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Application of the Extended Separated Pair Theory to the π-Electrons of Trans-Butadiene without Zero Differential Overlap Approximation

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Localized strongly orthogonal geminals are constructed by using the SCF orbitals of Parr and Mulliken. The best geminal product wave function is taken as zeroth order function and second order correction is calculated by the extended separated pair theory. 101.3% of the total "horizontal" correlation energy is obtained taking the result of the "full" CI calculation as standard. It is found that the contribution of terms neglected in the conventional separated pair theory is very important. The results are compared with those obtained by other variants of the Rayleigh-Schrödinger perturbation theory. As has been expected the result of the extended separated pair theory is superior to that of other perturbation theories discussed in the paper.

Lokalisierte stark orthogonale Geminale werden aus den SCF-Orbitalen von Parr und Mulliken konstruiert. Die beste Produktwellenfunktion aus Geminalen wird als Näherungsfunktion nullter Ordnung verwendet, und eine Korrektur zweiter Ordnung wird mit Hilfe der erweiterten Theorie der unabhängigen Elektronenpaare berechnet. 101,3% der gesamten „horizontalen" Korrelationsenergie wird erhalten, wenn man die „volle" CI-Rechnung als Standard nimmt. Es wird gefunden, daß der Beitrag von Termen, die in der konventionellen Theorie der unabhängigen Elektronenpaare vernachlässigt werden, sehr wichtig ist. Die Resultate werden mit denjenigen anderer Varianten der Rayleigh-Schrödinger Störungstheorie verglichen. Wie erwartet sind die Resultate der erweiterten Theorie der unabhängigen Elektronenpaare besser als diejenigen anderer hier diskutierter Störungstheorien.

Des géminales localisées fortement orthogonales sont construites en utilisant les orbitals SCF de Parr et Mulliken. La meilleure fonction d'onde produit de géminales est prise comme fonction d'ordre zéro et la correction du second ordre est calculée par la théorie des paires séparées étendue. Si l'on prend le résultat de l'I.C. «complète» comme référence, on obtient ainsi 101,3% de l'énergie de corrélation «horizontale». On trouve que la contribution des termes négligés dans la théorie des paires traditionnelle est très importante. Les résultats sont comparés à ceux obtenus à l'aide d'autres variantes de la théorie des perturbations de Rayleigh-Schrödinger. Comme il falleit s'y attendre, la théorie des paires séparées étendue donne un résultat supérieur à celui des autres traitements de perturbation.

1. Introduction

Recent calculations have shown that the separated pair (SP) theory using a single antisymmetrized product of strongly orthogonal geminals is able to account only for a fraction of the total correlation energy of the system [1–5]. Even in very favourable cases (two spatially strongly localized pairs as in Be and LiH) this fraction is only about 90% of the total correlation energy. Thus when accurate values are needed one has to go beyond the framework of the single geminal product scheme.

In a former paper the author has proposed a method in which the antisymmetrized product of the best possible strongly orthogonal geminals is regarded as zeroth order approximation and the remaining corrections may be calculated by perturbation theory (Extended SP theory) [6]. In principle this method can be applied to all systems if the best geminal product wave function is already known, but it will be convenient only when the corrections are really small, i.e., the higher order terms of the perturbation theory can be neglected.

Staemmler and Kutzelnigg have tested the SP theory (and other methods) on trans-butadiene using three different sets of integrals and the "zero differential overlap" approximation [7]. A single product of (localized) strongly orthogonal geminals was able to give about 90% of the total "horizontal" correlation energy in all cases.

It is felt that in order to obtain more appropriate information on the proportion of the "local" and "nonlocal" effects, the calculations should be carried out without the "zero differential overlap" approximation.

First the best possible (localized) geminal product wave function is constructed using the SCF orbitals (and integrals) of Parr and Mulliken [8]. The CI calculations using the same integrals had already been carried out by Pullman [9] and Nesbet [10]. The result of the "full" CI calculation of Nesbet, 2.32 eV, is taken as standard (100%) to which all results are referred. All second order corrections to the SP ground state are calculated by the extended SP theory. The second order corrections of other perturbation theories [10—14] are also evaluated and the results are compared with that obtained by the extended SP theory.

