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## EXCITED STATES AND PAIRING RELATIONS IN CERTAIN CONJUGATED SYSTEMS

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There is an increasing interest in molecular excited and highly excited states<sup>(1)</sup>. We have proposed a density matrix formalism for  $\pi$  electronic excited states in the frame of the simple PPP treatment<sup>(2)</sup>. It may be claimed that we are too unrealistic in contemplating states probably not comparable with experiment. Nevertheless, even if some states may have a purely academic character, their pairing properties with lower lying states earn both speculative and applied care<sup>(3-6)</sup>.

The complementarity relation<sup>(4)</sup> is an alternative formulation of the pairing theorem<sup>(6)</sup> which has led to very fruitful applications in calculating B terms in MCD spectra<sup>(7)</sup>. It has been pointed out that PPP calculations, despite their simplicity, may help to rationalize general trends<sup>(6)</sup>.

Recently, we have analyzed convergence problems appearing when calculating SC  $\pi$  bond orders  $P_{\mu\nu}$  in excited states of conjugated molecules<sup>(8)</sup>. The example we used there is the pyridazine molecule, for which we found that the three symmetry-allowed particular solutions<sup>(9)</sup><sup>(\*)</sup> divided the 27 states

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(\*) i.e. the two states which have all symmetric (antisymmetric) levels doubly occupied, and the reference state with all levels singly occupied by electrons with parallel spins.

considered into energetical regions.

Now, a mirror image of pyridazine in the sense adopted by Michl<sup>(6)</sup>, would be v-tetrazine. We could therefore advance another meaning for our formulation: the reference state<sup>(8)</sup> separates the configurations of a molecule from those of its mirror image. The anti-aufbau construction<sup>(8)</sup> helps to account for this interpretation. Note that this is not a merely mechanical transposition of results. If it were so, two complementary states would be always equidistant from the reference state, and this is not the case. Two species only approximately related in the sense of alternant pairing symmetry still have opposite sign MCD patterns<sup>(10)</sup>; this experimental result underlines the importance of pairing properties.

The reference state, also called hypermultiplet<sup>(11)</sup> is a most peculiar one. It is internally self-consistent<sup>(12)</sup>, as the other particular solutions<sup>(9)</sup>, and it is the only one which is self-complementary.

Let us thus look for other pairing relations involving the particular solutions. If two complementary states I and II are calculated with the same Hamiltonian, we have<sup>(4)</sup>

$$P_m^{(I)} + P_m^{(II)} = 2I_m \quad (1)$$

I being the unit matrix. If the Hamiltonians are different, let us say in a perturbation  $\Delta H$

$$H_m^{(I)} = H_m^{(II)} + \Delta H_m \quad (2)$$

it will be

$$P_m^{(I)} + P_m^{(II)} = 2I_m + \frac{\epsilon}{m}(\Delta H) \quad (3)$$

where  $\frac{\epsilon}{m}$  must be a functional of  $\Delta H_m$ .

When the U(3) symmetric matrices algebra is applied to the calculation of SC  $\pi$  bond orders<sup>(2)</sup>, the 27 solutions group together in three cases, according to the possibilities for  $N^+$  and  $N^-$  (number of electrons respectively in symmetric and antisymmetric levels). Pairing relations may be found for the 12 states where  $N^+ \neq N^-$  and singly occupied levels are allowed.

Let us name  $P_m^+$ ,  $P_m^0$  and  $P_m^-$  the  $\pi$  bond order matrices of the three particular solutions<sup>(9)</sup>, namely

$$P_m^+ = \begin{pmatrix} 1 & & & \\ & & & \\ & & & \\ & & & 1 \end{pmatrix} \quad P_m^- = \begin{pmatrix} 1 & & & \\ & & & \\ & & & \\ & & & -1 \end{pmatrix} \quad P_m^0 = \begin{pmatrix} 1 & & & \\ & & & \\ & & & \\ & & & 0 \end{pmatrix} \quad (4)$$

where the elements outside the diagonals are zero. The 12 mentioned states, if calculated with the same Hamiltonian, may be paired off, satisfying either

