

CONVERGENCE PROBLEMS AND ENERGETIC REGIONS IN  $\pi$  EXCITED  
STATES OF CERTAIN CONJUGATED MOLECULES

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AVE BOND INDEX IN THE H-BOND OF THE WATSON-CRICK PAIRS

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ABSTRACT

When calculating  $\pi$  bond orders of excited and superexcited states of conjugated molecules, difficulties arise in applying the variation method; besides, the convergence problems involved are well known. For pyridazine, chosen for discussion, 27 states are considered; the convergence problem is envisaged through two criteria in the choice of a parameter introduced in the compromise Hamiltonian. This convergence parameter is related to the variation method. There exist three particular solutions for bond orders, which divide the 27 states into energetical regions.

Running title:  $\pi$  excited states convergence problems and energetic regions.

## I. INTRODUCTION

The grounds for the success of effective PPP-type Hamiltonians have been very recently studied [1], and their application in different treatments of  $\pi$ -electron model systems persists [2]. In a series of papers, we have been concerned about the direct calculation of the SC  $\pi$  bond order matrix  $P$  for excited states without calculating first the wavefunctions [3,4,5]. The wavefunctions and corresponding energy levels reproducing these SC bond orders have been reported for butadiene [6].

The convergence problems for excited states are, as is well known, far from trivial. Our goal is to treat this question in its simplest possible form, and we have chosen to keep the PPP approach with the half-electron approximation for singly occupied levels [7,8], without configuration interaction. We have preferred the half-electron approach in order to preserve a restricted closed-shell scheme. We have applied elsewhere [9] the CNDO/2 approximation for triplet states in an open-shell unrestricted framework. Nevertheless, even in a simple system such as the allyl radical, an unrestricted PPP  $\pi$  treatment leads to violation of wavefunction spin and space symmetry (either one or both of them) [10]. As to CI, besides the difficulty in the selection of the configurations to be included [11], it is forcedly time demanding and expensive, even if it is becoming commonplace [12]. On the other hand, there are cases in which an appropriate modification of the molecular orbitals make the effect of CI negligible for intermediate excited states [13]. We have faced the problem through the introduction of a single parameter  $\xi$

for each state in the compromise Hamiltonian [3,5]

$$H_{\mu\nu} = H_{\mu\nu}^O + \xi P_{\mu\nu} C_{\mu\nu} \quad (1)$$

where  $H^O$  is the Hückel Hamiltonian, and the  $C_{\mu\nu}$  are proportional to the Coulomb repulsion integrals  $(\mu\nu|\nu\nu)$ . This formalism has been intended for 6-electron molecular systems possessing a twofold symmetry axis not passing through any  $\pi$  center, and applied to pyridazine [5].

The advantage of separating the basis set into symmetric (labelled as +) and antisymmetric (-) ones is that the variation method applies separately to the eigenfunctions and eigenvalues of each type.

Our basic equations are [3,5]

$$(J+C^+P^+ + C^-P^-)P^+ = J'P^+ = \text{symmetric}; \quad (K+C^-P^+ + C^+P^-)P^- = K'P^- = \text{symmetric} \quad (2)$$

where

$$J_{\mu\nu} = H_{\mu\nu}^O + H_{\mu, N+1-\nu}^O; \quad K_{\mu\nu} = H_{\mu\nu}^O - H_{\mu, N+1-\nu}^O; \quad P_{\mu\nu}^\pm = \sum_{i_\pm} n_{i_\pm}^{\pm} x_\mu^{i_\pm} x_\nu^{i_\pm} \quad (3)$$

$x_\mu^i$  is the coefficient of atomic orbital  $\mu$  whose occupation number is  $(2n^i)$ .

The 27 states considered are those for which  $n_\ell + n_h = I$  [3],  $n_\ell$  being a diagonal matrix with half the occupation numbers of the lowest energy levels,  $n_h$  a diagonal matrix with half the occupation numbers of the associated highest energy levels, and  $I$  the unit matrix.

The choice of  $\xi$  in (1) is not of course unique. We shall consider here two alternatives:

- 1)  $\xi = 1$  up to the reference state whenever possible, and

the closest possible to 1 otherwise;  $\xi = -1$  from the reference state on, and similarly the closest possible to -1 otherwise [5]. That is, the highest electronic interaction allowed by the convergence is taken.

