

ON THE BEEBE-LINDERBERG TWO-ELECTRON INTEGRAL APPROXIMATION

I. RØEGGEN and E. WISLØFF-NILSEN

Institute of Mathematical and Physical Sciences, University of Tromsø, P.O. Box 953, 9001 Tromsø, Norway

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The Beebe-Linderberg two-electron integral approximation, which is generated by a Cholesky decomposition of the two-electron integral matrix ($\{\mu\nu|\lambda\sigma\}$), is slightly modified. On the basis of test calculations, two key questions concerning this approximation are discussed: The numerical rank of the two-electron integral matrix and the relationship between the integral threshold and electronic properties. The numerical results presented in this work suggest that the modified Beebe-Linderberg approximation might be considered as an alternative to effective core potential methods.

1. Introduction

Within an orbital framework the treatment of two-electron integrals in quantum chemistry presents particular problems: First, the computational effort in generating the integrals. Even if this step is not the most time-consuming one in a quantum chemical calculation, it certainly represents a non-negligible part of the total computational time. Second, the associated storage and retrieval problem. For a large molecule and/or a system where a large number of basis functions are used, this problem may well be the "bottleneck" of the calculation. Third, if electron correlation is to be taken into account, a partial or a complete transformation of the two-electron integrals must be performed.

The Beebe-Linderberg two-electron integral approximation (the BL procedure) [1] has as its main aim the purpose of reducing the computational effort involved in the evaluation and storage of two-electron integrals. The procedure is based on a Cholesky decomposition of the positive definite two-electron integral matrix. By a particular ordering of the decomposition procedure, it is possible to obtain a matrix with a numerical rank which is considerably smaller than the theoretical limit. The procedure's merits depend on this numerical rank. However, the resulting numerical rank seems in general to be larger than anticipated by Beebe and Linderberg. This is likely to be

the main reason why this integral procedure has not obtained widespread application.

In spite of a larger numerical rank than anticipated on the basis of the first few test cases, the BL procedure has certain advantages which seem to have been overlooked: First, the number of elements of the integral tables generated by the Cholesky decomposition which are of magnitude greater than the integral threshold is smaller than expected on purely theoretical grounds. By storing only those elements of the integral tables which have a magnitude greater than the threshold, the BL procedure might represent an alternative to effective core potential or pseudo-potential methods [2-7]. Second, for theoretical models which require only a partial integral transformation, the BL procedure represents a simpler way of generating the necessary transformed integrals than conventional procedures based on the original two-electron matrix.

The structure of the paper is as follows: In section 2 we describe the essential elements of the BL procedure. Section 3 is devoted to a short description of an adaptation of this integral approximation to the extended geminal models devised by Røeggen [8-12]. In section 4 we discuss, on the basis of numerical experience, two key questions concerning this integral approximation: the numerical rank of the two-electron integral matrix and the relationship between the integral threshold and electronic properties.

2. The BL procedure

The starting point is the two-electron integral matrix ($V_{\mu\nu,\lambda\sigma}$), defined as

$$V_{\mu\nu,\lambda\sigma} \equiv [\mu\nu|\lambda\sigma] = \langle \chi_\mu \chi_\lambda | 1/r_{12} | \chi_\nu \chi_\sigma \rangle, \quad (1)$$

where $\{\chi_\mu; \mu = 1, \dots, m\}$ is the set of primary orbitals. The matrix \mathbf{V} is positive definite. It can be decomposed by the Cholesky procedure [13] into a product of a lower triangular matrix \mathbf{L} and its transpose, i.e.

$$\mathbf{V} = \mathbf{L}\mathbf{L}^T. \quad (2)$$

In the description of the algorithm for the construction of \mathbf{L} , it is convenient to represent the double indices of a distribution $\chi_\mu^*(1)\chi_\nu(1)$ by a single index, i.e. we set $I \equiv (\mu, \nu)$. The form of the algorithm is as follows: For $J = 1, 2, \dots, M$, where M is the index of the last row, set

$$L_{JJ} = \left(V_{JJ} - \sum_{K=1}^{J-1} L_{JK}^2 \right)^{1/2} \quad (3)$$

and

$$L_{IJ} = \left(V_{IJ} - \sum_{K=1}^{J-1} L_{IK} L_{JK} \right) / L_{JJ}, \quad I = J+1, \dots, M. \quad (4)$$

