Ionic structure and photoabsorption in medium sized sodium clusters

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We present ground-state configurations and photoabsorption spectra of Na-7+, Na-27+ and Na-41+. Both the ionic structure and the photoabsorption spectra of medium-size sodium clusters beyond Na-20 have been calculated self-consistently with a nonspherical treatment of the valence electrons in density functional theory. We use a local pseudopotential that has been adjusted to experimental bulk properties and the atomic 3s level of sodium. Our studies have shown that both the ionic structure of the ground state and the positions of the plasmon resonances depend sensitively on the pseudopotential used in the calculation, which stresses the importance of its consistent use in both steps.

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Important progress has recently been made in the measurement of photoabsorption spectra in small and medium-size sodium clusters. This calls for a critical re-evaluation of the theoretical description of the optical response of these systems. The earliest theoretical investigations of alkali clusters employed the jellium model and were followed by other groups (for a review, see [3]). The jellium model qualitatively explains many of the experimentally observed features. But a more realistic description of metal clusters is highly desirable, e.g. since the unrealistic sharp jellium edge gives rise to fundamental questions in the context of calculating optical properties of metal clusters.

The all-electron ab initio methods of quantum chemistry treat the ionic degrees of freedom on the most sophisticated level presently possible. But their computation times grow so rapidly with the size that only small systems could be studied so far. Treating only the valence electrons explicitly and describing nucleus plus core electrons by a pseudopotential leads to a considerable simplification of the electronic system. The unrestricted three-dimensional search for cluster ground-state configurations using Car-Parrinello or Monte-Carlo methods with non-local pseudopotentials is, however, still a task of considerable complexity.

Several approximate methods have been developed for the study of the ionic structure in larger clusters. The “spherically averaged pseudopotential scheme” (SAPS) optimizes the ionic positions in three dimensions while restricting the density of the valence electrons to spherical symmetry; the ion-valence electron interaction is described by the simplest pseudopotential possible, the Ashcroft empty-core potential. However, where more accurate methods can be applied, these predict ground-state geometries which differ considerably from the SAPS results. The pseudopotential perturbation theory and similar approaches greatly improve on the SAPS deficiencies in the treatment of the valence electrons, but they either consider only the volume-averaged effects of ionic structures, or require their geometries as an input. Approaching the problem from the opposite direction, a sophisticated extension of the Hückel model focuses on the prediction of ground-state configurations without explicitly taking the valence electrons into account. Its results are in good agreement with ab initio calculations. However, the parameters of this model must be adjusted to ab initio calculations and the optical response of the electrons cannot be calculated.

With the “cylindrically averaged pseudopotential scheme” (CAPS), a method has been developed that allows one to self-consistently calculate the ground states of clusters with several tens of atoms including ionic structure without restricting the valence electrons to spherical symmetry. The ionic configuration is hereby optimized by the method of simulated annealing that seems to be the best method for coping with the strong isomerism found in larger clusters. The electronic system is described in density functional theory; here we use the local density approximation (LDA) with the functional of Perdew and Wang. By an interlaced iteration, the set of equations

$$\frac{\partial E}{\partial R} = 0 \quad \frac{\partial E}{\partial n} = 0$$

is simultaneously solved self-consistently. Here $R$ denotes the set of all ionic positions, $n$ the electronic density and $E$ the energy functional

$$E[n; R] = T_s[n] + E_xe[n] + \frac{e^2}{2} \int \int \rho(r)\rho(r') d^3r' d^3r + \int n(r)\mu_i(r; R) d^3r + \sum_{i \neq j}^{N} \frac{1}{|R_i - R_j|}$$

for a cluster of $N$ ions with $Z$ valence electrons each.

The efficiency of the scheme results from two approximations that are made in the evaluation of the above energy functional. First, the interaction between valence electrons and ionic cores is described by a local pseudopotential:

$$\mu_i(r; R) = \sum_{i=1}^{N} V_{ps}(|r - R_i|).$$

In the present work, we have developed a more physical pseudopotential than that used in earlier applications of CAPS; it will be discussed below.
The second approximation is that while the ions are treated three-dimensionally, the electron density is restricted to cylindrical symmetry, i.e., in the solution of the electronic problem $V_{ps}(|r - R_i|)$ is replaced by its cylindrical average

$$V_{ps}(z, ρ, z, ρ_i) = \frac{1}{2\pi} \int_0^{2\pi} V_{ps}(|r - R_i|) dφ. \quad (2)$$

This certainly is a simplification whose detailed consequences are hard to judge a priori. However, since the photoabsorption cross sections of singly charged sodium clusters show that the electronic density of most clusters has an overall prolate, oblate or spherical shape[23], this approximation does not seem unreasonable for such systems. A severe test for the quality of this approximation will be a comparison of its results to those of fully three-dimensional methods.

