Ab initio calculations for structure and temperature effects on the polarizabilities of Na$_n$ ($n \leq 20$) clusters

Leeor Kronik, Igor Vasiliev, and James R. Chelikowsky

Department of Chemical Engineering and Materials Science, University of Minnesota, and Minnesota Supercomputing Institute, Minneapolis, Minnesota 55455

We present a rigorous, *ab initio* theoretical calculation of the dependence of Na cluster polarizability on cluster size, up to 20 atoms, obtained by combining *ab initio* pseudopotentials with a gradient-corrected density functional. Using molecular dynamics, we find that for clusters as small as nine atoms, a multitude of degenerate isomers exists even at $T=0$. By calculating the polarizability of these isomers, we reproduce the generally decreasing nature of the measured polarizability curve, as well as its dips at ''magic'' numbers corresponding to closed electronic shells. Moreover, we find that the effect of a finite temperature on the cluster structure suffices to account for most of the quantitative discrepancy between theory and experiment.

Small atomic clusters bridge between molecular and solid-state physics.[1] While each cluster can be viewed as a molecule, these molecules are metastable with respect to the addition of more atoms. Moreover, all properties (e.g., structural, mechanical, electronic, optical) of these ''molecules'' should gradually converge to their bulk values with increasing cluster size. In particular, much research is focused on sodium clusters.[2] This is because in Na, the ''quintessential simple metal,'' the size dependence of many properties is not obstructed by interactions between *valence* electrons that occur in more complicated elements.

One of the few cluster properties that can be measured with relative ease and accuracy is their polarizability, i.e., their change of dipole with applied electric field. A pioneering measurement of the size dependence of Na cluster polarizabilities was performed by Knight *et al.*[3] (shown in Fig. 3, discussed below). Three main features are observed in the experimental data: (a) Overall, the polarizability per atom gradually decreases from its atomic value towards its bulk value. (b) This gradual decrease is punctuated by significant ''dips'' at the ''magic'' atom numbers of 2, 8, and 18, corresponding to closed electronic shells of ''s''-, ''p''-, and ''d''-like nature, respectively. (c) Some residual fine structure is also displayed and is usually attributed to the detailed structure of the clusters.

Intrigued by these findings, many groups have attempted to reproduce these data theoretically, with techniques of varying degrees of sophistication.[4–10] A critical analysis of these studies shows that while significant progress has been made, theory is still lacking in two respects: (a) Rigorous, *ab initio* calculations[7–10] have been performed for clusters only up to 9 atoms due to computational difficulties, whereas computationally easier approaches[4–6,11] applicable to larger clusters, are not sufficiently accurate. (b) All calculations consistently and significantly underestimate the experimentally observed values.

In this paper, we present rigorous calculations of Na cluster structures and polarizabilities, based on *ab initio* pseudopotentials within gradient-corrected density-functional theory (DFT). We show that this results in a significant reduction of the computational load at essentially no loss of accuracy, which allows a theoretical simulation of the measured polarizability curve. We show that most of the remaining difference between theory and experiment is due to the effect of finite temperature on cluster structure.

Our computational approach is based on solving the Kohn-Sham DFT equations within the higher-order finite-difference pseudopotential method.[12] We employ pseudopotentials based on the Troullier-Martins scheme,[13] cast in a nonlocal Kleinman-Bylander form.[14] We used the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof[15] for the exchange-correlation term. For comparison purposes, we also used the local-density approximation (LDA) of Ceperley and Alder.[16] Both functionals were incorporated with a nonlinear partial core correction of the exchange-correlation term.[17]

As a first test of our computational approach, we calculated the Na dimer bond length, the experimental value of which is 5.82 atomic units (a.u.).[18] A recent all-electron calculation[10] yielded an LDA value of 5.70 a.u. and a GGA value of 5.85 a.u. for this bond length. Our pseudopotential-based calculations yielded values of 5.66 a.u. and 5.83 a.u., respectively. This is a relative error, compared to the all-electron values, of only 0.7% and 0.3%, respectively—which is well within the accepted accuracy of either calculation—especially given that the all-electron study relied on different density functionals than those used here. We conclude that the use of pseudopotentials essentially causes no inherent loss in accuracy. We also conclude that GGA provides for a practically perfect agreement with experiment, so that higher-order density functionals (e.g., ''meta-GGA''[19]) are not required for the present problem.

