A local MP2 periodic study of crystalline Argon

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Abstract. The CRYSCOR code, a computational tool for solving the second-order Møller-Plesset local equations (LMP2) for periodic systems, is used to study and compare the two crystalline Argon structures fcc and hcp. Binding energies, lattice parameters and bulk moduli are calculated; results are discussed in the framework of the latest experimental and theoretical literature data.

1. Introduction

Even if representing a minimal fraction of the total electronic energy, electron correlation is often fundamental for understanding chemical-physical phenomena, also in the case of solid state systems. In general, the observables of interest are energy differences between different electronic or nuclear arrangements which are of the same order of magnitude of the correlation corrections. Then, the latter can become decisive for determining the order of stabilities among different structures or for getting results in better agreement with the experimental ones. Moreover, when approaching a solid state problem, taking into account long-range cooperative effects becomes mandatory and an extended model of the system under investigation can be required. Wavefunction based correlation methods have a high scaling of the computational cost with the size of the problem. On the other hand, density functional theory (DFT), capable of treating at low cost periodic systems, has some disadvantages in comparison to correlated methods, such as the impossibility for systematic improvements and the inability to describe dispersive forces [1]. A general and robust computer program for the \textit{ab-initio} treatment of correlation effects in nonconducting crystals has recently been prepared. The code, named CRYSCOR, is based on the local correlation scheme originally proposed for molecules by Pulay and Saebø [3], developed and implemented by Werner and Schütz [4] in the \textsc{MOLPRO} code, and further extended to periodic systems by Pisani and coworkers [5]. The \textit{local} approach exploits the fact that dynamical electron correlation effects between remote parts of a system decay as the inverse sixth power of their distance, and can be disregarded. In adapting this technique to the case of crystalline systems, translational and point symmetry have been fully exploited and so the problem has been reduced to one concerning a cluster around the reference cell. Therefore, $O(N)$ scaling of the local methods is maintained, $N$ being the size of the crystal unit cell. The source of the Hartree-Fock (HF) reference is the well-known LCAO periodic code \textsc{CRYSTAL} [6], which solves efficiently the HF equations in a basis set of Gaussian type functions (GTF). This code also provides the symmetry information of the system and constructs the localized Wannier Functions (WF) spanning the occupied space. At the present time, only the second-order Møller-Plesset treatment is implemented in CRYSCOR.
A lot of work is going on to explore the capabilities and limitations of the code and to extend its range of applications: aim of this paper is its use in the study of the Argon crystal, trying to validate its ability to describe very weak long-range interactions.

Several attempts have been undertaken in the literature to explain the observed stability in standard conditions of the face centered cubic phase (fcc) for rare gas crystals, whose structure, according to calculations based on pair potentials performed by Born and his collaborators [7], should be somewhat less stable than that of hexagonal closed packed ones (hcp). In particular, this discrepancy has led to an intense debate on the effects accounting for the difference in the calculated energies of the fcc and hcp structures.

In fact, accurate ab-initio cluster approaches have provided remarkable results which however disagree with regard to the nature of this stability. Lotrich and Szalewicz [8], computing Argon binding energy by means of a symmetry-adapted perturbation theory three-body potential, conclude that short-range three-body forces are responsible for the stabilization of fcc over hcp. Fulde and coworkers [9, 10], using a coupled-cluster approach and an incremental expansion of the ground state energy, show that the stabilization due to the three-body terms is small and that the zero-point vibrational energy has to be added to yield fcc being preferred to hcp. Finally, Moyano et al. [11] argue that the use alone of more sophisticated two-body potentials can provide further insight into the stability of the two phases.

Recently, a periodic HF-like hybrid scheme approach, combining the HF exchange with the Wilson-Levy correlation functional (HF+WL) has been used in the study of weakly bonded systems [12]. Despite some interesting results for dimers, the authors conclude that long-range weak interactions are still not properly described.

In this context, our periodic approach is of interest because it permits us to improve the HF solution with electron correlation effects and long range dispersive contributions in a fully integrated code, with no extra parametrizations except for the optimization of the variational basis set. The case of the Argon dimer is considered for purposes of calibration of the computational settings.

