9 SCIENTIFIC HIGHLIGHT OF THE MONTH

A new theorem for embedding with application to a new hybrid method for difficult composite systems marrying configurational interaction and density functional calculations

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There are many situations where one would like to do electronic structure calculations but which are too large for *ab initio* treatment. Usually these contain some special central region which one is interested in, but the coupling to the remainder is too strong for one to neglect it entirely. A common approach has been "embedding" where one solves properly for the inner special part of the system, but with some sophisticated treatment of the boundary to represent more or less accurately the influence of the outer remaining part of the system.

The present article reports on two advances in this field. The first advance is a new theorem to achieve embedding. It replaces the outer region by a non-local separable potential (mathematically rather like a pseudopotential) around the boundary, which has been derived from a Hartree-Fock or Density Functional Theory calculation of the electronic structure in the outer region. The mathematics of the theorem is given in the appendix. Possible applications might include large biological molecules such as chlorophyl where one has an active centre around the Mg atom surrounded by a very large region that for some purposes may be rather inactive. The molecule is too large for a calculation on the whole molecule, but a calculation on the central part is sufficient provided one represents adequately the influence on it of the outer part of the molecule, all in the context of density functional theory or Hartree-Fock.

The theorem was discovered in the course of marrying Density Functional Theory (DFT) calculations in the outer region, with Configurational Interaction (CI) calculations in the central

region. This is the second advance reported here, and really occupies the whole paper, so that the theorem is described in that context. It was only later realised that other important applications of the theorem may lie elsewhere.

Hence the main purpose of this article is to introduce a new method for electronic structure calculations on systems that could not really be treated before. We have in mind a composite system such as a transition metal impurity in silicon or in an oxide host, where one small part has an "open shell" electronic structure at which it is necessary to take some configurations into account beyond the usual DFT approach. We want to be able to calculate the term splitting (in the sense of atomic energy levels) and other forms of excited states. Other examples of such composite systems might be defects with vacancies in a covalent material where the cut off dangling bonds may have some "open shell" character, and in biology a molecule such as haemoglobin containing the open shell Fe atom.

So far the only application (beside some simple tests) has been to one and two Ag atoms in solid P_2O_5, a material used in dosimetry of ionizing radiation. At present only the ground state has been considered, but it has been shown that two silver atoms have a tendency to coalesce into an Ag_2 molecule in the oxide. The method was developed by the group in St.Petersburg including Vladimir Bulatov and Ilia Tupitsyn with the help of Rex Godby, Mike Payne and others in Cambridge and the use of the CASTEP code for the DFT part of calculations. The open shell part of the calculations has been carried out by the Multi-Configurations Self-Consistent-Field (MCSCF) method using the code from the Swedish group of Prof.B.Roos, which has been well used and tested on atoms and molecules including those of open shell character. Both the DFT and MCSCF calculations are of course fully *ab initio* in the usual sense with Helmann-Feynman forces on the atomic nuclei.

The problem of course is how to marry DFT and MCSCF calculations because they represent such very different approaches. This is accomplished using two tricks, as we will describe below, the second of which is highly non-trivial and depends on a new theorem which may well have applications in other types of matching calculations. But first a few remarks about the MCSCF calculations are in order since they have not featured much in the Psi-k Newsletter. In an electronic structure calculation on, say, a single Fe atom, one wants to take two types of effects into account involving the mixing of several (or many) determinants in the wave function. The first is the energy splitting between different "terms" ^{5}F and ^{3}P etc (in the nomenclature of atomic energy levels) within the same $3d^74s$ configuration. Even in the lowest Hartree-Fock approximation, the wave function is not a single determinant (as is sometimes alleged) but for an atom is a linear combination of several determinants all from the same $3d^74s$ configuration, with Clebsh-Gordon coefficients to make the whole an eigenfunction of L^2 and S^2 operators with appropriate L(L+1) and S(S+1) eigenvalues. The ideas are extended to molecules and small clusters using S^2 and appropriate spatial symmetry. The second effect to be demonstrated by mixing in more determinants is electron correlations. For an atom this would mean determinants from a higher configuration constructed from a suitable basis set of local orbitals. For a cluster with low symmetry the two effects are mixed together.

