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SELF-CONSISTENT EMBEDDED CLUSTERS: BUILDING BLOCK EQUATIONS FOR LOCALIZED ORTHOGONAL ORBITALS

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Abstract

In order to be able to study a large electronic system following a building block approach, in which smaller tractable subsystems are handled at a time rather than the system as a whole, equations are proposed in this paper whose solutions are variational orthogonal orbitals localized on the subsystems. The equations for a given subsystem correspond to a molecular cluster embedded in the field created by the rest of the system, and are coupled to the corresponding equations for all subsystems under consideration, so that they must be solved self-consistently. While the localized nature of the solutions makes the equations appropriate for use in conjunction with local basis sets in practical implementations without significant loss of precision due to truncation errors, their orthogonality properties allow for the use of the advantages of the theory of separability of McWeeny in order to calculate total energies and (generalized product) wave functions. Since the building block equations proposed involve inter-subsystem interactions very cumbersome to calculate, an approximation is proposed in order to make their application to actual problems feasible: the representation of the cumbersome interaction operators by ab initio model potentials which are obtained directly from them, without resorting to any parametrization procedure based on a reference. This ab initio model potential approximation has been found to provide considerable computational savings without significant loss of accuracy in frozen-core calculations on molecules and frozen-lattice calculations on imperfect crystals.

1. Introduction

Although the size of a particular electronic system does not confine the applicability of quantum theory from a conceptual point of view, actual computations of electronic properties of large molecules or infinite systems (like solids) have been and still are considerably limited. This has been a challenge to many scientists and has promoted a tremendous effort to look for alternatives that drastically reduce the computational problems. The exploitation of point and translational symmetry and the development of efficient and specific algorithms has made ab initio calculations on moderately complex perfect crystalline systems at the Hartree–Fock level feasible [1]. Also, all-electron programs which take full advantage of point-symmetry, direct approaches, efficient transformation algorithms, rapid convergence methods, etc., are making the ab initio study of larger and larger molecules possible [2], although the computational difficulties still determine the interplay between the size and the sophistication of the methodological treatment.

A parallel effort has also been made on the development of basic theory. Here, the driving force has been the partition of the large problem into tractable subsystems which become the basis for a *building block* approach, whose final goal is to achieve variational solutions for the whole system [3–9]. The result is usually the formulation of a set of coupled equations (one for each subsystem under the effects of the others), which are simpler to treat than those for the entire system, and must be solved iteratively until the electronic densities and their mutual interactions are described self-consistently. However, few attempts have actually been made to solve the whole set of equations up to the final and self-consistent stage.

Many cases exist in which interest is focused on a relevant portion of the system rather than on the system itself. Examples are the valence electrons in a molecule, responsible for the bonding properties, or the cluster formed by an impurity and its closest coordination shells in a doped crystal, responsible for the local distortions caused by the impurity. In these circumstances, it may not be necessary to solve the building block equations completely, since the solutions for some subsystems may be known with sufficient accuracy from the beginning (atomic cores in molecules, unaffected lattice in doped crystals, . . .). The equations then become the basis for "frozen subsystem" approximations, for which only the equation for the relevant subsystem is tackled and no iteration over the whole set of equations is performed. These latter approximations have been extensively applied to valence-electron calculations in molecules (frozen core) [10–23] and, more scarcely, to embedded cluster calculations in crystals (frozen lattice) [24–27]. Also, embedded cluster methods have been proposed for solids which include lattice polarization effects through the use of empirically parametrized models [28–31].

Building block equations for large electronic systems have been proposed following two different lines. On the one hand, in 1960 Boys suggested the usefulness of localized orbitals to describe chemically invariant subsystems whose density matrix could be computed all at once and then transported to build up the wave function of systems containing such common blocks [3]. Gilbert developed further the idea of using localized orbitals as a basis for building block equations and proposed a transformation of the HF equation for the entire system into an equivalent set of smaller self-consistent subsystem equations for linearly independent localized orbitals which are nonorthogonal in general [4]. (We will be referring to these equations as Gilbert equations from now on.) Later, he extended his work to the formulation of a multiconfiguration self-consistent field theory for localized orbitals [5]. Particular forms of Gilbert equations have been proposed to study molecules and solid-state problems [6,32,33].

On the other hand, the idea of separability of a many-electron system and its quantum mechanical formulation led to a considerable amount of work [34–37] and, particularly, the formulation by McWeeny and Kleiner [7] and by Huzinaga et al. [8,9] of building block equations. Their work is based upon the proposition of the expansion of the total many-electron wave function in terms of a basis set of antisymmetric products of group wave functions which are required to fulfill strong-orthogonality conditions and, as a consequence, lead to a very convenient expression for the total energy as a sum of group energies plus interaction energies between groups. The expansion is expected to be a very good approximation (i.e. able to include intra-group electron correlation) to the total wave function when it is possible to partition the system into weakly interacting subsystems. Within this framework, Huzinaga et al. [8,9] have shown that the variational principle is very naturally partitioned and applied in steps by requiring the energy of each group (under the effects of the others) to be a minimum with respect to variations of its wave function under the requirement of strong-orthogonality between all group wave functions, this resulting in a set of building block equations which must be solved iteratively until self-consistent group functions lead to a final self-consistent solution for the whole system. In particular, when the expansion is reduced to only one antisymmetric product of group functions and each group function can be described by a single determinant, the solutions of Huzinaga equations are the standard Hartree–Fock orbitals for the entire system. Huzinaga building block equations have been the basis for the model potential method, which has been extensively applied (along the line of the frozen subsystem approach) to valence calculations in molecules [16–23] and, recently, to embedded cluster calculations in crystals [26,27].