The paper is organized as follows. In Section II the general features of the local MP2 method are briefly summarized. Section III is devoted to the computational details and strategies. In Section IV results on the Argon dimer and the two crystal structures are presented and discussed. All MP2 calculations have been carried out with a development version of the CRYSCOR code. Conclusions and perspectives are outlined in the last section.

2. Local MP2 method for periodic systems

This section summarizes how the original ideas of the local Pulay [3] approach have been implemented in the periodic CRYSCOR code. For an exhaustive description of the method, reference can be made to existing literature [5, 13].

1. Use of local, but differently constructed, basis sets to describe the occupied and virtual HF manifolds. The occupied space is spanned by orthonormal WFs, generated from the canonical Bloch orbitals produced by CRYSTAL using the Localization-Wannierization scheme by Zicovich-Wilson et al. [14] and then symmetrized a posteriori [15]. For the virtual manifold, as suggested by Pulay [16], projected atomic orbitals (PAO) are used, which are obtained by projecting out of the occupied space atomic orbitals (AO) of the basis set. PAOs form a redundant, non-orthogonal set, but at the same time are appreciably well localized and have the symmetry of the parent AOs.

2. Restriction of the pair excitation amplitudes, from two WFs to two PAOs, to a local set of WF pairs, exploiting the locality of the correlation effects. By virtue of the translational symmetry, the first WF is always confined in the reference cell and the second one in a finite
region around it. The set of WFs located in the reference 0 cell will be called reference-WFs.

3. Restriction of the excitation space to local domains. For each WF a symmetry-consistent set of atoms, whose corresponding PAOs are to be included in the domain, is determined according to a suitable criterion (like distance from the WF center, or atomic population). Each pair excitation domain is then defined as the union of local domains of the respective WFs.

4. Systematic exploitation of translational and point symmetry. Advantage is taken of the symmetry properties of the basis functions (AOs, PAOs and WFs) and of their product combinations, so that the estimate of all quantities of interest is restricted to an irreducible subset.

Then, the MP2 energy per unit cell can be expressed as follows:

\[ E_{\text{LMP2}} = \sum_i \sum_{j,J_{\text{near}i}} E_{i,j,J}^{\text{LMP2}} \]

\[ E_{i,j,J}^{\text{LMP2}} = \sum_{(a,A,b,B) \in [i,j,J]} K_{aA,bB}^{i,j,J} \left( 2T_{aA,bB}^{i,j,J} - T_{bB,aA}^{i,j,J} \right) \]

Here \((i, j)\) and \((a, b)\) number the reference WFs and PAOs, respectively; calligraphic indices \((I, J)\), \((A, B)\) denote lattice vectors and the corresponding crystal cell (the "0" for reference WFs, is omitted); \([i, j,J]\) indicates the pair domain of the two WFs. \(K_{aA,bB}^{i,j,J} \equiv (i0, aA | jJ, bB)\) are the 4-index electron repulsion integrals. \(T_{aA,bB}^{i,j,J}\) are the excitation amplitudes which are obtained by solving self-consistently the LMP2 equations, starting from the knowledge of the Fock matrix in the WF and PAO representation.

The partition of the energy by WF pairs, will permit us to analyze the role of the different types of contributions in the crystalline structures and to propose a new scheme for taking into account the basis set superposition error.

The LMP2 bottleneck, represented by the calculation of two-electron integrals in the AOs basis and their transformation to WFs and PAOs, has been overcome in CRYSCOR by an adaptation of the well known density fitting approximation [17] to the periodic case (DFP) [13, 18]. The basic idea behind DF is to approximate WF-PAO product densities, which appear in those integrals, with their projection onto a suitable auxiliary vector space. For the calculations presented here, DFP has been used in its Dual Range (DR-DFP) implementation, significantly different from those previously proposed, which will be the subject of a forthcoming paper. For distant WF pairs, a multipolar expansion technique can be adopted. Finally, an original procedure has been implemented to take into account far off LJ contributions [13], which are significant in extended systems.

