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Commentationes

The Method of Non-Paired Spatial Orbitals: Naphthalene and Azulene

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The method of non-paired spatial orbitals (NPSO) is applied to the π-electron systems of naphthalene and azulene. Calculations are made without spin projection and with the annihilation of the triplet component. The method leads to a substantial lowering of the energy for both molecules and for azulene the one parameter NPSO function gives results similar to the much more complicated alternant molecular orbital method. A form of NPSO wavefunction which can be used with modest effort is proposed. It is shown that the NPSO wavefunctions for these molecules can be reasonably written using a parameter deduced from calculations on smaller systems.

Die Methode der ungepaarten räumlichen Orbitale (NPSO) wird auf das π-Elektronensystem des Naphthalins und des Azulens angewendet. Die Berechnungen werden ohne Spinprojektion durchgeführt; die Tripletkomponente wird beseitigt. Die Methode führt zu einer bedeutenden Verringerung der Energie für beide Moleküle; für Azulen ergibt die NPSO-Funktion mit einem Parameter ähnliche Ergebnisse wie mit der weit aufwendigeren Methode der alternierenden Molekülorbitale. Es wird eine Form der NPSO-Wellenfunktion vorgeschlagen, die mit geringem Aufwand benutzt werden kann. Es wird gezeigt, daß die NPSO-Wellenfunktion für die genannten Moleküle mit Hilfe eines Parameters dargestellt werden kann, der aus Berechnungen an kleineren Systemen stammt.

1. Introduction

An effective way of calculating molecular wavefunctions which make allowance for electron correlation is to use the method of "different orbitals for different spins" (DODS) in which electrons of α and β spins are assigned to spatially different orbitals [1]. However, departure from doubly filled orbitals does mean that a spin eigenfunction can no longer be written as a single Slater determinant. The unrestricted Hartree-Fock method [2] overcomes this problem by minimising the energy of a single determinant in which electrons of different spins occupy different orbitals and then, if required, generating a spin eigenfunction by the use of a projection operator [1]. This procedure has been criticised on the grounds that after projection the wavefunction will not necessarily correspond to an energy minimum [3]. A more satisfactory, but much more difficult procedure is the extended or projected Hartree-Fock method in which a spin eigenfunction is generated first and the energy then optimised [1].

In view of the great difficulty of calculating optimum DODS wavefunctions there has been much interest in methods for which it is possible to work with a spin eigenfunction and to optimise the energy with respect to a small number of adjustable parameters. The aim of such work is to obtain wavefunctions which approximate closely to those which would be obtained by a complete configuration interaction (CI) calculation. As the number of electrons considered increases, the number of configurations to be included in a CI calculation rapidly becomes unmanageable. Because of the slow convergence of CI methods and of the fact that it is not easy to select the most important contributions to the wavefunction, alternative methods for including electron correlation are desirable.

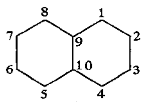
Two such methods are the "alternant molecular orbital" method (AMO) introduced by Löwdin [1] and reviewed in detail by Pauncz [4] and the method of "non-paired spatial orbitals" (NPSO) suggested by Linnett and his co-workers [5–8]. It is relatively easy to perform complete CI calculations for molecules containing up to six electrons and it is therefore possible to assess how closely the DODS wavefunctions approximate to the CI calculation. The AMO and NPSO methods both give energies close to the CI energies for these small systems. For example, in the case of benzene, the AMO method [9] gives 90% of the energy depression obtained by the complete CI calculation [10] and the NPSO method [6] gives 97% of the lowering. In general the NPSO method seems to be superior for systems containing up to six electrons [4]. Both methods work well for delocalized systems and for benzene the results are much better than those obtained by the separated pair calculation of Ebbing and Poplawski [20] which only gave 64% of the energy lowering of the complete CI calculation.

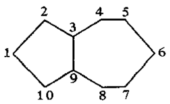
The AMO method has recently been shown to be successful for the ten electron systems of naphthalene [11] and azulene [12] and the results of preliminary NPSO calculations on naphthalene [8] were encouraging. This paper presents the application of the NPSO method to azulene and more extensive calculations on naphthalene. This work has two aims. Firstly we wish to investigate the feasibility of applying the NPSO method to larger systems and to evaluate its performance. Secondly, Empedocles and Linnett [7] showed that for several hydrocarbon π-electron systems the energy is minimised when the adjustable parameter k is in the region of 4 and that no serious errors would be introduced by assuming $k=4$ for the systems they considered. It is of interest to see if this value of k can also be used for these ten electron systems.