It is interesting to compare the building block eqautions set up by Gilbert with those of Huzinaga; this comparison is most simple and clear if we contrast their Hartree–Fock analogues instead of their respective multiconfigurational versions. At this stage, although the solutions of (i) any particular form of Gilbert equations, (ii) Huzinaga equations, or (iii) the HF equations for the entire system provide the same result (total energy and many-electron wave function) if the expansion method with a basis set common to all subsystems is used, their practical applications show specific advantages and disadvantages, and it is the balance between them that may guide the choice of equations for solving a particular problem. Along actual applications where finite basis sets are used, the choice of nonorthogonal localized orbitals represents an initial advantage over the use of orthogonal (non-localized) orbitals: One may expect the basis set for the subsystems to be more localized in the former case, so leading to smaller truncation errors and smaller subsystem equations. In this respect, we may remark that smaller basis sets than the ones required for the whole HF problem can be used to solve Huzinaga equations for a particular subsystem, because only a subset of the standard HF orbitals is obtained from them and has to be spanned. However, the basis set for each subsystem must be flexible enough so that the orbitals can fulfill the strong-orthogonality requirements with the other subsystems. This, in practice, means that some basic functions must span, to a certain extent, densities of other subsets and, therefore, the basis set can not be as small as in the nonorthogonal case. Some disadvantages are, however, inherent to the use of nonorthogonal orbitals. These are mainly associated to the calculation of the S^{-1} matrix which affects other magnitudes, like the Fock operator or the total energy. Moreover, the nonorthogonality complicates the implementation of the equations in standard programs, since they usually assume orthogonal-orbital algorithms, whereas Huzinaga equations are straightforwardly implemented by simply adding the new contributions to the one-electron integrals.

From the previous comments, it is expected that the practical advantages would increase if building block equations for subsystems were used for which the orbitals are localized in space while keeping the orthogonality between subsystems. The convenience of such a set of equations can be illustrated further if we consider two limiting situations which define a range of problems along which localization becomes increasingly necessary:

(i) There is a subset (or subsets) of the standard HF orbitals which is *actually* localized in space. This is the case, for instance, for an impurity in a perfect crystal which causes a local distortion on the host. For this case, it is expected that the standard HF manifold include a subset of orbitals strongly localized around the impurity. In this limit, Huzinaga equations can be used safely to solve the actually localized subsystem with small truncation errors and fast and accurate algorithms based on orthogonal orbitals.

(ii) The whole HF manifold is delocalized. This is the case, for instance, for the standard HF solutions of a perfect crystal. The HF orbitals are periodic orbitals and Huzinaga equations would require the use of basis sets extended over the whole crystal, making them useless, in practice, for this case. However, in perfect crystals it is still possible to use orbitals that retain the advantage of orthogonality while being localized (Wannier-like orbitals [38]) and, clearly, building block equations for localized orthogonal orbitals would be a safer choice in actual calculations, particularly when large unit cells make ab initio calculations of the whole system with periodic bases [1] prohibitive. Finally, intermediate situations can be found where the distortion caused by a defect propagates beyond first neighbours. Also, chemisorption problems could be cited to illustrate the convenience of using building block equations for localized orthogonal orbitals including intra-group electron correlation.

In this paper, we propose a modification of Huzinaga building block equations such that the solutions of the new set are orthogonal and localized on the subsystems, but they are not necessarily the standard HF orbitals: The equations retain the advantages shown by Huzinaga equations and widen the field of practical applicability to the problems illustrated above where, presumably, one or more subsets of interest of the standard HF orbitals are not localized. Other desirable features inherited from the original set are, first, the possibility of straightforwardly introducing relativistic effects through the use of appropriate one-electron operators [18,19,22] and, second, the inclusion of intra-group electron correlation along standard methods (and programs) like, for instance, CI [7,19,27].

In section 2 of this paper, the original building block equations of Huzinaga are shown to be related to Gilbert equations. We show that among all possible arbitrary choices of Gilbert equations, one of them leads to a set of subsystem equations which is equivalent to Huzinaga's. It is in the light of this relation that we propose, in section 3, a modification of Huzinaga equations which combines the convenient properties of localization and strong orthogonality.

Finally, in order to bring considerable computational savings to make the calculations feasible, some approximations to the inter-subsystem interaction terms present in the equations are necessary. Previous experience in frozen-core molecular calculations and frozen-lattice calculations in crystals with impurities has shown that an adequate balance between precision and economy can be achieved if the ab initio model potential approximation is followed in order to represent inter-subsystem interactions [19–22,26,27]. Within this approximation, a spectral representation of non-local operators (exchange) is used in such a way that the model potential operators to be used in the equation for a given subsystem are obtained directly from the wave functions of the other subsystems. They are not parametrized even in order to reproduce reference results. Recently, the use of the spectral representation has been extended to local operators [19,27] (Coulomb, relativistic operators), thus facilitating the obtention of ab initio model potentials not only for one-centre subsystems (such as atomic cores or complete-ion potentials), but also for many-centre subsystems [27]. Making use of this feature, we present in section 4 the ab initio model potential approximation for the modified Huzinaga equations; these model potential equations are the ones to be implemented in molecular programs and used in actual computations of molecules and solid state.

2. Gilbert and Huzinaga equations for subsystems

In this section, we first summarize the main features of Gilbert equations, which stem from the fact that the one-electron density operator in HF theory is a projection operator. Then, we see how Huzinaga building block equations for subsystems are related to them.

