

The 3-Centre Bond – Non Paired Spatial Orbital Method (NPSO)

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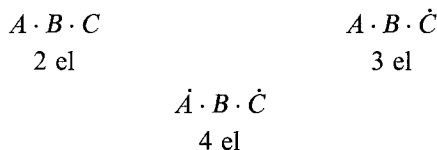
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The 3-centre bond with 2, 3 or 4 electrons has been reinvestigated using the non-paired spatial orbital (NPSO) method. Functions with two adjustable parameters in the spatial part of the wave function have been studied where previous work used only one parameter. In the 3 and 4 electrons cases where the spin part of the wave function can not be defined uniquely, use of two parameters makes the choice of spin function less crucial and is computationally more convenient than the use of parameters in the spin part of the wave function. In the 2 electron case the two adjustable parameters are a complex conjugate pair if the bond is highly ionic.

Die Dreizentrenbindung mit zwei, drei oder vier Elektronen ist erneut, und zwar mit einem auf nicht-gepaarten Ortsorbitalen beruhenden Verfahren, untersucht worden. Die Zahl der Parameter für die Einteilchenfunktion wurde gegenüber früher auf zwei erhöht. Im Fall von drei und vier Elektronen ist der Spin-Anteil nicht eindeutig definierbar und die jetzige Parameterzahl macht einerseits seine Festlegung nicht so gravierend und ist andererseits auch rechnerisch bequemer. Im Falle zweier Elektronen sind beide Parameter konjugiert komplex, wenn die Bindung stark ionisch ist.

La liaison à 3 centres avec 2, 3 ou 4 électrons a été réétudiée en utilisant la méthode des orbitales spatiales non appariées (NPSO). Des fonctions, avec deux paramètres ajustables pour la partie spatiale de la fonction d'onde, ont été utilisées là où les travaux précédents ne faisaient intervenir qu'un seul paramètre. Dans les cas à 3 et 4 électrons, lorsque la partie de spin de la fonction d'onde ne peut être définie d'une manière unique, l'emploi de deux paramètres rend le choix de la fonction de spin moins crucial et se trouve plus commode sur le plan du calcul que l'emploi de paramètres dans la partie de spin de la fonction d'onde. Dans le cas à deux électrons les deux paramètres ajustables forment un couple complexe conjugué si la liaison est fortement ionique.

The NPSO method for the 3-centre bond with 2, 3 or 4 electrons has been studied for a number of molecules [1–7]. The major problem is the difficulty of translating valence “pictures” such as



into wave functions.

In all three cases there are differences in the form of the spatial orbitals used and in the 3- and 4-electron cases there are differences in the spin functions used. In this paper, the relationship between these various functions is discussed using a more general NPSO wave function. This discussion will be limited to the symmetric 3-centre system $A-B-A$ with three atomic orbitals a , b and c centred on the three atoms. In each case it is convenient to expand wave functions into the full valence

bond basis sets. These are

$$\begin{aligned}
 \text{2 electrons} \quad \psi_1^{(2)} &= (a, b) + (b, a) + (b, c) + (c, b) \\
 \psi_2^{(2)} &= (a, c) + (c, a) \\
 \psi_3^{(2)} &= (a, a) + (c, c) \\
 \psi_4^{(2)} &= (b, b)
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 \text{3 electrons} \quad \psi_1^{(3)} &= 2(a, b, c) + (a, c, b) + (b, a, c) \\
 \psi_2^{(3)} &= (a, a, c) + (a, c, c) \\
 \psi_3^{(3)} &= (a, b, b) + (b, b, c) \\
 \psi_4^{(3)} &= (a, a, b) + (b, c, c)
 \end{aligned} \tag{2}$$

$$\begin{aligned}
 \text{4 electrons} \quad \psi_1^{(4)} &= (a, a, b, c) + (a, a, c, b) + (a, b, c, c) \\
 &\quad + (b, a, c, c) \\
 \psi_2^{(4)} &= (a, b, b, c) + (c, b, b, a) \\
 \psi_3^{(4)} &= (a, a, c, c) \\
 \psi_4^{(4)} &= (a, a, b, b) + (b, b, c, c)
 \end{aligned} \tag{3}$$