or

$$P_m^{(i)} + P_m^{(ii)} = P_m^+ + P_m^0 \quad (5)$$

$$P_m^{(i)} + P_m^{(ii)} = P_m^- + P_m^0$$

Again, if the Hamiltonian is not the same, we shall have

or

$$P_m^{(i)} + P_m^{(ii)} = P_m^+ + P_m^0 + \frac{\epsilon}{m}(\Delta H) \quad (6)$$

$$P_m^{(i)} + P_m^{(ii)} = P_m^- + P_m^0 + \frac{\epsilon}{m}(\Delta H)$$

Eq. (2) may also be written under the form

or else

$$\begin{aligned}
 \underline{P}^{(I)} + \underline{P}^{(II)} &= \underline{P}^+ + \underline{P}^- \\
 \underline{P}^{(I)} + \underline{P}^{(II)} &= 2\underline{P}^0
 \end{aligned}
 \tag{7}$$

which stresses the analogy between relations (1) and (5). Eqs. (5), (6) and (7) hold whenever the  $\pi$  system possesses a two-fold symmetry axis not passing through any  $\pi$  center.

The formalism we apply for excited states is a PPP-type one, writing it under the density matrix form, which has proven successful for other problems<sup>(13,14)</sup>

$$\underline{H} \underline{P} = E \underline{P} \tag{8}$$

As is well known, this is not an eigenvalue problem, for  $\underline{H}$  is a functional of the solution rather than a matrix,  $\underline{P}$  is a matrix instead of a vector, and must satisfy the constraints of symmetry and idempotency<sup>(13)</sup>. Although the density matrix approach permits convergence in some cases where the orbital formulation results in oscillation, care must be taken to preserve the constraints<sup>(13)</sup>.

Parametrization is generally intended for the ground state, so it is desirable to limit its influence. In this sense, hydrocarbons are more suitable than heteroatomic compounds, so we apply our formalism to hexatriene.

In the compromise Hamiltonian<sup>(2)</sup>

$$H_{\mu\nu} = H_{\mu\nu}^0 + \xi P_{\mu\nu} C_{\mu\nu} \tag{9}$$

$H^0$  is the Hückel Hamiltonian and  $C_{\mu\nu}$  are proportional to the Coulomb repulsion integrals  $(\mu\nu|\mu\nu)$ . The convergence parameter  $\xi$  plays the role of a damping constant<sup>(14)</sup>.

Of the two previously proposed criteria for the damping parameter<sup>(8)</sup>, we keep here the linear one:  $\xi = 1$  for the ground state,  $-1$  for the completely excited one and  $0$  for the reference state. We start from Hückel's solution and repeat the linear estimation of  $\xi$  with the obtained energy until self-consistency in this sense (each state is besides self-consistent in the usual sense, regarding the density matrix for that state). Unlike what happens for pyridazine<sup>(8)</sup>, in hexatriene the order of the states remains unaltered. Bond orders evidence instead the influence of relaxation; states with the same Hückel bond orders have different defrozen ones. The Figure shows total electronic energy from state 1 up to state 27; the spurious repulsion introduced by the half-electron model has been corrected for<sup>(8)</sup>. The particular solutions are less scattered for hexatriene than for pyridazine, where their positions corresponded to states 4, 14 and 23. As to the energetic regions we had alluded to, in hexatriene they appear dimmer.

In the Hartree-Fock equations

$$\underline{H}(\Psi)\Psi = \underline{E} \Psi \quad (10)$$

the wave function  $\Psi$  is supposed to be that of the state dealt with; virtual orbitals do not have therefore a clearcut physical meaning. In order to employ them to estimate properties of states other than the one for which self-consistency was achieved, they require modification. Even thus, the highest between them

are inadequate<sup>(15)</sup>, and this is not surprising.

As a starting matrix in eq. (8) we may use  $\underline{P}$  for the desired state built using  $\Psi$  (that is, some virtual orbitals also) of another state. Self-consistency then corrects the disagreements. We expected<sup>(8)</sup> that the solution may depend of the starting matrix. This uses to happen in more sophisticated treatments<sup>(14)</sup> and, at first sight, being or not near the solution could not only accelerate convergence but be decisive. It is not so in hexatriene, and we verified that neither in pyridazine. Given  $\xi$ , whatever it be the wavefunction  $\Psi$  used to build  $\underline{P}$ , it converges to the same solution.

