The Method of Increments —
a Wavefunction-based Ab-initio Correlation Method for Solids

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The method of increments is a wavefunction-based ab initio correlation method for solids, which explicitly calculates the many-body wavefunction of the system. After a Hartree-Fock treatment of the infinite system the correlation energy of the solid is expanded in terms of localised orbitals or of a group of localised orbitals. The method of increments has been applied to a great variety of materials with a band gap, but in this paper the extension to metals is described. The application to solid mercury is presented, where we achieve very good agreement of the calculated ground-state properties with the experimental data.

Keywords: Ab-initio calculation; Electron correlations; Method of increments; Mercury;

1. Introduction

Ab-initio electronic structure methods aim to solve the full electronic Hamiltonian (in atomic units):

$$H = \sum_i \left(-\frac{1}{2}\Delta_i - \sum_\alpha^K \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}. \tag{1}$$

The first two terms are the kinetic energy and the electron-nucleus interaction, both one-particle terms and properly described within a mean-field approach. The last term, the electron-electron interaction is a real many-body term, the two-body interaction can be solved only approximatively within a mean-field description.

Besides the very successful method to solve this Hamiltonian within the density-functional approach[1,2] (DFT), which relies on the ground-state density of the system and avoids the calculation of the many-body wavefunction of the system, it is desirable for many systems to calculate the many-body wave-function of the system explicitly yielding a deeper insight to the correlation effects of the system. The advantage of these methods, sometimes called quantum chemical methods, is that they can be improved systematically. As the starting point for such a calculation a single-particle wave-function is necessary. Nearly all methods rely on the Hartree-Fock wavefunction[3–5] of the systems. This independent electron approximation yields the lowest ground-state energy which is possible for independent elec-

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trons. "Independent electrons" means that the electron experiences an interaction field which is calculated as the spatial average over the positions of all other electrons. This field depends on the Hartree-Fock wavefunction, therefore the problem is solved in a self-consistent manner, until both the wavefunction and the field is converged. For a closed shell system the solution is a single Slater determinant, which is for weakly correlated systems a good starting point for successive correlation calculations. Moreover, the amount of electronic correlations, i.e. the instantaneous reaction of an electron due to the movement of any other electron, is defined as the difference between the Hartree-Fock solution and the true ground-state solution.

Quantum-chemical correlation methods rely on the Hartree-Fock solution of the system. Starting from the Hartree-Fock orbitals, which are divided into occupied and unoccupied ones with respect to the ground-state Slater determinant, in the configuration interaction (CI) ansatz[6,7] additional determinants are considered. In these determinants one, two or more occupied orbitals are replaced by unoccupied ones. The weights of these determinants in the ansatz for the many-body wavefunction are optimised by minimising the total energy of the system.

In order to apply the quantum-chemical correlation methods to an extended system the property that the correlation hole (i.e. the region, where the electrons interact instantaneously) is fairly local can be used. Therefore for a solid it is useful to switch from the description with delocalised Bloch orbitals to localised Wannier orbitals.[8] But even if the correlation hole extends only e.g. to the fourth-nearest neighbours, that would correspond to 64 atoms in a dense-packed three-dimensional solid and e.g. for carbon with its four valence electrons this would result in the need to correlate 256 electrons. It is hard to handle so many electrons with explicitly correlated methods, because the computational demand increases with N^5 to N^8, where N is the number of electrons, depending on the specific method used.

Therefore further approximations are necessary. For this purpose the method of increments was developed by Stoll.[9–11] In this approach the correlation energy is calculated in the first step as the sum of independent contributions of translationally invariant localised orbitals or groups of localised orbitals. As corrections the non-additive parts of two, three or more localised orbitals are added. If the group of localised orbitals is chosen reasonably, this partitioning of the correlation energy of the solid yields a fast converging series. Due to the partitioning it is necessary that the correlation method used for the individual increments is size-consistent and size-extensive.