(a, b) , (a, b, c) and (a, a, b, c) are the usual Slater determinants with the spins in order $\alpha\beta$, $\alpha\beta\alpha$ and $\alpha\beta\alpha\beta$ respectively. The energies of approximate wave functions can be compared with the energy of the general linear combination of the above valence bond configurations. The latter is a full configuration interaction (CI) function for the basis set of atomic orbitals a , b and c .

The electrons in NPSO functions are assigned to either atomic orbitals or to bond orbitals containing an adjustable parameter k which can appear in a symmetric manner (NPSO-A) or an asymmetric manner (NPSO-B). For the 2-electron case

$$\psi_A^{(2)} = (a + kb, kb + c) + (kb + c, a + kb) \tag{4}$$

$$\psi_B^{(2)} = (a + kb, b + kc) + (b + kc, a + kb) + (ka + b, kb + c) + (kb + c, ka + b). \tag{5}$$

The most general NPSO function is one containing 2 adjustable parameters (NPSO-C)

$$\begin{aligned}
 \psi_C^{(2)} &= (a + k_1b, k_2b + c) + (k_2b + c, a + k_1b) \\
 &\quad + (a + k_2b, k_1b + c) + (k_1b + c, a + k_2b).
 \end{aligned} \tag{6}$$

Spatial functions containing 2 parameters will similarly be derived for the 3- and 4-electron cases.

2-Electron Case

The three functions NPSO-A, NPSO-B and NPSO-C expand in terms of the valence bond set as follows:

$$\psi_A^{(2)} = k\psi_1^{(2)} + \psi_2^{(2)} + 2k^2\psi_4^{(2)} \tag{7}$$

$$\psi_B^{(2)} = (1 + k^2)\psi_1^{(2)} + 2k\psi_2^{(2)} + 4k\psi_4^{(2)} \tag{8}$$

$$\psi_C^{(2)} = (k_1 + k_2)\psi_1^{(2)} + 2\psi_2^{(2)} + 4k_1k_2\psi_4^{(2)}. \tag{9}$$

Table 1

| | Allyl ⁺ | | HCO ₂ ⁺ | |
|--------|--------------------|-------------------------------|-------------------------------|--------------------------------|
| | $E - 2W_{2p}$ (eV) | | (eV) | |
| NPSO-A | -30.038 | $k = 0.711$ | -53.2715 | $k = 0.67$ |
| NPSO-B | -30.201 | $k = 0.252$ | -53.0099 | $k = 0.345$ |
| NPSO-C | -30.375 | $k_1 = 2.34$ $k_2 = 0.198$ | -53.4583 | $k_1 = 1.561$ $k_2 = 0.275$ |
| CI | -30.398 | | -53.5077 | |

Table 2

| | k_1 | k_2 | NPSO-A k | NPSO-B k |
|------------------------------|-------|-------|------------|------------|
| O ₃ ⁺ | 1.816 | 0.103 | 0.507 | 0.170 |
| NO ₂ ⁺ | 1.879 | 0.231 | 0.670 | 0.292 |

NPSO-C becomes NPSO-A if $k_1 = k_2$ and NPSO-B if $k_1 = 1/k_2$. All NPSO functions exclude $\psi_3^{(2)}$ and the 2 parameter function NPSO-C will be the best function of the general form

$$\psi^{(2)} = c_1\psi_1^{(2)} + c_2\psi_2^{(2)} + c_4\psi_4^{(2)}. \quad (10)$$

Since c_3 in the full CI function is generally small, NPSO-C will be a very good function indeed.