In eqs. (3) and (4) the summations are to be omitted when the upper limit is zero. The column vectors of \mathbf{L} , $\{L_{IK}; I = K, \dots, M\}$, are called "integral tables" by Beebe and Linderberg. Wilkinson [13] has shown that this algorithm for the construction of \mathbf{L} is numerically very stable.

Beebe and Linderberg demonstrated that by an appropriate ordering of the indices only a small fraction of the \mathbf{L} matrix is needed in order to generate two-electron integrals with a fixed numerical accuracy. If the ordering of the indices is such that at any step in the procedure

$$L_{JJ}^2 \geq V_{NN} - \sum_{K=1}^{J-1} L_{NK}^2, \quad N = J+1, \dots, M, \quad (5)$$

the recurrence procedure can be terminated when

$$L_{JJ}^2 < \delta, \quad (6)$$

where δ is a preset threshold for the generation of the

integral tables. Beebe and Linderberg denoted the lowest value of J for which the inequality (6) is fulfilled, as the effective numerical rank of the two-electron integral matrix \mathbf{V} .

In a slight modification of the BL procedure we have neglected all elements of the integral tables which have a magnitude less than the integral threshold δ . In practice we have found that this last approximation leads to a drastic reduction in storage requirements even though this modified procedure requires that an index vector is stored for each integral table.

By returning to the original set of indices, we now have

$$[\mu\nu|\lambda\sigma] = \sum_{t=1}^{r_\delta} L_{\mu\nu;t} L_{\lambda\sigma;t}, \quad (7)$$

where r_δ is the effective numerical rank of the two-electron integral matrix. A large number of elements in a given integral table might be zero.

For a chosen orbital basis $\{\chi_\mu; \mu = 1, \dots, m\}$ we may then replace the two-electron operator by a sum of products of one-electron operators:

$$\frac{1}{r_{12}} \doteq \sum_{t=1}^{r_\delta} L_t(1) L_t(2), \quad (8)$$

where

$$\langle \chi_\mu | L_t | \chi_\nu \rangle = L_{\mu\nu;t}. \quad (9)$$

The replacement operator defined in eq. (8) will be particularly useful in approximation schemes where not all the transformed two-electron integrals are required.

3. Extended geminal models

The BL procedure is in a sense tailor-made for the extended geminal models devised by Røeggen [8–12]. In this section we sketch the essential features of the models which are needed for a discussion of the relationship between the integral threshold δ and electronic properties. A detailed description of computational aspects will be given elsewhere.

The particular model which we have adopted in this study is a recently proposed approximation scheme denoted the EXGEM4 model [14]. The main

features of the model are as follows:

For a closed-shell $2N$ -electron system we have the following ansatz for the electronic wavefunction:

$$\Phi^{\text{EXGEM4}} = \Phi^{\text{APSG}}$$

$$\begin{aligned} & + \sum_{K=1}^N M^{[N-1,1]} \mathcal{A}^{[2N]}(\Phi_{[K]}^{[2N-2]} \Omega_K^{[2]}) \\ & + \sum_{K < L}^N M^{[N-2,2]} \mathcal{A}^{[2N]}(\Phi_{[KL]}^{[2N-4]} \Omega_{KL}^{[4]}) \\ & = \Phi^{\text{APSG}} + \sum_{K=1}^N \Psi_K + \sum_{K < L}^N \Psi_{KL}. \end{aligned} \quad (10)$$

The first term in eq. (10) is the wavefunction corresponding to the APSG approximation (antisymmetric product of strongly orthogonal geminals), i.e.