2. Calculation of the Localized Strongly Orthogonal Geminals

We start with the occupied and unoccupied SCF orbitals of Parr and Mulliken [8]

$$\begin{aligned} a_u &= 0.3540\,(\chi_1+\chi_4)+0.4687\,(\chi_2+\chi_3)\,,\\ b_g &= 0.5081\,(\chi_1-\chi_4)+0.4229\,(\chi_2-\chi_3)\,,\\ a'_u &= 0.6452\,(\chi_1+\chi_4)-0.4698\,(\chi_2+\chi_3)\,,\\ b'_g &= 0.5343\,(\chi_1-\chi_4)-0.7268\,(\chi_2-\chi_3)\,, \end{aligned} \tag{1}$$

where the χ's are ordinary atomic $2p_z$ orbitals on the four carbon atoms.

First we construct from the SCF orbitals equivalent localized orbitals by a unitary transformation

$$\begin{aligned} \varphi_L &= 2^{-\frac{1}{2}}(a_u+b_g)\,, & \varphi_R &= 2^{-\frac{1}{2}}(a_u-b_g)\,,\\ \varphi'_L &= 2^{-\frac{1}{2}}(a'_u+b'_g)\,, & \varphi'_R &= 2^{-\frac{1}{2}}(a'_u-b'_g)\,. \end{aligned} \tag{2}$$

Orbitals φ_L, φ'_L are localized in the region of carbon atoms 1, 2 (left side of the molecule) and orbitals φ_R, φ'_R in the region of carbon atoms 3, 4 (right side of the molecule). The functions φ_L, φ'_L and φ_R, φ'_R span two mutually perpendicular subspaces L and R respectively. In the following considerations we regard the localized orbitals φ, φ' as fixed. The best localized equivalent (singlet) geminals can be written in the form [15–18]

$$\begin{aligned} \psi_L &= [c_1 \varphi_L \varphi_L + 2^{-\frac{1}{2}} c_2(\varphi_L \varphi'_L + \varphi'_L \varphi_L) + c_3 \varphi'_L \varphi'_L]\, 2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)\,, \\ \psi_R &= [c_1 \varphi_R \varphi_R + 2^{-\frac{1}{2}} c_2(\varphi_R \varphi'_R + \varphi'_R \varphi_R) + c_3 \varphi'_R \varphi'_R]\, 2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)\,. \end{aligned} \tag{3}$$

The coefficients c_i can be determined by minimizing the energy expression or by solving the secular equation

$$\det|\mathscr{H}^L_{ij} - \delta_{ij}\mathscr{E}| = 0 \tag{4}$$

and the corresponding linear equations

$$\sum_j c_j(\mathscr{H}^L_{ij} - \delta_{ij}\mathscr{E}) = 0\,, \qquad i = 1, 2, 3\,. \tag{5}$$

Here $\mathscr{H}^L_{ij}$ denotes the matrix elements of the two-electron operator [19, 20]

$$\begin{aligned} \mathscr{H}^L = {} & H(1) + H(2) + r_{12}^{-1} \\ & + 2\int d3\, d4 [r_{13}^{-1}(1 - P_{13}) + r_{23}^{-1}(1 - P_{23})]\, \psi_R(3', 4)\, \psi_R(3, 4)\,. \end{aligned} \tag{6}$$

As $\mathscr{H}^L$ depends itself on the coefficients c_i the solution should be carried out by SCF techniques.

The energy E_0 calculated by the antisymmetrized product of the best possible geminals

$$\Phi_0 = 6^{-\frac{1}{2}} \sum_P (-1)^p P \psi_L(1, 2)\, \psi_R(3, 4) \tag{7}$$

is lower by 2.160 eV than the HF energy. It means that Φ_0 gives 93.1 % of the total correlation energy. This result is very similar to those obtained by Staemmler and Kutzelnigg [7].

It should be noted that the wave function Φ_0 is of ${}^1A_g$ symmetry, independently of the coefficients c_i.

The total *intrapair* correlation energy may be identified with the difference $E_0 - E_{\mathrm{HF}}$.

In addition to the best possible geminals ψ_L, ψ_R, Eqs. (4), (5) have another four (singlet) geminal solutions ψ'_L, ψ''_L and ψ'_R, ψ''_R. The coefficients of these geminals in terms of the localized orbitals φ are the following

	c_1	c_2	c_3
ψ :	0.96603	0.00434	−0.25838
ψ' :	−0.01716	0.99873	−0.04738
ψ'' :	0.25785	0.05020	0.96488

We obtain also two (triply-degenerate) triplet geminals

$$\left.\begin{array}{l} \psi_L^+ \\ \psi_L^- \\ \psi_L^0 \end{array}\right\} = 2^{-\frac{1}{2}}(\varphi_L \varphi'_L - \varphi'_L \varphi_L) \left\{\begin{array}{l} \alpha\alpha\,, \\ \beta\beta\,, \\ 2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)\,, \end{array}\right.$$

$$\left.\begin{array}{l} \psi_R^+ \\ \psi_R^- \\ \psi_R^0 \end{array}\right\} = 2^{-\frac{1}{2}}(\varphi_R \varphi'_R - \varphi'_R \varphi_R) \left\{\begin{array}{l} \alpha\alpha\,, \\ \beta\beta\,, \\ 2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)\,. \end{array}\right.$$

We have altogether 12 linearly independent geminals (6 in subspace L and 6 in subspace R).