Solving (9) and (10) gives k_1 and k_2 as the roots:

$$\frac{c_1}{c_2} \pm \sqrt{\left(\frac{c_1}{c_2}\right)^2 - \frac{c_4}{2c_2}}. \quad (11)$$

Results for the π electron systems of Allyl⁺ and HCO₂⁺ using the integrals given by Hirst and Linnett [1, 2, 8] and by Kirchhoff, Farren and Linnett [7] are shown in Table 1.

For both Allyl⁺ and HCO₂⁺, k_1 and k_2 were evaluated using the correct coefficients in Eq. (10). Since c_3 is generally small, there is little error in using c_1 , c_2 and c_4 from published CI calculations when the full integrals are not readily available. The results in Table 2 use the CI coefficients from the work of Gould and Linnett [3] and Hirst and Linnett [5].

The interest in these results is not the energy of the 2-parameter function which is expected to be very good but the value of the parameters themselves. These show that the best result lies between NPSO-A and NPSO-B.

The parameters obtained from (11) are not always real. If the ionic function $\psi_4^{(2)}$ has a large contribution in the full CI function the parameters will be a complex conjugate pair. If k_1 and k_2 are replaced by $p \pm q$, $\psi_C^{(2)}$ can be rewritten as

$$\psi_C^{(2)} = p\psi_1^{(2)} + \psi_2^{(2)} + 2(p^2 - q^2)\psi_4^{(2)} \quad (12)$$

$\psi_C^{(2)}$ is thus $\psi_A^{(2)}$ with $k = p$ and an extra negative contribution from $\psi_4^{(2)}$. If the ionic function is more important than NPSO-A can allow, only an imaginary q

Table 3

| B ₂ H ₇ ⁻ | | |
|--|---------|---------------------------|
| E (a. v.) | | |
| NPSO-A | -1.4864 | $k = 2.15$ |
| NPSO-B | -1.4641 | $k = 1$ |
| NPSO-C | -1.4884 | $k_1 = 0.506 \pm i 1.589$ |
| CI | -1.4957 | |

can help. The 2-electron bridge region of the diborohydride ion studied by Duke and Linnett [6] shows this feature. The full CI function is

$$\psi_{\text{CI}}^{(2)} = 0.146 \psi_1^{(2)} + 0.121 \psi_2^{(2)} - 0.111 \psi_3^{(2)} + 0.525 \psi_4^{(2)} \quad (13)$$

c_4 is exceptionally high. An additional feature is that c_3 is large but negative. The function excluding $\psi_3^{(2)}$ is the NPSO-C function:

$$\psi^{(2)} = 0.061 \psi_1^{(2)} + 0.120 \psi_2^{(2)} + 0.665 \psi_4^{(2)} \quad (14)$$

which gives k_1 and k_2 as $0.506 \pm 1.589i$. Energies are shown in Table 3.

4-Electron Case

Following previous workers it is convenient to discuss the 4-electron case in terms of two functions which differ only in the spin terms, ψ_I and ψ_{II} . Both functions are correct eigenfunctions of S^2 .

The spin terms for ψ_I and ψ_{II} are

$$\begin{aligned} \text{for } \psi_I & \quad \{\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha\} \\ \text{for } \psi_{II} & \quad \{\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta\}. \end{aligned} \quad (15)$$

The spatial functions, similarly defined as in the 2-electron case, are

$$\psi_A^{(4)} = (a, a + kb, kb + c, c) \quad (16)$$

$$\psi_B^{(4)} = (a, a + kb, b + kc, c) + (a, ka + b, kb + c, c) \quad (17)$$

$$\psi_C^{(4)} = (a, a + k_1b, k_2b + c, c) + (a, a + k_2b, k_1b + c, c). \quad (18)$$