2)  $\xi$  linear;  $\xi = 1$  in the ground state;  $\xi = -1$  in the highest excited state and  $\xi = 0$  in the reference state (see section III). This should mean a linear variation of electronic interaction under excitation.

## II. CRITERION OF HIGHEST ELECTRONIC INTERACTION

Table I(a) shows the occupation numbers and the convergence parameter used in [5], for the 27 states numbered following the chosen criterion which, as we shall explain further in this section, gives rise to two branches appearing in the plot of the increasing total energy.

By Eqs. (2),  $J'$  and  $P^+$  commute (and so do  $K'$  and  $P^-$ ), so that they have the same eigenfunctions  $\phi_i$ . Now, the variation method associates  $\phi_1$  to the lowest  $J'$  eigenvalue and therefore to the highest  $P^+$  eigenvalue, for it is intended for the ground state built following the aufbau principle; its extension to excited states is by no means straightforward [14]. As long as the excited states obey the aufbau principle, and this holds up to state 5, we may employ directly our compromise Hamiltonian without the requirement of a convergence parameter. There is certainly trouble when the order of the occupation numbers is completely inverted relative to aufbau, as happens beyond state 23, and in some of the previous ones between state 14 and state 23. Difficulties are also expected even for partial inversion.

When the inversion is complete (the correlation term is

the dominating one in the Hamiltonian), changing  $\xi$  from 1 to -1 restores us to a situation where we may apply the variation method, the highest  $P^+$  eigenvalue corresponding thus to the highest  $J'$  eigenvalue. This is as if we built these states with the aufbau principle occupying the energy levels "downwards" from the "top", instead of "upwards" from the "bottom". Let us call this the anti-aufbau principle for the most excited states.

Hall's standard reference state [15] establishes a clear division. The four consequent energetic regions, separated by the particular solutions 5, 14 and 23 [4] are therefore:

A) up to state 5, where  $\xi = 1$ .

B) From state 5 up to state 14 the inversion in occupation numbers, when it occurs, is partial; we keep  $\xi = 1$  whenever possible.

C) From state 14 up to state 23 there is always inversion in occupation numbers, be it partial or complete (e.g. state 15); whenever possible, we choose  $\xi = -1$ .

D) From state 23,  $\xi = -1$ .

In the second and third regions,  $|\xi| = 1$  may lead to oscillating behaviours. In such cases we lessen  $|\xi|$  until convergence is attained. The sensibility to the  $\xi$  value is such, that it may be determined with two significant figures if desired.

In the three mentioned particular solutions, the density matrix is independent of the choice of the coefficient matrix, whatever the molecule is [4]; these are the so-called internally self-consistent states [16]. We shall see further that the behaviour of  $P_{\mu\nu}$  is also divided into energetical regions by the particular solutions.

We have tried hopelessly different variations of the damping procedure suggested by Montgolfier and Hoarau and used for hydrogen fluoride (HF) [17]. The damping still worsened the behaviour regarding convergence. It seems therefore that the damping procedure is applicable only under certain restricted conditions which are not clear to us. As to the energy-shift method [18], it proposes a different shift for each iteration, and is applied to the same case of HF with a highly deformed geometry.

Our single convergence parameter for each state involves a maximum simplicity criterion. Furthermore, in each pair of complementary states [19]  $\xi$  has opposite sign (and, aside from states 6 and 21, equal magnitude). This seems reasonable, for in these states  $P_{\mu\nu}$  has opposite signs, so that by changing signs in  $\xi$  the correlation term has the same stabilizing/destabilizing effect in both states. We ascribe to  $\xi$  all the factors that we do not take into account explicitly; physically, it may be thought as playing a role similar to the additional potential introduced in the Fock operator by Beebe [20] in order to modify the virtual orbitals.

When we obtained the SC bond orders in the 4-electron case [3,6], we did not meet the convergence problem because the equations could be solved directly and iteration was not required. In the 6-electron case, care has been taken so as to preserve the non-crossing rule [5]. Surely, if we allow violating it, the results may be quite different and perhaps the convergence problem does not even appear. The highest excited state of the 4-electron case does not obey the rule [6].