Geminals belonging to different subspaces are orthogonal in the strong sense, whereas those belonging to the same subspace are mutually orthogonal in the usual sense.

The best possible geminals ψ_L, ψ_R have been transformed into natural orbital form. In terms of the natural orbitals ω_L, ω'_L, ω_R, ω'_R the spatial part of ψ_L and ψ_R consists only of two terms

$$d_1 \omega \omega + d_2 \omega' \omega' .$$

3. Second Order Correction of the Extended SP Theory

In the extended SP theory the wave function Ψ of a $2N$-electron system is expanded in terms of an orthonormal set

$$\Psi = \sum_K A_K \Phi_K , \tag{8}$$

where Φ_0 is the best SP wave function and the Φ_K, $K \neq 0$, are generalized product functions containing *one* group function from each of the N subspaces. The group functions are constructed from the single-particle functions in terms of which the corresponding geminals are expanded [6].

The generalized product functions can be divided into two groups:

The functions of type A are products of strongly orthogonal geminals (one geminal from each of the N subspaces). All these configurations conform to the strong orthogonality conditions (SC's). In former generalizations of the SP theory exclusively these functions were considered [17–21], although attention was called to the fact that this set of functions is not a complete one [22].

The functions of type B contain also group functions with particle number $n = 0, 1, 3, 4, \ldots, 2N$ ("Electron transfer" configurations). These functions are called SC violating configurations because the occupation numbers of at least two subspaces differ from 2.

It has been shown [6] that the functions of groups A and B form a complete set if the set of single-particle functions in terms of which the geminals are expanded is a complete one. In this case, using series (8) as trial function, we obtain E, the exact energy of the system. If the set of the single-particle functions is not a complete one we get an energy which is equal to that obtained by the "full" CI calculation.

The direct solution of a secular equation of very high (or infinite) order is out of question. Instead the Rayleigh-Schrödinger perturbation theory should be used.

For the second order correction we obtain the following expression

$$\varepsilon^{(2)} = - \sum_{K \neq 0} \frac{|H_{K0}|^2}{H_{KK} - H_{00}} ,$$

where

$$H_{KL} = \int \Phi_K^* H \Phi_L \, d\tau .$$

The *interpair* correlation energy may be identified with the difference $E - \mathrm{E}_0$. In our case Φ_0 is identical with (7).

Configurations of Type A

From the 12 linearly independent geminals we can construct 36 product functions containing one geminal from each of the two subspaces. Among these functions only those have nonzero matrix elements with Φ_0 which are doubly-excited and belong to the eigenvalue $S_z = 0$.

They are as follows ($\mathscr{A}$ denotes the antisymmetrizer)

$$\mathscr{A}|\psi'_L\psi'_R|, \tag{9}$$

$$\mathscr{A}|\psi''_L\psi'_R|, \quad \mathscr{A}|\psi'_L\psi''_R|, \tag{10}$$

$$\mathscr{A}|\psi''_L\psi''_R|, \tag{11}$$

$$\mathscr{A}|\psi^+_L\psi^-_R|, \quad \mathscr{A}|\psi^-_L\psi^+_R|, \tag{12}$$

$$\mathscr{A}|\psi^0_L\psi^0_R|. \tag{13}$$

Configurations (10), (11), representing three- and four-particle correlations, yield a completely negligible correction of -0.00014 eV. Configurations (9), (12) and (13) represent two-particle interpair correlations. Their total contribution of -0.045 eV, although relatively small, cannot be neglected. (It is 1.9% of the standard value.)

Configurations of Type B

We have 16 linearly independent functions with $S_z = 0$ which contain one single-particle and one three-particle function belonging to different subspaces ("One electron transfer" configurations). By using the natural orbitals ω, they can be expressed in determinantal form

$$\det|\omega_L\alpha\,\omega_L\beta\,\omega'_L\alpha\,\omega_R\beta|, \tag{14}$$

$$\det|\omega_L\alpha\,\omega_L\beta\,\omega'_L\alpha\,\omega'_R\beta|, \tag{15}$$

$$\det|\omega'_L\alpha\,\omega'_L\beta\,\omega_L\alpha\,\omega_R\beta|, \tag{16}$$

$$\det|\omega'_L\alpha\,\omega'_L\beta\,\omega_L\alpha\,\omega'_R\beta| \tag{17}$$

[the other 12 can be derived from (14)–(17) if we carry out the changes $\alpha \leftrightarrow \beta$, $L \leftrightarrow R$, or both changes simultaneously].

