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Molecular Symmetry in Ab Initio Calculations

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A scheme is presented for the construction of the Fock matrix in LCAO-SCF calculations and for the transformation of basis integrals to LCAO-MO integrals that can utilize several symmetry unique lists of integrals corresponding to different symmetry groups. The algorithm is fully compatible with vector processing machines and is especially suited for parallel processing machines.

1. INTRODUCTION

Calculation of ab initio configuration interaction (CI) wavefunctions [1] involves essentially three major computational steps prior to the actual CI calculations:

(a) Generation of one-electron and two-electron integrals over basis functions (AOs) [2].

(b) Calculation of a wavefunction by the LCAO-SCF method [3].

(c) Transformation of the basis integrals in (a) to integrals over the LCAO-MOs from (b) [4].

The use of point group symmetry makes the computation of two-electron integrals more efficient [5–9] in that only symmetry non-equivalent (unique integrals) have to be computed. Two approaches are commonly employed for the subsequent processing of the symmetry unique list of integrals:

(1) A pre-transformation is carried out to integrals over symmetry-adapted basis functions [5, 10, 11] (primitive symmetry orbitals, PSO). The resulting complete list of integrals, which is considerably smaller because of the many integrals which are zero by symmetry, is then utilized for (b) and (c) above. In some cases, however, the pre-transformation can be time-consuming and, in addition, the list of PSO integrals has to be rearranged in canonical order for efficient processing in (c) [1].

(2) The symmetry-unique basis integrals are directly utilized in (b) and (c) above [5–8, 12]. This approach is based on the "equal contribution theorem" [6] and is only applicable to symmetric integrands.

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The above methods assume a single symmetry group for the complete system and do not recognize subsets of basis functions that may have higher symmetry which would result in additional gains during the integral evaluation. For example, in chemisorption studies of atomic/molecular adsorbates on surfaces, modelled by large clusters (e.g., ~50 atoms), it is most economical to compute the basis integrals in two subsets: (a) those involving basis functions of the surface (large cluster), computed with the full symmetry of the cluster, and (b) those involving the adsorbate (including adsorbate-surface integrals), computed with the symmetry of the chemisorbed system. In this paper, we report a simple symmetry scheme that has the following features:

(1) The scheme utilizes the full set of basis integrals which are effectively generated from sets of unique integrals corresponding to different symmetry groups. Canonical order is maintained.

(2) The scheme is readily suited for vector processing, single instruction multiple data (SIMD) machines and is especially advantageous for multiple instruction multiple data (MIMD) machines.

2. Generation of a Unique List of Integrals

The one-electron and two-electron electron integrals are given by

$$\int f_i^*(1)\, h(1)\, f_j(1)\, dv_1 \equiv (i/j)$$

and

$$\iint f_i^*(1)\, f_j(1)(1/r_{12})\, f_k^*(2)\, f_l(2)\, dv_1\, dv_2 \equiv (ij//kl),$$

respectively, where $\{f_i\} = \mathbf{f}$ is the set of basis functions (N in number). The integrals are invariant to an interchange of indices between the left and right and to a permutation of indices on the left and/or right. We define a symmetry group $S = \{R\}$, where the R are symmetry operations such that $R \times R' \in \{R\}$ and $R^{-1} \in \{R\}$. We further assume that $Rf_i \rightarrow \pm f_k$, i.e., an operation takes one function into another, to within a $\pm$ sign [13]. The scheme for generating a unique list of integrals in canonical order is essentially equivalent to that reported by Dupuis and King [8]; it is outlined below for the generation of two-electron integrals. The scheme for one-electron integrals is a trivial variation of that for two-electron integrals.

Four loops are set up over i, j, k and l, in that order, such that: $i = 1 \rightarrow N$, $j = i \rightarrow N$, $k = i \rightarrow N$ and $l = m \rightarrow N$ ($m = k$ if $i \neq k$, $m = j$ if $i = k$). This ensures the generation of a permutationally unique set of integrals in upper triangular form. It is assumed in all further discussion that the sets of integrals considered are permutationally unique.