Following Gilbert [4], let us start from the standard form of the Hartree–Fock (HF) equation,

$$\hat{F}|\psi_i\rangle = \varepsilon_i|\psi_i\rangle, \tag{1}$$

where $\hat{F}$ is the Fock operator for the complete system and $|\psi_i\rangle$ is one of the orthonormal standard spin-orbitals, which may be occupied, $|\psi_i^{\mathrm{occ}}\rangle$, or virtual, $|\psi_i^{\mathrm{vir}}\rangle$. This holds for the unrestricted HF and for the closed-shell restricted HF cases.

Let ψ^{occ} be a row vector containing all the occupied standard HF spin-orbitals,

$$\boldsymbol{\psi}^{\mathrm{occ}} \equiv (|\psi_1^{\mathrm{occ}}\rangle, |\psi_2^{\mathrm{occ}}\rangle, \ldots, |\psi_n^{\mathrm{occ}}\rangle), \tag{2}$$

and $\hat{\rho}$ the corresponding Fock–Dirac one-electron density operator

$$\hat{\rho} = \boldsymbol{\psi}^{\text{occ}} \boldsymbol{\psi}^{\text{occ}\dagger} = \sum_{i=1,n} |\psi_i^{\text{occ}}\rangle\langle\psi_i^{\text{occ}}|, \tag{3}$$

which is a projection operator, such that

$$\hat{\rho}|\psi_i^{\text{occ}}\rangle = |\psi_i^{\text{occ}}\rangle, \quad \hat{\rho}|\psi_i^{\text{vir}}\rangle = 0. \tag{4}$$

If $\hat{A}$ is an arbitrary one-electron operator, its projection onto the occupied HF manifold, $\hat{\rho}\hat{A}\hat{\rho}$, satisfies

$$\hat{\rho}\hat{A}\hat{\rho}|\psi_i^{\text{occ}}\rangle = \hat{\rho}\hat{A}|\psi_i^{\text{occ}}\rangle = \sum_j |\psi_j^{\text{occ}}\rangle A_{ji}, \tag{5}$$

where $A_{ji} = \langle\psi_j^{\text{occ}}|\hat{A}|\psi_i^{\text{occ}}\rangle$. Also, $\hat{\rho}\hat{A}\hat{\rho}|\psi_i^{\text{vir}}\rangle = 0$.

By subtracting (5) from (1), one obtains

$$[\hat{F} - \hat{\rho}\hat{A}\hat{\rho}]|\psi_i^{\text{occ}}\rangle = \sum_j |\psi_j^{\text{occ}}\rangle B_{ji}, \tag{6}$$

where $B_{ji} = \varepsilon_i \delta_{ji} - A_{ji}$, and

$$[\hat{F} - \hat{\rho}\hat{A}\hat{\rho}]|\psi_i^{\text{vir}}\rangle = \varepsilon_i|\psi_i^{\text{vir}}\rangle. \tag{7}$$

Since $\hat{\rho}\hat{A}\hat{\rho}$ has the same transformation properties as $\hat{F}$, one may require the matrix **B** in eq. (6) to be diagonal, thereby obtaining the Gilbert equations,

$$[\hat{F} - \hat{\rho}\hat{A}\hat{\rho}]|\varphi_i^{\text{occ}}\rangle = \beta_i|\varphi_i^{\text{occ}}\rangle. \tag{8}$$

where the $|\varphi_i^{\text{occ}}\rangle$, called by Gilbert the modified HF orbitals, are related to the standard occupied HF orbitals by a linear transformation:

$$\boldsymbol{\varphi}^{\text{occ}} = \boldsymbol{\psi}^{\text{occ}}\mathbf{C}, \tag{9}$$

with $\boldsymbol{\varphi}^{\text{occ}} \equiv (|\varphi_1^{\text{occ}}\rangle, |\varphi_2^{\text{occ}}\rangle, \ldots, |\varphi_n^{\text{occ}}\rangle)$. In contrast to the standard orbitals, the modified HF orbitals $|\varphi_i^{\text{occ}}\rangle$, are not necessarily orthogonal; however, they must be linearly independent and, therefore, able to be orthogonalized. The $|\varphi_i^{\text{occ}}\rangle$ are orthogonal if $\hat{A}$ is chosen to be Hermitean. Note also that $\hat{\rho} = \boldsymbol{\varphi}^{\text{occ}}\mathbf{S}^{-1}\boldsymbol{\varphi}^{\text{occ}\dagger}$, where $\mathbf{S} = \boldsymbol{\varphi}^{\text{occ}\dagger}\boldsymbol{\varphi}^{\text{occ}}$.

Gilbert equations (eqs. (8)) may be further generalized [4]. In effect, it is possible to add a term $(1 - \hat{\rho})\hat{A}'(1 - \hat{\rho})$, $\hat{A}'$ being an arbitrary one-electron Hermitean operator, to eqs. (8) which produces an analogous modification of the virtual subspace while the occupied subset is unaltered. As long as this new term does not mix the occupied and virtual manifolds, the wave function and energy remain intact. This fact was pointed out and used in order to improve the virtual orbitals prior to their use in correlation energy calculations [4,9].