The method of increments has been applied to ground-state properties of various material classes: From insulators[12–16] over semiconductors[9,10,17–21] to metals,[11,22,23,25] from strongly bound ionic or covalent systems to weakly bound van der Waals solids,[26–28] from large molecules[29–31] over polymers[32–39] to three-dimensional solids, from weakly correlated systems to strongly correlated ones such as transition-metal oxides[40,41] and rare-earth nitrides and oxides.[42–44] This large variety of applications is possible, because the method of increments allows for an individual selection of the localised orbital group for each system and for the choice of the

suitable correlation method used for the ansatz of the many-body wavefunctions. The results allow us to discuss the influence of electronic correlation on the cohesive energy, on the lattice constants, the bulk moduli and other ground-state properties. In addition we can determine the origin of the electronic correlations and the range of the correlation hole.

The generalisation to metals is discussed in this paper for the example of solid mercury.[23–25] Mercury condenses at 233 K into the rhombohedral structure with a bond length $a = 3.005$ Å and an angle of $70.53°$[45] (see Fig. 1). This is in contrast to
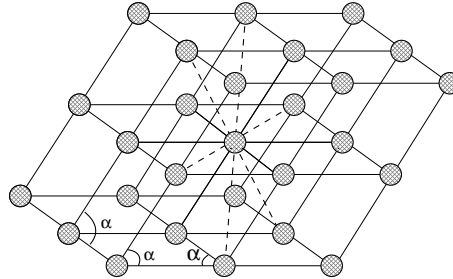

Fig. 1.   The rhombohedral structure occurring in solid mercury. The solid lines indicate the nearest neighbour distance a and the dashed lines show the second nearest neighbours, which form a regular hexagon.

zinc and cadmium, which adopt the hexagonal close-packed (hcp) structure, with an anomalous c/a ratio which is far from ideal hcp. Density functional methods fail to describe either of these structures accurately. Even in mercury some functionals yield a closed-packed fcc structure, and others a simple cubic structure. An application of the method of increments to mercury, including correlation via coupled cluster calculations on finite fragments of the solid, allows the systematic inclusion and comparison of the competing effects that leads to the observed structure.

The paper is organised as follows: In the next section the method of increments is presented and the extension to metals is described. In Sec. 3 the results for the ground-state properties of mercury are discussed. Conclusion follows in Sec. 4.

2. The Method of increments

The method of increments expands the correlation energy of the systems in terms of local increments (for a sketch see Fig.2). It is formally similar to treating the hierarchy of nth order atomic Bethe-Goldstone equations.[46] Here we want to sketch the basic ideas and some important formulae (for more details see Ref. [47,48]). The method relies on localised orbitals or a group of localised orbitals generated in a Hartree-Fock reference calculation. One-body correlation-energy increments ϵ_i are obtained by correlating each of the localised orbital groups separately while keeping the other ones inactive. In the present work we are using the coupled-cluster
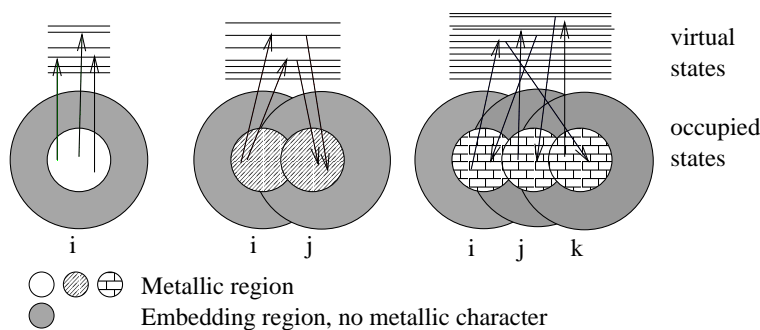
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Fig. 2.   Schematic overview of the procedure of the method of increments for metals.

approach with single and double substitutions with perturbative triples (CCSD(T)) as implemented in Molpro,[49–51] but every size-consistent correlation method is possible. This yields a first approximation of the correlation energy

$$E_{\text{corr}}^{(1)} = \sum_i \epsilon_i, \tag{2}$$

which corresponds to the correlation energy of independent orbital groups.