2. Method

The basis of the NPSO method is that a single determinantal wavefunction is formed by assigning electrons as far as possible to semi-localized bonding orbitals, which are usually combinations of two atomic orbitals from adjacent atoms, in such a way as to span the bonding regions of the molecule. As far as possible the spins are assigned so that electrons in adjacent semi-localized bonding orbitals have opposite spins.

For naphthalene and azulene the wavefunctions are constructed from the $2p\pi$ orbitals χ_i located on the carbon atoms. The numbering schemes for both molecules are indicated in the figure.





As will be apparent from the subsequent discussion the calculation would be very much easier if the initial single determinantal wavefunction had the symmetry of the molecule. Unfortunately the preliminary calculations on naphthalene [8] indicated that a symmetrical starting determinant is not sufficiently flexible. Previous work suggests that we should use the following initial single determinantal NPSO wavefunctions for these molecules:

Naphthalene

$$\begin{aligned}\psi_{\mathrm{I}}=A[&(\chi_1+k\chi_2)\alpha\ (\chi_3+k\chi_4)\alpha\ (\chi_{10}+k\chi_5)\alpha\ (\chi_6+k\chi_7)\alpha\\ &(\chi_8+k\chi_9)\alpha\ (\chi_2+k\chi_3)\beta\ (\chi_4+k\chi_{10})\beta\ (\chi_5+k\chi_6)\beta\\ &(\chi_7+k\chi_8)\beta\ (\chi_9+k\chi_1)\beta]\,,\end{aligned} \tag{1}$$

Azulene

$$\begin{aligned}\psi_{\mathrm{I}}=A[&(\chi_1+k\chi_2)\alpha\ (\chi_3+k\chi_4)\alpha\ (\chi_5+k\chi_6)\alpha\ (\chi_7+k\chi_8)\alpha\\ &(\chi_9+k\chi_{10})\alpha\ (\chi_2+k\chi_3)\beta\ (\chi_4+k\chi_5)\beta\ (\chi_6+k\chi_7)\beta\\ &(\chi_8+k\chi_9)\beta\ (\chi_{10}+k\chi_1)\beta],\end{aligned} \tag{2}$$

where A is the antisymmetrizer and k is a parameter to be varied to optimise the energy.

However determinantal wavefunctions constructed in this way are not satisfactory because they are not spin eigenfunctions and do not transform as one of the irreducible representations of the point group of the molecule. A wavefunction having the correct symmetry may be generated by the application of a symmetry projection operator [13] $P^{(j)}$

$$P^{(j)}=\frac{l_j}{h}\sum_R[\chi^{(j)}(R)]^*P_R \tag{3}$$

where j labels the irreducible representation, l_j is the dimensionality of the representation, h is the order of the group and $\chi^{(j)}(R)$ is the character of the group operator P_R for the j^{th} irreducible representation. Applying the operator for the A_{1g} representation to the naphthalene wavefunction (1) gives

$$\psi=[\psi_{\mathrm{I}}+\psi_{\mathrm{II}}-\psi_{\mathrm{III}}-\psi_{\mathrm{IV}}]\,, \tag{4}$$

where

$$\begin{aligned}\psi_{\mathrm{II}}=A[&(k\chi_1+\chi_2)\alpha\ \ (k\chi_3+\chi_4)\alpha\ \ (k\chi_{10}+\chi_5)\alpha\\ &(k\chi_6+\chi_7)\alpha\ \ (k\chi_8+\chi_9)\alpha\ \ (k\chi_2+\chi_3)\beta\\ &(k\chi_4+\chi_{10})\beta\ \ (k\chi_5+\chi_6)\beta\ \ (k\chi_7+\chi_8)\beta\\ &(k\chi_9+\chi_1)\beta]\end{aligned} \tag{5}$$

and ψ_{III} and ψ_{IV} are obtained from ψ_{I} and ψ_{II} respectively by interchanging α and β spins.