Gilbert equations provide a basis for localization, and some authors have been using particular forms of them in order to study parts of a system or a complete system following a building block approach [6,32,33]. As an example, let us look at Adams' choice [6], which was in fact proposed by him following a completely independent route: Suppose we divide a system into two subsystems A and B (what follows is general for a partition in any number of subsystems, the difference being a slightly more complicated notation), defined by two corresponding sets of occupied orbitals. The Fock operator for the whole system may be written as

$$\hat{F} = \hat{F}_A + \hat{V}_A^{\mathrm{env}} = \hat{F}_B + \hat{V}_B^{\mathrm{env}}, \tag{10}$$

where $\hat{V}_A^{\mathrm{env}}$ and $\hat{V}_B^{\mathrm{env}}$ are the environmental effects on A and B, respectively. Adams [6] used eqs. (8) with $\hat{A} = \hat{F} - \hat{F}_A$ for subsystem A, and $\hat{A} = \hat{F} - \hat{F}_B$ for subsystem B, obtaining

$$[\hat{F} - \hat{\rho}(\hat{F} - \hat{F}_A)\hat{\rho}]|\varphi_{Ai}^{\mathrm{Adams}}\rangle = \varepsilon_{Ai}^{\mathrm{Adams}}|\varphi_{Ai}^{\mathrm{Adams}}\rangle \tag{11}$$

and

$$[\hat{F} - \hat{\rho}(\hat{F} - \hat{F}_B)\hat{\rho}]|\varphi_{Bj}^{\mathrm{Adams}}\rangle = \varepsilon_{Bj}^{\mathrm{Adams}}|\varphi_{Bj}^{\mathrm{Adams}}\rangle. \tag{12}$$

Adams deduced these equations by minimizing the self-energy of the subsystems (that is, excluding the interaction with the rest of the system), under the constraints that (1) the orbitals within a subsystem be orthonormal, and (2) the orbitals of different subsystems be linearly independent. Kunz's choice for $\hat{A}$ was [32] $\hat{A} = \hat{\rho}_A \hat{V}_A^S \hat{\rho}_A$, where $\hat{\rho}_A = \sum_i |\varphi_{Ai}\rangle\langle\varphi_{Ai}|$, and $\hat{V}_A^S$ is the short-range component of the environmental effects on subsystem A (and similarly for B). Matsuoka [33] proposed the use of $\hat{A} = \hat{F} - \hat{\rho}_A \hat{F}_A \hat{\rho}_A$.

Let us now look at the formalism of Huzinaga [8,9]. He derived building block equations for subsystems such that their solutions are exactly the standard HF orbitals. This feature means an implicit definition of a subsystem as the subspace associated to a particular subset of the standard HF orbitals. So, by requiring the energy of a subsystem under the effect of the rest of the complete system to be a minimum, under the constraints of strong orthogonality between subsystem wave functions (in this case, the condition holds if $\langle \psi_{Ai}^{\mathrm{occ}} | \psi_{Bj}^{\mathrm{occ}} \rangle = \delta_{AB}\delta_{ij}$), Huzinaga obtained the following equations for subsystem A (and, of course, corresponding equations for the other subsystems):

$$[\hat{F} - \alpha\hat{\rho}_B\hat{F}]|\psi_{Ai}^{\mathrm{occ}}\rangle = \varepsilon_{Ai}|\psi_{Ai}^{\mathrm{occ}}\rangle, \tag{13}$$

α being an arbitrary constant. After making the operator Hermitean, the equation became

$$\left[\hat{F} - \frac{\alpha}{2}\left(\hat{\rho}_B\hat{F} + \hat{F}\hat{\rho}_B\right)\right]|\psi_{Ai}^{\text{occ}}\rangle = \varepsilon_{Ai}|\psi_{Ai}^{\text{occ}}\rangle. \tag{14}$$

We may comment here that the solutions of these equations are equivalent to the solutions of the HF equations for the entire system, and the strong orthogonality constraints must be regarded as a choice among multiple equivalent solutions and not as a variational constraint.

Huzinaga building block equations (eqs. (14)) become, at convergence,

$$\left[\hat{F} - \alpha\sum_j |\psi_{Bj}^{\text{occ}}\rangle\varepsilon_{Bj}\langle\psi_{Bj}^{\text{occ}}|\right]|\psi_{Ai}^{\text{occ}}\rangle = \varepsilon_{Ai}|\psi_{Ai}^{\text{occ}}\rangle. \tag{15}$$

These equations have been used in practice in order to obtain the solutions for the subsystem A, $|\psi_{Ai}^{\text{occ}}\rangle$, once the solutions for the subsystem B, $|\psi_{Bj}^{\text{occ}}\rangle$, *are known.* This is the case for the core and valence subsystems in a molecule, in which the (frozen) core orbitals are approximately known from the beginning and only the valence orbitals have to be obtained. So, eqs. (15) have been the basis for the core model potential methods. They have also been the basis for the study of impurities in crystals along embedded cluster calculations, where the target subsystem is the cluster formed by the impurity and its first nearest neighours, and the rest of the crystal is formed by a set of previously known frozen subsystems.