It has been recently demonstrated that energy is a functional of the truncated first-order contracted density matrix,



rather than a functional of the density matrix (Hohenberg-Kohn theorem) [21]. However, the validity of both theorems, at least as they stand, holds only for the ground state. Therefore these relations are still challenging questions.

We have used the McWeeny's energy formulae [22] as functions of the density matrix

$$E = E^+ + E^- \quad (4)$$

$$E^+ = \text{Tr}(J'P^+) + \text{Tr}(JP^+) ; E^- = \text{Tr}(K'P^-) + \text{Tr}(KP^-) \quad (5)$$

This total energy (4) must be corrected so as to take into account the spurious repulsion between the two half-electrons in each singly occupied level. As changing the sign of the convergence parameter amounts to changing the sign of the electronic interaction, from state 14 on the correction shall become that of a spurious attraction instead of that arising from a spurious repulsion; the correction is taken, as may be easily demonstrated, multiplied by  $\xi$  in each state.

As to the correction to the singly-occupied energy levels, we have shown elsewhere [8] that it depends on the process originating the state. That is, if  $n_i = 1/2$  comes from  $n_i = 0$  the correction has one sign, and the opposite if it comes from  $n_i = 1$ . Given a state, not a process, the sign of the correction to be applied is not clear any more. Besides, the energy levels corrected in this way are no more eigenvalues of the problem, and hence the corresponding eigenfunctions do not exist. We thus choose to leave the energy levels as they stand.

Fig. 1 shows the total energy from state 1 up to state 27. Since state 14 is internally self-consistent [4,16], it may be

calculated with any  $\xi$ . As it is seen, it falls either on the first straight line (with  $\xi = 1$ ) or on the second one (with  $\xi = -1$ ). It is a discontinuity point. We may look however at this figure from another viewpoint. If we shift the second branch it will match with the first one, the slope of both being the same (3.26 for the first one, 3.27 for the second one); this involves a shift in the zero-point energy. Under the present form, the two branches would mean that, if CI should be carried on, we must limit it within the same energy branch, avoiding mixing of configurations of one branch and configurations from the other one.

However, certain magnitudes on both branches are comparable. For instance, bond orders still follow the complementary condition, although not strictly due to the introduction of electronic correlation.

This is shown in Fig. 2, which reports  $P_{12}$  ( $P_{NC}$ ) for pyridazine, from states 1 up to 27. The values fall in the four energetic regions delimited by the particular solutions:

A)  $1 > P_{12} > 0.3$ ; B)  $0.4 > P_{12} > 0$ ; C)  $0 > P_{12} > -0.4$ ; D)  $-0.3 > P_{12} > -1$ .  
 $P_{23}$  follows the same trend. The bond orders crossing the symmetry axis ( $P_{16}$  and  $P_{34}$ ) do not.

Table 1(b) shows the behaviour of total energy regarding stability. These energy differences are calculated supposing that iteration does not affect the spurious repulsion correction; actually we have shown [8] that the corresponding integrals suffer very small variations due to relaxation, so we may safely neglect these differences in the present analysis. (We have required for self-consistency that the difference between any two iterated  $P_{\mu\nu}$  be less than 0.0004).

It is seen that of the 24 states aside from the particular solutions, 11 of them stabilize, 3 are neither stable nor unstable, and 10 destabilize. Now, the variation method ensures only a stationary point, the sign of the second derivative of the energy being difficult to determine [14] unless the geometry be near the equilibrium one [23], i.e. the ground state one.

Convergence is frequently slow and arduous, if achieved at all, for more sophisticated methods (e.g. the general MC-SCF for open shells) [24]. Besides, the fact of obtaining a convergence does not mean that we are even near the "true" value; it may depend, for instance, on our starting values being more or less far from the "true" ones [14] and this we have no means to verify. We cannot know if the stationary total energy is a minimum, a maximum or a saddle point. But we do know that the lowest eigenvalue is a minimum, the highest a maximum, and the others saddle points [14]. In our 6-electron problem, the separation into two basis sets shall mean then that of our 6 eigenvalues, we know that two are minima, two maxima and two saddle points. This, together with table I, helps us to understand better the stabilization of some states. Let us pick for example state 6, the first one of table I showing a slight destabilization; of the symmetric levels, the saddle point one has higher occupation number than the level corresponding to a minimum; in the antisymmetric ones, we have occupied the level which we know to be a maximum.