The contributions from these configurations to the second order correction are equally important. Their sum is -0.143 eV (6.2%).

We have two configurations which contain one four-electron function ("two electron transfer" configurations)

$$\det|\omega_L\alpha\,\omega_L\beta\,\omega'_L\alpha\,\omega'_L\beta|, \quad \det|\omega_R\alpha\,\omega_R\beta\,\omega'_R\alpha\,\omega'_R\beta|. \tag{18}$$

Their contribution is very small -0.002 eV.

In this way we obtain for $E_0 + \varepsilon^{(2)}$, the total correlation energy, -2.35 eV, that is 101.3% of the standard value.

It should be noted that most of the second order correction comes from the "one-electron transfer" configurations (14–17) which are left out in the conventional SP theory.

If we use the linear combination of configurations (7), (9–18) as trial function (including also the singly-excited configurations) we get for the correlation energy the standard value, 2.32 eV, of course.

4. Second Order Corrections Calculated by Other Variants of the Rayleigh-Schrödinger Perturbation Theory

By using the SCF orbitals and integrals of Parr and Mulliken we have calculated the second order correction to the Hartree-Fock ground state energy of trans-butadiene.

a) The usual (Møller-Plesset) variant of the Rayleigh-Schrödinger perturbation theory [11–14] gives only 47.7% of the total correlation energy.

b) The result obtained by the Epstein-Nesbet variant [10, 12–14], where the canonical SCF orbitals are used with the differences of the diagonal elements of the Hamilton operator in the denominators, is better and equals 82.7% of the total correlation energy (Nesbet's result).

c) A much more interesting result can be obtained if we use the localized SCF orbitals (2) instead of the canonical ones.

The configuration of the Hartree-Fock ground state in this representation has the following form

$$\det|\varphi_L\alpha\,\varphi_L\beta\,\varphi_R\alpha\,\varphi_R\beta|\,. \tag{19}$$

We have 18 doubly-excited configurations belonging to the eigenvalue $S_z=0$ which have nonzero matrix elements with the Hartree-Fock ground state.

Configurations which describe SP correlations

$$\det|\varphi'_L\alpha\,\varphi'_L\beta\,\varphi_R\alpha\,\varphi_R\beta|\,,\quad \det|\varphi_L\alpha\,\varphi_L\beta\,\varphi'_R\alpha\,\varphi'_R\beta| \tag{20}$$

give the second order correction -2.336 eV (100.7%).

The following 6 configurations represent interpair correlations which conform to the SC's (i.e., two electrons occupy L orbitals and two electrons R orbitals)

$$\det|\varphi_L\alpha\,\varphi'_L\beta\,\varphi_R\alpha\,\varphi'_R\beta|\,, \tag{21}$$

$$\det|\varphi'_L\alpha\,\varphi_L\beta\,\varphi_R\alpha\,\varphi'_R\beta|\,, \tag{22}$$

$$\det|\varphi_L\alpha\,\varphi'_R\beta\,\varphi'_L\alpha\,\varphi_R\beta|\,. \tag{23}$$

[The other three configurations can be derived from (21–23) by carrying out the changes $\alpha\leftrightarrow\beta$.] They give the second order correction -0.053 eV (2.3%).

We have 8 "one electron transfer" configurations (three electrons in L orbitals, one electron in R orbital and vice versa)

$$\det|\varphi_L\alpha\,\varphi_L\beta\,\varphi'_L\alpha\,\varphi'_R\beta|\,, \tag{24}$$

$$\det|\varphi_L\alpha\,\varphi_L\beta\,\varphi'_R\alpha\,\varphi'_L\beta|\,, \tag{25}$$

$$\det|\varphi'_L\alpha\,\varphi'_L\beta\,\varphi_L\alpha\,\varphi_R\beta|\,, \tag{26}$$

$$\det|\varphi'_L\alpha\,\varphi'_L\beta\,\varphi_R\alpha\,\varphi_L\beta|\,. \tag{27}$$

[The other four configurations can be derived from (24–27) by carrying out the changes $L\leftrightarrow R$.]

Their contribution to the second order correction is -0.016 eV (0.7%).

