Theor Chim Acta (1993) 86: 129–136

Theoretica Chimica Acta

Spin-projected Extended Hartree–Fock using a Valence Bond approach

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Received June 12, 1992/Accepted September 23, 1992

Summary. We describe spin-projected Extended Hartree–Fock calculations, performed with a Valence Bond Self-Consistent Field program. Potential energy curves are given for BH, BeH, and N_2. For BH the EHF function ranks well with the corresponding Spin-coupled and full CI wave functions. For BeH, the EHF function introduces spin contamination in the separated Be atom due to the rigidity of the wave function. This results in an inferior potential energy curve compared to Spin-coupled and full CI. The triple bond breaking in N_2 is again nicely described by EHF. The Extended Hartree–Fock method as suggested by Löwdin can be a feasible tool in describing bond breaking.

Key words: spin-projected Extended Hartree–Fock – Valence Bond

1. Introduction

The customary Hartree–Fock methods (RHF, UHF) possess the attractive quality that they present a simple physical model. These methods generally approximate the wave function by a single Slater determinant, which is the simplest function based on the independent-particle model with the correct symmetry [1]. Thus one has the opportunity to visualise the wave function in terms of orbitals, which is something sadly missed in more refined methods. There is a price to pay for this approach. Both the RHF and the UHF scheme have well-known inadequacies, amongst others: the RHF method fails to take into account properly the correlation between particles with different spins and the UHF method results in a wave function that is generally not a spin eigenfunction [2].

Löwdin [1] proposed the Extended Hartree–Fock (EHF) method to remedy these shortcomings, while preserving the physical simplicity of the ordinary HF methods. In the EHF method the wave function is a single Slater determinant projected to the desired symmetry. Löwdin [1] suggested a very elegant and general projection operator to accomplish this. As Löwdin saw it, the projection operator and the Slater determinant form a single conceptual entity [3]. The connection with the independent-particle model remains through the Hartree product. The most widely known form of the method is the spin-projected EHF method: the wave function is projected to the desired spin symmetry only. As in the UHF method, the restriction of doubly occupied spatial orbitals is not adhered to. In principle, the spin orbitals can be quite general, but for sake of simplicity they are mostly chosen to have pure alpha or beta spin [4]. The motive for this so-called different orbitals for different spins (DODS) idea is, quoting Löwdin [1]: "This new degree of freedom may now also be used for including correlation effects, since we may choose the two sets of orbitals associated with different spin functions in such a way that they let particles with different spins try to avoid each other".

In the EHF method the projected wave function is optimised variationally. A projection after the variational optimisation of the wave function usually gives an improvement in the energy too, but yields a rather poor potential energy surface that shows discontinuities [5].

The EHF method is conceptually simple, but never became very popular due to the complexity of the EHF equations [6, 7]. The amount of correlation energy that can be captured turned out to be less than expected [3]. High percentages (95%) are only reported for two-electron systems [8]. Mayer has written an extensive review article on the subject [8]. He considered the EHF method at the *ab initio* level to be best suited for the description of stretching and breaking of single bonds [5].

In this article we explore the EHF method by way of a Valence Bond (VB) approach. We show that EHF calculations can be done with a flexible VB program and shortly describe the program we use. For the dissociation of the singly bonded BH molecule and the BeH radical, we compare the performance of the EHF method to the Spin-coupled method [9] and the full CI approach. Finally we consider the dissociation of N_2 to show the capability of the EHF method to describe multiple bond breaking [8].

2. EHF and VB

A general one-configuration VB wave function is built of non-orthogonal orbitals (ϕ) and can be written as:

$$\Psi_{\mathrm{VB}} = \sum_k c_k \Psi_k = \sum_k c_k A \phi_1 \ldots \phi_N \Theta(N, S, M; k) \tag{1}$$

where A is the antisymmetrizer, and $\Theta(N, S, M; k)$ is an N-electron spin eigenfunction with eigenvalues S and M to $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$, respectively. The configuration state functions Ψ_k are also called structures. In modern VB calculations both the orbitals and the variational coefficients c_k are optimised. The dimension of Ψ_{VB} can be reduced if some structures are omitted, e.g. some spatial (core) orbitals are occupied twice. This becomes almost unavoidable in case of many electrons, because the number of independent structures grows very rapidly with the number of electrons [10].

One may distinguish two kinds of one-configuration Valence Bond approaches.