Before we present the results of our calculations, we discuss the local pseudopotential in some more detail. The most rigorous pseudopotentials in the sense of Philipps and Kleinman[24] and modern ab initio pseudopotentials[25] are always non-local in the sense that each angular momentum component of the valence electron feels a different potential. However, the use of non-local pseudopotentials in the search for cluster configurations quickly exhausts computational resources because of the multiple projections that have to be done at every step of the calculation, separately for each ion in the absence of any symmetry. Also, it has been shown that some ab initio pseudopotentials do not necessarily lead to a good agreement with experiment[24]. It therefore makes sense to address the pseudopotential question from a more pragmatic point of view.

Already early in the development of pseudopotential theory, it has been noted that by relaxing the Philipps-Kleinman condition, one can open up a new class of pseudopotentials[21]. They are called phenomenological pseudopotentials or model potentials since they are constructed by choosing some analytical function as a model potential and adjusting its parameters to experimentally known quantities, e.g., an atomic energy level or some bulk properties. Such model potentials can be nonlocal, or several partial-wave components may be chosen to be the same[22]. For metals with a simple electronic structure like that of sodium, one can in this way construct pseudopotentials that are effectively local. Various local pseudopotentials have, in fact, been successfully used (see, e.g., Refs. 21 and 22). But the question of how a valid local pseudopotential should be constructed is nontrivial. In Ref. 21 this question was addressed in detail with an emphasis on solid-state properties. There, an “evanescent core potential” was proposed, and we have used it in some test cases. Most of our calculations, however, were done with a pseudopotential that we have constructed especially for the use in finite sodium clusters, as explained below.

Whereas in solid-state physics an important criterion for the practical usefulness of a pseudopotential is its fast convergence in reciprocal space, our aim is its efficient handling in real space. We take up experience from CAPS[26] and parameterize the pseudopotential on the basis of pseudodensities, related to $\rho_3$ via Poisson’s equation, which can be angle averaged analytically. This allows for a more efficient solution of the Coulomb problem. Moreover, the short range of the pseudodensities ensures a fast repositioning of the ions. Our pseudopotential has the parameterization

$$V_{ps}(r) = \begin{cases} -\frac{2\pi}{R_1} g_1 r^2 + c_1 & r < R_1 \\ -\frac{2\pi}{3} g_2 r^3 + c_2 & R_1 \leq r < R_2 \\ -\frac{2\pi}{R_2} & r \geq R_2. \end{cases}$$

This corresponds to a pseudodensity with a two-step profile. Four of the seven parameters are fixed by requiring continuity of $V_{ps}(r)$ and its derivative. The remaining parameters $g_1$, $r_1$ and $r_2$ determine the physical properties of the pseudopotential. Clusters contain from a few up to several thousand atoms, thus spanning the region from the atom to the bulk material. Our aim is therefore to develop a local pseudopotential that interpolates between atomic and bulk properties. Thus we choose the parameters such that two quantities are reproduced correctly: the atomic $3s$ energy level $e_a$ on one hand, and the bulk Wigner-Seitz radius $r_0$ on the other hand. The latter is determined by the minimum of the bulk energy per electron $e_b$ in second order perturbation theory[27]. Using $r_s = 3.93a_0$ and the experimental value $e_a = -0.38$ Ry fixes $g_1 = -0.503a_0^{-3}$ and $r_2 = 3.292a_0$ and gives a constraint on $r_1$. The remaining freedom in choosing $r_1$ was exploited to fit the bulk compressibility $B$ as closely as possible to its experimental value $B_{exp} = 0.073$ Mbar[28], yielding $B = 0.0739$ Mbar for $r_1 = 0.641a_0$. With these parameters we obtain $e_b = -6.20$ eV, close to the experimental value $-6.25$ eV. The interstitial density, defined as the difference between the number of valence electrons in the Wigner-Seitz cell and in the muffin-tin sphere, takes the value 0.35 with our pseudopotential. This agrees within 3% with the value given in Ref. 29. The band-structure energy is 0.15 eV, in agreement with Ref. 30.

