Role of Self-Interaction Effects in the Geometry Optimization of Small Metal Clusters

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By combining the Self-Interaction Correction (SIC) with pseudopotential perturbation theory, the role of self-interaction errors inherent to the Local Density Approximation (LDA) to Density Functional Theory is estimated in the determination of ground state and low energy isomeric structures of small metallic clusters. Its application to neutral sodium clusters with 8 and 20 atoms shows that the SIC provides sizeable effects in Na\textsubscript{8}, leading to a different ordering of the low lying isomeric states compared with \textit{ab-initio} LDA predictions, whereas for Na\textsubscript{20}, the SIC effects are less pronounced, such that a quantitative agreement is achieved between the present method and \textit{ab-initio} LDA calculations.

36.40+d, 31.20.Sy, 31.50+w, 33.20.Kf

The use of Density Functional Theory (DFT), together with the Local (Spin) Density Approximation (L(S)DA) to perform structural optimization of small finite systems as well as to predict the stability of new, finite and infinite, materials, has increased dramatically in recent years, with a widespread use in Physics and Chemistry. In this framework, the problem reduces to the repeated determination of the self-consistent solution of the Kohn-Sham equations. Since in many materials (such as metals and the metallic clusters considered in this work) the interaction between the valence electrons and the ionic cores is weak - due to the effective screening of the nuclear charge by the tightly bound core electrons - the resulting electron-ion interaction can be formulated in terms of pseudopotentials. Several \textit{ab-initio} norm-conserving pseudopotentials are available which ensure a high degree of transferability, and are obtainable either via analytic formulæ, or their numerical tabulation requires a few CPU seconds. Indeed, \textit{ab-initio} LSDA-DFT methods, combined with norm conserving pseudopotentials, have been recently used to perform structural minimization of clusters with as many as 147 atoms.

Other \textit{ab-initio} methods, such as the Self-Consistent-Field Configuration Interaction (SCF-CI), which typically treat as active all the electrons of each atom, are more limited in cluster size, due to their higher computational cost, and also due to basis-set and size-consistency problems which preclude, e.g., the study of cluster trends as a function of size. However, these methods have no self-interaction problems, such as those well-known in LDA-DFT and, for some selected clusters (e.g., Na\textsubscript{8}), lead to ground-state structures which are distinct from the LDA-DFT results. The energy differences between close lying isomers of an alkali cluster are often associated with charge redistribution and charge polarization phenomena, which are relevant, not only to distinguish between isomers of the same cluster, but also to understand the difference between the ground-state geometry of isoelectronic clusters of different alkali species. Since these are aspects in which the self-interaction effects play a role, it is important to have an estimate of the size of these errors. In this Letter this problem is addressed by combining two well tested methods: Pseudopotential Perturbation Theory (PSP-PT) and the Self-Interaction Correction (SIC) as proposed in ref. \textsuperscript{1}, together with its extension to linear response theories, developed in ref. \textsuperscript{1}. It will be applied to optimize the geometries of two small neutral sodium clusters, with 8 and 20 atoms, starting from geometries associated with different isomers of these clusters, which have been identified in previous LDA-DFT \textit{ab-initio} calculations (for the octamer, also in SCF-CI structural minimization). It will be concluded that, for Na\textsubscript{20}, SIC-PSP-PT provides answers in quantitative agreement with the results of ref. \textsuperscript{2}, both for the bond-lengths and for the geometries of the low energy isomers. This seems to indicate that SIC does not play a sizeable role in the structural minimization of clusters with as many as 20 sodium atoms. However, for Na\textsubscript{8}, the results show an energy sequence for the three lowest isomers which does not follow the LDA-DFT \textit{ab-initio} results of ref. \textsuperscript{1}. As a result, it is observed that the T\textsubscript{d} structure is favoured with respect to the D\textsubscript{4d} isomer, in agreement with the SCF-CI calculations of ref. \textsuperscript{1}. This, in turn, seems to indicate that self-interaction effects play a sizeable role for the smaller clusters.

Pseudopotential perturbation theory has been applied to metallic clusters in ref. \textsuperscript{4}, using LDA-DFT. Being an approximation to the more sophisticated (and more time-consuming) \textit{ab-initio} methods, it has been shown \textsuperscript{4} to provide answers in quantitative agreement with these, in particular with \textit{state-of-the-art} Car-Parrinello structural minimization.

The SIC prescription, though lacking a first principles justification, has been applied with great success in different areas of physics and chemistry, including the study of both ground-state and excited state properties of small metallic clusters. At present, there is no...
first-principles workable scheme which can remedy completely the self-interaction errors in LDA-DFT. Therefore, we resort to SIC in order to estimate these effects. In this sense, the present study, more than conclusive, can be of guidance for future developments.