(a) In the Spin-coupled method [11] all the spin-couplings between the singly occupied orbitals of a one-configuration wave function are allowed for. As a result the method may describe any molecular dissociation process correctly. The singly occupied orbitals which result from a Spin-coupled calculation are uniquely defined and usually have a localised character.

(b) In the Generalised Valence Bond (GVB) method [12] in its usual form the non-orthogonality appears within pairs of orbitals only (strong orthogonality constraint). Mostly only one (perfect-pairing) structure is taken. This is sufficient for simple dissociation processes (one electron-pair bond).

Using the spin projection operator ($\boldsymbol{O}_S$) [1], the EHF wave function can be written as the projection of a single Slater determinant (Ψ_0) to the desired spin state (S):

$$\Psi_{\text{EHF}} = \boldsymbol{O}_S \Psi_0 = \prod_{L \neq S} \frac{[S^2 - L(L+1)]}{[S(S+1) - L(L+1)]} \Psi_0 \tag{2}$$

Although Eq. (2) is a very elegant expression, it is not easy to handle in case of many electrons. For other expressions and many properties see Pauncz [10, 13].

Starting from a one determinant Ψ_0 that is already an eigenfunction of S_Z with eigenvalues $M = S$ (the so-called principal case) and placing all μ orbitals that have alpha spin in the Hartree product first, the EHF wave function can be written as [10, 13]:

$$\Psi_{\text{EHF}} = \boldsymbol{O}_S |\phi_1 \ldots \phi_\mu \bar{\phi}_{\mu+1} \ldots \bar{\phi}_N| = \sqrt{\frac{2S+1}{\mu+1}} A\phi_1 \ldots \phi_N \Theta(N, S, S;1) \tag{3}$$

where $\Theta(N, S, S;1)$ is the branching-diagram function belonging to the highest spin path (i.e. the first one, if they are ordered according to the last-letter sequence [10]; cf. Fig. 3). This branching-diagram function can be interpreted as follows: first, all spin orbitals that have the same spin in the Hartree product are coupled together to the state of maximum multiplicity, next, these two subsystems are coupled to the desired spin state.

Comparison of Eqs. (1) and (3) suggests that the EHF wave function can be viewed as a VB wave function consisting of one special structure. The most compact way to express the EHF wave function in terms of structures asks for an ordering of the orbitals as in Eq. (3). If orbitals that have different spins in the Hartree product are exchanged, the EHF wave function becomes a fixed combination of several structures [10, 13]. Note that Eq. (3) is still usable if the starting determinant contains doubly occupied orbitals; μ and N then refer to the singly occupied orbitals only.

The EHF orbitals do inherit properties of the parent UHF wave function: orbitals that have the same spin before the projection may be made orthogonal to each other without loss of generality. Also, Amos and Hall [14] showed that the orbitals belonging to the different subsets can be transformed in such a way that they become biorthogonal (the pairing theorem). Due to their localised nature the paired orbitals are easily identified.

Smeyers et al. [15, 16] proposed a method related to EHF. Their omega function is obtained by a different spin projection operator, which has to be applied to a Hartree product of spin orbitals, followed by antisymmetrization (in that order, their projection operator does not commute with the antisymmetrizer). This results in a structure corresponding to the lowest spin path, which is for many purposes a good choice. We do not consider it here however, because it is not an EHF wave function in the original sense of the word, for it cannot be written as a projection of a single Slater determinant.

3. Method of calculation

The fact that the EHF wave function is a special case of a one-configuration VB function, implies that the EHF orbitals can be determined by a general VB program, that is capable of orbital optimisation. No additional programming effort is required. Using branching-diagram spin functions, the EHF wave function may be expressed as just one special structure, i.e. the structure with the highest spin path.

For all EHF and VB calculations we used the Valence Bond Self-Consistent Field (VBSCF [17, 18]) program TURTLE [19, 20]. We do not have to distinguish between even and odd number of electrons (cf. Mayer [8]).

The calculation of the non-orthogonal matrix elements is done using the generalised Slater–Condon rules [21] that are based on Löwdin's [22] general formula for matrix elements.

The orbital optimisation is based on the generalised Brillouin theorem [23] using the Super CI algorithm [24, 25]. Briefly: singly excited Brillouin states are formed by exciting orbitals of the reference wave function to a set of singly occupied and virtual orbitals [20]. A (non-orthogonal) CI calculation is performed with these Brillouin states and the corresponding coefficients are used in the subsequent orbital transformation. The process is repeated until convergence.

