Ab Initio Calculations on Large Molecules: The Multiplicative Integral Approximation

C. Van Alsenoy

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

In the multiplicative integral approximation (MIA), two-electron integrals are evaluated using an expansion of a product of two Gaussians in terms of auxiliary functions. An estimator of the error introduced by the approximation is incorporated in the self-consistent field (SCF) calculations and the integrals for which the error estimate is larger than a preset value are systematically corrected. In this way the results of a MIA-assisted calculation have the same accuracy as a conventional calculation. The full exploitation of the expansion technique while constructing the Fock-matrix allows important time savings. Results are presented for a number of test cases.

I. INTRODUCTION

The evaluation of two-electron integrals (2e integrals) has been the bottleneck in SCF-MO-LCAO calculations for a long time. Recently however, very efficient methods for the calculation of these integrals have been proposed.[1] But even so their number remains a crucial factor in self-consistent field (SCF) calculations. In particular, it is the limiting factor in the efficiency of the direct SCF approach.[2] This shows the importance of procedures which reduce the number of 2e integrals without causing significant loss of accuracy in the final results. Two general ways of addressing the problem have been followed so far. The first is the use of pseudopotential methods and the construction of effective Fock potentials. We will not discuss this method here and refer the reader to Ref. 3 for a general discussion of this topic.

The second method is to use auxiliary functions for the evaluation of 2e integrals. Boys and Shavitt[4] were probably the first to follow this line. They expanded a product of two functions as:

$$\phi_a \phi_b = \sum_\alpha c_\alpha \phi_\alpha \qquad (1)$$

to calculate two-center exchange integrals in H_2. In doing so, they used a number of auxiliary functions centered on both atoms as well as on the line connecting the two nuclei. The basis of this technique can be traced back to the well known Mulliken approximation[5]

$$\phi_a \phi_b = S_{ab}[\phi_a^2 + \phi_b^2] \qquad (2)$$

of which a number of variations were proposed, by among others, Sklar[6] and by Lowdin.[7]

In later years the technique formed the basis for the development of a number of approximate methods, namely the PDDO method by Newton et al.[8] and the LEDO method by Billingsley and Bloor,[9] the latter being based on earlier work of Harris and Rhein.[10] The VRDDO method by Kaufmann et al.,[11] based on a charge conserving integral approximation published by Wilhite and Euwema,[12] can also be placed under this heading. We refer to Refs. 8 and 9 for a more complete overview and more technical details of this earlier work. Auxiliary functions were also used by Clementi[13] in a number of calculations under the name "adjoint function method."

While most of the work was directed toward the calculation of 2e integrals over STOs, Campbell et al.[14] extended the ideas toward the use of GTOs. The authors named their method the "Core Valence Approximation." As the name suggests, it concerns the expansion of a core and a valence orbital in terms of auxiliary core functions:

$$\phi_{\text{core}} \phi_{\text{valence}} = \sum_\alpha c_\alpha \phi_{\text{core}, \alpha} \qquad (3)$$

which is taken into the calculation of $2e$ integrals:

$$(\phi_{\text{core}}\phi_{\text{valence}} \mid \phi_3\phi_4) = \sum_{\alpha} c_{\alpha}(\phi_{\text{core},\alpha} \mid \phi_3\phi_4)$$

$$(4)$$

An extension of this method to a valence–valence orbital expansion was announced, but has not, to our knowledge, been published. Campbell et al.[14] also realized an important gain of time in the SCF phase of a calculation by fully exploiting the expansion technique during the build up of the Fock matrix. In their procedure the expansion coefficients C_{α} of (3) are combined with elements of the density matrix and the resulting quantities are then combined with the three-function $2e$ integrals of (4) to construct the Fock-matrix.