In the next step we include the correlations of pairs of orbital groups. Only the non-additive part $\Delta\epsilon_{ij}$ of the two-body correlation energy ϵ_{ij} is needed.

$$\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j). \tag{3}$$

Higher order increments are defined analogously, e.g. the three-body increment

$$\Delta\epsilon_{ijk} = \epsilon_{ijk} - (\epsilon_i + \epsilon_j + \epsilon_k) - (\Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ik}). \tag{4}$$

The correlation energy of the system is finally obtained by adding up all the increments with appropriate weight factors:

$$E_{\text{corr}} = \sum_i \epsilon_i + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \Delta\epsilon_{ij} + \frac{1}{6} \sum_{\substack{ijk \\ i \neq j \neq k}} \Delta\epsilon_{ijk} + \cdots . \tag{5}$$

It is obvious that by calculating higher and higher increments the exact correlation energy is determined within the correlation method applied.

This partitioning of the correlation energy is only sensible if the series converges quickly enough, both with the order of increments (i.e., 3-body increments should be significantly smaller than two-body increments, etc.) and with the distance of the orbital groups involved in the increments. Increments involving distant orbital groups must decay faster than the number of increments increases in a 3-dimensional system. For a semiconductor or an insulator, increments with distant orbital groups interact only via van der Waals and thus decay like r^{-6}, whereas the number of pairs grows with r^2, so an overall decay of r^{-4} guarantees the convergence with respect to the distance of orbital groups.

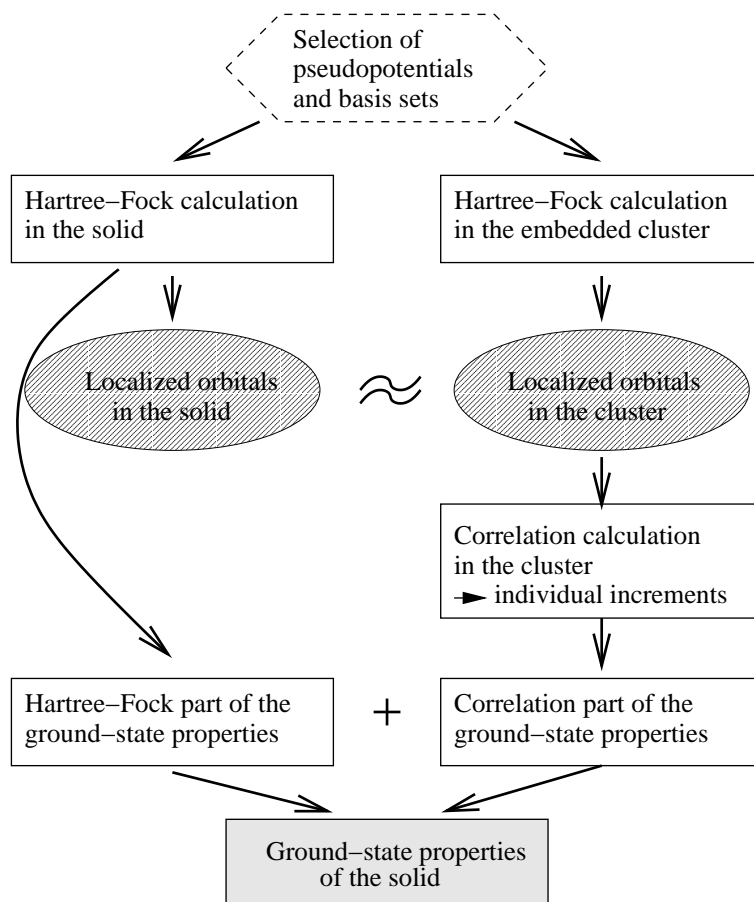 A direct transfer of this approach to metallic systems is not possible, however,

Fig. 3.   Schematic overview of the procedure of the ground-state calculations with the method of increments.