To obtain the ground-state structures of Na clusters and the length of all bonds involved in these structures, we used the simulated annealing approach, implemented using Langevin molecular dynamics,[20] followed by minimization of forces. Our results of the geometry of the ground-state structures of Na$_3$ to Na$_8$ agree with those reported previously[10] and all bond lengths agree to within $\sim 1\%$. For Na$_9$, we have reproduced the structure found in Ref. 10 [Fig. 1(a), left], but also found a degenerate isomer (whose ground state is lower in *total* energy by 27 meV) [Fig. 1(a), right]. Some representative structures for Na$_{10}$ to Na$_{20}$, for which

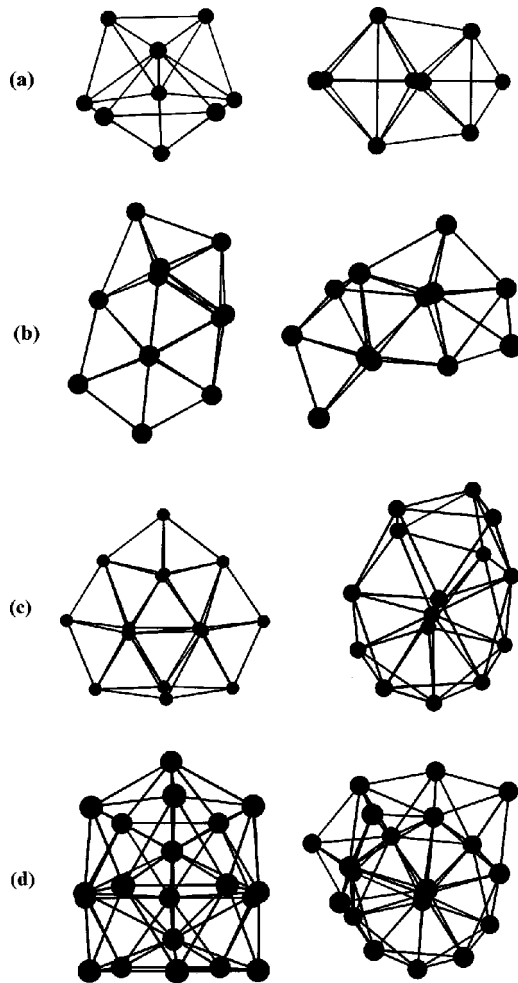FIG. 1. Selected low-energy Na cluster structures: (a) Na_9, (b) Na_{12}, (c) Na_{15}, and (d) Na_{20}.

all-electron calculations have not been performed due to computational limitations, are shown in Figs. 1(b)–1(d). We identified several general features common to all these clusters: First, they are characterized by a large number of degenerate isomers (i.e., of total-energy differences smaller than ~ 100 meV, and in many cases within ~ 20–30 meV). Second, many of the isomers feature ''motifs'' of pentagonal or hexagonal symmetry. Third, while some of these isomers [e.g., those displayed on the left-hand side of Figs. 1(c)–1(d)] feature an overall degree of symmetry, many others [e.g., those displayed on the right-hand side of Figs. 1(b)–1(d)] do not. These findings agree with, and generalize, previous results obtained for a few of the cluster sizes by Röthlisberger and Andreoni.[21] We verified directly that some symmetric structures suggested in the literature [e.g., the stacked pentagonal pyramids suggested for Na_{12} (Ref. 11) or the cubo-octahedron suggested for Na_{13} (Ref. 22)] are *not* ground-state structures and are higher in energy than the low-lying isomers by ~ 0.5 eV. Both the multitude of isomers and the possible lack of overall symmetry are due to the weak and nondirectional nature (often dubbed ''floppy''[8]) of Na-Na bonds.