The spin function arising from the usual projection operator is $\psi_I + \psi_{II}$ and the most general spin function is defined as

$$\psi_{III} = \sin(\gamma\pi) \psi_I + \cos(\gamma\pi) \psi_{II}. \quad (19)$$

Expanded in terms of the VB basis set, the functions for the 4-electron case are

$$\psi_{I-A}^{(4)} = k\psi_1^{(4)} + 2k^2\psi_2^{(4)} + 2\psi_3^{(4)} \quad (20)$$

$$\psi_{II-A}^{(4)} = 2k\psi_1^{(4)} + k^2\psi_2^{(4)} + 4\psi_3^{(4)} \quad (21)$$

$$\psi_{I-B}^{(4)} = (1 + k^2) \psi_1^{(4)} + 4k\psi_2^{(4)} + 4k\psi_3^{(4)} \quad (22)$$

$$\psi_{II-B}^{(4)} = 2(1 + k^2) \psi_1^{(4)} + 2k\psi_2^{(4)} + 8k\psi_3^{(4)} \quad (23)$$

$$\psi_{I-C}^{(4)} = (k_1 + k_2) \psi_1^{(4)} + 4k_1k_2\psi_2^{(4)} + 4\psi_3^{(4)} \quad (24)$$

$$\psi_{II-C}^{(4)} = 2(k_1 + k_2) \psi_1^{(4)} + 2k_1k_2\psi_2^{(4)} + 8\psi_3^{(4)}. \quad (25)$$

The general spin function for ψ_C is thus

$$\begin{aligned} \psi_{III-C}^{(4)} = \{ \sin(\gamma\pi) + 2 \cos(\gamma\pi) \} \{ (k_1 + k_2) \psi_1^{(4)} + 4 \psi_3^{(4)} \} \\ + \{ 4 \sin(\gamma\pi) + 2 \cos(\gamma\pi) \} k_1 k_2 \psi_2^{(4)}. \end{aligned} \quad (26)$$

This is identical to the complete CI function with ψ_4 excluded. The coefficient of ψ_4 in the complete CI function is normally small. ψ_{III-C} is over determined. Only two parameters are necessary to define the best function and the general spin functions arising from ψ_A and $\psi_B - \psi_{III-A}$ and ψ_{III-B} are identical when the optimum values of k and γ are chosen. The variation of k_1 and k_2 with γ in ψ_{III-C} is however of interest. Defining

$$\psi_{III-C}^{(4)} = c_1 \psi_1^{(4)} + c_2 \psi_2^{(4)} + c_3 \psi_3^{(4)} \quad (27)$$

and

$$a = \frac{2 \sin(\gamma\pi) + \cos(\gamma\pi)}{2 \{ \sin(\gamma\pi) + 2 \cos(\gamma\pi) \}} \quad (28)$$

and solving (26) and (27) gives k_1 and k_2 as the roots

$$2C_1/C_3 \pm \sqrt{4 \left(\frac{C_1}{C_3} \right)^2 - \frac{C_2}{aC_3}}$$

k_1 and k_2 are real only for values of γ such that $a > \frac{C_2 C_3}{4 C_1^2}$ or $a < 0$. Allyl⁻ and HCO₂⁻, using the integrals given by Hirst and Linnett [1, 2, 8] and by Kirchhoff, Farren and Linnett [7], have been studied in some detail. k_1 and k_2 for Allyl⁻ plotted against γ are shown in Fig. 1. The region with k_1 and k_2 complex is small, lying between $\gamma = 0.85$ and $\gamma = 0.92$. Similar results are obtained for HCO₂⁻.