since localised orbitals become very long-range entities here and a many-body expansion in terms of such orbitals cannot be expected to have useful convergence characteristics. In order to make the expansion still computationally feasible, we have suggested[23,30] to start from suitable model systems where long-range orbital tails are absent, and to allow for delocalisation only successively in the course of the expansion; more specifically, when calculating pair contributions for a given orbital group combination (i, j), we allow for delocalisation $i \rightarrow j$ and $j \rightarrow i$, and similarly with the 3-body terms we allow for delocalisation over the triples of atoms, etc. It is clear that the final result is not affected, only the convergence properties of the many-body expansion are changed. As an additional advantage, we can calculate individual terms of the expansion from (suitably modelled/embedded) finite clusters of reasonable size. In the case of mercury, for example, we can force localisation of the solid by using a s-type atomic basis set for describing the valence-electron

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system. This way, delocalisation due to sp-mixing is avoided, but still each atom has its correct crystal surroundings concerning the electrostatic interaction. Due to the metallic embedding scheme even the conduction bands are localised in the central region. The incremental expansion has to take care subsequently of the non-additive effects of correlation and delocalisation.

Here we want only briefly sketch the technical details necessary to apply the method of increments to real systems. The first question is the selection of the pseudopotentials, if necessary, and the basis set which is usually a set of contracted Gaussian functions centred at the atoms involved in the system. Because we want to use standard correlation methods as implemented in quantum chemical programs we have to calculate the correlation energy increments in finite fragments of the solid. Therefore we generate a proper embedding, so that the localised orbitals in the cluster are very simular to the one in the solid. The localisation procedure is mostly according to Foster and Boys.[52] An schematic overview of the procedure is given in Fig.3.

3. Application to solid mercury

The Hartree-Fock ground-state properties are calculated with CRYSTAL[53] supplying a 20-valence-electron pseudopotential[54] for mercury and the corresponding crystal-optimised basis set.[30] The value for the cohesive energy is corrected for the basis set superposition error[55] by a counterpoise correction with the atomic energy calculated in the presence of basis sets placed at the positions of neighbouring atoms in the solid (convergence required 12 nearest neighbours for Hg). As shown in Fig.4,5 the HF treatment yields no binding for mercury, the cohesive energy at the experimental structure is repulsive by about the same amount as the experimental cohesive energy is binding.

For the correlation calculation we use an embedding scheme where the part of the cluster which is not correlated is described with 2-valence-electron scalar relativistic pseudopotentials[56] which simulate the Hg $5s^2 5p^6 5d^{10}$ shells within the atomic core. Thus, only the $6s$ shell is explicitly treated in the embedding region. The critical part in the application of the method of increments to metals is the possibility of describing the metallic orbitals calculated in the embedding region in a local way. This localization is done in our approach by a unitary transformation of the occupied canonical orbitals according to the criterion of Foster and Boys.[52] Good localisation characteristics are achieved by using an s-type atomic basis set ($2s$ basis, with contraction coefficients optimised for the free atom) on the embedding and thereby avoiding delocalisation due to sp-mixing. Within this localised environment we can use the full basis for the 1, 2, or 3 atoms that we are calculating the correlation energy of, for the 1-, 2-, or 3-body increments, respectively. This approach allows us to successively include metallic delocalisation in an incremental way.

