

An approximate theory of large molecules and molecular complexes[†]

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Abstract. We present here an approximate *ab initio* formalism where a large molecule is treated in terms of its small subunits in such a way that both the integral generation and energy minimization problems are simplified. In this approach one can concentrate on one part of a molecular system and thus tailor the theoretical analysis to observations relating to this part of the system only.

Keywords. *Ab initio* theory; large molecules.

1. Introduction

All molecular systems in their ground state are known to consist of smaller subunits that, despite varying degrees of interaction, retain their identity to a large extent. This fact is of immense importance in a theoretical treatment of large molecules and has been utilized by various authors (Christoffersen and Maggiora 1969; Diner *et al* 1970; Christoffersen 1972; Shipman and Christoffersen 1973; Davis *et al* 1974; Pullman and Bethod 1978). This general characteristic allows one to break up the problem into a set of small steps involving these subunits. Theoretically speaking, this implies that one can set up meaningful equations relating to the local behaviour of a subunit even though the other parts of the molecule are only approximately described.

An actual rigorous development of a computational scheme for treating the subunits of a molecular system individually is, however, a non-trivial problem. The approaches in vogue in this area are of three kinds. While all three rely on reducing the basis set burden to minimal sets, the molecular-fragments approach (Christoffersen and Maggiora 1969; Christoffersen 1972; Shipman and Christoffersen 1973; Davis *et al* 1974) performs a conventional SCF and/or CI once the basis is selected. The Perturbation-CI with Localized Orbitals (PCILO) approach (Diner *et al* 1970) assumes a starting wavefunction that depends on bond orbitals, a concept of limited validity (particularly for complex systems). The molecular electrostatic potential model (Pullman and Bethod 1978) does not allow (at least explicitly) any scope for reoptimization of the parts of the system being replaced by such potentials.

We shall, in what follows, develop a formalism that allows one to handle a large molecule part by part. This implies that, no matter how large the system is, one can

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use this approach to get meaningful and accurate information on any part of the system.

2. A new scheme of integral management

What we propose to achieve here is an unconventional scheme by virtue of which one obtains an *ab initio* energy expression that uses segmented integral sets over basis functions spanning a given system.

First consider the energy expression. Exactly what form this takes depends on the nature of the wavefunction. Let us consider first a set of orbitals $\{\phi_{ap}\}$, a , denoting a molecular fragment which can be simply one of the constituent atoms. We shall denote the molecular orbitals as $\{\psi_i\}$ and assume them to be orthonormal and have the 'LCAO' form:

$$|i\rangle \equiv \psi_i = \sum_{a,p} c_{ap}^{(i)} \phi_{ap}. \quad (1)$$

In terms of the MO we shall assume an energy expression of the form,

$$E = \sum_i n_i h_i + \frac{1}{2} \sum_{i,j} n_i n_j (v_{ij}^J J_{ij} - v_{ij}^K K_{ij}), \quad (2)$$

where n_i are the occupancies, v_{ij}^J and v_{ij}^K are the vector-coupling coefficients,

$$h_i = \langle i | h | i \rangle$$

$$J_{ij} = \iint |\phi_i(\mathbf{r})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\phi_j(\mathbf{r}')|^2 \mathbf{dr} \mathbf{dr}' \quad (3)$$

$$K_{ij} = \iint \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \mathbf{dr} \mathbf{dr}'.$$