Nonorthogonality between the ground and excited states wavefunctions is a troublesome question [25,26,27,28]. In order to verify how large the departure from orthogonality could be for our sixth-order determinantal wavefunctions  $\psi_i$ , we calculated the integrals  $(\psi_i, \psi_j)$  for all the closed-shell sta

tes. Most of these integrals vanish identically for symmetry reasons. Only six of the 28 integrals do not and their values are:

$$\begin{aligned}(\psi_1, \psi_{12}) &\cong 10^{-8} ; (\psi_1, \psi_{24}) \cong 10^{-5} ; (\psi_4, \psi_{16}) \cong 10^{-3} ; (\psi_4, \psi_{27}) \cong 10^{-6} ; \\ (\psi_{12}, \psi_{24}) &\cong 10^{-4} ; (\psi_{16}, \psi_{27}) \cong 10^{-7} .\end{aligned}$$

Thus, even starting from different orbital wavefunctions, our closed-shell determinantal wavefunctions built from them are very nearly orthogonal for pyridazine.

State 14 deserves particular attention. Hall [15] intends this reference standard excited state as having every orbital singly occupied and associated with the same spin, let us say  $\alpha$ . It is the only open-shell state for which an unrestricted calculation (being the  $\beta$  levels virtual ones they are of no importance) will yield the same result as a restricted one, in the sense that the  $\alpha$  levels are already the appropriate levels. There would be then no need to appeal to the half-electron hypothesis, for there will be no contaminations from other multiplets. It has besides the remarkable property of being spin-orthogonal to all the other 26 states. Hoffmann compares this state with his "average state" [16], with which it may coincide. The wavefunction of the "average state" is a compromise one describing all the electronic states of a molecule "in a democratic fashion". This is the sense too of our compromise Hamiltonian [3,5] , which does not single out the ground state [29], but leads to different wavefunctions for each state. The standard reference state is described by a single-determi-

nant wavefunction [15]. Its energy levels will be the Hückel ones (in our case), more or less shifted depending on the  $\xi$  value.

### III. CRITERION OF LINEAR CONVERGENCE PARAMETER

If in Fig. 1 we take for the standard state 14  $\xi = 0$ , the energy will have the mean value of those corresponding to  $\xi = +1$  and  $-1$ . It is seen that this falls between the ground state and the highest excited state. Being the particular solutions independent of the  $\xi$  value, we may choose freely any one, particularly zero. For the above mentioned reasons, this would mean adopting the Hückel levels for that state. The wavefunctions are simply the 6 basis symmetry functions.

It is then quite tempting to see whether an appropriate choice of  $\xi$  can lead us to a monotonous behaviour in the energy, avoiding the disturbing situation of highly excited states falling lower than others which may be less excited. The simplest hypothesis for a variation in the  $\xi$  parameter is the linear one, with  $\xi = 1$  in the ground state,  $\xi = 0$  in the reference state and  $\xi = -1$  in the highest excited state; calculations about the effects of electron correlation [26] show that it is much more important in the ground state than in the intermediate excited states.

Plotting  $\xi$  as a function of the Hückel total energy gives the values reported in Table II(a), where the order is not Hückel's but the SC one calculated with the present  $\xi$ . The total energy takes into account the half-electron correction in the same way as mentioned in the previous section. This order, in turn, shows inversions when comparing with Table I.

We have no elements to decide between both. We could still follow further the underlined procedure, by plotting again  $\xi$  as a linear function of the obtained energy, and so on until self-consistency.

Fig. 3 shows that the energy has now a monotonic behaviour. We can draw the analogous of Fig. 2 for  $P_{12}$ , and it exhibits a quite similar trend leading again to energetic regions delimited by the particular solutions. Only, it is less symmetrical due to the fact that in this case the particular solutions 4 and 23 are not symmetrical around the standard state. The  $P_{\mu\nu}$  values are qualitatively similar with both criteria, and for two thirds of them differences are not larger than 0.05. This is quite striking for states such as 11 (12 of Table I), where  $\xi$  is respectively 1 and 0.18 for criteria 1 and 2.

Table II(b) reports the same magnitudes that Table I(b) in the present approximation. There are more states which neither stabilize nor destabilize. (From both tables it is seen that this happens sometimes after an appreciable number of iterations). The speed of convergence, measured by  $\nu$ , is not proportional to  $|\xi|$ .