$$\Phi^{\text{APSG}} = M^{[N]} \mathcal{A}^{[2N]} \left(\prod_{K=1}^N \Lambda_K(x_{2K-1}, x_{2K}) \right), \quad (11)$$

where $\mathcal{A}^{[2N]}$ is the antisymmetrizer and $M^{[N]}$ is a normalization constant defined by the equation

$$\langle \Phi^{\text{APSG}} | \Phi^{\text{APSG}} \rangle = 1. \quad (12)$$

In eq. (11) x_i represents the combined space and spin coordinates of electron i . The geminals $\{\Lambda_K\}$ are products of an orbital function and a singlet-coupled spin function, i.e.

$$\Lambda_K(x_1, x_2) = \Lambda_K(r_1, r_2) \theta_0(\sigma_1, \sigma_2). \quad (13)$$

The orbital space is partitioned into $N + 1$ orthogonal subspaces, one subspace for each electron pair and a common orbital space. The geminals used in the APSG approximation are defined in terms of the orbitals of the associated subspaces. By using natural orbitals, the spatial geminals can be written in the form

$$\Lambda_K(r_1, r_2) = \sum_{k=1}^{n_K} a_k^K \varphi_k^K(r_1) \varphi_k^K(r_2), \quad (14)$$

where n_K is the dimension of the orbital space associated with electron pair K .

The determination and the interpretation of the correction term Ψ_K in eq. (11) is such that the truncated wavefunction

$$\Psi^{[K]} = \Phi^{\text{APSG}} + \Psi_K \quad (15)$$

describes the correlated motion of electron pair K when the rest of the system is described by an APSG approximation. Similarly, the correction term Ψ_{KL} is in principle determined by the requirement that the truncated wavefunction

$$\Psi^{[KL]} = \Phi^{\text{APSG}} + \Psi_K + \Psi_L + \Psi_{KL} \quad (16)$$

should describe the correlated motion of the electron pairs K and L when the rest of the system is described by an APSG approximation. The EXGEM4 model [14] is characterized by a particular approximation for the correction terms Ψ_{KL} .

The energy can be evaluated within the framework of the method of moments. Since by construction we have

$$\langle \Phi^{\text{APSG}} | \Phi^{\text{EXGEM4}} \rangle = 1, \quad (17)$$

it follows

$$\begin{aligned} E^{\text{EXGEM4}} & = \langle \Phi^{\text{APSG}} | H \Phi^{\text{EXGEM4}} \rangle \\ & = E^{\text{APSG}} + \sum_{K=1}^N \epsilon_K + \sum_{K < L}^N \epsilon_{KL}, \end{aligned} \quad (18)$$

where

$$E^{\text{APSG}} = \langle \Phi^{\text{APSG}} | H \Phi^{\text{APSG}} \rangle, \quad (19)$$

$$\epsilon_K = \langle \Phi^{\text{APSG}} | H \Psi_K \rangle, \quad (20)$$

$$\epsilon_{KL} = \langle \Phi^{\text{APSG}} | H \Psi_{KL} \rangle, \quad (21)$$

and H is the Hamiltonian in question.

4. Test cases

In this section we shall discuss two key questions related to the BL procedure. In section 4.1 we display results concerning the effective numerical rank of the two-electron matrix as a function of the integral threshold δ . In section 4.2 we look at the relationship between the integral threshold and electronic properties.

