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Role of self-interaction effects in the geometry optimization of small metal clusters

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Abstract. – 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_8, leading to a different ordering of the low-lying isomeric states compared with *ab initio* LDA predictions, whereas for Na_{20} the SIC effects are less pronounced, such that a quantitative agreement is achieved between the present method and *ab initio* LDA calculations.

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 [1]. 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 *ab initio* norm-conserving pseudopotentials are available which ensure a high degree of transferability, and are obtainable either via analytic formulae, or their numerical tabulation requires a few CPU seconds [2], [3]. Indeed, *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 [4].

Other *ab initio* methods, such as the Self-Consistent–Field Configuration Interaction (SCF-CI)[5], which typically treat all the electrons of each atom as active, are more limited in cluster size, due to their higher computational cost, and also due to basis-set [6], [7] and size-consistency [8] 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 kown in LDA-DFT [6] and, for some selected clusters (*e.g.*, Na_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 [4], 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 [4]. 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 paper this problem is addressed by combining two well-tested methods: Pseudopotential Perturbation Theory (PSP-PT) [9], [10] and the Self-Interaction Correction (SIC) as proposed in ref. [6], together with its extension to linear-response theories, developed in ref. [11]. 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 *ab initio* calculations [12] (for the octamer, also in SCF-CI structural minimization [13]). It will be concluded that, for Na_{20}, SIC-PSP-PT provides answers in quantitative agreement with the results of ref. [12], 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_8, the results show an energy sequence for the three lowest isomers which does not follow the LDA-DFT *ab initio* results of ref. [12]. As a result, it is observed that the T_{d} structure is favoured with respect to the $D_{4\mathrm{d}}$ isomer, in agreement with the SCF-CI calculations of ref. [13]. 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. [10], using LDA-DFT. Being an approximation to the more sophisticated (and more time-consuming) *ab initio* methods, it has been shown [10] to provide answers in quantitative agreement with these, in particular with *state-of-the-art* Car-Parrinello structural minimization [12].

The SIC *prescription* [6], 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 [11]. 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, in particular for what concerns the study of excited-state properties of clusters.

Because the LDA-PSP-PT results are available for these clusters [10], the role of self-interaction errors can be estimated unambiguously. We would like to point out that SIC has been used before in this context, not only to test its ability to predict the bond length in alkali dimers [7], [14], but also in the more general framework of structural minimization [15]. Whereas in the case of dimers the role of SIC in the chemical bonding of atoms in a cluster cannot be investigated, this role has been carefully studied in ref. [15], where it has been found that a spin-polarized, SIC-DFT formulation may be essential to allow for reliable predictions of the stable geometries of small metallic clusters. Indeed, it has been shown in ref. [15] that the ground state of Na_6 is planar in SIC-LSDA, in contrast to LSDA, in which the ground-state structure is three-dimensional. For the clusters considered in this work, which are closed shell in the "jellium" model, the spin-polarization effects are minimal. Therefore, we apply the perturbative formulation in LDA instead of LSDA. Furthermore, it will be concluded that already for a 20-atom sodium cluster, the role of SIC in the assignment of the equilibrium geometry is negligible. This is rewarding, in view of the increased computational load involved in SIC formulations [15].

In the following, we briefly summarize the SIC-PSP-PT formulation used, before discussing the results and writing down the conclusions.

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

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

In this equation, N is the number of ions (also the number of valence electrons for the neutral clusters considered here), and $\mathbf{R}$ represents a set of given ionic positions, which ultimately should be determined by minimizing the total energy of the system. $v_{\mathrm{ps}}(\mathbf{r}-\mathbf{R}_i)$ represents the pseudopotential at point $\mathbf{r}$, centred at the atomic site $\mathbf{R}_i$. We shall adopt the local pseudopotential used in ref. [10], with the parametrization adequate for sodium, taken from ref. [16]. With respect to any chosen centre of the cluster, the sum of the pseudopotentials can be expanded as follows:

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

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 [6], [11] for the N valence electrons moving self-consistently in this spherical potential ([1]). The remaining terms are included perturbatively up to second order, which leads to a contribution $\Delta E_{\mathrm{ps}}^{(2)}$ to the total energy reading [10]

$$\Delta E_{\mathrm{ps}}^{(2)} = \frac{1}{2}\int \mathrm{d}\mathbf{r}\,\delta n_2(\mathbf{r},\mathbf{R})\,v_{2,\mathrm{ex}}(\mathbf{r},\mathbf{R})\;, \tag{3}$$

where $\delta n_2(\mathbf{r},\mathbf{R})$ is the screened induced density change caused by the external potential $v_{2,\mathrm{ex}}(\mathbf{r},\mathbf{R})$. The total energy is then given by the sum of the monopole part, obtained via the SIC-LDA self-consistent solution, plus the term $\Delta E_{\mathrm{ps}}^{(2)}$ 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 $\delta n_2(\mathbf{r},\mathbf{R})$ 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 ref. [11]). 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 $\delta n_2(\mathbf{r},\mathbf{R})$ [11].