In all methods previously developed, the authors recognized the approximate nature of the expansions of the type (1) for the evaluation of $2e$ integrals. They either applied the method to all integrals involved in a calculation, being aware that the resulting method was only approximate,[8] or, applied it only to those integrals for which the approximation was good enough to give results with a negligible loss of accuracy.[14] In this last case, testing is needed, which unfortunately interferes with a fast and efficient construction of the Fock matrix. It would be more advantageous to apply the expansion technique to all $2e$ integrals involved and to make the necessary corrections afterward, if the majority of the integrals do not need to be corrected. Therefore, we propose to use the expansion technique in combination with an error estimate of the resulting $2e$ integral. Furthermore, we will incorporate this error estimate into the SCF part of the calculations, correcting only those integrals for which the accuracy is below a preset threshold.

In Section II we discuss the nature of the auxiliary functions used, as well as the error estimate. The implementation of this method in closed-shell SCF calculations will be dealt with in Section III and the results will be described in Section IV.

II. THE EXPANSION OF A PRODUCT OF TWO GAUSSIANS

The multiplicative integral approximation (MIA)[15] involves the expansion of a product of two basis functions $\phi_h\phi_l$ (ϕ_h with a high exponent and ϕ_l with a low exponent) in terms of auxiliary functions $\phi_{h,\alpha}$ of the basis function with the high exponent:

$$\phi_h\phi_l = \sum_{\alpha} c_{\alpha}\phi_{h,\alpha}$$

$$(5)$$

The auxiliary functions are obtained by taking the original function with the high exponent (ϕ_h), adding a small constant value to the exponent of the function, and multiplying it by a polynomial factor. If, for example, we have a simple Gaussian function (centered on the origin)

$$\phi = x^l y^m z^n \exp(-kr^2)$$

$$(6)$$

we have auxiliary functions of the following form:

$$\phi_{\text{aux}} = x^{l+l'} y^{m+m'} z^{n+n'} \exp(-k'r^2);$$

$$k' = k + a$$

$$(7)$$

If the original function is a contracted one, the associated auxiliary functions have the following general form:

$$\phi_{\text{aux}} = x^{l+l'} y^{m+m'} z^{n+n'} \sum_{i} c_i' \exp(-k_i'r^2);$$

$$k_i' = k_i + a$$

$$(8)$$

The c_i' are the normalized contraction coefficients.

The expansion coefficients are determined by a least-squares fit of the exact product and the expanded form under the condition that the charge and dipole of the original charge distribution are conserved. The charge and dipole moment of the original distribution are defined by:

$$\text{charge} = q = \int \phi_h\phi_l \, dv$$

$$(9)$$

$$\text{dipole} = \mathbf{d} = \int \phi_h \mathbf{r}\phi_l \, dv$$

$$(10)$$

Thus we construct the following functional, where L_1 and $\mathbf{L}_2$ are Lagrange multipliers:

$$F = \int \left(\phi_h\phi_l - \sum_{\alpha} c_{\alpha}\phi_{h,\alpha} \right)^2 dv$$

$$+ L_1 \left\{ \int \phi_h\phi_l \, dv - \int \sum_{\alpha} c_{\alpha}\phi_{h,\alpha} \, dv \right\}$$

$$+ \mathbf{L}_2 \cdot \left\{ \int \phi_h \mathbf{r}\phi_l \, dv - \int \mathbf{r} \sum_{\alpha} c_{\alpha}\phi_{h,\alpha} \, dv \right\}$$

$$(11)$$

The derivatives of this functional versus the coefficients c_α and the Lagrange multipliers lead to a set of equations, which can be solved to give values for the coefficients c_α.

Preliminary tests showed that the set, given in Table I, consisting of 13 auxiliary functions performs satisfactorily, provided the exponents of the hard and the soft Gaussian have a ratio of about 3. Consequently, we will be able to apply our expansion to products of core–valence-type functions as well as to products of valence–valence-type functions.