Due to the special form of the EHF wave function, Brillouin states resulting from excitations within the subsets of orbitals with the same spin in the Hartree product vanish. We did not exploit the pairing theorem.

The spatial parts of the corresponding singly occupied orbitals of opposite spin, become strongly non-orthogonal in the EHF calculations. If they are used to form Brillouin states as described above, the resulting non-orthogonal CI, that yields the orbital transformation coefficients, becomes nearly dependent, resulting in large CI coefficients. This may seriously hamper convergence. Therefore excitations to these orbitals were excluded in the EHF calculations, and the alpha and beta set orbitals were given their own realisation of the virtual space [20]. In our current preliminary implementation this doubles the size of the basis in the calculation. The convergence behaviour then is satisfactory: some 10 iterations for an accuracy of 10^{-8} Hartree in the energy.

This trick is not usable in the Spin-coupled calculations, since it would make the orbital basis excessively large: all active orbitals would need their own virtual space. Consequently, our Spin-coupled calculations required many iterations. It is therefore not useful within the present context to compare timings. We note that the EHF function contains all determinants present in the Spin-coupled function, so that in the basis of determinants both methods require the evaluation of the same matrix elements. However the orthogonalisations allowed by the special nature of the EHF function, may be exploited to make the EHF calculation much more economical, using the generalised Slater–Condon rules [21].

We used a DZP basis set, based on a van Duijneveldt [26] Gaussian basis set augmented with polarisation functions [27] and contracted to $(4sp)/[2sp]$ for H and $(9s5pd)/[4s2pd]$ for Be ($\zeta_d = 0.255$), B ($\zeta_d = 0.70$) and N ($\zeta_d = 0.80$). Cartesian d functions were used. As a reference serve full CI calculations (for BH, BeH), which were done with GAMESS [28].

We did not use projection operators to select the desired spatial symmetry of the wave function. The Σ^+ symmetry was achieved by restricting the basis in which the orbitals were expanded to orbitals of σ-symmetry. In N_2 the gerade symmetry was imposed.

4. Results and discussion

4.1. *BH*

The best potential energy curves for each method, with no orbitals restricted to be doubly occupied, are given in Fig. 1. All curves run quite parallel and the EHF and Spin-coupled curve give almost the same equilibrium distance, 2.42 and 2.41 Bohr, respectively. The full CI curve lies considerably lower and gives a shorter equilibrium distance of 2.37 Bohr.

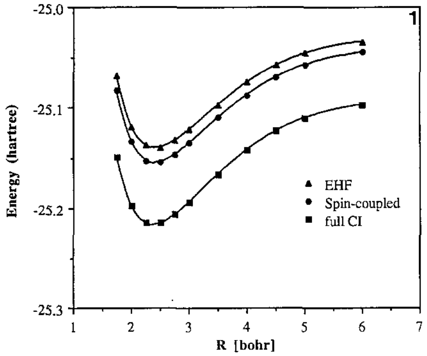
The total energies at 2.5 Bohr are −25.139544, −25.154075 and −25.214908 Hartree respectively for the EHF, Spin-coupled and full CI approaches. From this we can deduce binding energies at 2.5 Bohr of 288.8 kJ/mol, 299.3 kJ/mol and 324.3 kJ/mol, respectively.

The penalty on occupying the 1*s* core orbital twice is very small in EHF: maximal 0.13 mHartree (at 1.75 Bohr). It simplifies the calculation considerably, for the EHF wave function now consists of six instead of twenty determinants. For the Spin-coupled calculation, the rise in the total energy is not negligible, but constant: 10 mHartree over the whole range. If the 2*s* is also doubly occupied, the Spin-soupled and the EHF wave function coincide to a two-determinant GVB wave function. The energy curve rises another 6 to 8 mHartree (compared to the Spin-coupled curve). The binding energy at 2.5 Bohr is calculated at 295.3 kJ/mol.

At the dissociation limit the boron orbitals resulting from the EHF and Spin-coupled calculations are not pure *s*- and *p*-orbitals. The EHF and Spin-coupled calculations with all orbitals singly occupied gain 5.5 and 3.5 mHartree, respectively, by this symmetry breaking. The total wave function was consistently of Σ^+ symmetry.