For azulene the application of the symmetry projection operator for the A_1 representation gives

$$\psi=\psi_{\mathrm{I}}-\psi_{\mathrm{IV}}\,, \tag{6}$$

where

$$\begin{aligned}\psi_{\mathrm{IV}}=A[(k\chi_1+\chi_2)\beta\ \ (k\chi_3+\chi_4)\beta\ \ (k\chi_5+\chi_6)\beta\ \ (k\chi_7+\chi_8)\beta\\ (k\chi_9+\chi_{10})\beta\ \ (k\chi_2+\chi_3)\alpha\ \ (k\chi_4+\chi_5)\alpha\\ (k\chi_6+\chi_7)\alpha\ \ (k\chi_8+\chi_9)\alpha\ \ (k\chi_{10}+\chi_1)\alpha].\end{aligned}\tag{7}$$

A spin eigenfunction can then be generated by the application of a spin projection operator [1]. The singlet wavefunction ψ_s for the A_{1g} state of naphthalene or the A_1 state of azulene can now be written as

$$\psi_s=O_s(\psi_{\mathrm{I}}+\psi_{\mathrm{II}}),\tag{8}$$

where O_s is a singlet projection operator. (ψ_{III} and ψ_{IV} are, in fact, included in the spin projection of ψ_{I} and ψ_{II} respectively.) The energy is given by

$$E=\frac{\langle(\psi_{\mathrm{I}}+\psi_{\mathrm{II}})|H|O_s(\psi_{\mathrm{I}}+\psi_{\mathrm{II}})\rangle}{\langle(\psi_{\mathrm{I}}+\psi_{\mathrm{II}})|O_s(\psi_{\mathrm{I}}+\psi_{\mathrm{II}})\rangle}\tag{9}$$

because the spin projection operators are idempotent and commute with the Hamiltonian.

For the ten electron case ψ_s is now a linear combination of 504 Slater determinants. There are well established methods [4, 14–16] for calculating the energy of a wavefunction generated by the application of a spin projection operator to a single determinant provided that the orbitals have been transformed to the "corresponding orbitals" of Amos and Hall [17] or the "paired orbitals" of Löwdin [18]. If u_i and v_i are transformed orbitals containing electrons of α and β spins respectively in the unprojected determinant, they satisfy the orthogonality conditions.

$$\begin{aligned}\langle u_i|u_j\rangle=\langle v_i|v_j\rangle=\delta_{ij}\\ \text{and}\qquad \langle u_i|v_j\rangle=\lambda_i\delta_{ij},\end{aligned}\tag{10}$$

where δ_{ij} is the Kroenecker δ. This transformation is readily applied to ψ_{I} and ψ_{II} and the contributions to the energy from $\langle\psi_{\mathrm{I}}|H|O_s\psi_{\mathrm{I}}\rangle$ and $\langle\psi_{\mathrm{II}}|H|O_s\psi_{\mathrm{II}}\rangle$ are thus easily calculated. Unfortunately there is no easy way of calculating the integral $\langle\psi_{\mathrm{I}}|H|O_s\psi_{\mathrm{II}}\rangle$ where ψ_{I} and ψ_{II} are determinants with different spatial parts having no particular orthogonality relationships between them. This is the major difficulty in the application of the NPSO method.

The unprojected wavefunctions ψ are in effect combinations of wavefunctions of all the possible multiplicities allowed for the number of electrons under consideration. The effect of the spin projection operator is to remove the unwanted multiplicities – triplets, quintets etc. to give a singlet function. If one is interested in the singlet state, the major contaminating species is the triplet and Amos and Hall [17] suggested that the annihilation of the triplet state would be a good approximation to full projection. Making the further assumption, which is not quite valid, that the spin annihilation operator is idempotent, the calculation of $\langle\psi_{\mathrm{I}}|H|O_s\psi_{\mathrm{II}}\rangle$ reduces to $\langle\psi_{\mathrm{I}}|H|A_{s+1}\psi_{\mathrm{II}}\rangle$ where A_{s+1} is an operator annihilating the component with spin quantum number $s+1$ from the wavefunction. $A_{s+1}(\psi_{\mathrm{II}}-\psi_{\mathrm{IV}})$ is a combination of 52 determinants and it is feasible to calculate this integral directly using the method of King *et al.* [19] for each individual integral in the expansion.