The symmetry-unique list of integrals, henceforth referred to as the unique list, is defined as all integrals $(ij//kl)$ such that if $RiRjRkRl = i'j'k'l'$ then $Z_{i'j'k'l'} > Z_{ijkl}$ for all operations R in the symmetry group, where the integral index Z_{ijkl} and pair index Z_{ij} are defined as follows:

$$Z_{ij} = L \times \min(i, j) + \max(i, j), \qquad L > N$$

and

$$Z_{ijkl} = L \times \min(Z_{ij}, Z_{kl}) + \max(Z_{ij}, Z_{kl}).$$

For the case of several symmetry groups $\{S_K\}$, Q in number, the basis functions are arranged in subsets, $G_1, G_2, \ldots, G_Q$, with $G_i \cap G_j = 0$, where the superset $\bigcup_{i=1}^{K} G_i$ is closed to the operations of symmetry groups S_K and the full set $\bigcup_{i=1}^{Q} G_i = \{f_i\}$ has the overall symmetry of the system, S_Q. Q unique lists of two-electron integrals $\{I_K\}$ are generated, where I_K is the set of unique integrals corresponding to the subset of basis functions $\bigcup_{i=1}^{K} G_i$, transforming according to symmetry S_K, in which at least one of the basis functions belongs to G_K. This last constraint ensures that the sets of integrals, including symmetry equivalent integrals, associated with the unique lists contain no members in common.

To exemplify the above discussion, for adsorbates on large clusters, one would consider two symmetry groups S_1 and S_2 corresponding to the symmetry of the bare cluster and chemisorbed system, respectively. The basis functions are divided into two subsets: $G_1 \equiv$ basis functions of the cluster and $G_2 \equiv$ basis functions of the adsorbate. Two unique lists, I_1 and I_2, of two-electron integrals are generated corresponding to the subsets G_1 and $G_1 \cup G_2$, where at least one basis function belongs to G_2 in the latter case. A point to note is that if the set G_2 (isolated adsorbate) transforms according to a third symmetry S_3, higher than S_2, one can achieve additional economy by generating three unique lists, I_1, I_2 and I_3, where I_1 and I_3 are generated with subsets G_1 and G_2, respectively, and I_2 is generated as before with the additional constraint that there also be at least one basis function that belongs to G_1. In practice, for a significant gain, the sets G_1 and G_2 must be appropriately large. One may also generalize to many symmetry groups, though the integral generation scheme becomes more involved. In general, one may have $Q' \geqslant Q$ unique lists providing the sets of integrals, including symmetry equivalent integrals, associated with the unique lists contain no members in common.

The operator $h(1)$, for the one-electron integrals, can be expressed as $T(1) + V(1)$, where $T(1)$ is the kinetic energy operator and $V(1)$ is the potential energy operator which includes nuclear-electronic interactions and one-electron pseudo-potentials, if any. Since $V(1)$ transforms according to the overall symmetry of the system (symmetry group S_Q) only one unique list of one-electron integrals is generated with the complete basis $\bigcup_{K=1}^{Q} G_K$.

3. Processing of the Unique List of Integrals

Applying all operations of a symmetry group S_K to a unique integral $(ij//kl)$ in the corresponding unique list I_K generates a set of integrals which are characteristic in that they cannot be generated from any other unique integral in I_K or in $I_{L \neq K}$ (see the definition of uniqueness and Ref. [14]). Different symmetry operations acting on $(ij//kl)$ may produce identical integrals or integrals differing only by a permutation of indices as discussed in Section 2. A convenient way to detect and bypass these redundant integrals is to associate a packed index with each unique integral defined by

$$U = \sum_{R}^{M} 2^{R-1} P_R,$$

where M is the number of symmetry operations in S_K and $P_R = 1$ for a new integral and $P_R = 0$ for a redundant integral. The summation is over symmetry operations and $P_E = 1$ corresponds to the unique integral (identity operation). Thus, the complete set of integrals associated with the unique list I_K may be generated by applying the symmetry operations of S_K successively to the list I_K and taking into account only those integrals with $P_R = 1$ for symmetry operation R. Computationally, it is only necessary to determine if $U/2^{R-1}$ is odd, then $P_R = 1$, or even, then $P_R = 0$. It also follows that the superset of all such sets of integrals, generated above, is the complete list of permutationally unique two-electron integrals. A similar argument holds for the one-electron integrals, although there is only one unique list corresponding to the symmetry group S_Q.

While the unique lists of integrals are generated in canonical order, as defined in Section 2, the application of a symmetry operation $R \in S_K$ transforms the set of unique integrals $I_K \equiv \{(ij//kl)\}$ into $I'_K \equiv \{(i'j'//k'l')\}$, where the primed set is no longer in canonical order with respect to the unprimed set. In order to preserve canonical order, we define a transformation of the basis

$$\mathbf{f}_R = (f_{R1} f_{R2} \cdots f_{RN}) = (f_1 f_2 \cdots f_N)\, R = \mathbf{f}R$$

for each operation $R \in S_K$, where $\mathbf{f}$ is the original basis used to compute the unique list I_K. The generated set I'_K, when expressed in terms of the transformed basis $\mathbf{f}_R$, is identical to the unique list I_K, where the labels now correspond to the set $\mathbf{f}_R$, and is therefore in canonical order.