#### IV - CONCLUSIONS

1) The convergence parameter  $\xi$  ( $|\xi| \leq 1$ ) is changed in sign for the excited states beyond the reference one. This is justified through the "anti-aufbau" principle.

2) Two criteria are proposed for choosing  $\xi$ , being the first one the highest possible  $|\xi|$  value and the second a linear variation of  $\xi$  with energy.

3) The first criterion gives two linear branches for the total electronic energy, matchable by shifting the zero of the energy. The second criterion results in a monotonic parabolic behaviour.

4) All determinantal wavefunctions of closed-shell states are found to be very nearly orthogonal, the most unfavourable case giving  $10^{-3}$ . The standard reference state is orthogonal to all the others.

5) In both criteria, the particular solutions lead us to four energetical regions.

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## FIGURE CAPTIONS

Fig. 1 - SC total electronic energy following the criterion of maximum electronic interaction. The 27 states of pyridazine are numbered in the order reported in Table I. States 5, 14 and 23 correspond to the particular solutions.

Fig. 2 - SC  $P_{12}$  ( $P_{NC}$ ) for the 27 states of pyridazine. The four energetic regions delimited by the particular solutions are: A)  $1 > P_{12} > 0.3$ ; B)  $0.4 \geq P_{12} > 0$ ; C)  $0 > P_{12} \geq -0.4$ ; D)  $-0.3 > P_{12} > -1$ .

Fig. 3 - SC total electronic energy following the criterion of linear convergence parameter. The 27 states of pyridazine are numbered in the order of Table II. States 4, 14 and 23 correspond to the particular solutions.

TABLE I. Criterion of highest electronic interaction for 27 states of pyridazine.

(a)  $2n_i^+$ , occupation numbers of symmetric levels;  $2n_i^-$ , occupation numbers of antisymmetric levels;  $\xi$ , convergence parameter.

(b)  $\Delta E = E_{\text{tot}}(\text{final}) - E_{\text{tot}}(\text{first iteration})$ ;  $\nu$ , number of iterations required to attain self-consistency.

State	(a)			(b)	
	$2n_i^+$	$2n_i^-$	$\xi$	$\Delta E(\text{eV})$	$\nu$
1	2 2 0	2 0 0	1	-0.10	8
2	2 2 1	1 0 0	1	-0.04	4
3	2 1 0	2 1 0	1	-4.81	25
4	2 0 0	2 2 0	1	-8.0	20
5	2 2 2	0 0 0	---	---	--
6	1 2 0	2 0 1	0.8	+0.32	20
7	2 1 1	1 1 0	1	-0.72	9
8	2 1 2	0 1 0	0.8	+0.26	18
9	2 0 1	1 2 0	0.8	+2.22	25
10	2 0 2	0 2 0	0.4	+0.46	21
11	1 1 0	2 1 1	1	-0.04	5
12	1 2 1	1 0 1	1	+0.20	14
13	1 0 0	2 2 1	1	+4.0	7
14	1 1 1	1 1 1	---	---	--
15	1 2 2	0 0 1	-1	+0.14	6
16	1 0 1	1 2 1	-1	-0.10	13
17	1 1 2	0 1 1	-1	$\sim 0$	4
18	0 2 0	2 0 2	-0.4	-0.16	17
19	0 1 0	2 1 2	-0.8	$\sim 0$	13
20	0 2 1	1 0 2	-0.8	-1.40	20
21	1 0 2	0 2 1	-1	-0.34	35
22	0 1 1	1 1 2	-1	+0.14	7
23	0 0 0	2 2 2	---	---	--
24	0 2 2	0 0 2	-1	-4.78	17
25	0 0 1	1 2 2	-1	$\sim 0$	4
26	0 1 2	0 1 2	-1	+2.70	19
27	0 0 2	0 2 2	-1	+0.22	7

TABLE II. Criterion of linear convergence parameter for 27 states of pyridazine.

(a)  $2n_i^+$ , occupation numbers of symmetric levels;  $2n_i^-$ , occupation numbers of antisymmetric levels;  $\xi$ , convergence parameter.

(b)  $\Delta E = E_{\text{tot}}(\text{final}) - E_{\text{tot}}(\text{first iteration})$ ;  $v$ , number of iterations required to attain self-consistency.