The contribution from the "two electron transfer" configurations (four electrons in L orbitals or four electrons in R orbitals)

$$\det|\varphi_L\alpha\,\varphi_L\beta\,\varphi'_L\alpha\,\varphi'_L\beta|\,,\qquad \det|\varphi_R\alpha\,\varphi_R\beta\,\varphi'_R\alpha\,\varphi'_R\beta| \tag{28}$$

is -0.005 eV (0.2%).

The total second order correction equals -2.410 eV which is 103.9% of the standard value.

It is apparently a much better result than those obtained by variants a) and b). Compared with the results of the extended SP theory it can be noticed, however, that variant c) underestimates the interpair correlations (by 5.0%) and overestimates the SP correlations (by 7.6%). The reason for this is as follows. The matrix element H_{0K} of configurations (19) and (20) is rather large, 0,1428 a.u., and the corresponding states are nearly-degenerate. As a consequence the terms

$$-\frac{|H_{0K}|^2}{H_{KK}-H_{00}}$$

are not small corrections.

5. Conclusion

The extended SP theory gives a very satisfactory result for the correlation energy of trans-butadiene if we terminate the perturbation series at the second order. The explanation of this fact is not very difficult. The SP theory picks out the dominant configurations which would give large corrections in the perturbation theory and treats them variationally. The effect of the less important configurations can be successfully taken into account by second order perturbation theory. It should be noted, however, that the contribution from the "one electron transfer" configurations to the second order correction will be enhanced in the extended SP theory due to the choice of the zeroth order wave function. Even the contribution from the singly- and triply-excited configurations (14), (17), which vanishes in ordinary second order perturbation theories, is significant. At the same time the contribution from the "two electron transfer" configurations will be reduced by half.

Now the question arises how the extended SP theory works for systems where the geminal product wave function is not a good approximation, i.e., where the intrapair and the interpair correlation energies are of the same order of magnitude. The enhancement of the contribution from the interpair correction, although less pronounced, will take place even in this case. It may happen, however, that we should include some third (and higher) order terms of the perturbation series if more accurate values are needed. The practicability of the method depends on the convergence of the perturbation expansion.

Finally it should be emphasized that in this paper the π-electron system of trans-butadiene serves as the simplest possible model on which several methods can be easily tested. The advantage of the extended SP theory over the "full" CI calculation becomes apparent only for systems where the number of configurations is very large provided that the localized geminals can be determined.

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References

1. Miller, K. J., and K. Ruedenberg: J. chem. Physics **43**, S 88 (1965).
2. Ebbing, D. D., and R. C. Henderson: J. chem. Physics **42**, 2225 (1965).
3. Ahlrichs, R., and W. Kutzelnigg: J. chem. Physics **48**, 1819 (1968).
4. — — Chem. Physics Letters **1**, 651 (1968).
5. — — Theoret. chim. Acta (Berl.) **10**, 377 (1968).
6. Kapuy, E.: Theoret. chim. Acta (Berl.) **6**, 281 (1966).
7. Staemmler, V., and W. Kutzelnigg: Theoret. chim. Acta (Berl.) **9**, 67 (1967).
8. Parr, R. G., and R. S. Mulliken: J. chem. Physics **18**, 1338 (1950).
9. Pullman, A.: J. Chim. physique **51**, 188 (1954).
10. Nesbet, R. K.: Proc. Roy. Soc. (London) A **230**, 312, 322 (1955).
11. Møller, C., and M. S. Plesset: Physic. Rev. **46**, 618 (1943).
12. Claverie, P. S., S. Diner, and J. P. Malrieu: Internat. J. Quantum Chem. **1**, 751 (1967).
13. Diner, S., J. P. Malrieu, and P. Claverie: Theoret. chim. Acta (Berl.) **8**, 390 (1967).
14. Malrieu, J. P., P. Claverie, and S. Diner: Theoret. chim. Acta (Berl.) **8**, 404 (1967).
15. Parks, J. M., and R. G. Parr: J. chem. Physics **28**, 335 (1958).
16. Parr, R. G.: Quantum theory of molecular electronic structure. New York: W. A. Benjamin, Inc. 1963.
17. McWeeny, R.: Proc. Roy. Soc. (London) A **253**, 242 (1959).
18. — Rev. mod. Physics **32**, 335 (1960).
19. Kapuy, E.: Acta Physic. Acad. Sci. Hung. **15**, 147 (1962).
20. — Physics Letters **1**, 205 (1962).
21. — Acta Physic. Acad. Sci. Hung. **12**, 351 (1960).
22. Lycos, P. G., and R. G. Parr: J. chem. Physics **24**, 1166 (1956).

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