4.1. The effective numerical rank of the two-electron integral matrix

As emphasized in section 1, one of the reasons for the lack of interest in the BL procedure seems to be

Table 1

The relationship between the integral threshold, δ , and the effective numerical rank, r_δ , of the two-electron integral matrix

Molecule	Integral threshold δ ^{a)}	Number of basis functions m	Numerical rank r_δ (r_δ/m)	Number of non-negligible elements in the integral tables
F ₂	10 ⁻²	48	109 (2.27)	6635
	10 ⁻³	48	151 (3.15)	19372
	10 ⁻⁴	48	211 (4.40)	37381
	10 ⁻⁵	48	251 (5.23)	54176
	10 ⁻⁶	48	292 (6.08)	69741
	10 ⁻⁷	48	348 (7.25)	86118
	10 ⁻⁸	48	392 (8.17)	97896
PH ₃	10 ⁻²	54	97 (1.80)	11723
	10 ⁻³	54	161 (2.98)	53188
	10 ⁻⁴	54	215 (3.98)	122791
	10 ⁻⁵	54	286 (5.30)	210609
	10 ⁻⁶	54	356 (6.59)	306626
	10 ⁻⁷	54	456 (8.44)	453188
	10 ⁻⁸	54	556 (10.30)	609243
O ₄	10 ⁻²	80	182 (2.28)	19776
	10 ⁻³	80	271 (3.39)	82999
	10 ⁻⁴	80	351 (4.39)	211660
	10 ⁻⁵	80	444 (5.55)	384514
	10 ⁻⁶	80	540 (6.75)	626315
CaF ₂ ^{b)}	10 ⁻²	107	234 (2.19)	23751
	10 ⁻³	107	361 (3.37)	90841
	10 ⁻⁴	107	483 (4.51)	220582
	10 ⁻⁵	107	593 (5.54)	381064
	10 ⁻⁶	107	685 (6.40)	561304
	10 ⁻⁷	107	832 (7.78)	847592

^{a)} In atomic units. ^{b)} Linear structure.

due to the disappointingly large effective numerical rank of the two-electron integral matrix. To throw some light on this aspect of the BL procedure, we present a few numerical test calculations on the molecules F₂, PH₃, O₄ and CaF₂. In table 1 we display the effective numerical rank, r_δ , of the two-electron integral matrices for these molecules for selected values of the integral threshold. We also display the number of non-negligible integral table elements, i.e. the number of elements such that $|L_{\mu\nu, \tau}| > \delta$.

Pertaining to the results in table 1 we would like to emphasize the following points: First, if the integral threshold is written as $\delta = 10^{-p}$, then the effective numerical rank, r_δ , in most cases satisfies the inequality

$$pm < r_\delta < (p+1)m, \quad (22)$$

where m is the number of basis functions. This result gives support to Beebe and Linderberg's conjecture that the effective numerical rank is considerably smaller than its theoretical maximum value, which is $\frac{1}{2}m(m+1)$. However, the relative value of the rank, i.e. $r_\delta / \frac{1}{2}m(m+1)$, which as a rule of thumb, satisfies the inequality

$$\frac{2p}{m+1} < \frac{r_\delta}{\frac{1}{2}m(m+1)} < \frac{2(p+1)}{m+1}$$

depends strongly both on the chosen integral threshold and the number of basis functions. On the other hand, these numerical results do not lend support to another conjecture by Beebe and Linderberg that the number of basis functions, m , is a likely value for the effective

numerical rank. The second point we would like to consider is the storage requirement of this modified BL procedure. In our version we store only those elements of the integral tables which have magnitude greater than the integral threshold δ . In the last column of table 1 we display the number of non-negligible elements for selected values of the integral threshold. If we consider CaF_2 , the number of stored elements is 847592 for $\delta = 10^{-7}$ au. The number of stored two-electron integrals computed with the same integral threshold, is approximately 4.0×10^6 . The storage requirement is therefore reduced by a factor of 4.7 compared with a conventional approach. We also note that if a larger value of δ is chosen, a further substantial reduction in the storage requirement can be obtained.

4.2. Test calculations on HF and Li_2

To examine the relationship between the integral threshold, δ , and electronic properties we select two small molecules with very different characteristics. The HF molecule has a large electric dipole moment, a small internuclear equilibrium distance and a large binding energy in the ground state. Li_2 on the other hand is a non-ionic molecule with a large internuclear distance in the ground state and a small binding energy. The ground state electronic potential curve has a sharp minimum for HF, while the Li_2 minimum is quite shallow.