The increments are calculated for selected cluster models which reflect the geometry of the Hg crystal. The rhombohedral structure of the infinite crystal can be
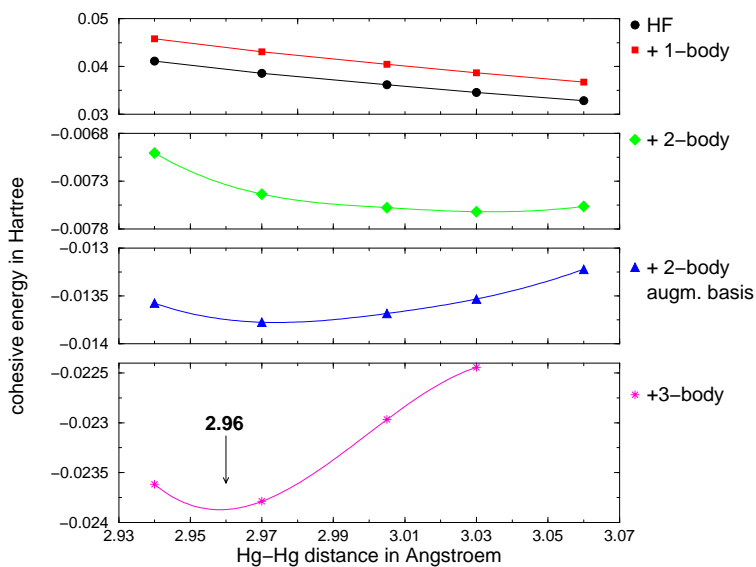
Fig. 4.   The cohesive energy of Hg with respect to the nearest neighbour-distance a.
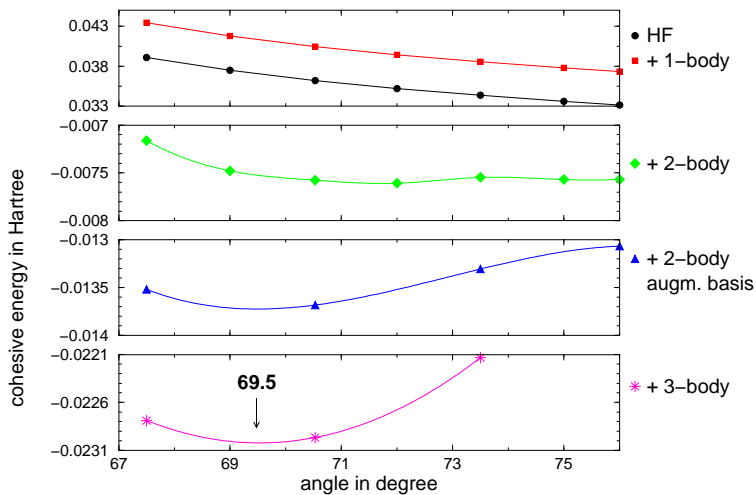

Fig. 5.   The cohesive energy of Hg with respect to the angle in the rhombohedral structure.

viewed as a central atom surrounded by atom shells of various size. We select for the embedding the first shell containing 12 atoms, 6 of them at distance a(nn) (=3.005 Å) and 6 at 1.155 a(nn); For calculating a few-body term, we include all atoms in the embedding which are in the first shell of one of the atoms to be correlated. The description of the atoms to be correlated is much more important for the final correlation energy, as we will keep frozen the localised orbitals of the atoms of the

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embedding region when calculating correlation energies.

The basis sets of the correlated atoms were described in Ref. 30. A $(10s9p7d2f1g)/[8s7p6d2f1g]$ set is used for the 20 valence electrons of mercury, and an even tempered augmented version of the same basis to gain an impression of the basis set completeness for these calculations. Using these basis sets, we recalculate the integrals and reoptimise the orbitals of the atoms to be correlated, in a HF calculation, within the frozen environment of the embedding. Thus we have reasonably delocalised orbitals within the interior of our cluster over the atoms $i, j, ..$ to be correlated, but localised orbitals with respect to the embedding. Then we calculate the correlation energy of these atoms in a coupled-cluster calculation with single and double excitations and perturbative treatment of the triples (CCSD(T)).[50,51] We can do this with different definitions of the core in order to see the different contributions of the valence $6s$, $5d$, and core $5sp$ electrons. All these calculations are performed using the MOLPRO suite of ab-initio programs.[49]

The results for the lattice parameters, the cohesive energy and the bulk modulus are summarised in Table 1. In order to discuss the dependence of the energy of

Table 1.   Results for the structure and bulk modulus of solid mercury. a is in Å, α in degrees, E_{coh} in eV and B in Mbar. For the LDA value in the hcp structure, $a = a(\text{nn})$ is given.