If the expansion is applied to the product ij of two Gaussians in a $2e$ integral (ij, kl), we obtain:

$$(ij, kl) = \sum_{\alpha=1}^{13} c_\alpha^{ij}(i_\alpha, kl) \qquad (12)$$

The error involved in using (12) for the evaluation of the integral (ij, kl) can be estimated from:

$$\frac{\Delta Q_{ij} S_{kl}}{r_{i,kl}^3} \qquad (13)$$

S_{kl} stands for the charge in the distributions $\phi_k \phi_l$,

ΔQ_{ij} represents the largest difference in a component for the quadrupole moment of the expanded charge distribution and $r_{i,kl}$ is given by the expression:

$$\mathbf{r}_{i,kl} = \frac{1}{2}(\mathbf{r}_{ik} + \mathbf{r}_{il}) \qquad (14)$$

We can derive (13) starting from the following expression for a $2e$ integral (ij, kl):

$$(ij, kl) = \int dv_2 \phi_k(2)\phi_l(2) \underbrace{\int dv_1 \frac{\phi_i(1)\phi_j(1)}{r_{12}}}_{V(2)}$$

$$(15)$$

Table I. Set of 13 auxiliary functions[a] used in this work.

$\phi_h(.2)$	$x\phi_h(.2)$	$x\phi_h(1.)$	$x^2\phi_h(.2)$
	$y\phi_h(.2)$	$y\phi_h(1.)$	$y^2\phi_h(.2)$
	$z\phi_h(.2)$	$z\phi_h(1.)$	$z^2\phi_h(.2)$
			$xy\phi_h(.2)$
			$xz\phi_h(.2)$
			$yz\phi_h(.2)$

[a] An expression of the form $x\phi_h(.2)$ means that a value of 0.2 is added to the exponent of the original Gaussian and the factor x means that the original Gaussian is multiplied by a factor x. If the Gaussian is centered in a point with coordinates A_x, A_y, and A_z, the function is multipled by a factor $(x - A_x)$.

The last integral represents the potential felt by electron 2 due to the charge distribution of electron 1. This potential can be expanded in terms of its multipole components:

$$V(2) = \frac{q}{r} + \frac{\mathbf{d} \cdot \mathbf{r}}{r^3} + \frac{1}{2}\frac{\mathbf{r} \cdot \overline{Q} \cdot \mathbf{r}}{r^5} + \dots \qquad (16)$$

Since we have expanded the distribution (ij) in terms of auxiliary functions under the condition that charge and dipole moments are strictly conserved, the first term of the series (16) which differs from the exact expansion, will be the term containing the quadrupole moment. Taking this term as error estimate, we obtain:

$$\Delta_{ijkl} = \sum_{\alpha\beta} \Delta Q_{\alpha\beta}^{ij} \int dv_2 \phi_k(2)\phi_l(2) \frac{x_\alpha x_\beta}{r^5} \qquad (17)$$

Since we wish to make all decisions on the level of shells rather than on the level of individual integrals, we use formula (18) to estimate the error in all integrals with shell indices (IJ, KL).

$$\Delta_{IJKL} = \frac{\Delta Q_{IJ} S_{KL}}{r_{I,KL}^3} \qquad (18)$$

In this expression ΔQ_{IJ} stands for the largest error in quadrupole moment components between any two basis functions belonging to the shells I and J, while S_{KL} stands for the largest overlap between any two basis functions belonging to the shells K and L.

III. IMPLEMENTATION IN AN SCF CALCULATION

As stated before we will apply the MIA expansion to all products of basis functions (IJ) in the $2e$ integrals (IJ, KL) encountered, when looping over all four shell combinations. We want to ensure that the shell with shell index I contains in general Gaussian functions having a higher exponent than the Gaussians contained in shell J. Hence, before starting the calculations, we order the shells according to their hardness in such a way that softest shell comes first and the hardest shell comes last.

Furthermore, since the three function $2e$ integral

$$(\phi_{i,\alpha} | \phi_k \phi_l)$$

is no longer dependent on the index j, the loops for the construction of the Fock matrix can be reorganized such that a very fast build-up is

possible. Application of the MIA expansion to all 2e integrals results in contributions to the different elements of the Fock matrix given by the expressions (19):