State	(a)			(b)	
	$2n_i^+$	$2n_i^-$	$\xi$	$\Delta E(\text{eV})$	$v$
1	2 2 0	2 0 0	1	-0.10	8
2	2 2 1	1 0 0	0.74	-0.02	3
3	2 1 0	2 1 0	0.80	-2.66	17
4	2 2 2	0 0 0	0.48	---	--
5	2 0 0	2 2 0	0.60	-1.91	10
6	1 2 0	2 0 1	0.44	+0.02	5
7	2 1 1	1 1 0	0.55	-0.05	5
8	2 1 2	0 1 0	0.28	+0.20	6
9	2 0 1	1 2 0	0.34	$\sim 0$	4
10	1 1 0	2 1 1	0.25	$\sim 0$	2
11	1 2 1	1 0 1	0.18	$\sim 0$	2
12	2 0 2	0 2 0	0.08	$\sim 0$	3
13	1 0 0	2 2 1	0.06	$\sim 0$	1
14	1 1 1	1 1 1	0	---	--
15	1 2 2	0 0 1	-0.06	$\sim 0$	1
16	0 2 0	2 0 2	-0.08	$\sim 0$	1
17	1 0 1	1 2 1	-0.18	$\sim 0$	2
18	1 1 2	0 1 1	-0.25	$\sim 0$	2
19	0 2 1	1 0 2	-0.34	-0.12	6
20	0 1 0	2 1 2	-0.28	$\sim 0$	3
21	1 0 2	0 2 1	-0.44	-0.01	5
22	0 1 1	1 1 2	-0.55	-0.01	5
23	0 0 0	2 2 2	-0.48	---	--
24	0 2 2	0 0 2	-0.60	+0.93	9
25	0 1 2	0 1 2	-0.80	+1.41	13
26	0 0 1	1 2 2	-0.74	$\sim 0$	2
27	0 0 2	0 2 2	-1	+0.22	7

