Application of wavefunction-based *ab initio* methods to extended systems

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Abstract. The quantum-mechanical problems of solving the electronic Hamiltonian of realistic system on an *ab initio* level is mainly tackled with the density functional approach, which relies on the ground-state density of the system and avoids the calculation of the many-body wavefunction of the system. However, the present DFT-based approaches are not amenable to systematic improvements. Therefore, it is desirable to include correlations within the many-body wavefunction, using so-called quantum-chemical methods for the correlation. Especially for the strong-correlated systems (like molecular magnets) the explicit determination of the many-body wavefunction is of great importance with respect to proper description of their electronic properties.

1 Introduction

The field of many-body theory has been developing at high speed in recent years. A significant amount of effort is directed toward affordable descriptions of electronic correlation. The most widely used approach here is density-functional theory. Within a DFT-based formalism one avoids constructing the many-body wavefunction of the system and instead computes directly ground-state properties from its charge density. However, the exact form of the functional embodied in the Hohenberg-Kohn theorem is unknown and, therefore, approximations are required. One of the most important, local-density approximation, works successfully for the ground-state properties of weakly correlated systems. For the systems with strong electronic correlation effects like molecular magnets it is desirable to determine explicitly the many particle wavefunction of the system; this allows for a deeper insight into their electronic properties. The advantage

of the so-called quantum-chemical methods is their amenability to systematic improvements (by enlarging the basis set and by including more terms in the expansion of the wavefunction of the system). As a starting point for such a calculation a single-reference wavefunction is necessary. Nearly all methods rely on the Hartree-Fock wavefunction of the system.

2   Quantum-chemical approach to cohesive properties of solids

Ab initio Hartree-Fock (HF) and post-HF electron correlation methods are standard tools in computational chemistry nowadays of atoms and molecules. For solids, HF calculations have become possible with the advent of the program package CRYSTAL [1]. However, the problem of an accurate treatment of electron correlation is not fully settled. Recently, using the idea of local excitations in the electronic structure theory of solids, Stoll developed the so-called "method of increments" [2]. This method combines Hartree-Fock (HF) calculations for periodic systems with correlation calculations on the corresponding finite embedded cluster, where the total correlation energy per unit cell (u.c.) of a solid is written in terms of interactions of increasing complexity among the electrons assigned to localized orbitals comprising the solid under consideration:

$$E_{\text{corr}}^{\text{solid}} = \sum_{\substack{A\in\text{u.c.}}} \varepsilon_A + \frac{1}{2!} \sum_{\substack{A\neq B \\ A\in\text{u.c.} \\ B\in\text{solid}}} \Delta\varepsilon_{AB} + \frac{1}{3!} \sum_{\substack{A\neq B\neq C \\ A\in\text{u.c.} \\ B,C\in\text{solid}}} \Delta\varepsilon_{ABC} + \cdots. \qquad (1)$$

The ε_A (one-body increment) is computed by considering excitations only from the A-orbitals, freezing the rest of the solid at the HF level. The two-body increment is defined as $\Delta\varepsilon_{AB} = \varepsilon_{AB} - [\varepsilon_A + \varepsilon_B]$, where ε_{AB} is the correlation energy of the joint orbital system AB. Higher-order increments are defined in an analogous way. Thus, for the three-body term we get: $\Delta\varepsilon_{ABC} = \varepsilon_{ABC} - [\varepsilon_A + \varepsilon_B + \varepsilon_C] - [\Delta\varepsilon_{AB} + \Delta\varepsilon_{BC} + \Delta\varepsilon_{AC}]$. Finally, summing up all increments, with the proper weight factors (according to their occurrence in the solid), one obtains the correlation energy per unit cell of the infinite system. In order to get reliable results a size-extensive correlation method must be used. Of course, the incremental expansion only makes sense if it is well convergent, i.e., if $\Delta\varepsilon_{AB}$ rapidly decreases with increasing distance between the positions A and B and if the three-body terms are significantly smaller than the two-body ones. This means that only a few increments need to be calculated, yet a full account of the short range correlations is achieved this way.

Calculations based upon the method of increments have been performed on a variety of solids with band gap [3–5], where in all cases very good agreement of the calculated ground-state properties with the experimental data was achieved. Metals require special treatment: Since the conduction bands are only partially filled, we cannot construct well localized orbitals from them. To fix this problem we suggest to apply a special embedding scheme [6]. One should start from a system where long-range orbital tails are absent, and to allow for delocalization only

successively in the course of the incremental expansion. More specifically, when calculating pair contribution for a given orbital group combination (A,B), we allow for delocalization $A \rightarrow B$ and $B \rightarrow A$, and similarly with the higher-order terms we allow for delocalization over the triples, tetraples, etc. It is clear, that the final result is not affected, only the convergence properties of the many-body expansion are changed. Recently, this approach has been successfully applied to group 2 and 12 metals [7, 8].