This 'diagonal' form of energy, though restricted, corresponds to many valid and accurate wavefunctions. Given (2), we shall indicate how, in general, one can reduce its evaluation to that of terms relating to fragments. Consider the one-electron terms:

$$h_i \equiv \langle i | h | i \rangle$$

$$= \sum_{pq,a} c_{ap}^{(i)} c_{aq}^{(i)} \langle ap | h | aq \rangle \quad (4)$$

$$+ \sum_{pq, a \neq b} c_{ap}^{(i)} c_{bq}^{(i)} \langle ap | h | bq \rangle.$$

For large molecular systems even within the conventional *ab initio* framework where all the necessary integrals are calculated accurately and are readily available, the calculation of h_i (as well as other terms of the energy) is facilitated by blocking the integrals $\langle ap | h | bq \rangle$ in terms of the blocks $B = [a, b]$, where a, b are individual fragments. Introducing the block index B and the corresponding differential

overlap $\rho_{B,pq} = \phi_{ap} \phi_{bq}$ and the density matrix element $D_{B,pq}^{(ii)}$, one can rewrite the one-electron matrix element as

$$h_i = \sum_B \sum_{pq} h_{B,pq} D_{B,pq}^{(ii)}, \quad (5)$$

or using matrix notation,

$$\mathbf{h} = \mathbf{h}^+ \mathbf{D}^{(ii)}. \quad (6)$$

The two-electron Coulomb repulsion terms can similarly be written in terms of the blocked J-supermatrix as

$$J_{ij} = \sum_{B, B'} \sum_{pq, rs} D_{B,pq}^{(ii)} \mathcal{J}_{Bpq, B'rs} D_{B'rs}^{(jj)}, \quad (7)$$

or in matrix notation,

$$J_{ij} = \mathbf{D}^{(ii)} \mathbf{J} \mathbf{D}^{(jj)}. \quad (8)$$

The exchange integrals will be expressed in terms of the supermatrix integrals as follows:

$$K_{ij} = \sum_{B, B'} \sum_{pq, rs} c_{ap}^{(i)} c_{a'r}^{(i)} c_{bq}^{(j)} c_{b's}^{(j)} \mathcal{J}_{Bpq, B'rs} \quad (9)$$

where $B = [ab]$ and $B' = [a'b']$. The greatest advantage that one can derive from this fragment-based blocking of integrals is by making sure that all the elements of an individual blocked supermatrix fit into the core. This implies that the blocks themselves must not be too large. As we shall see in the illustrations given below, this condition will be satisfied for many problems.

For large molecules it is essential to approximate the potential of distant blocks. A 'point-charge' model of the following description should be adequate in many cases. Assume that some of the blocks do not have appreciable differential overlap between the orbitals of its constituent fragments. These blocks clearly disappear from our energy expression as given by (5), (6) and (7). Furthermore for calculating the Coulomb integrals between the blocks $B = [ab]$ and $B' = [a'b']$, for which any of $[aa']$, $[ab']$, $[ba']$ or $[bb']$ has vanishing differential overlap. We use the approximation:

$$\rho_{Bpq} \cong S_{B,pq} \delta(\mathbf{r} - \mathbf{R}_{Bpq}), \quad (10)$$

where $\mathbf{R}_{B,pq}$ is a point (lying on the line joining the centres of the functions p and q) where $|\rho_{B,pq}|$ attains its maximum. In this approximation J_{ij} takes the form:

$$J_{ij} \cong \sum_{B, B'} \sum_{pq, rs} \frac{S_{Bpq} S_{B'pq} D_{Bpq}^{(ii)} D_{B'rs}^{(jj)}}{|\mathbf{R}_{Bpq} - \mathbf{R}_{B'rs}|} \quad (11)$$

Clearly (11) will hold only for large $|\mathbf{R}_{Bpq} - \mathbf{R}_{B'rs}|$.

3. A new ansatz of wavefunction of large molecular systems

The basic problem of treating a large molecular system by *ab initio* means is the fact that each molecular orbital spreads out over all the centres leading to the appearance of large matrices and supermatrices. It is also frequently true that the wavefunctions expressed in such molecular orbitals are not size-consistent and a monumental effort is needed in terms of configuration-mixing in order to 'dissociate' them properly.