We have used a modification of this idea. Following Löwdin [23], the function ψ_{I} can be represented by $[\alpha^5]\,[\beta^5]$ where it is understood that the first five spatial orbitals contain electrons of α spin and the last five electrons of β spin. $(-\psi_{\mathrm{III}})$ is similarly represented by $[\beta^5]\,[\alpha^5]$ with the same convention regarding the spatial orbitals. The effect of the singlet projection operator O_s on ψ_{I} is written

$$O_s \psi_{\mathrm{I}} = \sum_{k=0}^{5} C(0,k)\, T_k\,,$$

where $T_k = [\alpha^{5-k}\beta^k]\,[\alpha^k\beta^{5-k}]$ and represents all possible determinants for which there are $(5-k)\,\alpha$ spins and $k\,\beta$ spins among the first five spatial orbitals and $k\,\alpha$ spins and $(5-k)\,\beta$ spins among the last five spatial orbitals and the coefficient $C(0,k)$ for the 10 electron case is given by

$$C(0,k) = \frac{1}{6}(-1)^k \binom{5}{k}^{-1}.$$

Instead of applying the annihilation operator A_{s+1} to $(\psi_{\mathrm{I}} - \psi_{\mathrm{II}})$ we have simply omitted the terms T_2 and T_3 from the expression $O_s\psi_{\mathrm{I}}$. Thus we have included the same terms that would be given by annihilation of the triplet component but with the coefficients given by spin projection. This function will be written as $A'_{s+1}\psi_{\mathrm{I}}$. The method of Pauncz [4] was used to calculate

$$\langle \psi_{\mathrm{I}} | H | A'_{s+1}\psi_{\mathrm{I}} \rangle \quad \text{and} \quad \langle \psi_{\mathrm{II}} | H | A'_{s+1}\psi_{\mathrm{II}} \rangle\,.$$

Calculations were also made with the unprojected function ψ (Eq. (4)) for naphthalene and a function derived from the unprojected azulene function (6) by including the determinants obtained by exchanging α and β spins.

We assumed the same geometries as Pauncz and his coworkers for naphthalene [11] and azulene [4] and used the integrals tabulated in their work so that our results are directly comparable with theirs. The integrals were calculated by the method of Ruedenberg [21].

3. Results

a) *Naphthalene*

The results of the NPSO calculations described above for the naphthalene molecule are in Table 1 along with the results of Silberman and Pauncz [11]. The unprojected NPSO energy reported previously [8] was, unfortunately, found to be in error. The correct value is reported in Table 1. Annihilation of the triplet component is seen to improve the energy somewhat but the result is disappointing compared with the AMO results, although the NPSO energies are considerably lower than that given by the MO method. Further improvement might be expected for full spin projection. In order to get an indication of any possible further lowering we calculated the energy

$$E_1 = \frac{\langle \psi_{\mathrm{I}} | H | O_s \psi_{\mathrm{I}} \rangle + \langle \psi_{\mathrm{I}} | H | A'_{s+1}\psi_{\mathrm{II}} \rangle}{\langle \psi_{\mathrm{I}} | O_s \psi_{\mathrm{I}} \rangle + \langle \psi_{\mathrm{I}} | A'_{s+1}\psi_{\mathrm{II}} \rangle}\,. \tag{11}$$

Table 1. *Energies for wavefunctions for naphthalene*

Method	Energy (eV)	k
SCF-LCAO-MO[a]	-494.4805	
Unprojected NPSO	-497.1048	0.2482
NPSO with annihilation	-497.7234	0.214
of triplet component	$(-497.6699$	0.25)
NPSO E_2	-497.9909	0.221
	$(-497.9449$	0.25)
NPSO E_1	-498.0896	0.215
	$(-498.0338$	0.25)
AMO 1 parameter[a]	-498.5394	
AMO 5 parameter[a]	-499.5259	

[a] Ref. [11].

This is seen to lower the energy by a further 0.35 eV with the value of k remaining approximately the same.

In view of the fact that the calculation of $\langle \psi_{\mathrm{I}} | H | A'_{s+1} \psi_{\mathrm{II}} \rangle$ is time consuming, we considered the possibility of calculating the energy by

$$E_2 = \frac{\langle \psi_{\mathrm{I}} | H | O_s \psi_{\mathrm{I}} \rangle + \langle \psi_{\mathrm{I}} | H | \psi_{\mathrm{II}} \rangle - \langle \psi_{\mathrm{I}} | H | \psi_{\mathrm{IV}} \rangle}{\langle \psi_{\mathrm{I}} | O_s \psi_{\mathrm{I}} \rangle + \langle \psi_{\mathrm{I}} | \psi_{\mathrm{II}} \rangle - \langle \psi_{\mathrm{I}} | \psi_{\mathrm{IV}} \rangle} . \tag{12}$$

Table 1 shows that this procedure yields an energy close to the minimum of E_1, although the value of k does shift slightly. We can, therefore, suggest that this is a reasonable way of doing the calculation without excessive computation.