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 centre of mass of the cluster. This strategy (similar to those adopted in ref. [10], [13]), being

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([1]) Although in ref. [10] it is shown that PSP-PT and SIC-PSP-PT work well also for open-shell systems, the choice of closed-shell systems adopted in this work (closed shell in a spherical jellium sense), with 8 and 20 valence electrons, minimizes the contribution of $v_{2,\mathrm{ex}}(\mathbf{r},\mathbf{R})$.

Table I. – *Results for* Na_{20}*, for the two lowest isomers found in ref.* [12]*, obtained using standard* PSP-PT [10]*, 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, for each method, corresponds to the absolute minimum.*

Na_{20}	A	B
PSP-PT	0.000(1.02)	0.197(1.02)
SIC-PSP-PT	0.000(1.00)	0.237(1.00)

incomplete, will prove sufficient for the present purpose. In table I the results obtained with this methodology for Na_{20} are given. Two low-energy isomers have been identified in ref. [12], 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, for each row the energy differences always refer 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 [7], [14]. 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 difference in the restoring force coefficient for the breathing mode [10].

The situation is quite different for Na_8. The results are shown in table II, where we keep the same notation as in table I. The 3 structures considered are identified in fig. 1. SIC-PSP-PT leads to structures which favour geometries in accordance with ref. [13]. 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 (cf. ref. [15]). In this context, it is worth mentioning the recent measurements of the photoabsorption cross-section of Na_9^+ clusters [17] in a cold beam, which reveals a multi-peak structure which can be reproduced [18] by computing the absorption from the ground-state geometry found with the self-interaction free SCF-CI [5], 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 ref. [10], [12]. However, it should be pointed out that a fully consistent structural

Table II. – *Results for* Na_8*, for the three lowest isomers found in ref.* [12], [13]*, illustrated in fig.* 1. *The notation used here is the same as in table* I.

Na_8	$D_{2\mathrm{d}}$	T_{d}	$D_{4\mathrm{d}}$
PSP-PT	0.000(1.02)	0.160(1.00)	0.108(1.02)
SIC-PSP-PT	0.000(1.00)	0.104(1.00)	0.159(1.00)

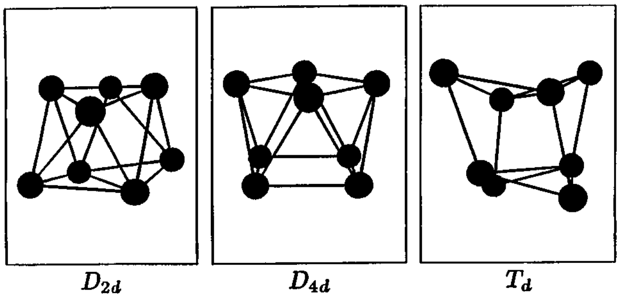

Fig. 1. – The 3 different geometries obtained in ref. [12] for Na_8, corresponding to the ground state and two lowest isomers (energy is increasing from left to right), and used as starting geometries which are minimized as a function of a dimensionless scaling parameter, which uniformly and simultaneously changes the radial distances of all the atoms with respect to the centre of mass of the cluster. The structure on the left displays $D_{2\mathrm{d}}$ symmetry, the one in the middle $D_{4\mathrm{d}}$ symmetry, and the one on the right T_d symmetry (see main text for details).

minimization of a cluster would require the use of SIC-generated pseudopotentials. In this sense, it remains an open problem how different from the LDA results are the average bond lengths obtained in a consistent SIC-LDA structural minimization. It is noteworthy that the present results are in contrast with those obtained via SCF-CI [5], which lead to an average bond length in small alkali clusters which is larger, on the average, than what is known in the bulk limit [12]. Whereas the values obtained here are physically more appealing, in the sense that, 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, 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, as 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. These results are likely to have a sizeable influence in the computation of the optical properties of small metallic clusters, an issue which is presently under investigation [19]. 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 [19].

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