$$F_{ik}: \sum_{j,l} P_{jl}(ij,kl) = \sum_{j,l} P_{jl} \sum_a C_a^{ij}(i_a,kl)$$

$$= \sum_{a,l} (i_a,kl) \sum_j P_{jl} C_a^{ij}$$

$$F_{il}: \sum_{j,k} P_{jk}(ij,kl) = \sum_{j,k} P_{jk} \sum_a C_a^{ij}(i_a,kl)$$

$$= \sum_{a,k} (i_a,kl) \sum_j P_{jk} C_a^{ij}$$

$$F_{kl}: \sum_{i,j} P_{ij}(ij,kl) = \sum_{i,j} P_{ij} \sum_a C_a^{ij}(i_a,kl)$$

$$= \sum_{a,i} (i_a,kl) \sum_j P_{ij} C_a^{ij}$$

$$F_{jk}: \sum_{i,l} P_{il}(ij,kl) = \sum_{i,l} P_{il} \sum_a C_a^{ij}(i_a,kl)$$

$$= \sum_{a,i} C_a^{ij} \sum_l P_{il}(i_a,kl)$$

$$F_{jl}: \sum_{i,k} P_{ik}(ij,kl) = \sum_{i,k} P_{ik} \sum_a C_a^{ij}(i_a,kl)$$

$$= \sum_{a,i} C_a^{ij} \sum_k P_{ik}(i_a,kl)$$

$$F_{ij}: \sum_{k,l} P_{kl}(ij,kl) = \sum_{k,l} P_{kl} \sum_a C_a^{ij}(i_a,kl)$$

$$= \sum_a C_a^{ij} \sum_{k,l} P_{kl}(i_a,kl) \quad (19)$$

We consider only closed-shell calculations, although the extension to open-shell calculations is possible without difficulty. The formulas (19) are obtained if the MIA expansion is applied to all 2e integrals involved.

We want to retain the same accuracy as in a conventional SCF calculation. Hence, after the fast build-up of the Fock matrix, we have to make a second loop over all 2e integrals and correct those integrals for which the error estimated by (18) is larger than a preset threshold. We take the threshold equal to the limit for the neglect of small integrals (in this paper: $10^{**} - 7$). In fact, to decide whether a certain batch of integrals needs to be corrected we use the expression:

$$\Delta_{IJKL} \cdot P_{IJKL} \quad (20)$$

In this expression P_{IJKL} stands for the largest element in the batches of density matrix elements:

$$\mathbf{P}_{IJKL} = \max(P_{ij}, P_{ik}, P_{il}, P_{jk}, P_{jl}, P_{kl})$$

$$\forall_{i\epsilon I}, \quad \forall_{j\epsilon J}, \quad \forall_{k\epsilon K}, \quad \forall_{l\epsilon L}$$

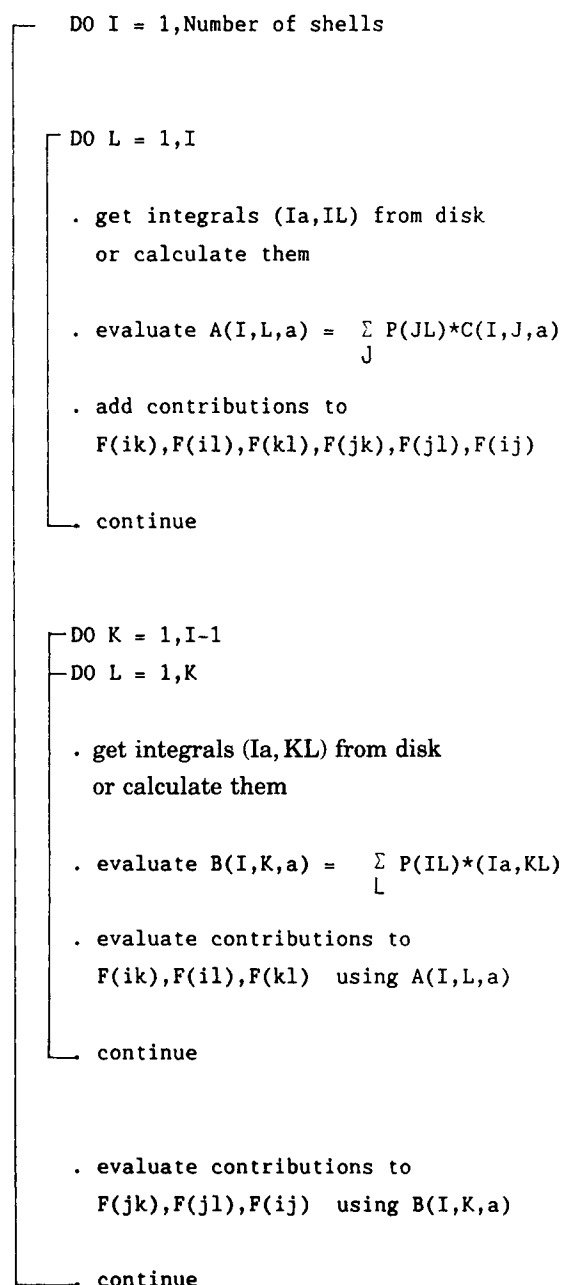The loop structures for the fast build-up and the corrections are presented in Figures 1 and 2, respectively.

```
┌── DO I = 1,Number of shells
│
│  ┌─ DO L = 1,I
│  │
│  │  . get integrals (Ia,IL) from disk
│  │    or calculate them
│  │
│  │  . evaluate A(I,L,a) =  Σ P(JL)*C(I,J,a)
│  │                         J
│  │  . add contributions to
│  │    F(ik),F(il),F(kl),F(jk),F(jl),F(ij)
│  │
│  └── continue
│
│  ┌─DO K = 1,I-1
│  ├─DO L = 1,K
│  │
│  │  . get integrals (Ia,KL) from disk
│  │    or calculate them
│  │
│  │  . evaluate B(I,K,a) =   Σ P(IL)*(Ia,KL)
│  │                          L
│  │  . evaluate contributions to
│  │    F(ik),F(il),F(kl)  using A(I,L,a)
│  │
│  └── continue
│
│  . evaluate contributions to
│    F(jk),F(jl),F(ij)  using B(I,K,a)
│
└──── continue
```