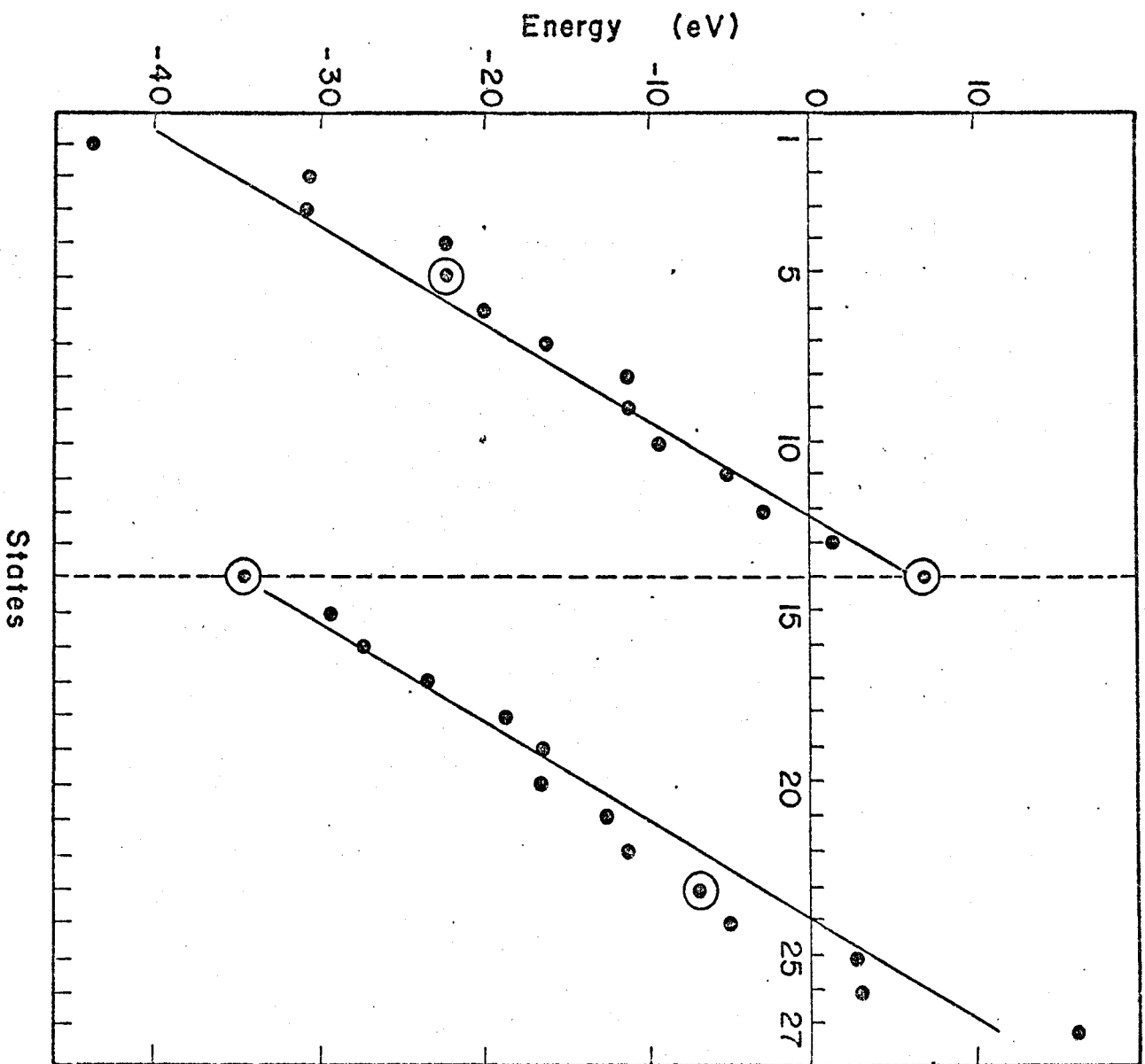


FIG. 1

SC P<sub>12</sub>