For the HF calculations, we used van Duijneveldt's [15] (10s, 6p, 1d) GTO basis for fluorine contracted to [6s, 4p, 1d]. The contraction scheme for the s- and

p-type functions was $\langle 5, 1, 1, 1, 1, 1/3, 1, 1, 1 \rangle$, where the expansion coefficients of the atomic 1s and 2p orbitals are used as contraction coefficients. We used a d exponent of 1.0. For hydrogen we used van Duijneveldt's [15] (5s) GTO basis contracted to [4s] with the contraction scheme $\langle 2, 1, 1, 1 \rangle$. The expansion coefficients of the atomic 1s orbital were used as contraction coefficients. This set of s-type functions on hydrogen was augmented with a set of p functions with exponent 0.8. The basis set used for the Li_2 calculations was a [9s, 5p, 2d] set of contracted CTO [15].

The results for HF are displayed in tables 2 and 3. In table 2 we give the EXGEM4 energy components and the electric dipole moment as a function of the integral threshold, relative to values for $\delta = 10^{-8}$ au. All quantities in this table refer to the ground state of HF and a fixed internuclear distance of 1.70 au. In table 3 we present the equilibrium distance and binding energy of HF in the ground state as a function of the integral threshold for both the APSG and EXGEM4 models.

Regarding the results in tables 2 and 3, we would like to emphasize the following points: First, an integral threshold as large as $\delta = 10^{-2}$ au yields meaningful results for HF. Second, for $\delta \leq 10^{-5}$ au, the errors in the calculated equilibrium distance, binding energy and the electric dipole moment are insignificant and are orders of magnitude smaller than errors due to the use of an incomplete basis and to the approximate treatment of electron correlation. Third, the variationally determined quantities, i.e. those obtained by

Table 2

EXGEM4-energy components and electric dipole moment of HF as a function of the integral threshold, relative to the values for $\delta = 10^{-8}$ au a,b,c)

δ	ΔE	$\Delta \left(\sum_{K=1}^N \right) \epsilon_K$	$\Delta \left(\sum_{K < L}^N \right) \epsilon_{KL}$	$\Delta E(\text{EXGEM4})$	$\Delta \mu(\text{APSG})$
10^{-2}	-0.02497803	0.00006342	-0.00252042	-0.02743703	0.004614
10^{-3}	-0.00058644	0.00002062	-0.00007889	-0.00064471	0.000808
10^{-4}	-0.00007195	0.00000099	-0.00000638	-0.00007733	-0.000096
10^{-5}	0.00000132	0.00000021	0.00000172	0.00000326	-0.000011
10^{-6}	0.00000014	0.00000003	0.00000155	0.00000171	-0.000006
10^{-7}	0.00000001	0.00000001	0.00000113	0.00000155	-0.000002
10^{-8}	0.00000000	0.00000000	0.00000000	0.00000000	0.000000

a) All quantities in atomic units. b) Internuclear distance: $R = 1.70$ au. c) All calculations for the ground state.

Table 3

Equilibrium distance and binding energy of HF as a function of the integral threshold, relative to the values for $\delta = 10^{-8}$ au a,b,c)

δ	ΔR_e^{APSG}	$\Delta R_e^{\text{EXGEM4}}$	ΔD_e^{APSG}	$\Delta D_e^{\text{EXGEM4}}$
10^{-2}	-0.005016	-0.008456	-0.008909	-0.006293
10^{-3}	-0.000760	-0.000875	0.000319	0.000347
10^{-4}	-0.000101	-0.000340	-0.000009	-0.000011
10^{-5}	0.000007	0.000017	0.000000	-0.000002
10^{-6}	0.000000	0.000010	0.000000	-0.000004
10^{-7}	0.000000	0.000004	0.000000	-0.000002
10^{-8}	0.000000	0.000000	0.000000	0.000000

a) All calculations for the ground state of HF.

b) All quantities in atomic units.

c) For $\delta = 10^{-8}$ au, we have $R_e^{\text{APSG}} = 1.741419$ au, $R_e^{\text{EXGEM4}} = 1.747612$ au, $D_e^{\text{APSG}} = 0.180193$ au and $D_e^{\text{EXGEM4}} = 0.220894$ au. Experimental values: $R_e = 1.733$ au [16], $D_e = 0.225$ au [17].

the APSG model, seem to be slightly less sensitive to the value of the integral threshold than those generated by the EXGEM4 model. However, the overall picture from the calculations on HF is that a relatively large value of the integral threshold can be used with a negligible sacrifice in accuracy.