Figure 1. Loop structure for the fast build-up of the Fock matrix.

```
┌─ DO I = 1,Number of shells

├─ DO K = 1,I

├─ DO L = 1,K

├─ DO J = 1,J1      if I=K then J1=L

│                        else J1=I


│  . IF ( ΔP.GT. 10⁻⁷ )   THEN


│  . get corrections (IJ,KL) -  Σ C(IJ,a)*(Ia,KL)
│                               α
│    from disk or evaluate them


│  . add corrections to
│    F(ij),F(ik),F(il),F(jk),F(jl),F(kl)


│              ENDIF


└─→ continue
```

Figure 2. Loop structure for the calculations of the corrections to the Fock matrix.

IV. RESULTS

To compare the results of our approach with those of a conventional SCF calculation, the molecules given in Table II were chosen as test cases.

Since our strategy is based on the assumption that most of the 4-shell combinations do not need correction, the first point we want to check is whether this is true. The results are given in Table II under the heading Percentage. We see that, in most cases, the percentage of 4-shell combinations in need of correction is less that 50%. Moreover, the percentage decreases rapidly as the size of the molecule increases. Since the MIA expansion should

work better in cases where the ratio of hard versus soft functions is higher, it may seem surprising that the percentage for alanine–dipeptide (4-21G) is smaller than the one for serine (6-311G) (both calculations have about the same number of basis functions). However, when we compare the actual number required of 4-shell combinations, we see that for serine we need to calculate 447107 4-shell combinations, while for alanine–dipeptide we only need 325170 4-shell combinations. Thus, while the percentage of 4-shell combinations increases by 37%, the percentage of corrections rises only by 9%, indicating that indeed, relatively fewer shells need to be corrected for a larger basis set.

The difference in total energy with or without the MIA approximation is almost negligible as can be seen from the values given in Table II, last column. Also, it is important to note that this difference in converged SCF energies is already present in the first iteration of the calculation, and remains constant throughout the iterations (conventional and MIA calculations also take the same number of iterations before reaching convergence). This allows us to conclude that the error estimate (18) gives the correct order of magnitude of the error in a 2e integral.

Finally, in Table III we compare the time difference with and without the MIA approximation for the build-up of the Fock matrix from a list of integrals. For a conventional calculation there is usually one list of 2e integrals. In a MIA calculation there are two lists of integrals: one of approximate integrals and a second list of corrections. The Fock matrix is built from the list of approximate integrals using formulae (19). The time needed to do so is given under the heading MIA. The time

Table II. Some examples of calculations with and without the MIA approach.