Because the LDA-PSP-PT results are available for these clusters [10], the role of self-interaction errors can be estimated unambiguously, the only possible source of inaccuracy being related to the SIC itself. We would like to point out that SIC has been used before in this context, but only to test its ability to predict the bond-length in alkali dimers. In such calculations, the role of SIC in the chemical bonding of atoms in a cluster cannot be investigated.

On the foregoing, we briefly summarize the SIC-PSP-PT formulation used, before discussing the results and writing down the conclusions. A more detailed and extended analysis will be published elsewhere.

By replacing the nuclei and core electrons by pseudopotentials, leaving as active quantum particles the valence electrons, one can write, for the ionic contribution to the total potential,

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

In this equation, $N$ is the number of ions (also the number of valence electrons for the neutral clusters considered here), and $\vec{R}$ represents a set of given ionic positions, which ultimately should be determined by minimizing the total energy of the system. $v_{ps}(\vec{r} - \vec{R}_i)$ represents the pseudopotential at point $\vec{r}$, centered at atomic site $\vec{R}_i$. We shall adopt the local pseudopotential used in ref. [10], with the parametrization adequate for sodium, taken from ref. [14]. With respect to any chosen center of the cluster, the sum of the pseudopotentials can be expanded as follows:

$$v_{ex}(\vec{r}, \vec{R}) = v(\vec{r}, \vec{R}) + v_{2,ex}(\vec{r}, \vec{R})$$

$$= v_0(r, \vec{R}) Y_{0,0}(\vec{r}) + \sum_{l=1}^{\infty} \sum_{m=-l}^{l} v_{l,m}(r, \vec{R}) Y_{l,m}(\vec{r}) .$$

The first term is just the monopole, spherical part of the total ionic contribution, which will be taken into account exactly in SIC-LDA by solving the set of SIC Kohn-Sham-like equations [12] for the $N$ valence electrons moving self-consistently in this spherical potential [17]. The remaining terms are included perturbatively up to second order, which leads to a contribution $\Delta E_{ps}^{(2)}$ to the total energy reading [10].

$$\Delta E_{ps}^{(2)} = \frac{1}{2} \int d\vec{r} \delta n_2(\vec{r}, \vec{R}) v_{2,ex}(\vec{r}, \vec{R}) ,$$

where $\delta n_2(\vec{r}, \vec{R})$ is the screened induced density change caused by the external potential $v_{2,ex}(\vec{r}, \vec{R})$. The total energy is then given by the sum of the monopole part, obtained via the SIC-LDA self-consistent solution, plus the term $\Delta E_{ps}^{(2)}$ given by eq.(3). As in ref. [10], the screened induced density will be computed making use of linear response theory, which incorporates, in a self-consistent manner, the screening of the external perturbation by the valence electrons. Since $\delta n_2(\vec{r}, \vec{R})$ is built out of SIC-LDA spherical self-consistent solution, it is in fact computed in a numerically exact way via Green’s functions techniques (for an elaborated discussion of the methods and techniques, the reader is referred to refs. [11,15]). As shown in ref. [11], the standard LDA-DFT linear response theory, known as Time-Dependent LDA (TDLDA), introduces a spurious self-polarization effect, which leads to an erroneous overscreening of the external field. The extension of SIC to the linear response theory has been formulated in ref. [11], and it is this SIC response formulation which is used in computing $\delta n_2(\vec{r}, \vec{R})$.

Instead of performing a fully-relaxed structural optimization, we started from the given LDA-DFT low-energy isomeric structures found in ref. [12], and then minimize the total energy using SIC-PSP-PT by scaling uniformly the radial distance of the constituent atoms from the center of mass of the cluster. This strategy (similar to those adopted in refs. [10,14]), being incomplete, will prove sufficient for the present purpose. In table 1 are given the results obtained with this methodology for Na$_{20}$. Two low energy isomers have been identified in ref. [13], labelled $A$ and $B$, respectively. The $A$ structure corresponds to the lowest isomer, with an extra binding with respect to the $B$ structure of 0.136 eV [12]. In the first row the PSP-PT results obtained in ref. [10] are shown for these 2 isomers, within LDA-DFT, using the minimization strategy adopted here. In the second row, the SIC-PSP-PT results of the present calculation are tabulated. All the ingredients of the 2 calculations are the same, except for SIC. Furthermore, and for each row the energy differences are always referring to the structure which has minimum energy. Furthermore, the numbers in parenthesis indicate the value of the scaling factor at which a given structure minimizes its energy. One can observe that SIC leads to a (small) reduction of the bond length in comparison with PSP-PT, in agreement with the previous results for dimers [6,13]. More important, however, is the fact that SIC-PSP-PT keeps the same energy ordering for the 2 isomers, therefore evidencing no measurable effect, apart from the expected differences in the restoring force coefficient for the breathing mode [14].