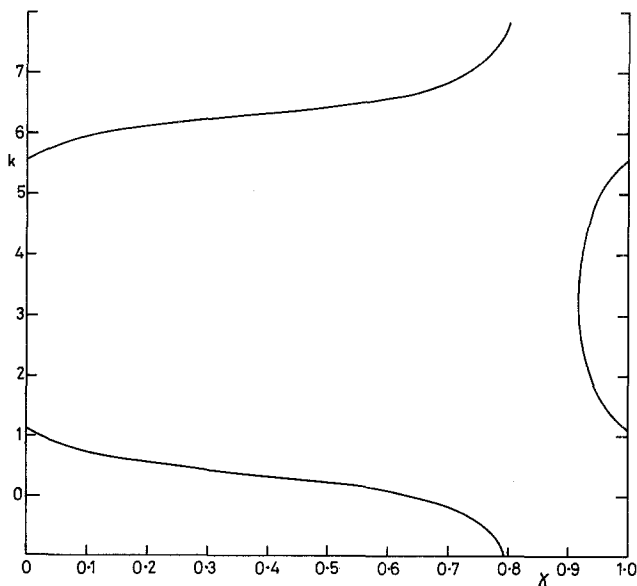


Fig. 1. Allyl⁻ - k_1 and k_2 as functions of γ for best NPSO function

These results suggest that the 4-electron case would be better approached with a simple spin function, satisfying the S^2 operator and the use of two parameters in the spatial function, rather than with only one parameter in the spatial function and the general spin function. In larger problems where it is not always convenient to expand NPSO functions in terms of a VB basis set, a simple spin function would ease the computational effort even though extra parameters are introduced in the spatial part of the function. No physical interpretation can be given to the value of the spatial parameters which depend on the choice of the spin function.

$\psi_C^{(4)}$ is similar to $\psi_A^{(4)}$ but with a smaller contribution from $\psi_2^{(4)}$. A larger contribution from $\psi_2^{(4)}$ than $\psi_A^{(4)}$ allows could be achieved if necessary, as in the 2-electron case, with k_1 and k_2 as a complex conjugate pair.

3-Electron Case

The 3-electron case, like the 4-electron case, has no unique spin form. ψ_I and ψ_{II} are both correct eigenfunctions of S^2 , but differ in the choice of spin terms

$$\begin{aligned} \text{for } \psi_I & \quad \{\alpha\beta\alpha - \alpha\alpha\beta\} \\ \text{for } \psi_{II} & \quad \{\alpha\beta\alpha - \beta\alpha\alpha\}. \end{aligned} \quad (29)$$

Similar spatial functions to those employed for the 4-electron case are

$$\psi_C^{(3)} = (a, a + k_1 b, k_2 b + c) - (c, c + k_1 b, k_2 b + a) \quad (30)$$

$\psi_A^{(3)}$ is $\psi_C^{(3)}$ with $k = k_1 = k_2$ and $\psi_B^{(3)}$ is $\psi_C^{(3)}$ with $k = k_2 = 1/k_1$. Expansion in terms of the VB basis set gives

$$\psi_{I-A}^{(3)} = k\psi_1^{(3)} + \psi_2^{(3)} + 2k^2\psi_3^{(3)} + k\psi_4^{(3)} \quad (31)$$

$$\psi_{II-A}^{(3)} = k\psi_1^{(3)} + 2\psi_2^{(3)} + k^2\psi_3^{(3)} + 2k\psi_4^{(3)} \quad (32)$$

$$\psi_{I-B}^{(3)} = \psi_1^{(3)} + k\psi_2^{(3)} + 2k\psi_3^{(3)} + k^2\psi_4^{(3)} \quad (33)$$

$$\psi_{II-B}^{(3)} = \psi_1^{(3)} + 2k\psi_2^{(3)} + k\psi_3^{(3)} + 2k^2\psi_4^{(3)} \quad (34)$$

$$\psi_{I-C}^{(3)} = k_1\psi_1^{(3)} + \psi_2^{(3)} + 2k_1k_2\psi_3^{(3)} + k_2\psi_4^{(3)} \quad (35)$$

$$\psi_{II-C}^{(3)} = k_1\psi_1^{(3)} + 2\psi_2^{(3)} + k_1k_2\psi_3^{(3)} + 2k_2\psi_4^{(3)}. \quad (36)$$