Molecule	Basis set	# Basis-functions	Percentage[a]	Energy Difference[b]
Glycerol	4-21G	70	44.3	−0.00042
Threonine	4-21G	90	40.5	−0.00035
Alanine–dipeptide	4-21G	114	34.8	−0.00050
Glycinealdehyde	6-311G	67	59.5	−0.00009
Methyl–ethylketone	6-311G	89	48.0	−0.00007
Serine	6-311G	112	43.0	−0.00028

[a]Percentage of 4-shell combinations in need of correction, calculated with respect to the actual number of 4-shell combinations after the neglect of small integrals (threshold at 10** − 7).
[b]Energy difference (in a.u.) as total energy (MIA approach) minus total energy (conventional approach).

Table III. Time needed to build the Fock matrix from a list of integrals in a conventional and a MIA calculation.

	MIA	Correction	Total	Refer	Gain (%)
Glycerol	131	302	433	613	20
Threonine	252	612	864	1347	35
Alanine–dipeptide	446	976	1422	2350	39
Glycine–aldehyde	115	279	394	494	20
Methyl–ethylketone	253	730	983	1400	30
Serine	466	1374	1840	3200	42

Source: From Ref. 16.

MIA. The time needed to add the corrections to the Fock matrix using the integrals from the correction list is also shown. The Total column sums the two previous values. These values are compared with the value needed for the build-up of the Fock matrix in a conventional calculation, given under Refer.

We see that for a calculation involving about 70 orbitals, the gain of time is negligible. Nevertheless, as the number of basis functions increases, we see that the percentage of time gained approaches 40%. Perhaps more important than the actual gain of about 1000 s in the largest calculation, is the fact that the gain of time shows a rapidly increasing trend when we go from a smaller to a larger molecule. The actual value of the percentage may change when the program is run on a different computer, because certain parts of the program may be optimized more on one type of computer than on another. However, the trend that our approach steadily gains over the conventional one, will remain constant.

We see from Table III that the corrections to the Fock matrix are time consuming, even for the largest calculation (serine, 6311G).

The extension, for the calculation of the corrections, from a conventional to a direct SCF approach[2] is quite natural, since in this type of approach the density matrix itself is replaced by its change between different iterations. Consequently, as the calculation converges, fewer integrals will need correction as judged by Eq. (2). The two largest calculations (serine, 6-311G; alanine-dipeptide, 4-21G) need 10 iterations to reach convergence. Table IV gives for each iteration the time needed to make the corrections in the conventional SCF approach and in the direct SCF approach. In the conventional approach, the corrections take the same amount of time in every iteration, which is no longer true in the direct SCF approach. In the latter the necessary integrals are recalculated in every iteration. As a result the time to build the Fock matrix increases even for the second cycle. However, iteration time decreases very rapidly as convergence is approached. Another striking phenomenon is the relatively small total gain in the case of serine, which can be attributed to the more time-consuming recalculation of the integrals of their high degree of contraction.

Table IV. Time (s) needed for each iteration in the calculation of serine and alanine dipeptide.

Iteration #	Serine (6-311G)		Alanine dipeptide (4-21G)	
	Direct	Conventional	Direct	Conventional
1	1374	1374	976	976
2	3324	.	1803	.
3	2251	.	1253	.
4	1636	.	966	.
5	1362	.	679	.
6	917	.	526	.
7	790	.	432	.
8	654	.	383	.
9	619	.	369	.
10	573	1374	355	976
Total time	13500	13740	7742	9760

In view of the preceding, the overall conclusion is that, for large calculations the direct SCF approach has a distinct time advantage for the calculation of the corrections.

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15. The name "Multiplicative Integral Approximation" was suggested by Dr. P. Pulay.

16. All calculations were performed on a Micro-VAX II. Therefore, the values given are somewhat different from those reported previously (5th International Congress on Quantum Chemistry, Montreal (Quebec), Canada 1985) for calculations performed on a VAX II/780.