In conclusion, therefore, the MCSC method uses an expansion in determinants for the wave function, where each determinant is constructed out of localized orbitals (usually atomic-type

orbitals) chosen to give good convergence for term splittings and correlation, based on experience in quantum chemical calculations. The Achilles heel of the MCSCF method is, of course, that the number of determinants grows exponentially with the size of the system which makes it impossible for solid applications by itself.

We now turn to the two tricks needed to marry the MCSCF and DFT methods. The first trick is illustrated in Fig.1, where space is divided into three regions, with the region I containing the "open shell" part of the system and regions II and III amenable to DFT calculations. In the case of Fe as a substitutional impurity in Si, region I would be the Fe atom, region II the four Si neighbours plus the twelve other bonds that they make to further neighbours, while III is the rest of the Si in the supercell (Fig.2). The MCSCF calculations are carried out in the whole of regions I+II, while the DFT calculations comprise regions II+III. The overlap region II treated by both methods will serve to match the two types of calculation. From DFT calculations of regions II+III an influence of III onto II is extracted which will serve as an embedding potential for MCSCF calculations of regions I+II. Similarly, from MCSCF calculations of the regions I+II the influence of I onto II is extracted to be used as an embedding potential for DFT calculations for regions II+III.

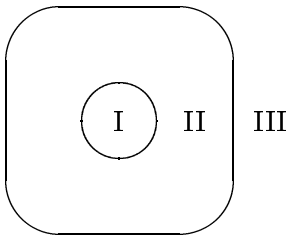

Figure 1: The three regions.

The method is not confined to impurities or defects in a bulk solid. For example regions II and III may be a solid with a surface in the usual "slab" representation, while region I is an adatom on the surface. For hamoeglobin region I would be the Fe atom, region II its close neighbourhood, and region III the distant part of the molecule.

We turn now to the second trick, which is the crucial one, with the new theorem and wider application.

It concerns what we do at the outer surface of region II when doing the cluster calculations on I+II, to represent the fact that there is the region III outside the boundary. Let us introduce the issue like this: when people have wanted to do an electronic structure calculation related to something in bulk amorphous Si, they have sometime used a finite cluster and terminated the dangling bonds of the outermost Si atoms with hydrogen atoms. It was found that the covalent bond between an outer Si atom and its H atom is rather similar to that between two Si atoms. Thus from the point of view of the outer Si atom, the H does a fairly good job of replacing the bulk amorphous Si that has been chopped off to make the finite cluster. The new theorem enables us to construct a non-local separable hermitian potential operator V'_{sep} to do

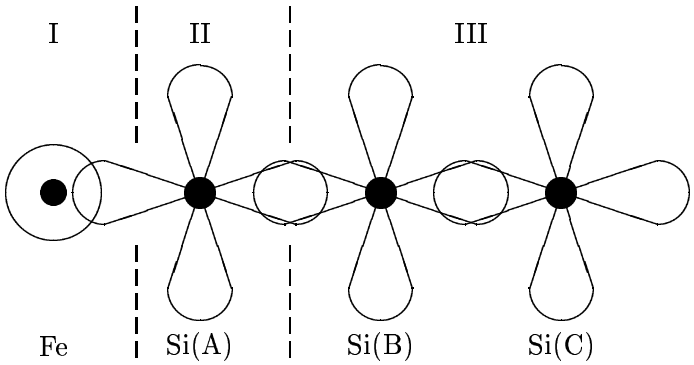

Figure 2: An Fe impurity atom in a Si host crystal.

the job exactly. The V'_{sep} is a hydrogen-like potential in the sense that it carries one electron, not four, and hence terminates the cluster. But V'_{sep} is also silicon-like in that its filled "valence" eigenstate is a silicon directed sp^3 hybrid type valence orbital, whose bond to an outer Si atom of the region II is exactly the same as that from a proper Si atom. At the same time the empty "conduction band" states of Si are preserved in V'_{sep}.