The results for Li_2 are displayed in table 4. These results and others not included in the table, suggest that one should be a bit cautious regarding the upper limit of the integral threshold. Calculations based on $\delta = 10^{-4}$ au gave disastrous results for Li_2 . Even though the APSG energy seemed to be meaningful, the single pair correction terms $\{\epsilon_K\}$ were far from their correct values. On the other hand, when $\delta \leq 10^{-5}$ au, the errors due to the selected integral threshold are (in magnitude) considerably smaller than the combined errors due to a finite basis set and the unavoidable approximate treatment of electron correlation.

5. Concluding remarks

The numerical results presented in section 4.2 suggest that an integral threshold as large as $\delta = 10^{-5}$ au can be used with a negligible loss in accuracy. If we then consider table 1 once more, it can be seen that the storage requirement of the BL procedure is substantially reduced compared with a conventional approach. For CaF_2 , the storage requirement is reduced by approximately a factor of 10 with an integral threshold of 10^{-5} au. Accordingly, we suggest that the modified BL procedure might be considered as an alternative to effective core potential methods.

When considering a comparison between the effective core potential methods and the modified BL procedure, we would like to emphasize the following points:

(1) Effective core potential methods yield no prac-

Table 4

Equilibrium distance and binding energy of Li_2 as a function of the integral threshold, relative to the values for $\delta = 10^{-8}$ au a,b,c)

δ	ΔR_e^{APSG}	$\Delta R_e^{\text{EXGEM4}}$	ΔD_e^{APSG}	$\Delta D_e^{\text{EXGEM4}}$
10^{-5}	0.000052	0.000230	0.000005	0.000062
10^{-6}	0.000065	0.000884	0.000000	-0.000004
10^{-7}	0.000000	0.000361	0.000000	-0.000005
10^{-8}	0.000000	0.000000	0.000000	0.000000

a) All calculations for the ground state of Li_2 .

b) All quantities in atomic units.

c) For $\delta = 10^{-8}$ au, we have $R_e^{\text{APSG}} = 5.099125$ au, $R_e^{\text{EXGEM4}} = 5.081332$ au, $D_e^{\text{APSG}} = 0.036587$ au and $D_e^{\text{EXGEM4}} = 0.036723$ au. Experimental values: $R_e = 5.051$ au [18] and $D_e = 0.0385 \pm 0.0005$ au [19].

tical reduction in storage requirements or computation time for systems comprising only of light atoms. The properties of the modified BL procedure can be utilized for any molecular system.

(2) Effective core potential methods are based on the frozen core approximation, with the non-local potentials involving the core electrons approximated by local potentials. These approximations might be too crude when there is a large rearrangement of the valence electrons, e.g. in a polar molecule. The modified BL procedure can be used in all-electron calculations thereby avoiding the problems created by a frozen core.

(3) The modified BL procedure is a "continuous" approximation, i.e. it can be gradually improved simply by reducing the integral threshold. In our opinion this is a very useful property since we can choose an integral threshold which is adapted to other approximations introduced in the calculation.

The implementation of this modified BL procedure for extended geminal models will be described elsewhere. We note additionally that use of second-order perturbation theory to incorporate electron correlation is particularly suited to the BL procedure. The necessary two-electron integrals are given by eq. (7) when the integral tables $\{(L_{\mu\nu};t)\}$ are replaced by the transformed two-electron integral tables.

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