In view of the disappointing performance of the one parameter NPSO function we investigated the effect of introducing a second parameter into the wavefunction. Two alternative schemes were explored with unprojected functions. Firstly, the same parameter k_1 was used for bonds 12, 23, 34, 56, 67 and 78 and k_2 for bonds 19, 410, 510 and 89. The energy minimum occurs in the region of $k_1 = 0.27$, $k_2 = 0.21$ giving an energy of -497.1418 eV. Bond length considerations suggest that a better choice would be k_1 for bonds 12, 34, 56 and 89 and k_2 for bonds 23, 410, 510, 67, 89 and 19. However, the improvement was insignificant. For $k_1 = 0.29$, $k_2 = 0.22$ the energy obtained was -497.1520 eV. Thus the energy lowerings were not sufficient to suggest that it would be worth introducing a second parameter in this way.

The most probable reason for the poor performance relative to the AMO method is that the NPSO method does not explicity consider the 9–10 bond which is comparable in length to the 1–9 and 2–3 bonds. A comparison of the first order density matrices for the unprojected NPSO function and the AMO wavefunction (Table 2) indicates that the NPSO method gives a poor description of the electron distribution in the 9–10 bond.

In these calculations k can be replaced by $1/k$ and the figures in Table 1 show that the energy is minimised for values of k close to 0.25. Energy values for $k = 0.25$ are shown in parentheses and are seen to be close to the minimum. Thus it is apparent that the value of $k = 4$ suggested by Empedocles and Linnett [7] is also applicable in the case of naphthalene.

Table 2. *First order density matrix for naphthalene*

	Unprojected NPSO ($k = 0.2482$)	AMO (5 parameters)
11	0.9039	0.8355
22	0.9016	0.8703
99	0.9109	0.9426
12	0.2072	0.3763
23	0.2078	0.1311
19	0.2096	0.1378
910	−0.0178	0.2803

b) *Azulene*

Table 3 contains the results of the energy calculations for azulene along with the results of Pauncz [4] and Silberman, Gershgorn and Pauncz [12] obtained by the AMO method. As we were not able to obtain exact agreement with the MO energy and eigenvectors of the overlap matrix obtained by Pauncz and his coworkers, we include the MO energy obtained in this work along with our SCF-LCAO-MO energy. The SCF orbitals are given in Table 4. The alternant molecular orbitals of Silberman *et al.* were constructed from the eigenvectors of the overlap matrix.

The Coulson-Rushbrooke theorem does not apply to non-alternant systems. However, the AMO method is applicable to such systems if the alternant molecular orbitals are constructed by taking combinations of bonding and antibonding orbitals having the same symmetry in such a way as to localise the two groups of AMO on different sets of atoms in the molecule. The calculations reported by

Table 3. *Energies of wavefunctions for azulene*

Method	Energy (eV)	k
MO (Eigenvectors of overlap matrix)		
Pauncz[b]	−490.0192	
Silberman *et al.*[a]	−490.0606	
This work	−490.0134	
SCF-LCAO-MO	−490.7623	
AMO (1 parameter)[b]	−491.9428	
AMO (5 parameters)[b]	−493.1266	
Unprojected NPSO	−494.4050	0.2555
NPSO (E_2)	−495.2340	0.2273
	(−495.2050	0.25)
Optimized AMO[a]	−495.3652	
Annihilated NPSO	−495.5472	0.23
	(−495.5230	0.25)
NPSO (E_1)	−495.8820	0.228
	(−495.8516	0.25)

[a] Ref. [12].
[b] Ref. [4].