The situation is quite different for Na$_{18}$. The results are shown in table 2, where we keep the same notation as in table 1. The 3 structures considered are identified in fig.1. Whereas SIC-PSP-PT leads to structures in which the volume of delocalization of the valence electrons, controlled by the scaling factor, is in excellent agreement with the results of ref. [12], the energy or-
dering of the isomers is different in SIC-PSP-PT, when compared with the predictions of refs. [10,12]. This, in view of the ingredients of the calculations used, turns out to be a pure self-interaction effect. Interestingly, the results obtained with the present method show a favouring of geometries which correlates well with the results of ref. [14], which makes use of a truly self-interaction free theory. This, in turn, reinforces the results of the present calculation, which shows that self-interaction effects should not be overlooked in the important issue of predicting the lowest isomeric structures of small alkali clusters. In this context, it is worth mentioning the recent measurements of the photoabsorption cross-section of Na$_{20}$ clusters [13] in a cold beam, which reveals a multiplex peak structure which can be reproduced by computing the absorption from the ground-state geometry found with the self-interaction free SCF-CI [7], after an appropriate scaling of the bond-lengths.

Finally, we would like to comment on the average bond-length obtained using the present calculation. The present results lead to bond-lengths in quantitative agreement with the findings in refs. [11,12], as opposed to the results of SCF-CI [5], which lead to an average bond-length in small alkali clusters which is larger, on the average, that what is known in the bulk limit [12]. As the cluster size decreases, one expects a contraction of the average bond-length, due to the corresponding increase of the surface to volume ratio. This qualitative reasoning, as well as the comparative performance of LDA-DFT methods and SCF-CI methods for the sodium dimer (cf. ref. [12]) lend support to the results of the present calculation. In any case, the reason behind this difference cannot be attributed to a self-interaction problem but, instead, to the different treatment of correlations between the active electrons.

In summary, in what concerns the geometry optimization of small alkali metal clusters, one has shown that self-interaction effects cannot be overlooked, and may be crucial for an accurate assignment and sorting of the low energy isomers. This feature decreases with increasing cluster size, and seems to be unimportant already for Na$_{20}$. As is well known [11], self-interaction effects still manifest themselves in other properties of these clusters, such as the energy of the one-electron orbitals, modifying also the topology of the potential energy surface, which is reflected in a different vibrational spectrum [12].

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TABLE I. Results for Na$_{20}$, for the two lowest isomers found in ref. [12], obtained using standard PSP-PT [14], and the SIC-PSP-PT developed in this work. For each of the 2 geometries selected, two sets of values are given, associated to the result of a total energy minimization as a function of the scaling parameter. The value of the scaling parameter at minimum is given in parenthesis, whereas the value of the total energy constitutes the other result tabulated. The values quoted for the energies (eV) are referred to the state which, in turn, reinforces the results of the present calculation, which shows that self-interaction effects should not be overlooked in the important issue of predicting the lowest isomeric structures of small alkali clusters. In this context, it is worth mentioning the recent measurements of the photoabsorption cross-section of Na$_{20}$ clusters [13] in a cold beam, which reveals a multiplex peak structure which can be reproduced by computing the absorption from the ground-state geometry found with the self-interaction free SCF-CI [7], after an appropriate scaling of the bond-lengths.

| Na$_{20}$ | A | B |
|----------|---|---|
| PSP-PT   | 0.000(1.02) | 0.111(1.01) |
| SIC-PSP-PT | 0.000(1.00) | 0.237(1.00) |
TABLE II. Results for Na$_8$, for the three lowest isomers found in refs. [12][14], illustrated in fig.1. The notation used here is the same as in table 1.

|       | $D_{2d}$  | $T_d$  | $D_{4d}$ |
|-------|-----------|--------|----------|
| PSP-PT| 0.000(1.02)| 0.159(1.02)| 0.111(1.01) |
| SIC-PSP-PT| 0.000(1.00)| 0.104(1.00)| 0.159(1.00) |

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FIG. 1. The 3 different geometries obtained in ref. [12] for Na$_8$, corresponding to the ground-state and two lowest isomers (energy is increasing from left to right), and used as starting geometries which are minimized as a function of a dimensionless scaling parameter, which uniformly and simultaneously changes the radial distances of all the atoms with respect to the center of mass of the cluster. The structure on the left displays $D_{2d}$ symmetry, the one in the middle $D_{4d}$ symmetry, and the one on the right $T_d$ symmetry (see main text for details).