The precise definition of region II for our system when calculating on region I+II is therefore as shown by Fig.3. It includes the inward pointing hybrid and terminating potential V'_{sep} of Si(B). But in calculating region II+III the Si(B) atom is a full Si pseudopotential (Fig.2). Similarly the Fe atom could be represented by a constructed terminating potential in the LDA calculation on system II+III but in this case it would be easiest and best just to use an Fe DFT potential, at least for a ground state calculation.

The theorem in its simplest form runs like this. Suppose we have the Hamiltonian

$$H_0 \;=\; -\frac{1}{2}\nabla^2 + V, \tag{1}$$

where V is an ordinary potential, and this H_0 has eigenvalues ϵ_n and eigenfunctions ψ_n

$$H_0\psi_n \;=\; \epsilon_n\psi_n. \tag{2}$$

We can now construct

$$H \;=\; H_0 + V_{sep} \tag{3}$$

such that its eigenvalues and eigenstates are as follows

$$\begin{aligned} H\psi'_n \;&=\epsilon_n\psi'_n, \qquad n>1 \\ H\phi \;&=E\phi \end{aligned} \tag{4}$$

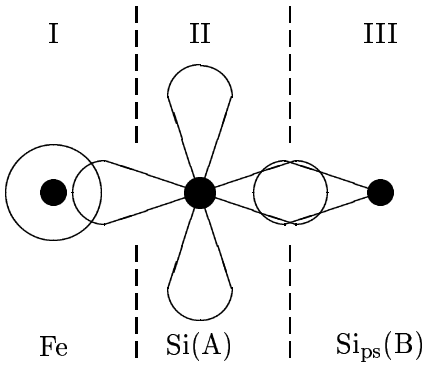

Figure 3: A pseudo-Si directed valence orbital modelling the influence of region III.

where E and ϕ are given. From (1) and (3), the desired V'_{sep} is

$$V'_{sep} = V + V_{sep} \tag{5}$$

the lowest eigenstate is the desired ϕ with desired E, and all the higher eigenvalues $\epsilon_n (n > 1)$ are preserved. The theorem shows that V_{sep} has the form

$$V_{sep} = \sum_{i,j=1}^{3} |f_i\rangle \, U_{ij} \, \langle f_j| \tag{6}$$

where

$$f_1 = \phi, \quad f_2 = \psi_1, \quad \text{and} \quad f_3 = H_0\phi, \tag{7}$$

and where the U_{ij} involve E, ϵ_1, and various scalar products of f_i. The precise form of the U_{ij} and the proof of the theorem are given in the mathematical appendix.

The use of the theorem in our example is not completely straightforward. The ϕ is our desired sp^3 type hybrid directed valence orbital, pointing towards an outer Si atom of region II. But we do not know a priori what ϕ is, nor its appropriate E. What we can get from a DFT calculation on pure Si is a set of identical bonding orbitals ϕ_{bj} centered at each bond j in the crystal. The set of all ϕ_{bj} span the same functional space as the set of Bloch functions of the the valence bands ψ_k and ϕ_{bj} is constructed as linear combinations of ψ_k. The ϕ_{bj} can be chosen to be as localized as possible, or to have maximum bond order. The ϕ_{bj} are not mutually orthogonal (unlike the Wannier functions) but one can define matrix elements between them and an energy E from which the valence band structure can be generated again. The ϕ_b can be thought of as the sum of two hybridised sp^3-like orbitals on the two atoms, but there is no unique way of splitting up ϕ_b in that way. Therefore the theorem is applied to the pair of atoms and a pair of V_{sep} are produced which together give E and ϕ_b exactly. The calculations proceed iteratively

from approximate atomic V's in (1) which have been tuned to give some quantity such as the correct lowest excited states of Si or the bottom of the conduction band of bulk Si and this is of course conserved by the operation of the theorem.

As already remarked, the method in its simplest form has been applied to Ag atoms in P_2O_5 including their movement to coalesce into Ag_2 dimers. Both the $3d^{10}$ and $3d^9 4s$ configurations had large amplitudes in the ground state and were particularly involved in the dimer formation.

Finally, the group in St.Petersburg WOULD WELCOME COLLABORATORS to apply and develop the method further. Please contact Prof Igor Abarenkov at e-mail: aiv@iva.usr.pu.ru .