Table 4. SCF-LCAO *molecular orbitals for azulene*

		χ_1	$\chi_2 \pm \chi_{10}$	$\chi_3 \pm \chi_9$	$\chi_4 \pm \chi_8$	$\chi_5 \pm \chi_7$	χ_6
1	b_2	0.0232	0.0645	0.2095	0.2738	0.3446	0.3853
2	a_2	0.0	0.1841	0.3242	0.3914	0.2990	0.0
3	b_2	0.2620	0.2677	0.3427	0.0902	−0.2143	−0.3433
4	b_2	0.5916	0.3018	−0.2952	−0.1941	0.1016	0.2490
5	a_2	0.0	0.4164	0.3505	−0.1517	−0.4090	0.0
6	b_2	0.2983	−0.0729	−0.3549	0.4996	0.1355	−0.5568
7	a_2	0.0	0.4476	−0.2188	−0.3961	0.4753	0.0
8	b_2	0.6005	−0.4522	0.0714	0.2274	−0.4600	0.5532
9	a_2	0.0	−0.3778	0.6673	−0.4914	0.2622	0.0
10	b_2	0.5186	−0.4522	0.3005	−0.3818	0.4299	−0.4477

Pauncz [4] were made in this way. Subsequent work has shown that this is not necessarily the best method because one can take linear combinations of the antibonding orbitals of a particular symmetry before forming the AMO. Silberman *et al.* [12] found the optimum unitary transformations of the antibonding orbitals as well as optimising the energy with respect to the usual AMO parameters. This calculation is referred to as the "optimised AMO method" in Table 3.

The results in Table 3 show that for azulene the performance of the NPSO method is very good and that a one parameter wavefunction compares very well with the rather complicated AMO wavefunction of Silberman *et al.* [12] which involves two unitary transformations among the antibonding orbitals and five non-linear parameters mixing the bonding and antibonding orbitals.

Again the energy minima are given by values of k close to 0.25. The energies for $k = 0.25$ are given in parentheses. The assumption of a value of k of 0.25 would not introduce any serious errors into the calculation.

It is of interest to consider why the NPSO method should be relatively better for azulene than for naphthalene. The first order density matrix for the unprojected NPSO function is given in Table 5 and shows that the NPSO wavefunction is

Table 5. *First order density matrix for azulene*

	Unprojected NPSO ($k = 0.2555$)	Optimized AMO
11	0.9021	0.8516
22	0.9057	0.9626
33	0.9354	0.8308
44	0.8989	0.7934
55	0.9001	0.8481
66	0.8964	0.8040
12	0.2098	0.2934
23	0.2190	0.2143
34	0.2155	0.3242
45	0.2125	0.3450
56	0.2113	0.3008
39	−0.1693	0.0713

antibonding for the 3–9 bond. However, this is the longest bond in the molecule (1.483 Å) and is considerably longer than the next longest bond (2–3) (1.413 Å). It would thus appear that the 3–9 bond has much less π-bond character than the 9–10 bond in naphthalene. The length of a "pure" sp^2-sp^2 single bond has been the subject of some controversy [22] but one may say that it is in the region of 1.50 Å. Thus in the case of azulene, it is reasonable to suppose that the lack of explicit consideration of the bridge bond will be less serious that in the case of naphthalene.

We also used the energy expressions E_1 and E_2 (Eqs. (11) and (12) respectively) and obtained results similar to those for naphthalene. Including full spin projection of ψ_{I} again lowers the energy by about 0.35 eV. Satisfactory results can be obtained by the use of expression E_2.

4. Conclusions

Even though we have not performed NPSO calculations with fully spin projected wavefunctions, we conclude that the method is successful for these ten electron systems. Full spin projection would not lower the energy appreciably. The fact that the value of k is virtually the same for the annihilated calculation and energy expressions (11) and (12) suggests that the optimum value of k for E_2 will give a minimum energy (or very close to it) for the fully projected function. In view of the difficulties of performing fully spin projected calculations, we suggest that the use of $(O_s\psi_{\mathrm{I}})+\psi_{\mathrm{II}}-\psi_{\mathrm{IV}}$ is a very reasonable approximation.

The results for azulene are particularly good compared with the AMO calculations [12] which involve many more adjustable parameters.

For both naphthalene and azulene the energy is minimized for values of k close to 0.25. Thus these molecules follow the pattern observed by Empedocles and Linnett [7] and our results support their assertion that it is possible to write accurate NPSO wavefunctions for the ground states of complex molecules without performing laborious energy calculations.

Our calculations and previous applications of the NPSO method suggest that this is a good way of calculating correlated wavefunctions for delocalized systems.

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