The transformation and relabeling is illustrated in Table I for three basis functions related by a single C_2 two-fold rotation which interchanges basis functions 1 and 3. The unique list of two-electron integrals is shown along with the list of integrals generated by the C_2 operation. The latter are expressed in terms of the original basis labels and the labels of the transformed basis which is then identical to the unique list.

TABLE I

Processing of the Symmetry Unique List of Integrals

Symmetry operations	Basis functions		
E	1	2	3
C_2	3	2	1

Unique list of integrals $P_E = 1$	Symmetry-generated integrals		
	Original basis notation	Transformed basis notation	P_{C2}
1111	3333	1111	1
1112	3332	1112	1
1113	3331	1113	1
1122	3322	1122	1
1123	3321	1123	1
1133	3311	1133	0
1212	3232	1212	1
1213	3231	1213	1
1222	3222	1222	1
1223	3221	1223	0
1313	3131	1313	0
1322	3122	1322	0
2222	2222	2222	0

Fock matrix

$F_{11} = (F_E)_{11} + (F_{C2})_{33}$; $F_{12} = (F_E)_{12} + (F_{C2})_{23}$
$F_{13} = (F_E)_{13} + (F_{C2})_{13}$; $F_{22} = (F_E)_{22} + (F_{C2})_{22}$
$F_{23} = (F_E)_{23} + (F_{C2})_{12}$; $F_{33} = (F_E)_{33} + (F_{C2})_{11}$

Molecular orbital integrals

$V = V_E + V_{C2}$

Note. The symmetry operation C_2 interchanges basis functions 1 and 3. Two-electron integrals are denoted by indices of basis functions and are generated as discussed in Section 2. The transformed basis corresponds to $\mathbf{f}_{C2} = \mathbf{f}C_2$. The intermediate Fock matrices F_E and F_{C2} are combined, as shown, to construct the Fock matrix F. The intermediate vectors of transformed LCAO-MO integrals, V_E and V_{C2}, are directly added together to obtain V (Section 4).

The application of the algorithm to the construction of the Fock matrix [2], central to the LCAO-SCF procedure, and to the transformation to LCAO-MO integrals is discussed below. In the discussion, the Fock matrix is denoted by F and the LCAO-MO integrals are denoted by a vector V. Each element of V corresponds to a MO integral $(PQ//RS)$, where the indices represent MOs. The indices are ordered in a manner identical to those corresponding to basis integrals (Section 2).

4. THE FOCK MATRIX AND LCAO-MO TRANSFORMATION

The Fock matrix element F_{ij} is defined as

$$F_{ij} = (i/j) + \sum_m [(ij//\phi_m \phi_m) - (i\phi_m//j\phi_m)].$$

The set $\{\phi_m\}$ is the set of LCAO-MOs [3], defined by

$$\boldsymbol{\phi} = \mathbf{f}C, \text{ where } C \text{ is the coefficient matrix such that}$$

$$\phi_i = \sum_k C_{ki} f_k.$$

Substituting the expansion for ϕ_i gives

$$F_{ij} = (i/j) + \sum_k \sum_l D_{kl}[(ij//kl) - (ik//jl)],$$

where $D_{kl} = \sum_m C_{km} C^*_{lm} = (CC^\dagger)_{kl}$ is called the density matrix. In terms of permutationally unique integrals, an integral $(ij//kl)$ contributes to all Fock matrix elements obtained from pairwise combinations of the four indices, and a permutational factor can be associated with each integral to account for permutational redundencies (e.g., $(ij//kl) = (ji//kl)$ if $i = j$). We assume that this factor is incorporated into the value of $(ij//kl)$.

From previous discussions, one may express the Fock matrix $F = \sum_{S_K} F(S_K)$, where $F(S_K)$ is the Fock matrix constructed with the full set of integrals associated with the unique set I_K. An important point to note is that the one-electron part of the Fock matrix, exclusively contained in $F(S_Q)$ (Section 2), is constructed with the full set of one-electron integrals associated with the single unique list, corresponding to symmetry group S_Q.