As a test-case study, we have calculated the ground state of Na-7+ with our pseudopotential, with the evanescent-core potential[21], and with the empty-core like pseudopotential[28]. The $D_{5h}$-geometry of Na7+ is well known from ab initio calculations[31] and we find the pentagonal bipyramid, shown in Fig. 1, with all three pseudopotentials. This demonstrates that CAPS can give realistic results even for very small systems, and that the cylindrical averaging is not too restrictive. The influence of the pseudopotential can be seen in the bonding lengths, e.g. the distance between the two edges of the bipyramid: our pseudopotential and the evanescent core potential result in a distance of 6.03a0 and 6.02a0, respectively, whereas the empty-core like pseudopotential leads to a shorter distance of 5.64a0. All these values lie in the range found in fully three-dimensional calcu-
A blueshift of the dipole resonance in sodium clusters with respect to its experimental position has been found in many calculations, and there has been a longstanding discussion about its origin. Our results show that the detailed form of the pseudopotential does strongly influence the resonance position, but that other effects must also contribute to the discrepancy with experiment. We think that one important effect is the finite temperature, present in most experiments, which results in an increased cluster volume, and thus to a decrease of the plasma frequency of a few percent. The experiments of Ref. 20 show, indeed, that the average resonance positions are shifted to lower energies when the temperature is increased.

This must be borne in mind when comparing the results of calculations performed at T=0 to those experimental data of larger clusters, where the photoabsorption was measured only at finite temperature. On the other hand, the LDA leads to well known errors that also affect the optic response.

Encouraged by the correct prediction of the structure of Na-7+, we have employed our scheme to calculate ground-state structures and photoabsorption spectra of sodium clusters in a size region where no self-consistent calculations with ionic structure have been made so far. In Figures 2 and 3 we present the ionic geometries and photoabsorption cross section \( \sigma \) of Na-27+ in arbitrary units against eV. Upper panel left: Experimental data. Lower panel left: LRPA photoabsorption spectrum. Right-hand side: CAPS structure.

Although these differences might appear small, they have noticeable consequences for the photoabsorption spectrum, as shown in Fig. 1. Here we plot the percentages of the energy-weighted dipole sum rule \((m_1)\) obtained in the “localized” random-phase approximation for different pseudopotentials. Full line: present pseudopotential; dashed line: evanescent-core potential; dotted line: empty-core like pseudopotential. A phenomenological Lorentzian line broadening is applied.

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FIG. 1. Right-hand side: CAPS-geometry of Na-7+. Left-hand side: percentages of the dipole \( m_1 \) sum rule obtained in the “localized” random-phase approximation for different pseudopotentials. Full line: present pseudopotential; dashed line: evanescent-core potential; dotted line: empty-core like pseudopotential. A phenomenological Lorentzian line broadening is applied.

FIG. 2. Ionic structure and photoabsorption cross section \( \sigma \) of Na-27+ in arbitrary units against eV. Upper panel left: Experimental data. Lower panel left: LRPA photoabsorption spectrum. Right-hand side: CAPS structure.
In contrast, Na-41+ has a “magic” configuration of 40 valence electrons, leading to a nearly spherical density and almost no splitting of the dipole resonance. The two strongest close-lying transitions exhaust 64% of the total oscillator strength. It is very interesting to note that, besides 20% of the strength lying outside the region of the experiment, another 16% of the strength are scattered around 3.4 eV. In the LRPA, these subpeaks are interpreted as internal compressional modes and modes of higher multipolarity that are coupled to the dipole oscillation by the ionic structure. Their contributions are seen to be in good qualitative agreement with the high-energy shoulder observed in the experiment.

In summary, our studies have shown that CAPS, combined with the localized random-phase approximation, provides a powerful tool for calculating ionic geometries and photoabsorption spectra of medium-sized sodium clusters where \textit{ab initio} procedures are computationally not possible with a full search of ionic structures. With a local pseudopotential fitted to bulk and atomic properties, we reproduce the global features of the dipole resonances, apart from a slight blue shift that leaves room for temperature and non-LDA effects. We believe that CAPS gains additional importance since its results can serve as an input to three-dimensional calculations, thus bringing closer an explanation of the recent observation of the melting of clusters which depends on a detailed knowledge of their ionic structure.

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