3. Computational details

The computational settings adopted for the present LMP2 study are here described and the role of the various parameters is examined. As concerns the reference CRYSTAL calculations, for obtaining the HF solution, all parameters have been set so as to guarantee good accuracy [6]. For the sake of comparison, DFT calculations have been performed on cubic Argon, using B3LYP and PWGGA functionals [19]. The cubic lattice contains one atom per cell while the hexagonal lattice has two atoms per cell, so all the quantities of interest (reference WFs, WW-pairs, etc.) in the latter are doubled.

**Basis set (BS).**

This is a critical issue. As it is well known and will be shown in the following, BSs which are adequate for the HF calculation are not appropriate for the MP2 correction, where the use of diffuse functions becomes decisive. The selection of a suitable BS must be compatible with the
restrictions imposed by periodic HF calculations in terms of basis set linear dependency and computational costs. All present MP2 corrections are restricted to excitations from the valence space (4 WFs per atom). This permits us to adopt pseudopotentials in order to get rid of core electrons with substantial savings. We have adopted the valence basis set with a semiempirical effective core relativistic pseudopotential optimized by Dolg et al. [20] for the Argon atom and used as a starting point by Fulde [9] and coworkers in their study on Argon crystal. This basis set, referred to in the following as A, is a (6s6p3d1f)/[4s4p3d1f] one. For the reasons outlined above, we could not use the more extended basis set developed in [9]. A check of the basis set reliability at the HF level has been performed by calculating HF cohesive energies with an all-electron basis set [21], which represents at the moment the HF limit for Argon atom: the agreement in the energy results is excellent (figure 2).

In order to improve our MP2 description, we have tried a second basis set, called A+, containing a second f function, with an exponent equal to 0.46. **MP2 parameters.** A set of preliminary calculations have been done, in order to define the settings which achieve the best balance between computational costs and accuracy: results are collected in table 1. The first analyzed parameter (test cases 1, 2, 3) is the cutting of WF and PAO tails, in their expansion as a linear combination of AOs: AO coefficients smaller than the thresholds qw and qp, defined by input, are set to zero. For the dimer a value of 1x10^-6 has been used for both parameters, while for extended systems, the rather accurate setting qw = qp = 1x10^-4 has been adopted.

Then, the effect of the domain size is considered (test cases 4, 5, 6); we have used for each reference WF a domain made of PAOs projected out from AOs centered on the 13 atoms closer to the reference ones. This choice introduces relatively small errors, both for fcp and hcp, with great savings of computational time.

Finally, the number of WW pairs to include in equation 1 has been investigated (test cases 7 and 8 and figure 1). WF pairs can be classified according to a distance d criterion between WFs centroids as: strong (d = 0), weak (0 < d < d1) and distant (d1 < d < d2); the main idea is that excitations from two WFs become progressively less important with increasing distance, so that the respective contributions can be treated in a less accurate way. In particular, distant pairs can be evaluated by means of the multipolar approximation and contributions arising from pairs farther than d2 are derived from the LJ extrapolation and added a-posteriori. In the case of the dimer, all pairs have been included and calculated by means of the DFP technique. For crystals, d1 and d2 have to be accurately calibrated; the good agreement between test cases 7 and 8 and the corresponding gain in time induced us to use the multipolar approximation for pairs whose WFs are farther than 6 Å. The convergence with respect to d2 is shown in figure 1: the correlation energy neglected because of the truncation is recovered through the LJ energy estimation so that E(MP2+LJ) converges much more rapidly than E(MP2) with respect to d2. The default settings are gathered in test 9.

**Correction of basis set superposition error (BSSE).** All the interaction energies have been corrected for the BSSE effects. The standard Boys-Bernardi [22] counterpoise procedure (CP) has been used to correct the HF or DFT formation energy, whereas for MP2 calculations two schemes have been adopted: the CP one and an alternative approach which exploits the intrinsic additivity of the MP2 contributions in terms of WF-WF pairs. In fact, if we consider in summation 1 only the pairs formed by one reference WF and the other one in the surrounding crystal, we directly estimate the MP2 binding energy (no intra-atom contributions are taken into account). This technique, referred to as partition method (PM), provides an MP2 energy which is almost BSSE-free.
Table 1. Data concerning preliminary MP2 calculations for the fcc crystal with basis set A, $a_0 = 5.20$. In the sixth column, in parentheses is reported the number of WW pairs evaluated by means of the multipolar expansion. For each atom 37 PAOs are included in the WF domain. Calculations have been performed on an Opteron processor, 2.2 GHz CPU, 4 Gb of memory.