Method	a	α	E_{coh}	B
Hartree-Fock	—	—	+0.985	—
Incremental correlation (2b:aug. basis,s-only)	—	—	+0.245	—
Incremental correlation (2b:aug. basis)	2.97	70.0	-0.375	0.132
Incremental correlation (3b:s-only)	2.97	69.2	-0.561	0.383
Incremental correlation (3b)	2.96	69.5	-0.649	0.360
Expt.[45,57]	3.005	70.53	-0.670	0.322

the lattice on its structure, we vary the lattice distance and angle of the structure around the experimental lattice parameters. The HF energy decreases with increasing distance (see Fig. 4) as is normal for a purely repulsive potential. It also decreases with increasing angle (see Fig. 5) which corresponds to an opening of the structure and lowering of the density. The one-body terms of the correlation-energy expansion are repulsive for mercury and have nearly no dependence on the lattice parameter. The first term in the expansion to examine closely with respect to the effect of the lattice parameter is therefore the two-body increment. Here the potential is actually very flat, and thus the minimum can be shifted noticeably by the use of an augmented basis set, if we are only considering the two-body increments. In Fig. 5 the angular dependence of the two-body part is shown to be even weaker. Only with the augmented basis set does a shallow minimum appear. With the augmented basis, we find a minimum with $a = 2.97$ Å, and $\alpha = 70.0°$. If we include

only the correlation of the valence s-electrons in the two-body increments we still have no minimum. Only with the inclusion of d-correlation in the two-body part do we find a bound solid. We have chosen to truncate the expansion of the three-body correlation after 8 increments. We concentrate on these eight geometries because they contribute about 80% to the 3-body part of the cohesive energy. These 8 clusters all have 2 nearest or second-nearest-neighbour distances connecting the atoms. Including the contributions of the three-body increments the rhombohedral lattice structure is stabilised with only a very small shift to a smaller interatomic distance and somewhat smaller angle. Overall the lattice parameter agree within 1.4% with the experimental values.

The results for the cohesive energy are summarised in the third column of Table 1. The HF part of the cohesive energy is repulsive, the 1-body correlation contribution to the cohesive energy is repulsive, too. The main contribution to the binding comes from the 2-body increments, with about half of this originating from the core-valence correlation of the d shell. Without correlating the d shell solid mercury would not be bound. The 3-body contributions are attractive, both for the valence as for the d shell, whereas the latter one contribute by about one third to the total 3-body contributions. The most important four-body contributions have been calculated, they are small (≤ 0.08 eV) and repulsive. The spin-orbit contribution to the binding and the zero-point energy can be neglected. In summary, the method of increments allows us to determine the cohesive energy of solid mercury within the same accuracy compared to the experimental value (error less than 15% within the given finite basis set) as was achieved for semiconductors and insulators.

Our calculated values for the bulk modulus are given in Tab. 1. The bulk modulus calculated with two-body increments only is 0.132 Mbar, considerably lower than the experimental value. When only the s-correlation of the three-body increments is included, the bulk modulus increases to a value of 0.383 Mbar. The final result of the method of increments, with the inclusion of d-correlation for the three-body increments, gives 0.360 Mbar in good agreement with experiment.

4. Conclusion

We have presented here the generalisation of the method of increments to metals. Only the correlation part of the energy is treated by means of the incremental scheme. To obtain localised orbitals, we start from embedded clusters without any metallic character. Within the incremental scheme we allow for a delocalisation of the orbitals and therefore account for the metallic character of the systems. With this approach the convergence rate, especially with the order of increments, is not as good as for insulators, but still three- and higher-body terms account for only about 15% of the correlation contribution to the binding. For the first time we could solve the puzzling problem of the binding in solid mercury, where the binding is entirely due to electronic correlations. The lattice structure of solid mercury has been calculated using the method of increments. With this wavefunction-based

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method, we can reproduce the lattice constant and rhombohedral angle to within 99% of the experimental values, and obtain a cohesive energy of -0.65 eV, 97% of the experimental value, and a bulk modulus well within the experimental error bars.

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