4.2. *BeH*

The potential energy curves obtained with EHF, Spin-coupled and full CI are given in Fig. 2. In this case the EHF and Spin-coupled curves differ more substantially, the Spin-coupled curve being much closer to the full CI. Again the



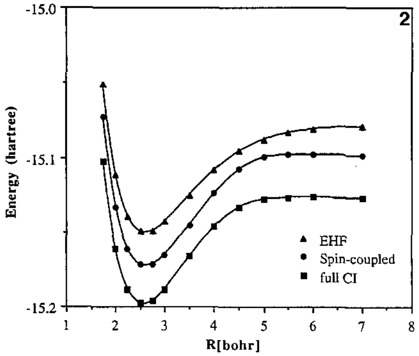


Fig. 1. Potential energy curves for BH

Fig. 2. Potential energy curves for BeH

equilibrium geometries differ very little between EHF and Spin-coupled (2.65 Bohr and 2.66 Bohr respectively), whereas the full CI predicts a shorter distance (2.62 Bohr). The total energies at 2.5 Bohr are −15.149776, −15.172055 and −15.197804 Hartree for EHF, Spin-coupled and full CI respectively. From these numbers we calculate dissociation energies ($E_{2.50} - E_{\infty}$) of 187.1 kJ/mol for EHF, 191.6 kJ/mol for Spin-coupled and 186.1 kJ/mol for full CI, again showing the EHF to produce very similar results to the Spin-coupled method, and surprisingly close to full CI.

As observed in the BH calculations, the Be atomic orbitals show symmetry breaking at infinite separation.

The Spin-coupled curve shows a slight barrier in the total energy in between the minimum and the dissociation limit, which is not found in the EHF calculation. This barrier is also found in previous Spin-coupled calculations [29] and is confirmed by our full CI calculations. The failure of the EHF method to reproduce this barrier may be explained by the fact that the Be atomic wave function is not a pure singlet spin state at infinite internuclear distance, but suffers some triplet contamination. This causes the curve to rise too steeply at larger internuclear distances (see Fig. 2).

The triplet contamination is easy to see by rearranging [13, 30] the orbitals in the EHF wave function (*h* corresponds to the hydrogen 1*s*) and giving the wave function in terms of branching-diagram functions in Fig. 3.

Only the fourth and fifth branching-diagram function describe a singlet Be atom. In the EHF function the coefficients of the branching-diagram functions are fixed, since it is one special CSF. In the Spin-coupled wave function the coefficients of the triplet contributions may be varied and thus be eliminated at infinite internuclear distance.

4.3. N_2

The EHF N_2 wave function with all orbitals singly occupied contains 3432 determinants. For both the EHF and the Spin-coupled calculations, we choose to keep the 1*s* and 2*s* doubly occupied, resulting in twenty determinants. The potential energy curves are given in Fig. 4. The curves are very similar. The equilibrium distance is, respectively, 2.10 and 2.12 Bohr. The energies at 2.1 Bohr are −109.027831 and −109.044583 Hartree for EHF and Spin-coupled respectively. At this distance the binding energies are 622.1 and 666.1 kJ/mol.

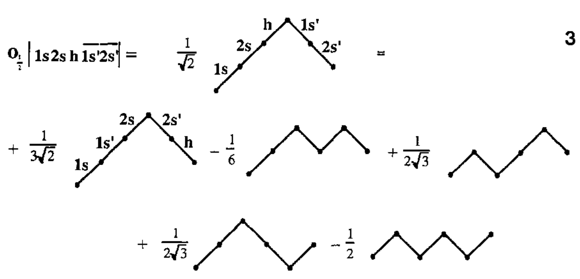


Fig. 3. The Extended Hartree–Fock function for BeH in terms of branching-diagrams

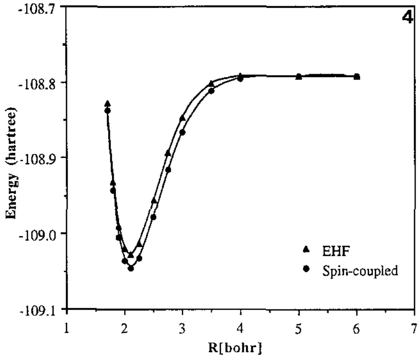


Fig. 4. Potential energy curves for N_2

The EHF spin-coupling scheme is well suited for this molecule: the two subsystems of maximum multiplicity now correspond to the valence electrons of the two nitrogen atoms. Both models lead to proper dissociation to the separate ^4S N atoms and yield in fact identical wave functions for an infinite distance between the nitrogen atoms.