For calculating the polarizability of these clusters, we relied on a finite-field approach, which solves the Kohn-Sham equations with and without a small applied electric field.[23] The polarizability tensor is calculated explicitly via finite
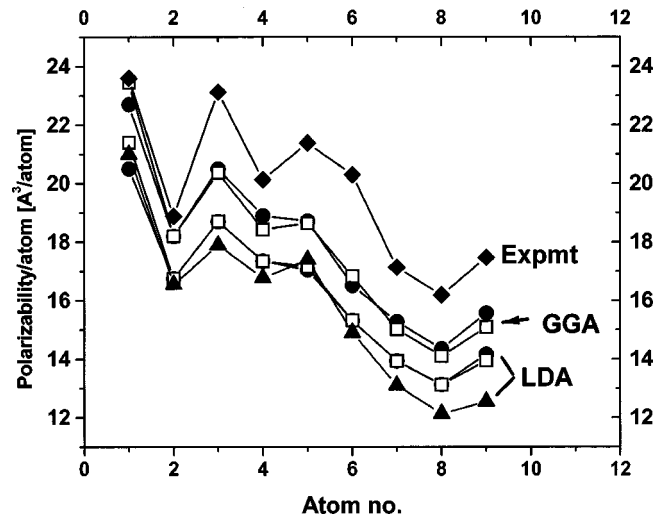

FIG. 2. A comparison of various theoretical calculations for the polarizability of Na clusters up to 9 atoms: diamonds—experimental data, after Ref. 3; circles—all-electron LDA and GGA calculations, after Ref. 10; open squares—pseudopotential based LDA and GGA calculations, this paper; triangles—previous pseudopotential-based LDA calculations, after Ref. 7.

differences, and the average polarizability (which is measured experimentally) is the average of the diagonal elements of this tensor. A detailed comparison between our calculations, a recent *ab initio* all-electron calculation, a previous *ab initio* pseudopotential calculation, and experiment, for clusters up to 9 atoms, is given in Fig. 2. It is readily observed that GGA-based calculations offer a significantly improved agreement with experiment with respect to LDA-based calculations. Our use of pseudopotentials results in no inherent loss in accuracy. This also implies that the contributions of the core electrons to the polarizability, often invoked to explain the discrepancy between all-electron and pseudopotential calculations,[8] are actually quite negligible. We find that the evident difference between the all-electron LDA calculations and the old pseudopotential-based LDA data in Fig. 2 is, instead, due to the absence of nonlinear partial core corrections in the latter calculations. These core corrections contribute to the polarizability indirectly only, by modifying the bond lengths.

Having verified the validity of the polarizability computations, we have performed the same calculation for all low-lying isomers found for clusters with 9 atoms or more. The resulting curve, shown in Fig. 3, is, to the best of our knowledge, the first complete theoretical reproduction of the experimental curve. Both general trends of the experimental curve—an overall decreasing polarizability with increasing cluster size and significant dips at ''magic'' numbers—are reproduced in the theoretical curve. We note that for the second decade of clusters, a *band* of polarizability values, rather than a single value, is found. This is due to the numerous degenerate isomers. The shape of this band is smooth. We therefore attribute the residual fine structure seen in the experimental data to experimental inaccuracies, rather than to a physical source. We also note that a new set of experimental polarizability values, recently given by Rayane *et al.*,[9] generally agrees with the main features of the original experiment. However, it features a greatly enhanced fine structure of polarizability oscillations between odd and even
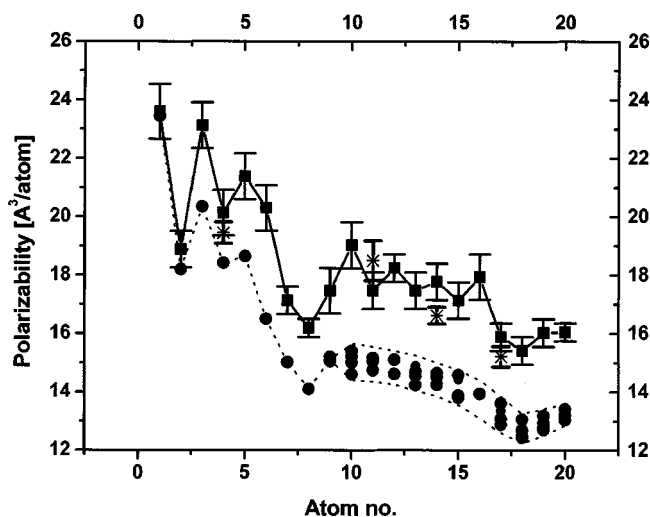
FIG. 3. Polarizability of Na clusters: squares—experimental data, after Ref. 3; circles—theory at $T = 0$ K (dashed lines are a guide to the eye); stars—theory at $T = 750$ K.

