efficient method to study ionic effects in jellium clusters. This is supported by the good agreement obtained with fully relaxed total-energy minimizations. Furthermore, the isotropic approximation is found to work well for closed-shell clusters, whereas the anisotropic response is found to be essential for a correct description of the open-shell clusters. The extension of the present formalism to the study of large clusters is under way.

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