We can now see how Huzinaga building block equations (eqs. (14)) are related to Gilbert equations (eqs. (8)): Once we define the subsystems A and B as the subspaces associated to particular subsets of the standard HF occupied orbitals, we can define the following row vectors,

$$\begin{aligned}
\boldsymbol{\psi}^{occ} &= (|\psi_{A1}^{\text{occ}}\rangle, \ldots, |\psi_{An_A}^{\text{occ}}\rangle, |\psi_{B1}^{\text{occ}}\rangle, \ldots, |\psi_{Bn_B}^{\text{occ}}\rangle),\\
\boldsymbol{\psi}_A^{\text{occ}} &= (|\psi_{A1}^{\text{occ}}\rangle, \ldots, |\psi_{An_A}^{\text{occ}}\rangle),\\
\boldsymbol{\psi}_B^{\text{occ}} &= (|\psi_{B1}^{\text{occ}}\rangle, \ldots, |\psi_{Bn_B}^{\text{occ}}\rangle);
\end{aligned} \tag{16}$$

and the Fock–Dirac one-electron density operators of subsystems A and B,

$$\hat{\rho}_A = \boldsymbol{\psi}_A^{\text{occ}}\boldsymbol{\psi}_A^{\text{occ}\dagger}, \quad \hat{\rho}_B = \boldsymbol{\psi}_B^{\text{occ}}\boldsymbol{\psi}_B^{\text{occ}\dagger}, \tag{17}$$

which fulfill the following properties:

$$\begin{aligned}
&\hat{\rho} = \hat{\rho}_A + \hat{\rho}_B, \qquad &&\hat{\rho}_A\hat{\rho}_B = \hat{\rho}_B\hat{\rho}_A = 0,\\
&\hat{\rho}\hat{\rho}_A = \hat{\rho}_A\hat{\rho} = \hat{\rho}_A, \qquad &&\hat{\rho}\hat{\rho}_B = \hat{\rho}_B\hat{\rho} = \hat{\rho}_B.
\end{aligned} \tag{18}$$

If we choose in Gilbert equation $\hat{A} = \alpha\hat{\rho}_B\hat{F}\hat{\rho}_B$ for subsystem A, we obtain

$$\left[\hat{F} - \alpha\hat{\rho}_B\hat{F}\hat{\rho}_B\right]|\varphi_i^{\mathrm{occ}}\rangle = \beta_i|\varphi_i^{\mathrm{occ}}\rangle. \tag{19}$$

This equation is completely equivalent to eq, (14) and, in fact, it could also have been derived from eq. (13) by using a different Hermitezation procedure. It is easily seen that the standard HF occupied orbitals which define the subsystem *A* are solutions of eq. (19):

$$\left[\hat{F} - \alpha\hat{\rho}_B\hat{F}\hat{\rho}_B\right]|\psi_{Ai}^{\mathrm{occ}}\rangle = \varepsilon_{Ai}|\psi_{Ai}^{\mathrm{occ}}\rangle, \tag{20}$$

and a property of this choice of equations is that the standard HF orbitals defining the other subsystems are also solutions of the same equation,

$$\left[\hat{F} - \alpha\hat{\rho}_B\hat{F}\hat{\rho}_B\right]|\psi_{Bj}^{\mathrm{occ}}\rangle = (1-\alpha)\varepsilon_{Bj}|\psi_{Bj}^{\mathrm{occ}}\rangle. \tag{21}$$

Similarly, for subsystem *B* we obtain

$$\left[\hat{F} - \alpha\hat{\rho}_A\hat{F}\hat{\rho}_A\right]|\psi_{Bj}^{\mathrm{occ}}\rangle = \varepsilon_{Bj}|\psi_{Bj}^{\mathrm{occ}}\rangle, \tag{22}$$

$$\left[\hat{F} - \alpha\hat{\rho}_A\hat{F}\hat{\rho}_A\right]|\psi_{Ai}^{\mathrm{occ}}\rangle = (1-\alpha)\varepsilon_{Ai}|\psi_{Ai}^{\mathrm{occ}}\rangle, \tag{23}$$

which may be used to obtain $|\psi_{Bj}^{\mathrm{occ}}\rangle$. The standard virtual orbitals are eigenfunctions of the equations for any subsystem,

$$\left[\hat{F} - \alpha\hat{\rho}_A\hat{F}\hat{\rho}_A\right]|\psi_i^{\mathrm{vir}}\rangle = \left[\hat{F} - \alpha\hat{\rho}_B\hat{F}\hat{\rho}_B\right]|\psi_i^{\mathrm{vir}}\rangle = \varepsilon_i|\psi_i^{\mathrm{vir}}\rangle. \tag{24}$$

We can now compare some features of Huzinaga building block equations with those of the previously mentioned equations on the basis of a common root: Gilbert equations. For this purpose, it is useful to analyze the action of the operators chosen to be added to $\hat{F}$ in eqs. (8).

The $\hat{A}$ operators proposed by Adams [6], Kunz [32], and Matsuoka [33], referred to above, produce nonorthogonal localized orbitals which are linear combinations of all the standard HF occupied orbitals. As a consequence, one may use truncated local basis sets along actual applications. In Huzinaga equations (eqs. (19)), $\hat{A}$ is rather a picking out operator, since it provides the means to select a specific subset of the *standard* occupied spin-orbitals among all the solutions obtained in the equations for a subsystem. In this case, the basis set of a subsystem may be reduced with respect to the one used for the complete system, since it must span only a subset of the standard HF orbitals, but not as much as in the localized orbital equations. This is the advantage of Gilbert–Adams-like equations, which becomes important as the localization in space of subsets of the standard HF orbitals can not be expected.