One should, however, realize that this behaviour of molecular orbitals is more a mathematical artifact than reality; the orbitals spread out because of orthogonality and symmetry requirements. In any event a localization of the molecular orbitals can always be carried out, although this also implies that the wavefunctions using such orbitals are expanded in order to retain the same degree of accuracy. We present here an ansatz that depends on a special approximate treatment of the local orbitals. We first decouple the bond orbitals by introducing pair functions such as

$$\psi_{12} = a\phi_1^2 + b(\phi_1\phi_2)_0 + c\phi_2^2, \quad (12)$$

where ϕ_1 and ϕ_2 are the orbitals, suitably orthogonalized and belonging to the fragments M_1 and M_2 respectively, that participate in the bond. The notation $(\phi_1\phi_2)_0$ implies singlet coupling:

$$(\phi_1\phi_2)_0 = (2)^{-\frac{1}{2}} (\phi_1\alpha\phi_2\beta - \phi_1\beta\phi_2\alpha). \quad (13)$$

The main objective of the above construction is to be able to derive fragment-wise contributions to the total energy that can be independently optimized. To illustrate this let us consider a molecule consisting only of the fragments M_1 and M_2 and that there is only a single bond between them defined by the pair function ψ_{12} , all other orbitals being doubly-occupied. The matrix elements are:

$$\begin{aligned} H_{11} &= \langle \phi_1 | 2h_{\text{eff}} + J_1^{\text{op}} | \phi_1 \rangle \\ H_{22} &= \langle \phi_1 | h_{\text{eff}} + J_2^{\text{op}} + K_2^{\text{op}} | \phi_1 \rangle + \langle \phi_2 | h_{\text{eff}} | \phi_2 \rangle \\ H_{33} &= \langle \phi_2 | 2h_{\text{eff}} + J_2^{\text{op}} | \phi_2 \rangle \\ H_{21} &= 2^{\frac{1}{2}} \langle \phi_1 | h_{\text{eff}} + J_1^{\text{op}} | \phi_2 \rangle \\ H_{31} &= K_{12} \equiv \langle \phi_1 | K_2^{\text{op}} | \phi_1 \rangle \\ H_{32} &= 2^{\frac{1}{2}} \langle \phi_1 | h_{\text{eff}} + J_2^{\text{op}} | \phi_2 \rangle \end{aligned} \quad (14)$$

In the above h_{eff} consists of potentials generated by the occupation of the orbitals other than ϕ_1 and ϕ_2 :

$$h_{\text{eff}} = -\frac{1}{2}\nabla^2 + \sum_I V_I + \sum_i' (2J_i^{\text{op}} - K_i^{\text{op}}), \quad (15)$$

where summation over I runs over all the nuclei, that over i goes over all the occupied orbitals except ϕ_1 and ϕ_2 , $\{J_i^{\text{op}}\}$, $\{K_i^{\text{op}}\}$ being the Coulomb and exchange operators corresponding to the orbitals $\{\phi_i\}$.

Next we introduce a 'truncated overlap' concept as follows: We assign sets of basis functions spanning individual fragments. In general the functions of one fragment have non-zero overlap with those of the neighbouring fragments. However, the contribution of the overlaps falls off rapidly, roughly as the square of

the overlaps of individual orbitals multiplied by their occupancy in their respective fragments. Thus one can devise different levels of accuracy on the basis of a cut-off parameter below which all inter-fragment overlaps are set to zero. In such approximation the orthogonalization of orbitals on one fragment to those on the other will use only a truncated overlap matrix of a much smaller dimension than the full-blown one. Let the orbitals $\phi_i^{(1)}$ and $\phi_j^{(2)}$ centred on the fragments M_1 and M_2 be written as:

$$\begin{aligned}\phi_i^{(1)} &= \sum c_{ip}^{(1)} \chi_p^{(1)} \\ \phi_j^{(2)} &= \sum c_{jp}^{(2)} \chi_p^{(2)}\end{aligned}\quad (16)$$