| test case | $q_w = q_p$ | domain size | $d_1$ (Å) | $d_2$ (Å) | tot WW-pairs | CPU (sec.) | $E_{HF+MP2}^{tot}$ (µHa) |
|-----------|-------------|-------------|-----------|-----------|-------------|-----------|---------------------|
| 1         | 1x$10^{-3}$ | 13          | 6.        | 6.        | 9(0)        | 13800     | 2293.0              |
| 2         | 0.0005      | 13          | 6.        | 6.        | 9(0)        | 14000     | 2258.1              |
| 3         | 0.0001      | 13          | 6.        | 6.        | 9(0)        | 14500     | 2258.2              |
| 4         | 0.0001      | 1           | 4.        | 4.        | 3(0)        | 300       | 1616.7              |
| 5         | 0.0001      | 13          | 4.        | 4.        | 3(0)        | 8000      | 2009.4              |
| 6         | 0.0001      | 19          | 4.        | 4.        | 3(0)        | 16000     | 2058.6              |
| 7         | 0.0001      | 13          | 6.        | 8.        | 15(6)       | 20000     | 2726.2              |
| 8         | 0.0001      | 13          | 8.        | 8.        | 15(0)       | 32000     | 2693.1              |
| 9         | 0.0001      | 13          | 6.        | 12.       | 36(27)      | 38000     | 2857.3              |

Figure 1. MP2 and LJ+MP2 energy contributions (in Hartree) for different settings of the $d_2$ parameter (in Å) for the fcc phase, basis set A, $a_0 = 5.20$. The asymptotic convergence of the second serie, achieved for $d_2 = 12$, means that a full estimate of the contribution has been reached.

4. Results

The dimer.
Calculations on the Argon dimer have permitted us to calibrate the basis set and to test the reliability of our approach: the results are reported in table 2. BSSE corrections at the HF level are negligible for all the basis sets; on the contrary, the correction due to the not complete basis sets can represent a sensitive amount of the MP2 binding energies: because the CP and PM techniques give equivalent results only one value is reported in the table. The use of $f$ functions appears of fundamental importance in the evaluation of correlation energy and equilibrium bond
distance: a clear trend is seen from the all-electron basis set (no f functions) to the A$^+$ one.  

The crystals.

As for the dimer, BSSE corrections are small both for HF and DFT crystalline calculations. As regards the MP2 energies, CP and PM techniques give an energy per atom which is 0.3 and 0.1 percent more stable than the one evaluated for the isolated atom, respectively; obviously, these corrections represent a tiny percentage of the total atomic energy, but their difference (444 $\mu$Ha) becomes significant in the estimation of the cohesive energy. In our opinion, the CP method applied to a LMP2 approach overestimates the BSSE correction by overweighting the contribution due to the singlet excitations from the occupied WF to the domain of the ghost ones. For this reason, we have used the PM data in the binding energy evaluations.

Let us comment on the results summarized in figure 2, referring to cubic Argon. The HF approach, regardless of the adopted basis set, is unable to provide a positive binding energy at any distance. Also B3LYP drastically fails. PWGGA predicts a low binding energy (1906 $\mu$Ha) for a lattice parameter of 6.0 Å. This is probably due to its underestimation of the exchange contribution, with a consequent loss of physically relevant repulsive interactions.

The LMP2 correlation correction to HF corrects the former results, providing a crude but essentially correct estimate of the cohesive energies for the fcc structure. The geometry optimization yields an equilibrium lattice parameter in good agreement with the experiment and the differences between BSs A and A$^+$ can be fully appreciated.