On the other hand, the use of nonorthogonal orbitals poses some difficulties. First, once the equations are solved, an algorithm for the calculation of the total energy of the system is needed which involves the evaluation of the S^{-1} matrix of the entire system. For large systems, this is not an easy task. Moreover, the operators $\hat{F}$ and $\hat{\rho}$ in eq. (11) depend on S^{-1} and, since the accuracy of the approximations used to calculate the inverse matrix may vary along the self-consistent procedure, convergence problems may easily arise. Also, the selection of n_A spin-orbitals from the equations for subsystem A, n_B from the equations for subsystem B, etc., along the self-consistent procedure may affect the convergence. In the case of Gilbert–Adams-like equations, this selection may not be simple, since the necessary requirement of linear independency between orbitals of different subsystems is not automatically guaranteed, either explicitly or implicitly. This makes the use of ad hoc methods for the achievement of convergence compulsory. In this respect, Matsuoka [33] has found that a preorthogonalization of orbitals before every iteration, as well as the use of shift operators such as $\sum_i |\varphi_i\rangle \varepsilon_i \langle\varphi_i|$ during the first iterations, are necessary to attain convergence. Also, spurious tunnelling effects have been observed in some embedded cluster calculations using Gilbert–Adams-like equations [29] which might be related to this problem.

If Huzinaga equations (eqs. 19)) are used, the difficulties associated to the calculation of the S^{-1} matrix for the entire system and to ensuring linear independency among the solutions disappear, since the strong orthogonality constraints are built in. In effect, the fulfillment of $\hat{\rho}_A \hat{\rho}_B = \hat{\rho}_B \hat{\rho}_A = 0$ is inherent to the fact that both $|\psi_{Ai}^{\text{occ}}\rangle$ and $|\psi_{Bj}^{\text{occ}}\rangle$ are eigenfunctions of a common Hermitean operator (see eqs. (20) and (21)), and during the iterative process it is only necessary to be sure that none of the $|\psi_{Ai}^{\text{occ}}\rangle$ are used to construct $\hat{\rho}_B$ for the next iteration, and vice versa: an arbitrary value for α large enough (eq. (21)) would shift all the $(1-\alpha)\varepsilon_{Bj}$ eigenvalues above the ε_{Ai} ones, allowing in this way a proper selection of the $|\psi_{Ai}^{\text{occ}}\rangle$ solutions during the iterations. This, at the same time enforcing orthogonality, facilitates the convergence.

Finally, we may comment that the orthogonality between different subsystem solutions facilitates the implementation of the equations in standard computer programs for molecular systems, which usually work with orthogonal orbitals.

3. Modified Huzinaga equations for subsystems

In this section, we propose building block equations which combine the advantages of orthogonality with those of localization.

The driving idea for the formulation of the equations is the following. We look for a choice of the arbitrary operator $\hat{A}$ for each subsystem in Gilbert equations (eq. (8)) such that the set of n_A solutions to be taken from the equation for subsystem A, φ_A^{occ}, n_B solutions to be taken from the equation for subsystem B, φ_B^{occ}, etc., comes from a localizing unitary transformation of the standard occupied HF spin-orbitals [39]. The orthogonality between the solutions of a particular subsystem is guaranteed if its $\hat{A}$ operator is chosen to be Hermitean. In order to ensure the orthogonality between the solutions of different subsystems, we may require all the solutions $\varphi_A^{\text{occ}}, \varphi_B^{\text{occ}}, \ldots,$ to be eigenfunctions of a common Hermitean operator, as in the case of Huzinaga equations. (They will, in fact, be eigenfunctions of all the Hermitean operators for the subsystems.) These conditions are fulfilled with the following choice of $\hat{A}$ in eq. (8).

$$\hat{A} = \hat{F} + \sum_I \hat{\rho}_I \hat{\Omega}_I \hat{\rho}_I , \tag{25}$$

where I runs over the different subsystems, $\hat{\rho}_I = \varphi_I^{\text{occ}} \varphi_I^{\text{occ}\dagger}$, and the $\hat{\Omega}_I$ are arbitrary Hermitean operators. In the equations for a given subsystem, A for instance, $\hat{\Omega}_A$ produces a localization on subsystem A if it is chosen to be $\hat{\Omega}_A = \hat{W}_A - \hat{F}$, and $\hat{W}_A$ is an arbitrary Hermitean localizing operator for A. On the other hand, $\hat{\Omega}_I (I \neq A)$ must be chosen so as to make all the $|\varphi_{Ii}^{\text{occ}}\rangle$ be solutions of the equations for subsystem A. This is satisfied by choosing

$$\hat{\Omega}_I = (1 - \alpha_I)(\hat{W}_I - \hat{F}), \quad (I \neq A), \tag{26}$$

α_I being an arbitrary constant. As in Huzinaga equations, large enough values for the constant α_I ensure that all the solutions $|\varphi_{Ai}^{\text{occ}}\rangle$ are the lowest ones, so providing an automatic selection of orbitals for the next iteration which guarantees the fulfillment of the strong orthogonality properties between subsystems and facilitates convergence.

The equations for subsystem A are:

$$\hat{O}_A |\varphi_i\rangle = \lambda_i |\varphi_i\rangle, \tag{27}$$

where

$$\hat{O}_A \equiv \hat{F} - \hat{\rho}\hat{F}\hat{\rho} - \hat{\rho}_A(\hat{W}_A - \hat{F})\hat{\rho}_A - \sum_{I \neq A} \hat{\rho}_I \{(1 - \alpha_I)(\hat{W}_I - \hat{F})\} \hat{\rho}_I . \tag{28}$$