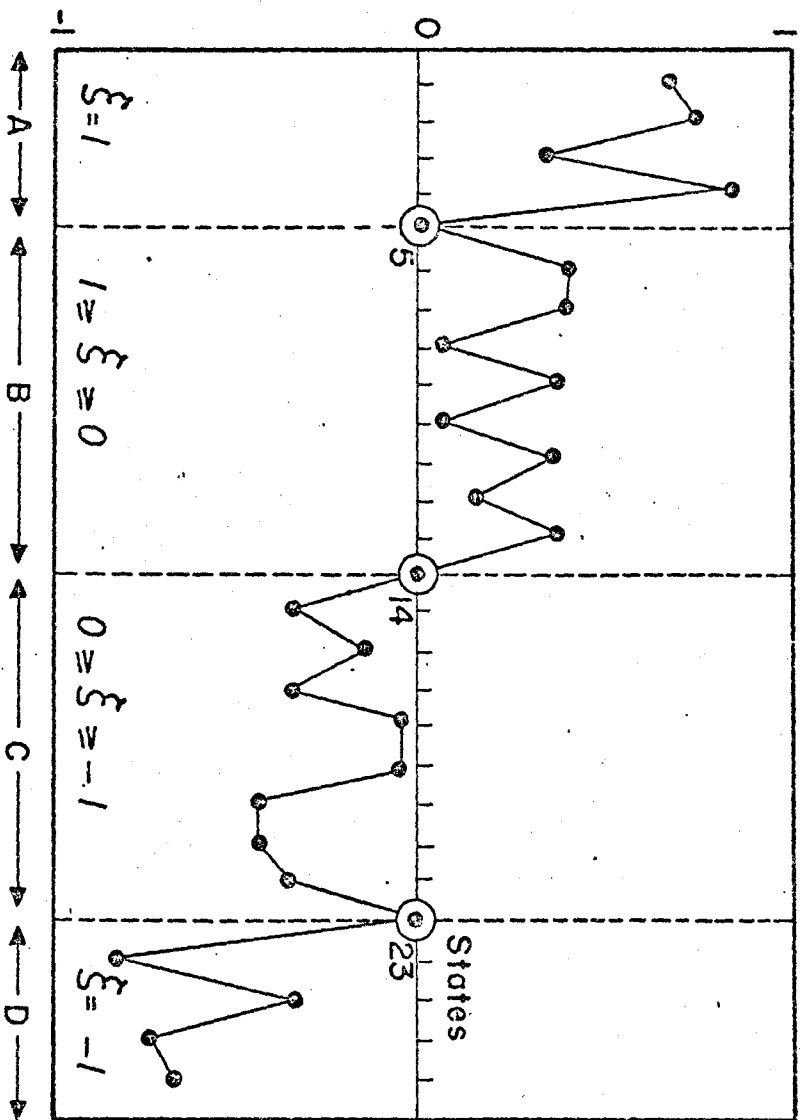


FIG. 2

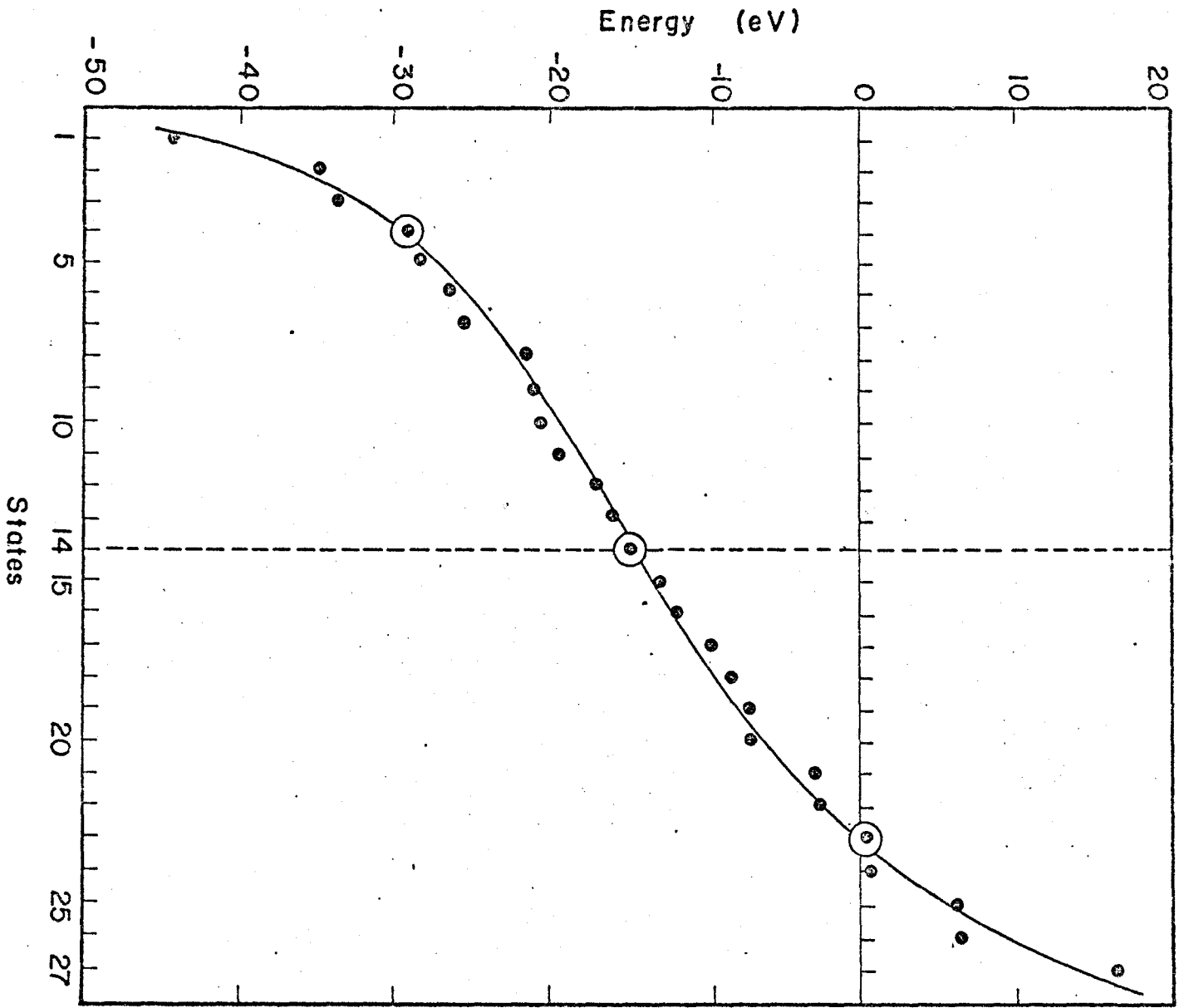


FIG. 3