3   Treatment of magnetic materials

If one is intersted in the local properties of the solid, e.g. in the spin state of the particular ion in a magnetic material, it is necessary to use multi-reference correlation methods, which can deal with the degeneracy resulting from the partially occupied d or f shells. We have applied such highly accurate methods to the determination of the spin-states of cobalt ions in $RBaCo_2O_{5.5}$ ($R = Ho, Gd$) (Fig. 1) depending on the oxygen coordination of Co, the lattice parameter changes at structural phase transition, and the rare earth element (R) involved [9]. We con-
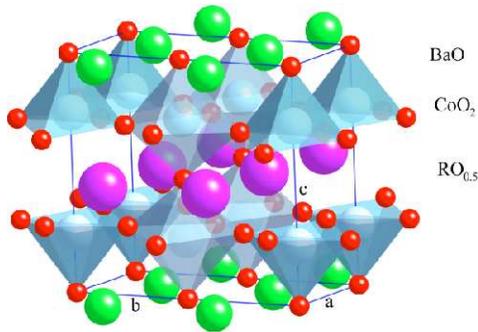

Fig. 1. The lattice structure of $RBaCo_2O_{5.5}$ ($R = Ho, Gd$); the frame is for elementary cell.

sider the peculiar behavior of the trivalent ions $Co^{3+}(3d^6)$ in either octahedral or pyramidal oxygen coordinations, which is related to a structural first-order phase transition in both compounds. Relative energy positions of low spin ($S = 0$), intermediate spin ($S = 1$) and high spin ($S = 2$) electron configurations are calculated for the low- and high-temperature lattice structures of $RBaCo_2O_{5.5}$. A combined analysis of the calculated results and experimental structural data leads to a simple model that captures the most prominent features of the phase transition common to both. The calculations supported the expected result that the lowest spin state of the CoO_6 cluster is extremely sensitive to the actual changes of the lattice structure, in contrast to the behavior obtained for the CoO_5 cluster spin states. The dominant role of the octahedral Co ions in the

spin-state transitions in both compounds was also supported by a supplementary cluster analysis of the evaluated electronic energy changes accompanying the structural changes in $RBaCo_2O_{5.5}$ (R=Ho, Gd).

As an example of the spin-spin interaction we present *ab initio* calculations on a cluster model of a vanadium containing ring-like molecular magnet (Fig. 2, Left panel). There the question arises, how the spin-spin interaction between two vanadium ions depends on the geometry of the V-V binding via the bridging oxygen. DFT calculations show a significant dependence on the functional used,
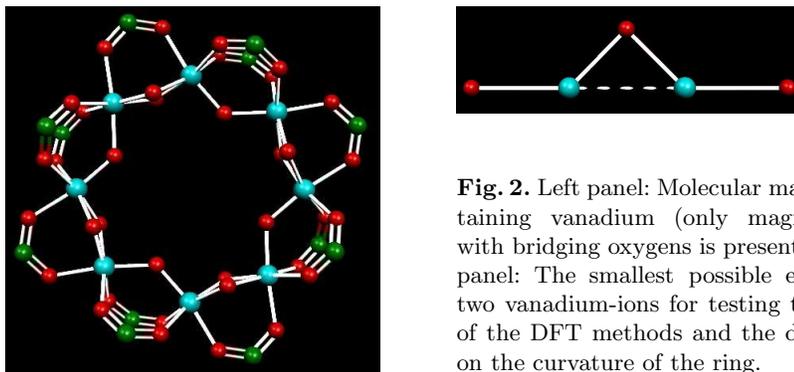

Fig. 2. Left panel: Molecular magnets containing vanadium (only magnetic part with bridging oxygens is presented). Right panel: The smallest possible entity with two vanadium-ions for testing the quality of the DFT methods and the dependence on the curvature of the ring.

therefore it is desirable to get reliable results with quantum-chemical methods for small model systems like V_2O_3 (Fig. 2, Right panel) and compare them with the different DFT approaches.

References

1. Pisani, C., Dovesi, R., Roetti, C.: Hartree-Fock *ab-initio* of crystalline systems. In: Berthier, G., Dewar, M. J. S., Fischer, H., *et al.* (eds.), Lecture Notes in Chemistry, vol. 48, Spinger, Heidelberg (1988)
2. Stoll, H. Phys. Rev. B 46, 6700 (1992); Stoll, H. Chem. Phys. Lett. 191, 548 (1992); Stoll, H. J. Chem. Phys. 97, 8449 (1992).
3. Paulus, B. Phys. Rep. 428, 1 (2006).
4. Voloshina, E., Paulus, B. J. Chem. Phys. 124, 234711 (2006).
5. Voloshina, E., Paulus, B. J. Comp. Chem. (accepted).
6. Voloshina, E., Gaston, N., Paulus, B. J. Chem. Phys. 126, 134115 (2007).
7. Paulus, B., Rosciszewski, K., Gaston, N., Schwerdtfeger, P., Stoll, H. Phys. Rev. B 70, 165106 (2204); Paulus, B., Rosciszewski, K. Chem. Phys. Lett. 394, 96 (2004); Gaston, N., Paulus, B., Rosciszewski, K., Schwerdtfeger, P., Stoll, H. Phys. Rev. B 74, 094102 (2006).
8. Voloshina, E., Paulus, B. Phys. Rev. B 75, 245117 (2007); Voloshina, E., Paulus, B. Mol. Phys. 105, 2849 (2007); Gaston, N., Paulus, B. Phys. Rev. B 76, 214116 (2007); Voloshina, E., Paulus, B. In: Simos, T. E., Maroulis, G. (eds.), Computation in Modern Science and Engineering, CP963, vol. 2, part A, p.274 (2007).
9. Siurakshina, L., Paulus, B., Yushankhai, V. Eur. J. Phys. B (submitted).