Their solutions are the following: First,

$$\hat{O}_A |\varphi_{Ai}^{\text{occ}}\rangle = \lambda_{Ai}^{\text{occ}} |\varphi_{Ai}^{\text{occ}}\rangle, \tag{29}$$

where φ_A^{occ} are the occupied solutions to be taken from this equation and fulfill $\varphi_A^{\text{occ}} = \psi^{\text{occ}} U_A$, U_A being a rectangular matrix made up of n_A columns of a unitary matrix. Second,

$$\hat{O}_A |\varphi_{Bj}^{\text{occ}}\rangle = (1 - \alpha_B)\lambda_{Bj}^{\text{occ}} |\varphi_{Bj}^{\text{occ}}\rangle, \tag{30}$$

where the $|\varphi_{Bj}^{\text{occ}}\rangle$ are the same spin-orbitals which are the occupied solutions for the equivalent equations for subsystem B but are, however, *discarded* when obtained from the equations for subsystem A (similarly for subsystems $C, D, \ldots$). Finally,

$$\hat{O}_A |\psi_i^{\text{vir}}\rangle = \varepsilon_i^{\text{vir}} |\psi_i^{\text{vir}}\rangle, \tag{31}$$

which are the virtual orbitals, useful for a correlation energy calculation, either directly or after a modification through some suitable $(1-\hat{\rho})\hat{A}'(1-\hat{\rho})$ operator [4,9] as commented above.

Although it should be noted that *any* Hermitean localizing form for $\hat{W}_I$ [6,24,39] is compatible with eqs. (27) and (28), the comparison with Gilbert–Adams-like equations is facilitated if the $\hat{W}_I$ are chosen to be $\hat{W}_I = \hat{F} - \hat{F}_I$ [6], the environmental effects on I. Then, eqs. (27) and (28) reduce to Matsuoka equations [33] if the fourth term on the right-hand side of eq. (28) is omitted. In this case, the orbitals for different sybsystems are not required to be orthogonal, since they are not solutions of a common Hermitean operator; however, care must be taken while choosing solutions for the next iteration in order to preserve linear independency, since it is not guaranteed by any characteristics built into the resulting equations. In this sense, the explicit requirement that $\hat{\rho}_I\hat{\rho}_J = 0$ $(I \neq J)$ during the first iterations has been found to be necessary to attain convergence [33]; it should be noted that if this requirement is met all along the self-consistent procedure using Matsuoka's equations, they should produce the same results as eqs. (27) and (28). The proposed equations reduce to Kunz equations [32] if, in addition to discarding the fourth term on the right-hand side of eq. (28), the second term is also omitted. Finally, they reduce to Huzinaga equations when all the localizing operators are set to zero, $\hat{W}_A = \hat{W}_B = \ldots = 0$, and the second and third terms are omitted. If these two terms are not deleted, the resulting equations are equivalent to Huzinaga's, that is, their solutions are also the standard HF orbitals.

The self-consistent solutions of the building block equations, eq. (27), provide an adequate and convenient basis to proceed to the calculation of the total energy using the formalism of generalized antisymmetric product wave functions of McWeeny [7]. In effect, since the solutions of eqs. (27) for all groups show the following orthogonality properties,

$$\langle \varphi_{Ii\rangle}^{\text{occ}} | \varphi_{Jj}^{\text{occ}} \rangle = \delta_{IJ}\delta_{ij}, \ \langle \varphi_{Ii}^{\text{vir}} | \psi_k^{\text{vir}} \rangle = 0, \ \langle \psi_k^{\text{vir}} | \psi_l^{\text{vir}} \rangle = \delta_{kl}, \tag{32}$$

they can be used to construct many-electron antisymmetric group wave functions, $\Phi^I(1, 2, \ldots, n_I)$, so that the strong orthogonality requirements stated in the theory are satisfied [7]:

$$\int \Phi^{I^*}(1,i,j,\ldots)\Phi^J(1,k,l,\ldots)\,\mathrm{d}x_1 = 0, \quad (I \neq J). \tag{33}$$

These antisymmetric group wave functions Φ^I can be either one- or many-configuration wave functions. Then, according to the theory [7], a very good approximation to the total wave function of the system can be the following single generalized product:

$$\Psi = M\hat{A}\prod_I \Phi^I, \tag{34}$$

where M is a normalization factor, $\hat{A}$ is an inter-group antisymmetrizer, and the strong-orthogonal set Φ^J is used. (In particular, if the one-configuration approximation is adopted for the Φ^J's, the total wave function Ψ is the Hartree–Fock wave function for the entire system, and its corresponding energy is a minimum if the one-electron solutions of eqs. (27) are used.) The total energy for the entire system corresponding to eqs. (34) and (33) can be conveniently expressed as a sum of subsystem energies, plus interaction energies between subsystems (see ref. [7] for details),

$$E = \sum_I E_I + \frac{1}{2} \sum_I \sum_{J \neq I} E_{IJ} . \tag{35}$$

4. Ab initio model potential approximation

The localized character of the solutions of eq. (27) on the different subsystems has been described above as a very necessary feature for practical applications, since it allows for the use of finite local basis sets without considerable truncation errors. However, even if local basis sets are used, the building block eqs. (27), which have to be iteratively solved for all the subsystems into which the entire problem has been partitioned, involve inter-subsystem interactions very cumbersome to calculate which should be approximated by efficient and accurate forms if the solution of the equations for actual problems is to be feasible. Here, we propose the application of the ab initio model potential approach to model the inter-subsystem interactions. This method has been found to provide considerable computational savings, without significant loss of accuracy, when applied to frozen-core calculations on molecules [20–23] and to frozen-lattice calculations on imperfect crystals [26,27]. The driving idea of the ab initio model potential approximation is to use a representation (model potential) of the cumbersome operators, which is obtained directly from them without resorting to any parametrization procedure; this is achieved by means of local model potentials in the case of simple local operators (i.e. one-centre Coulomb) and of spectral representations on appropriate basis sets in the case of nonlocal operators (exchange) and more complicated local operators (many-centre Coulomb, relativistic operators) [19,20,22,27].