5. Conclusions

We show that Extended Hartree–Fock wave functions may be routinely obtained, using a general Valence Bond program, with orbital optimisation.

The EHF method is capable of describing the dissociation of bonds in well-chosen systems.

In the case of BeH, the separated Be atom is not a pure spin state in the EHF model. This drawback is absent in the Spin-coupled wave function.

Both the EHF and the Spin-coupled approach display symmetry breaking in the separated atoms.

Acknowledgement. We thank J. H. Langenberg for stimulating discussion and useful suggestions.

References

1. Löwdin P-O (1955) Phys Rev 97:1509
2. Pauncz R (1967) Alternant molecular orbital method. WB Saunders, Philadelphia
3. Löwdin P-O (1966) The projected Hartree–Fock method. An extension of the independent-particle scheme. In: Löwdin (ed) Quantum theory of atoms, molecules, and the solid state. Academic Press, NY
4. Howat G, Lunell S (1976) Projected Hartree–Fock calculations on the ground and first excited $^1\Sigma_g^+$ states of the hydrogen molecule. In: Calais, Goscinski, Linderberg and Öhrn (eds) Quantum science. Plenum Press, NY
5. Mayer I (1978) Int J Quantum Chem 14:29
6. Handy NC, Rice JE (1988) Gradient theory; Its application to the Extended Hartree–Fock method. In: Carbó (ed) Quantum chemistry: basic aspects, actual trends, vol 62. Elsevier, Amsterdam
7. Mayer I, Kondász J (1975) Int J Quantum Chem 9:517
8. Mayer I (1980) The spin-projected Extended Hartree–Fock method. In: Advances in quantum chemistry, vol 12. Academic Press, NY
9. Gerratt J (1971) Adv atom mol Phys 7:141

10. Pauncz R (1979) Spin eigenfunctions, construction and use. Plenum Press, NY
11. Cooper DL, Gerratt J, Raimondi M (1991) Chem Rev 91:929
12. Goddard III WA (1967) Phys Rev 157:73
13. Pauncz R (1976) Investigations into the properties of projected spin functions. In: Calais, Goskinski, Linderberg, and Öhrn (eds) Quantum science, Plenum Press, NY
14. Amos AT, Hall GG (1961) Proc R Soc London 263:483
15. Smeyers YG, Delgado-Barrio G, Doreste-Suárez L, Martin-González JM (1986) Int J Quantum Chem 29:1705
16. Smeyers YG, Delgado-Barrio G, Doreste-Suarez L, Martin-González JM (1986) J Mol Struct 143:561
17. van Lenthe JH, Balint-Kurti GG (1980) Chem Phys Lett 76:138
18. van Lenthe JH, Balint-Kurti GG (1983) J Chem Phys 78:5699
19. Verbeek J, Langenberg JH (1989) TURTLE – an *ab initio* VB/VBSCF/VBCI program, Utrecht
20. Verbeek J (1990) Nonorthogonal orbitals in *ab initio* many-electron wavefunctions, Ph.D. Thesis, University of Utrecht
21. Verbeek J, Lenthe JHv (1991) Int J Quantum Chem 15:201
22. Löwdin P-O (1955) Phys Rev 97:1474
23. Levy B, Berthier G (1986) Int J Quantum Chem 2:307
24. Grein F, Chang TC (1971) Chem Phys Lett 12:44
25. Banerjee A, Grein F (1976) Int J Quantum Chem 10:123
26. van Duijneveldt FB (1971) Gaussian basis sets for the atoms H–Ne for use in molecular calculations, Internal Report. IBM Research Laboratory, San Jose, California
27. Dunning Jr TH, Hey PJ (1977) Gaussian basis sets for molecular calculations. In: Schaefer III (ed) Methods of electronic structure theory, vol 3. Plenum Press, NY
28. Dupuis M, Spangler D, Wendoloski JJ (1980) NRCC Program QG01, GAMESS, Lawrence Berkeley Laboratory; M. F. Guest, R. J. Harrison, J. H. van Lenthe and L. C. H. van Corler (1987) Theor Chim Acta 71:117; S. Zarrabian and R. J. Harrison (1989) Chem Phys Lett 81
29. Gerratt J, Raimondi M (1980) Proc R Soc Lond A 371:525
30. Ruttink PJA (1978) Theoret Chim Acta 49:223