In table 3 our results are compared to literature data. As expected, the use of basis set A$^+$ does not alter the equilibrium geometry but significantly improves the MP2 contribution to cohesive energy and slightly corrects the calculated bulk modulus. The remaining discrepancy with respect to literature data may be attributed to the intrinsic limitation of the LMP2 approximation and to basis set inadequacy.

The hexagonal Argon, which seems to be the stable crystalline form under high-pressure conditions, has then been addressed at the same level of accuracy. Since the potential energy surface is very flat, it has been difficult to unambiguously identify the minimum configuration. However, in our opinion, to discriminate which of the two phases result as the most stable, a comparison at equal volume and Ar-Ar distances becomes mandatory. In table 4 are reported the energy results for the two structures, in a geometry corresponding to the fcc equilibrium ones.

In agreement with experimental evidence and previous theoretical investigations [10, 11] the fcc packing appears to be favoured, and this is true for the whole set of addressed geometries. The total correlation energy has been partitioned into four contributions, according to the distance criterion between WF pairs. It emerges that the stabilization of the cubic structure is mainly due to long-range effects: the close-by contributions are practically equivalent in the two lattices while energy differences are relevant for all pairs starting from the second star of neighbour atoms.

5. Conclusions

CRYSCOR, a general-purpose code for evaluating electron correlation in crystals at an LMP2 level, has been used in the study of the energetic properties of fcc and hcp Argon crystals. Despite the low level of sophistication and the not complete convergence on the truncation parameters due to inherent limits of the local method, the code has provided reliable results. In particular, the cohesive energy and the lattice parameter for cubic Argon are in good agreement with experimental data. Also the sensitivity of the technique has been confirmed by the right prediction of the exact order of stability between the two crystalline phases. In this regard, it has been of fundamental importance to take advantage of the description (within the basis set limit) of long-range interactions.
Table 2. Structural and energetic properties of Ar dimer, with different techniques and different basis sets. Equilibrium distances $r$ in Å. Dissociation energies $D_e$ in $\mu$Ha. In parentheses, the percentage of BSSE correction with respect to MP2 binding energy. In the case of [9], results referring to basis set $A$ and to the more complete basis set $C$ are reported.

| Technique                  | $r$ (Å) | $D_e$ (μHa) |
|----------------------------|---------|------------|
| GGA-PW91 [23]             | 3.96    | -521.8     |
| HFWL [12]                 | 3.72    | -202.5     |
| CCSD(T) ($A$) [9]         | 4.01    | -238.7     |
| CCSD(T) ($C$) [9]         | 3.83    | -375.3     |
| HF+MP2 (all-el.)          | 4.00    | -231.0     |
| HF+MP2 ($A$)              | 3.95    | -302.6 (31%) |
| HF+MP2 ($A^+$)            | 3.88    | -359.0 (22%) |
| Exp. [23]                 | 3.76    | -453.6     |

Figure 2. Binding energies (Ha) as a function of the lattice parameter (Å) for the fcc structure calculated with different Hamiltonians and basis sets.

Application of CRYSCOR to the whole set of rare-gas crystals is a close perspective, while implementation of finest levels of theory lies farther in the future.

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Table 3. Structural and energetic properties of Ar fcc crystal, with different techniques and different basis sets. Equilibrium distances \( r \) in Å. Bulk moduli \( B \) in GPa. Cohesive energies \( E_{\text{bind}} \) in \( \mu \)Ha. The data reported from [9] are without zero point energy correction.

| Structure | \( a \) (Å) | \( d_{\text{Ar}-\text{Ar}} \) (Å) | Volume (Å\(^3\)) | \( E_{\text{HF+MP2}}^{\text{bind}} \) | MP2 contributions |
|-----------|-------------|-----------------|-----------------|----------------|-----------------|
| fcc       | 5.30        | 3.75            | 37.22           | 2930.4         | 219408          |
| hcp       | 3.75        | 6.12            | 3.75 3.75 3.75  | 37.22 2830.6   | 219410          |

Table 4. Energy comparison between the two lattices in the geometry corresponding to the cubic optimized ones. Energies are in (\( \mu \)Ha). Percentage deviation from experimental fcc is 4.1\%. Calculations performed with basis set A. Binding energies are corrected for the BSSE (PM technique).

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