The Fock operator $\hat{F}$ involved in eq. (27) can be expressed as

$$\hat{F} = \hat{F}_A + \hat{V}_A^{\text{env}} = \hat{F}_A + \sum_{I \neq A} \hat{V}^I = \hat{T} + \hat{V}^A + \sum_{I \neq A} \hat{V}^I , \tag{36}$$

where the potential due to the environment of A, $\hat{V}_A^{\text{env}}$, has been expressed in terms of the potentials created by the subsystems, $\hat{V}^I$, which are [27]:

$$\hat{V}^I(i) = -\sum_{\alpha \in I} \frac{Z_\alpha}{r_{\alpha i}} + \hat{J}^I(i) - \hat{K}^I(i) + \hat{V}^I_{\text{MV,DW}}(i); \tag{37}$$

here, the index α runs over the nuclei included in subsystem I, $\hat{J}^I$ and $\hat{K}^I$ are the one-electron Coulomb and exchange operators associated to the group wave function of subsystem I [27], and $\hat{V}^I_{\text{MV,DW}}$ is an optional relativistic mass–velocity and Darwin potential, which appears if the Cowan–Griffin one-component relativistic approximation is adopted [19,22,40]. When $\hat{F}$ is used in the equation for a given subsystem, let us say A, it is convenient to approximate the terms $\hat{V}^I$ for all $I \neq A$ as follows: First, $\hat{V}^I$ is split into long-range and short-range terms,

$$\hat{V}^I = \hat{V}^I_{lr} + \hat{V}^I_{sr} = \left[-\sum_{\alpha\in I} \frac{Z_\alpha - N_\alpha}{r_{\alpha i}} \right] + \left[-\sum_{\alpha\in I} \frac{N_\alpha}{r_{\alpha i}} + \hat{J}^I - \hat{K}^I + \hat{V}^I_{\text{MV,DW}} \right], \tag{38}$$

where N_α are arbitrary numbers chosen in order to enforce the long/short-range behaviour of the components of the electrostatic potential. Then, $\hat{V}^I$ is substituted by a model potential $\hat{V}^{I,\text{MP}}$, defined by

$$\hat{V}^{I,\text{MP}} = \hat{V}^I_{lr} + \hat{P}_I \hat{V}^I_{sr} \hat{P}_I , \tag{39}$$

where $\hat{P}_I$ is the projection operator on a given basis set of the subsystem I, $\boldsymbol{\chi}_I = (|\chi_{I1}\rangle, |\chi_{I2}\rangle, \ldots)$,

$$\hat{P}_I = \boldsymbol{\chi}_I \mathbf{S}_I^{-1} \boldsymbol{\chi}_I^\dagger , \tag{40}$$

being $\mathbf{S}_I = \boldsymbol{\chi}_I^\dagger \boldsymbol{\chi}_I$. A convenient choice for $\boldsymbol{\chi}_I$ is the set of primitive basis set functions used to expand the solutions of eq. (27) for subsystem I. (Alternatively, if the subsystem I includes only one nucleus, the $-N_\alpha/r_{\alpha i} + \hat{J}^I$ contribution to the long-range potential can be approximated by a simple local model potential [26].) So, the $\hat{F}$ operator to be used in the equations of subsystem A is approximated by

$$\hat{F} \cong \hat{T} + \hat{V}^A + \sum_{I\neq A} \left(\hat{V}^I_{lr} + \hat{P}_I \hat{V}^I_{sr} \hat{P}_I \right), \tag{41}$$

with obvious changes when it is used in subsystem B, C, etc.

The second term on the right-hand side of eq. (28) can be approximated, following the same kind of approach, by $\hat{\rho}\hat{P}_A\hat{F}\hat{P}_A\hat{\rho}$, where $\hat{P}_A$ (see eq. (40)) is the projection operator on an appropriate basis set, a convenient choice being the set of primitive basis set functions used to expand $\boldsymbol{\varphi}_A^{\text{occ}}$.

The last two terms on the right-hand side of eq. (28) involve the calculation of

$$\hat{\rho}_I(\hat{W}_I - \hat{F})\hat{\rho}_I = \boldsymbol{\varphi}_I^{\text{occ}} \left[\boldsymbol{\varphi}_I^{\text{occ}\dagger} (\hat{W}_I - \hat{F}) \boldsymbol{\varphi}_I^{\text{occ}} \right] \boldsymbol{\varphi}_I^{\text{occ}\dagger} \tag{42}$$

for all subsystems. The elements of the matrix between square brackets are output of the calculation on subsytem I; therefore, these terms do not require any further approximations.

Finally, we would like to make some comments related to the computations involved along the iterative solution of the building block equations for all subsystems. In effect, each cycle, (i) say, requires as many molecular calculations as subsystems are considered (along each molecular calculation, eqs. (27) are solved for a particular subsystem), this resulting in the (i)th density operator: $\hat{\rho}^{(i)} = \sum_I \hat{\rho}_I^{(i)}$. However, it is important to note that the time consuming two-electron basic integrals for a given subsystem are to be computed only once and stored to be used along all iterations necessary to achieve the required convergence in $\hat{\rho}$. This means that after the first cycle, the molecular calculations involved in subsequent cycles are considerably faster.

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