These will have a net overlap given by

$$\langle \phi_i^{(1)} | \phi_j^{(2)} \rangle = c_{i1}^{(1)} c_{j1}^{(2)} S_{11}^{(12)}, \quad (17)$$

where $S_{11}^{(12)} = \langle \chi_1^{(1)} | \chi_1^{(2)} \rangle$, provided only the functions $\chi_1^{(1)}$ and $\chi_1^{(2)}$ overlap appreciably. Obviously the easiest way to achieve orthogonalization is to include in the sets $\{\chi_p^{(1)}\}$ and $\{\chi_p^{(2)}\}$ the functions $\chi_1^{(2)}$ and $\chi_1^{(1)}$ respectively. Rewriting $\phi_i^{(1)}$ and $\phi_j^{(2)}$ as

$$\begin{aligned}\phi_i^{(1)} &= \sum c_{ip}^{(1)} \chi_p^{(1)} + c_{i1}^{(2)} \chi_1^{(2)} \\ \phi_j^{(2)} &= \sum c_{jp}^{(2)} \chi_p^{(2)} + c_{j1}^{(1)} \chi_1^{(1)}\end{aligned}\quad (18)$$

we have

$$\langle \phi_i^{(1)} | \phi_j^{(2)} \rangle = \sum_{p,q=1}^2 c_{ip}^{(p)} c_{jq}^{(q)} S_{pq}^t, \quad (19)$$

where the truncated overlap-matrix is given by:

$$S_{pq}^t = \langle \chi_1^{(p)} | \chi_1^{(q)} \rangle. \quad (20)$$

We shall describe below how the above approach brings in considerable simplifications in connection with some typical bonding situations. Before that we consider the question of wavefunction optimization in the context of the present ansatz.

4. Wavefunction optimization

Once the Hamiltonian matrix along with all the basic matrices and supermatrices are in place, we concern ourselves with the optimization of the wavefunction. There are three levels of optimization to be distinguished. First consists of solving the secular equation for the coefficients a , b and c . Secondly, the orbital-vectors of a given fragment are to be optimally rotated amongst themselves. Finally the occupied orbitals are to be mixed with the virtual orbitals belonging to the same fragment. In order to optimize the mixing of the occupied orbitals of the fragment M_1 we use the criterion obtained from the multi-configuration self-consistent field

(MCSCF) formulation. If $\mathbf{e}_i^{(1)}$ and $\mathbf{c}_j^{(1)}$ are properly optimized orbital-vectors belonging to the fragment M_1 , they must satisfy (Hinze 1974):

$$\mathbf{c}_i^{(1)+} (\mathbf{F}_i^{(1)} - \mathbf{F}_j^{(1)}) \mathbf{c}_j^{(1)} + \mathbf{c}_j^{(1)+} \mathbf{f}_i^{(1)} - \mathbf{c}_i^{(1)+} \mathbf{f}_j^{(1)} = 0, \quad (21)$$

where $\mathbf{F}_i^{(1)}$ and $\mathbf{F}_j^{(1)}$ are the corresponding Fock operators, $\mathbf{f}_i^{(1)}$ and $\mathbf{f}_j^{(1)}$ being the respective 'inhomogeneities':

$$\mathbf{\Delta}_i^{(1)} \equiv \mathbf{F}_i^{(1)} \mathbf{c}_i^{(1)} + \mathbf{f}_i^{(1)} - \left(\sum \varepsilon_{ij}^{(1)} \mathbf{S}^{(1)} \mathbf{c}_j^{(1)} + \sum \varepsilon_{ij}^{(2)} \mathbf{S}^t \mathbf{c}_j^{(2)t} \right) = 0, \quad (22)$$

where $e_j^{(2)t}$ is the 'truncated' part of $\mathbf{c}_j^{(2)}$.

