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Lower Excited State Wavefunctions for some Conjugated Carbon Compounds — NPSO Method

By

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The method of Non-Paired Spatial-Orbitals is applied to the excited states of three typical conjugated hydrocarbons, Benzene, Fulvene and Hexatriene.

Die NPSO Methode wird auf die angeregten Zustände von drei typischen konjugierten Kohlenwasserstoffen, Benzol, Fulven und Hexatrien angewandt.

La méthode des orbitales spatiales non-appariées (NPSO) est appliquée aux états excités de trois hydrocarbures conjugués typiques, soit le benzène, le fulvène et l'hexatriène.

The application of the method of Non-Paired Spatial-Orbitals (NPSO) to conjugated hydrocarbons is complicated by the need to include adjustable parameters in the wavefunction. Their values can only be determined rigorously by resort to a laborious variational energy calculation. The present paper extends the work of two previous papers [*2*, *3*]. The attempt is made to suggest ways in which the adjustable parameters in the excited states wavefunctions may be determined a priori. Indeed, if we are to make calculations at all on systems much bigger than naphthalene by this method, some such simplification is essential.

In the NPSO method wavefunctions of the lower excited states are constructed from the same set of spatial orbitals as are used for the ground states; only the spin combination is changed. It is therefore analogous to the valence bond method. But in some ways it has a wider significance because of the various ways in which the Exclusion Principle can affect the electron density. A parallel case in atomic structure was considered by Shull and Løwdin [*7*]. They used the Hylleraas-Eckart function:

$$N_1\,(1s\,1s' + 1s'\,1s)$$

to represent the ground state of the Helium atom, and a function:

$$N_2\,(1s\,1s' - 1s'\,1s)$$

to represent the ^3S excited state. This excited state is usually described by a wavefunction based conventionally on $1s$ and $2s$ spatial orbitals, but Shull and Løwdin's description neatly provides a lower energy. Extending the idea it might be profitable to write the ground state wavefunction for lithium using three $1s$-type orbitals with different exponents, $1s$, $1s'$ and $1s''$. The same is true for the ground and excited states of any "different orbitals for different spins" (DODS)

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function; (e.g. it could be applied to the Alternant Molecular Orbital approach). The electron distributions in ground and excited states are of course, quite different, both because of the consequences of the antisymmetry requirement on the total wavefunction, and also, as far as the NPSO approach is concerned, because the variable parameters assume different values.

There are two independent but related problems with the NPSO method. They are the determination of the spin combination for minimum energy for any state, and the determination of the optimum value of the space constant k for that state.

In the present study, we have made a non-empirical calculation of the wavefunctions and energies of the lower excited states of fulvene and hexatriene, using the NPSO full spin-CI treatment. The figures for benzene have already been published [*2*]. We accept, for the moment the limitations inherent in non-empirical calculations using the Goeppert-Mayer-Sklar approximation, although some of these may be particularly drastic in calculations for excited states. A semi-empirical approach to these problems is made in another paper [*4*].

The energies of the $^1B_1$, $^3B_1$, and $^3A_1$ excited states of fulvene and of the ^3B_u, ^1A_g and ^3A_g excited states of hexatriene which have been calculated here are found to be below the energies estimated for these molecules in their ground states using the SCF–LCAO–MO treatment of ROOTHAAN [*5*, *1*]. Any discussion of the spectrum in terms of the SCF treatment is consequently hard to justify, because both ground and excited states are incorrectly located on the energy scale by several electron volts. It did not seem worthwhile therefore to compare the results of the present NPSO treatment with those of simpler approximate non-empirical treatments.

Table 1. *Excitation energies for fulvene and hexatriene calculated using the* NPSO *full spin*-CI *treatment and minimising the energies of each state with respect to k*

Fulvene State	Excitation Energy (eV)	approx $k_{\min}$	Hexatriene State	Excitation Energy (eV)	approx $k_{\min}$
$^1A_1$ (g. s.)	(0.00)	4.2	^1A_g (g. s.)	(0.00)	3.9
$^1A_1$	3.60	4.2	^1A_g	3.20	3.9
$^3A_1$	< 1.7	3.8	^3A_g	< 3.13	—
$^5A_1$	4.80	4.0	^5A_g	4.90	3.6
$^1B_1$	1.79	3.7	^1B_u	4.20	3.6
$^3B_1$	0.99	4.1	^3B_u	1.31	3.9
$^5B_1$	—	—	^5B_u	5.70	4.5
$^7A_1$	10.17	any	^7B_u	9.70	any

For fulvene and hexatriene the calculated energies of several lower excited states above that of the ground state are shown in Tab. 1. It is seen that with fulvene there are more low-lying energy levels than for hexatriene, (or benzene [*2*]).

For the ground state we find that the energy is a slowly varying function of k, and of the spin combination, and that the value of k which minimises the energy of the lowest excited levels, (those within 5 eV of the ground state), is always between 3.5 and 4.2. This is also found for benzene [*2*]. Consequently we may hope, as for benzene, to use an empirical value of 4.0 for all states without great loss of accuracy in the calculation of excitation energies.

Methods 2 and 3 of the previous paper [*3*] have been used to generate a single component of the spin combination to represent the levels of the lower excited state functions for benzene, fulvene and hexatriene.

The spin projection operator can be used in a straightforward way to eliminate the unwanted parts from the spin combinations generated by method 1. For example with benzene (see ref. [*2*] for definition of symbols), the starting functions are:

$$\begin{array}{ll} \Phi_6 + \Phi_{15} - \Phi_{26} - \Phi_{35} & A_{2g} \\ \Phi_6 - \Phi_{15} - \Phi_{26} + \Phi_{35} & B_{1u} \\ \Phi_6 - \Phi_{15} + \Phi_{26} - \Phi_{35} & B_{2u}\,. \end{array} \tag{1}$$

For states having other symmetries, e.g. E_{2g}, we must use a starting function in which two pairs of adjacent NPSOs bear the same spin function.

Table 2. *Energies of excited functions (in* eV *relative to* 6 W_{2p}*) calculated using* NPSO *full spin-*CI *treatment, compared with that calculated using an* NPSO *function with no adjustable parameters*

	State	Full spin-CI for $k = k_{\min}$	Method 2	Method 3
Benzene	$^3B_{1u}$	−115.93	−115.57	−115.86
	$^3E_{1u}$	−114.61	—	−113.25
Fulvene	$^3B_1$	−116.34	−114.16	−114.39
Hexatriene	^3B_u	− 99.11	− 98.35	− 98.45

In order to use method 3 to construct a triplet function for example, we use the same starting function (1). From each term a combination of determinants is generated which is antisymmetric in the interchange of all but one pair of electrons in adjacent NPSOs. That is, as for the ground state [*3*], we choose the maximum number of adjacent pairs to give the state of lowest energy for any symmetry class.

Some examples of the energies of lower excited state functions calculated in this way are shown in Tab. 2.

These results are somewhat less accurate than those for the ground state, but the order of the problem is much greater. In the $^3B_1$ and ^3B_u states of fulvene and hexatriene for example nine adjustable parameters have been fixed a priori. This is part of the price; loss of accuracy is inevitable if a complex function is to be drawn into a simple scheme which uses no adjustable parameters. However it should be possible to improve the numerical performance greatly by the careful use of empirical data.

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