The most general spin function is $\psi_{III}^{(3)}$ where

$$\psi_{III} = \sin(\gamma\pi)\psi_I + \cos(\gamma\pi)\psi_{II} \quad (37)$$

$\psi_{III-C}^{(3)}$ is identical to the complete CI function at the optimum values of γ , k_1 and k_2 . The interest in the case lies in the variation of E (for optimum values of k_1 and k_2) as a function of γ . Fig. 2 shows this variation for the Allyl radical along with the variation of E (for optimum k) for $\psi_{III-A}^{(3)}$ and $\psi_{III-B}^{(3)}$ as a function of γ . The energy scale shown is greatly enlarged to show the behaviour near to the CI energy. $\psi_{III-A}^{(3)}$ gives a good energy only for a very narrow range of γ . For γ in the range 0–0.5, the energy of $\psi_{III-A}^{(3)}$ is between –25.6 and –27.1. $\psi_{III-B}^{(3)}$ gives a good energy for positive combinations of ψ_I and ψ_{II} . $\psi_{III-C}^{(3)}$ however behaves in a very interesting manner. For γ between 0 and 0.643 (the latter point being where $\psi_{III-A}^{(3)}$ reaches its best result) the energy is remarkably independent of the choice

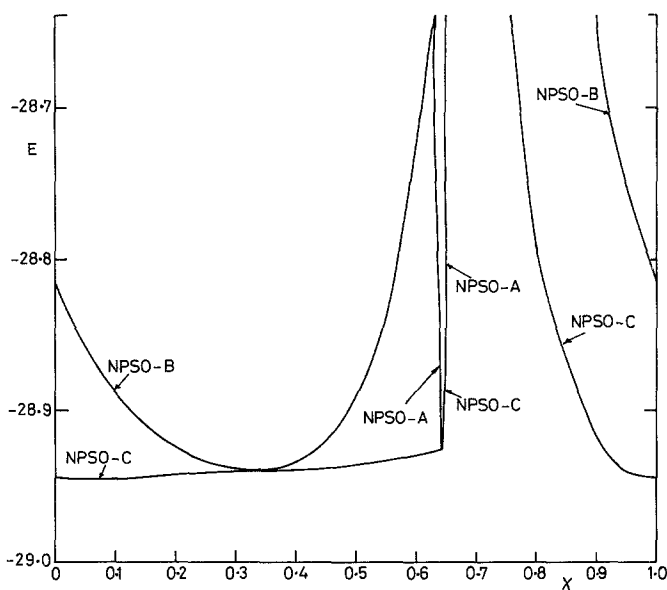


Fig. 2. Allyl radical – energy as function of γ for NPSO-A, NPSO-B and NPSO-C

of γ . For $\gamma > 0.643$ the energy rises although by obviously keeping below the energy of both $\psi_{III-A}^{(3)}$ and $\psi_{III-B}^{(3)}$ the wave function is still good. Similar results have been found for the HCO_2 radical.

The conclusion here is similar to that in the 4-electron case. If a simple spin function is chosen, satisfying the S^2 operator, variation of two spatial parameters will give a good result and will be computationally easier than choosing one spatial parameter and one parameter to give the most general spin function. In $\psi_{III-A}^{(3)}$ the energy is highly critical on the choice of γ . This is not found for $\psi_{III-B}^{(3)}$ but $\psi_{III-C}^{(3)}$ behaves consistently better. Since the NPSO functions include all four VB basis functions, three parameters are needed to achieve the best NPSO function while only two were required in the 2 and 4 electron cases. Two parameters in the spatial functions appear to give good results unless the spin function choice is a particularly poor one.

Conclusion

This work using two parameters in the spatial part of the function rather than one as previously used leads to very good wavefunctions. This is expected in view of the increased flexibility in the function. The important result is that the use of a greater number of parameters in the spatial part of NPSO wavefunctions may resolve some of the problems and complexity that arise from the nonunique choice of the spin terms. This study of the simple 3-centre system suggests that providing the S^2 operator is satisfied the choice of spin terms is not crucial if sufficient parameters are included in the spatial part of the wavefunction. In certain cases with high contributions from ionic terms the spatial parameters need to be considered in complex conjugate pairs.

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