Turning to the question of optimization of the orbitals by mixing them with the virtual orbitals of the same fragment, we consider the Fock equations, themselves: We apply a Newton-Raphson type procedure (Wahl 1977):

$$\left[\begin{aligned} & \mathbf{F}_i^{(1)} - \sum_j (|\mathbf{S}\mathbf{c}_j^{(1)}\rangle \langle \mathbf{F}_i^{(1)} \mathbf{c}_j^{(1)}| + |\mathbf{F}_i^{(1)} \mathbf{c}_j^{(1)}\rangle \langle \mathbf{S}\mathbf{c}_j^{(1)}|) \\ & - \sum_j (|\mathbf{S}^t \mathbf{c}_j^{(2)t}\rangle \langle \mathbf{F}_i^{(1)t} \mathbf{c}_j^{(2)t}| + |\mathbf{F}_i^{(1)t} \mathbf{c}_j^{(2)t}\rangle \langle \mathbf{S}^t \mathbf{c}_j^{(2)t}|) \\ & - \varepsilon_i \mathbf{S}^{(1)} \end{aligned} \right] \delta \mathbf{c}_i^{(1)} = -\mathbf{\Delta}_i^{(1)}, \quad (23)$$

and require that $\delta \mathbf{c}_i^{(1)}$ are orthogonal to the orbitals $\{\mathbf{c}_j^{(2)}\}$ through the truncated overlap matrix \mathbf{S}^t .

5. Specific applications

We apply the above formulation to two different kinds of systems, those characterized by covalent and coordination bonding. We restrict ourselves to relatively small systems. However, the extension to larger systems will be seen to be straightforward. We do not attempt here to present any numerical tests, deferring them to a later report.

5.1 Covalent-bonded systems

We shall restrict ourselves to a simple covalent structure such as ethane consisting of two components (CH_3) bonded by a two-electron bond. We choose the wavefunction as:

$$\psi_{\text{tot}} = \tilde{A} \psi_1 \psi_2 [a \phi_1^2 + b (\phi_1 \phi_2)_0 + c \phi_2^2], \quad (24)$$

where ψ_1 , ψ_2 are composed of the closed-shell orbitals representing the CH-bonds and ϕ_1 , ϕ_2 the localized orbitals taking part in the C-C bond. Denoting the CH_3 fragments by the symbols M_1 and M_2 , the blocks are $[M_1 M_1]$, $[M_1 M_2]$ and $[M_2 M_2]$. However, using the 'truncated overlap-matrix' idea, the block $[M_1 M_2]$ is eliminated automatically by introducing the functions that overlap between M_1 and M_2 in each of the blocks $[M_1 M_1]$ and $[M_2 M_2]$. This is easily shown as follows. The part of energy that depends on ϕ_1 and ϕ_2 , when the orbitals are expanded in their respective fragment basis sets:

$$\begin{aligned}
 \varepsilon_{12} = & a^2 \mathbf{D}_1^+ (2\mathbf{h}_{\text{eff}} + \mathcal{F} \mathbf{D}_1) \\
 & + b^2 [\mathbf{D}_1^+ \{\mathbf{h}_{\text{eff}} + (\mathcal{F} + \mathcal{K}) \mathbf{D}_2\} + \mathbf{D}_2^+ \mathbf{h}_{\text{eff}}] \\
 & + c^2 \mathbf{D}_2^+ (2\mathbf{h}_{\text{eff}} + \mathcal{F} \mathbf{D}_2) \\
 & + 2ab 2^{\frac{1}{2}} \mathbf{D}_{12}^+ (\mathbf{h}_{\text{eff}} + \mathcal{F} \mathbf{D}_1) \\
 & + 2bc 2^{\frac{1}{2}} \mathbf{D}_{12}^+ (\mathbf{h}_{\text{eff}} + \mathcal{F} \mathbf{D}_2) \\
 & + 2ac \mathbf{D}_1^+ \mathcal{K} \mathbf{D}_2
 \end{aligned} \tag{25}$$

where ϕ_i is represented by the vector \mathbf{c}_i ,

$$\mathbf{h}_{\text{eff}} = \mathbf{h} + \sum'_{i \in M_1, M_2} (2\mathcal{F} \mathbf{D}_i - \mathcal{K} \mathbf{D}_i), \tag{15'}$$