cluster sizes, as well as a polarizability minimum at $n = 20$, rather than at $n = 18$. Our calculations agree well with the old experimental data,[3] but do not reproduce the additional features found in the new data.[9]

While the above calculations adequately reproduce the *qualitative* trends of the experiment, the *quantitative* experimental result is still consistently underestimated. Because the experiment is thought to be conducted at many hundreds of degrees K (Ref. 2) (the exact temperature of the cluster being very difficult to measure directly), it is reasonable to expect that temperature may play a significant role in increasing the polarizability. In the most simple picture, the polarizability increase is obtained through the change of shape of the cluster in general[8,21,24] and the extension of its average bond length in particular.[11,25] Indeed, the fact that temperature influences the polarizability, mostly by changing the cluster structure, is hinted at by closely observing Fig. 3: Whereas the theoretical result for the single atom is a perfect fit with experiment, given the experimental uncertainty, and the discrepancy for the Na dimer is small, a significant gap between theory and experiment develops from Na_3 and on, i.e., as soon as the geometry of the cluster starts playing a significant role in the polarizability.

To assess how much of the quantitative discrepancy can be explained by temperature effects, we have performed Langevin molecular dynamics[20] at the fixed temperature of 750 K (i.e., at the upper limit of the experimental range) for four select cluster sizes: 4, 11, 14, and 17. For each cluster size, we computed the average polarizability, sampled at four select cluster structures with high, low, and average binding energies. The average polarizability obtained from these

structures is shown in Fig. 3. It is readily observed that the inclusion of a finite temperature effect strongly decreased the gap between theory and experiment—from 8.5% to 3.3% for Na_4, from 14.0% to 5.7% for Na_{11}, from 18.2% to 6.0% for Na_{14}, and from 16.8% to 4.2% for Na_{17}. We note that the experimental polarizability value typically includes an additional contribution from the static dipole rotating in the external electric field.[23] However, we have estimated this contribution and found it to be restricted to several tenths of an $Å^3$/atom. Thus, we find that the most simple picture of temperature effects suffices to account for most of the discrepancy between theory and experiment. Indeed, the fact that the polarizability value for Na_{11} slightly overestimates the experimental value also suggests that our calculations did not fail to take into account a major mechanism contributing to the polarizability.

On the theoretical side, we attribute the residual difference to higher-order effects not included in our calculations (such as field-induced ionic movements, and the corresponding distortion they impart on the electronic structure). However, this residual error may well be instead due to the limited accuracy of the experiment, recently discussed by Kümmel et al.[11] Indeed, the stated uncertainty of the experiment is several percent.[3] Moreover, the above-mentioned ''fine structure'' of the experiment, which theory does not predict, as well as the strong discrepancy between different experiments[3,9] suggests that systematic errors (such as a preferential measurement or certain cluster structures or orientations) may also be involved. In this sense, we believe that further refinement of the theory beyond the level of sophistication used in the present paper is probably unwarranted until more precise experimental data emerge.

In conclusion, we have used pseudopotentials within gradient-corrected density-functional theory in order to reproduce theoretically the entire Na polarizability curve up to 20 atoms at $T = 0$. For clusters with 10 atoms and above, we have found a multitude of degenerate isomers. By calculating their polarizability we have reproduced both the generally decreasing nature of the experimental curve and its dips at ''magic'' numbers corresponding to closed electronic shells. However, contrary to experiment, we have found that all ''fine structure'' in the curve is smeared out by the multitude of isomers. We have then shown that by taking into account the effect of a finite temperature on the cluster structure, one accounts for the quantitative difference between theory and experiment, within the stated accuracy of both, or very close to it.

[1] For a recent overview see, e.g., *Theory of Atomic and Molecular Clusters: With a Glimpse at Experiments*, edited by J. Jellinek (Springer-Verlag, Berlin, 1999).

[2] For review articles see, e.g., W.A. de Heer, Rev. Mod. Phys. **65**, 611 (1993); M. Brack, *ibid.* **65**, 677 (1993); V. Bonacic-

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