Mathematical appendix

We now define the V_{sep} and prove the theorem by constructing the required H of equations (3) and (4). It is convenient to change the notation slightly and to refer to all the eigenvalues and eigenstates of H by ϵ' and ψ' and we have $\epsilon'_n = \epsilon_n$ for $n > 1$. Thus the V_{sep} of (6) now has

$$f_1 \;=\; \psi'_1, \quad f_2 \;=\; \psi_1, \quad \text{and} \quad f_3 \;=\; H_0\psi'_1. \tag{8}$$

We start by considering the unitary transformation U

$$U \;=\; I \;-\; 2P, \tag{9}$$

where P is the projector operator

$$\begin{aligned} P &= a|\psi_1 + \psi'_1\rangle\,\langle\psi_1 + \psi'_1| \\ a &= 1/[2(1 + \langle\psi_1|\psi'_1\rangle)] \end{aligned} \tag{10}$$

with the properties

$$P^+ \;=\; P, \qquad \text{and} \qquad P^2 \;=\; P, \tag{11}$$

from which the unitary property $UU^+ = I$ follows readily. Here we employed the fact that by adjusting the phase factors of ψ_1 and/or ψ'_1 the scalar product $\langle\psi_1|\psi'_1\rangle$ can always be made real. We also have

$$(H_0P)^+ \;=\; PH_0 \;=\; a|f_1 + f_2\rangle\,\langle\epsilon_1 f_2 + f_3| \tag{12}$$

We now construct the set of ψ'_n by the unitary transformation U operating on the set of ψ_n:

$$|\psi'_n\rangle \;=\; U|\psi_n\rangle. \tag{13}$$

We can now write down the H that has the required eigenstates and eigenvalues

$$\begin{aligned} H \;=\; \sum_n |\psi'_n\rangle\,\epsilon'_n\,\langle\psi'_n| \;&=\; \sum_n |\psi'_n\rangle\,\epsilon_n\,\langle\psi'_n| \;+\; |\psi'_1\rangle\;(\epsilon'_1 - \epsilon_1)\;\langle\psi'_1| \\ &=\; UH_0U^+ \;+\; |\psi'_1\rangle\;(\epsilon'_1 - \epsilon_1)\;\langle\psi'_1| \end{aligned} \tag{14}$$

where we have written $\epsilon'_n = \epsilon_n + (\epsilon'_n - \epsilon_n)$ and used the fact that $\epsilon'_n = \epsilon_n$ except for $n = 1$. From(10) and (14) we now have

$$V_{sep} = [UH_0U^+ - H_0] + |\psi'_1\rangle\ (\epsilon'_1 - \epsilon_1)\ \langle\psi'_1|, \tag{15}$$

and it remains to simplify the term in square brackets which will turn out to have the required form (6), (8) as the last term of (15) already does. We have from (9), (11)

$$UH_0U^+ - H_0 = -2PH_0 - 2H_0P + 4PH_0P \tag{16}$$

where from (12) PH_0 already has the required form (6), and so does $H_0P = (PH_0)^+$. Finally for (16), (15) we need

$$PH_0P = a^2|\psi_1 + \psi'_1\rangle\,\langle\psi_1 + \psi'_1|H_0|\psi_1 + \psi'_1\rangle\,\langle\psi_1 + \psi'_1|, \tag{17}$$

where the inner matrix element has the value

$$\langle\psi_1 + \psi'_1|\epsilon_1\psi_1 + H_0\psi'_1\rangle = \langle f_2 + f_1|\epsilon_1 f_2 + f_3\rangle, \tag{18}$$

which we denote by b. Thus

$$PH_0P = a^2b\,(|f_1\rangle\,\langle f_1| + |f_1\rangle\,\langle f_2| + |f_2\rangle\,\langle f_1| + |f_2\rangle\,\langle f_2|) \tag{19}$$

and collecting everything from (15) to (19) gives V_{sep} in the required form (6) with (8), where all the U_{ij} coefficients (not to be confused with the operator U in (9)) depend on scalar products of the f_i which are all calculable.