the summation excluding $\phi_1, \phi_2, \{\mathbf{D}_i \equiv \mathbf{c}_i \mathbf{c}_i^+\}$ are the 'diagonal' density matrices and $\mathbf{D}_{12} \equiv \frac{1}{2}(\mathbf{c}_1 \mathbf{c}_2^+ + \mathbf{c}_2 \mathbf{c}_1^+)$. It is immediately seen that the terms $\mathbf{D}_{12}^+ \mathcal{F} \mathbf{D}_1, \mathbf{D}_{12}^+ \mathcal{F} \mathbf{D}_2$ use integrals of either the block $[M_1 M_1]$ or $[M_2 M_2]$. Also one can write, using the approximation in (10),

$$\begin{aligned}
 \mathbf{D}_1^+ \mathcal{F} \mathbf{D}_2 = & (\mathbf{D}'_2)^+ \mathcal{F} \mathbf{D}_1 + (\mathbf{D}'_1)^+ \mathcal{F} \mathbf{D}_2 - (\mathbf{D}'_1)^+ \mathcal{F} \mathbf{D}'_2 \\
 & + \sum'_{pq, rs} \frac{S_{pq} S_{rs} c_{1p} c_{1q} c_{2r} c_{2s}}{|R_{pq} - R_{rs}|},
 \end{aligned} \tag{26}$$

and

$$\mathbf{D}_1^+ \mathcal{K} \mathbf{D}_2 = (\mathbf{D}'_1)^+ \mathcal{K}' \mathbf{D}'_2.$$

The summation over pq, rs excludes the 'overlapping' basis functions. All the \mathcal{F} and \mathcal{K} integrals required belong to either block $[M_1 M_1]$ or $[M_2 M_2]$.

It is easy to see how one can generalize this approach to, for example, the straight-chain hydrocarbons in which case our wavefunctions will look like:

$$\begin{aligned}
 \psi_{\text{tot}} = & \tilde{A} \psi_1 \psi_2 \psi_3 \dots \times [a_{12} \phi_1^2 + b_{12} (\phi_1 \phi_2)_0 + c_{12} \phi_2^2] \\
 & \times [a_{23} \psi_2^2 + b_{23} (\psi_2 \psi_3)_0 + c_{23} \psi_3^2] \times \dots,
 \end{aligned} \tag{27}$$

where $(\phi_1, \phi_2), (\psi_2, \psi_3)$ etc. are the pairs forming the bonds.

5.2 Coordination-bonded systems

We shall consider in this category those bonds that are characterized by the following feature: There is a central atom (usually a transition metal) that binds together several ligands around itself by virtue of a 'sharing' of charge between its valence-orbitals and those on the ligands. Consider, for example, the coordination complex $\text{K}_3\text{Fe}(\text{CN})_6$. We construct the wavefunction in the following way: First we strip each potassium of its valence electron, donating the latter to the CN ligands. The potassium ions will serve only as charge centres yielding a potential field. Traditionally the wavefunction is constructed in an 'aufbau' fashion by distributing the 65 valence electrons into 32 doubly-occupied orbitals and one singly-occupied orbital. The single-determinant wavefunction that follows is then optimized in a semi-empirical framework (Reschke 1979). No *ab initio* work exists in the literature

(except those based on $X\alpha$ -techniques) to the best knowledge of the present authors.

Taking advantage of the very weak overlap of the CN^- -ligands with one another, we propose here a different kind of wavefunction. We construct the wavefunction in the following form (assuming that K^+ ions provide only potential fields and no additional electrons):