This kind of calculation (where the constraints are preserved with no additional requirement) could be used, for example, as a first step towards more accurate alternant molecular orbitals, obtained coupling occupied MO's with virtual ones<sup>(16)</sup>.

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FIGURE CAPTION

SC total electronic energy for the 27 considered states of hexatriene. At the right the occupation numbers of symmetric and antisymmetric levels respectively are indicated.

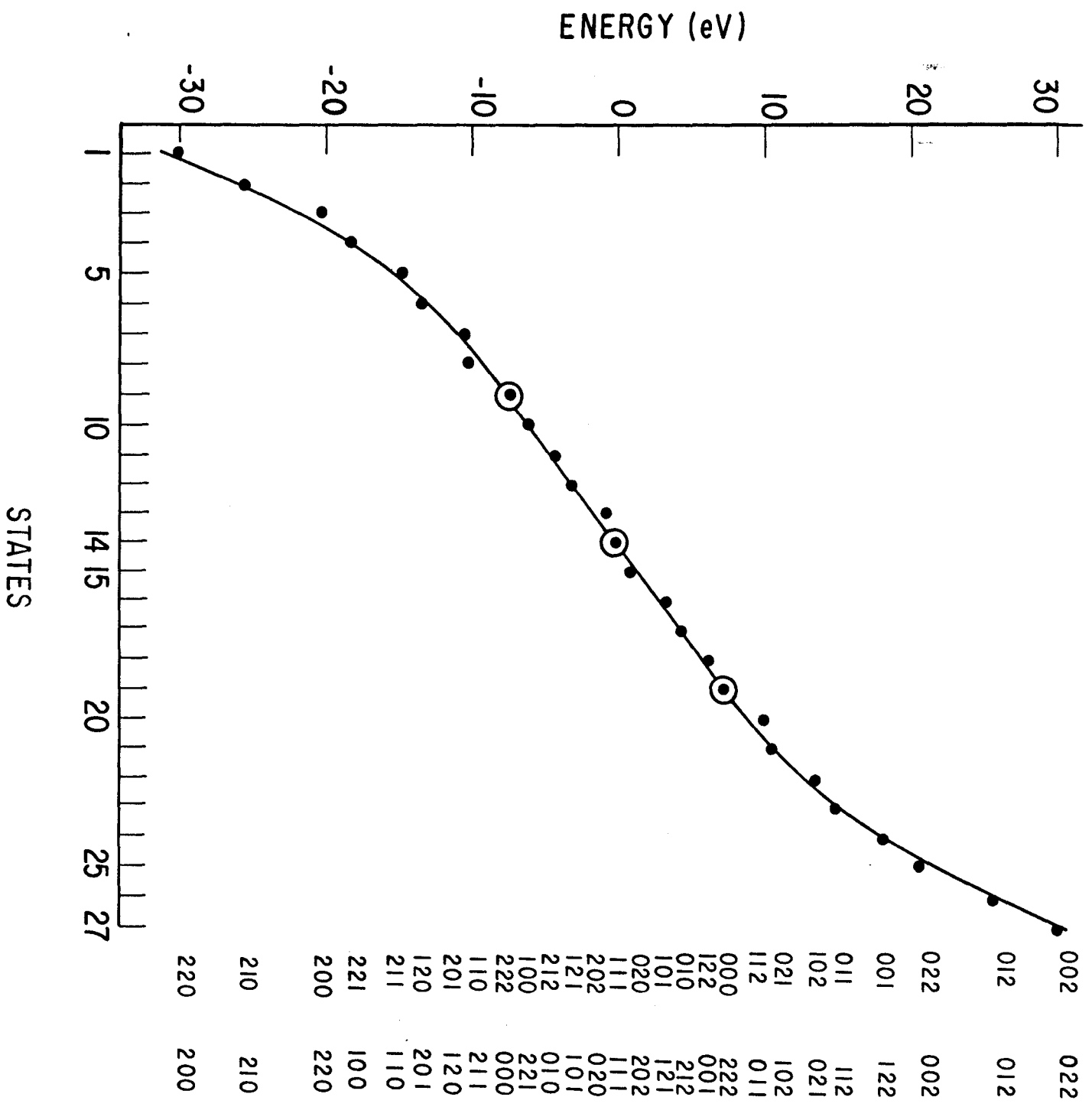


FIG.