One can further express the $F(S_K)$ in terms of a set of partial Fock matrices $F_R(S_K)$ for all $R \in S_K$, where $F_R(S_K)$ is the partial Fock matrix constructed with the transformed basis $\mathbf{f}_R$ utilizing the set I'_K, generated from I_K by the symmetry operation R, and taking into account only those integrals for which $P_R = 1$. The density matrix corresponding to the transformed basis $\mathbf{f}_R$ is $D_R = R^\dagger D R$. Since the set I'_K is identical to I_K when expressed in the basis $\mathbf{f}_R$, one can repeatedly utilize the integrals in I_K with $P_R = 1$ along with the density matrix D_R to construct $F_R(S_K)$ for all $R \in S_K$. $F(S_K)$ is then obtained by transforming back the $F_R(S_K)$ to the original basis, $\mathbf{f}$, and taking the sum

$$F(S_K) = \sum_R R F_R(S_K) R^\dagger.$$

This is shown in Table I, where F_E is the Fock matrix constructed with the list of unique integrals, while F_{C2} is the matrix constructed with the basis $\mathbf{f}_{C2}$, utilizing the integrals in the unique list with $P_{C2} = 1$. The final Fock matrix is obtained by adding F_E and the transformed F_{C2}.

Turning to the transformation of basis integrals to integrals over the LCAO-MOs, the element V_{PQRS} is given by

$$V_{PQRS} = (PQ//RS) = \sum_i \sum_j \sum_k \sum_l C_{iP} C_{jQ} C_{kR} C_{lS}(ij//kl).$$

As in the case of the Fock matrix, we can express

$$V = \sum_{S_K} \sum_R V_R(S_K).$$

$V_R(S_K)$ is constructed with the transformed basis $\mathbf{f}_R$, utilizing the integrals in I_K, with $P_R = 1$, and the C matrix corresponding to $\mathbf{f}_R$ ($C_R = R^\dagger C$). Since the MO integrals do not depend on the labels of the basis functions, the $V_R(S_K)$ do not have to be transformed prior to the summation as in the case of the $F_R(S_K)$.

We have implemented the symmetry algorithm in our LCAO-MO integral transformation program and general SCF program. The former program utilizes a $\mathcal{O}(N^5)$

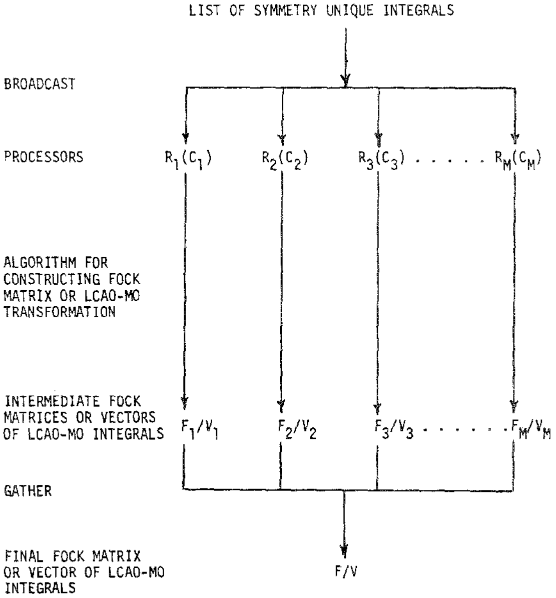

FIG. 1. Parallel processing of unique integrals. Each processor is assigned to a symmetry operation R_m along with the corresponding LCAO-MO matrix C_m. The algorithm is executed in parallel by the processors to construct the intermediate Fock matrices or vectors of transformed LCAO-MO integrals which are then combined.

algorithm [1] and vectorizes completely on the Cray-XMP computer whereas the SCF program vectorizes partially. Both programs are designed for SIMD/vector machines and loop over the symmetry operations so that a single list of symmetry unique integrals is processed repeatedly utilizing the C_R generated for each symmetry operation R. The algorithm is especially suited for parallel processing, as shown in schematic form in Fig. 1. A processor is designated to handle a symmetry operation so that the $\{F_R\}$, or $\{V_R\}$, are constructed in parallel utilizing duplicate lists of unique integrals or a single list which is broadcast to the various processors. The total time required to construct F, or V, is then comparable to the time for processing the unique list of integrals.

5. SUMMARY

A scheme is presented for the construction of the Fock matrix in LCAO-SCF calculations and for the transformation of basis integrals to LCAO-MO integrals that can utilize several symmetry unique lists of integrals corresponding to different symmetry groups. The scheme utilizes the complete set of integrals which are effectively generated by repeatedly processing the set of unique integrals in a manner such that the canonical order is preserved. The algorithm is fully compatible with SIMD/vector processing machines and is especially suited for parallel processing (MIMD) machines.

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13. This restriction is not a serious disadvantage if the integral program permits the orientation of functions independent of the global coordinate system; see, for example, The utility of lobe Gaussians (J. L. Whitten, *J. Chem. Phys.* **44**, 359 (1966). In many, but not all, cases one can choose the orientation according to the internal symmetry co-ordinates of the system.
14. This follows from the fact that if two unique integrals generate the same integral on applying symmetry operations of the group, then they have to be related by some symmetry operation in the group; this contradicts the assumption of uniqueness.