$$\begin{aligned} \psi_{\text{tot}} = & \tilde{A}(\text{Fe} - \text{core})(\Pi_i \psi_{\text{CN}^+,i}) \phi_4^2 \phi_5^2 \phi_6 \phi_{\text{CN}4}^2 \phi_{\text{CN}5}^2 \phi_{\text{CN}6}^2 \times \\ & [a_1 \phi_1^2 + b_1(\phi_1 \phi_{\text{CN}1})_0 + c_1 \phi_{\text{CN}1}^2] \times \dots \\ & [a_2 \phi_2^2 + b_2(\phi_2 \phi_{\text{CN}2})_0 + c_2 \phi_{\text{CN}2}^2] \times \\ & [a_3 \phi_3^2 + b_3(\phi_3 \phi_{\text{CN}3})_0 + c_3 \phi_{\text{CN}3}^2], \end{aligned} \quad (28)$$

where ψ_{CN^+} are the individual CN^+ wavefunctions, $\phi_i \equiv \phi_{\text{Fe}i}$, $i = 1, 2, \dots, 6$ are the iron orbitals and $\phi_{\text{CN}i}$, $i = 1, 2, \dots, 6$ are the openshell CN-orbitals. This wavefunction is based on the model of 'back-donation' where three of the CN^- -ligands actually form two-electron bonds with the three valence electrons on the iron. Of course any three ligands other than those used in (28) qualify for this. But because of negligible overlap between the CN ligands such resonant wavefunctions do not contribute significantly to the energy especially since we are principally interested only in the description of the electrons populating the Fe-orbitals.

Upon identifying the fragments as the Fe atom and the six CN-ligands, we note that only 13 blocks (seven diagonal and six off-diagonal) lead to non-negligible integrals assuming that orbitals on different CN-ligands do not overlap. The variational part of the total energy (i.e. those terms that contain the Fe and CN^- valence orbitals) is given by

$$\begin{aligned} \varepsilon_{\text{val}} = & \frac{1}{2} \sum_{A=\text{CN, Fe}} \sum_{i=1}^6 n_{Ai} \mathbf{D}_{Ai}^+(\mathbf{h}_{\text{eff}} + \mathbf{F}_i^0) \\ & + \sum_{i=1}^3 [a_i^2 \mathbf{D}_{\text{Fe}i} \mathcal{J} \mathbf{D}_{\text{Fe}i} + b_i^2 \mathbf{D}_{\text{Fe},i}^+(\mathcal{J} + \mathcal{K}) \mathbf{D}_{\text{CN},i} + c_i^2 \mathbf{D}_{\text{CN},i}^+ \mathcal{J} \mathbf{D}_{\text{CN},i}] \\ & + 2 \sum_{i=1}^3 [(a_i + c_i) b_i 2^{\frac{1}{2}} \mathbf{c}_{\text{Fe}i}^+ \mathbf{F}_i^0 \mathbf{c}_{\text{CN}i} + a_i c_i \mathbf{D}_{\text{CN}i}^+ \mathcal{K} \mathbf{D}_{\text{Fe}i}] \\ & + 2 \times 2^{\frac{1}{2}} \sum_{i=1}^3 \mathbf{c}_{\text{Fe}i}^+ (a_i b_i \mathcal{J} \mathbf{D}_{\text{Fe}i} + c_i b_i \mathcal{J} \mathbf{D}_{\text{CN}i}) \mathbf{c}_{\text{CN}i}, \end{aligned} \quad (29)$$

$$n_{Ai} = 2, A = \text{Fe or CN}, i = 4, 5, 6$$

$$n_{\text{Fe}i} = 2a_i^2 + b_i^2, n_{\text{CN}i} = 2c_i^2 + b_i^2, i = 1, 2, 3$$

$$\mathbf{D}_{Ai} = \mathbf{c}_{Ai} \mathbf{c}_{Ai}^+$$

$$\mathbf{F}_i^0 = \mathbf{h}_{\text{eff}} + \sum_{B=\text{CN, Fe}, B \neq i} n_{Bj} (\mathcal{J} - \frac{1}{2} \mathcal{K}) \mathbf{D}_{Bj}. \quad (30)$$

Again using the argument from the previous example one can simplify the evaluation of all the terms such that they involve only the integrals belonging to individual fragments (i.e. only the seven diagonal blocks).

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