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OCCUPATION NUMBER DEPENDENCE OF MOLECULAR ENERGY LEVELS[*]

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ABSTRACT

The Roothaan expression for the energy of a closed-shell molecular system is generalized in order to apply to open shells. A continuous variation from 0 to 2 is supposed for each level's occupation number, extending to this range the correction due to the spurious repulsion appearing in the half-electron method. The characteristic equations of the $X\alpha$ method are applied to the energy expressions. The one level case is discussed in detail. Ionic and excited states of the 1,3 transbutadiene π system are analyzed.

1. INTRODUCTION

The Hartree-Fock treatment of atoms and molecules [1] based on single-determinant wavefunctions is straightforward in the closed shell case, but presents difficulties for open shells. If it is required that $\underset{\sim}{H}$ commutes with $\underset{\sim}{S}^2$, $\underset{\sim}{S}$ is not well defined in open shell systems. On the other hand, the complications arisen by the use of unrestricted wavefunctions are well known [2] . To circumvent this problem Roothaan [3] has proposed a multi-determinant wavefunction, leading to an eigenvalue problem of quite a different kind. Dewar, on the other hand, proposed his half-electron method [4,5,6] in which the open shell is described as a closed shell with two half electrons and the resulting spurious electron repulsion is subs tracted at the end of the calculation.

The success of the SCF-Xα method for the calculation of electron binding energies has been ascribed not to relaxation, but to the "correct" handling of the electron-repulsion terms of the multiplet barycenter [7,8] . It is not apparent, however, whether the electronic relaxation effects of the Xα techniques (thawing of the eigenfunctions) are the same as understood in molecular orbital (MO) theory [9] . In a previous paper on the excited states of transbutadiene [10] , the individual eigenvalues seemed to be rather independent of the occupation number of the other functions.

In the present paper, this point is discussed in detail through an analysis of the dependence of orbital energies and the

total electronic energy considered as continuous functions of the occupation numbers. In this context the formalism of the $X\alpha$ method is particularly suitable.

2. ELECTRONIC π ENERGY, ENERGY LEVELS AND THEIR DEPENDENCE ON OCCUPATION NUMBERS.

In the closed-shell PPP method [11] , the expression for the total π-electron energy is written as a function of the bond orders $P_{\mu\nu}$ between atoms μ and ν :

$$E_\pi = \sum_\mu P_{\mu\mu} (U_{\mu\mu} + \frac{1}{4} P_{\mu\mu}\gamma_{\mu\mu}) + 2 \sum_{\mu<\nu} P_{\mu\nu}\beta_{\mu\nu} + \sum_{\mu<\nu} \{(P_{\mu\mu}-1)(P_{\nu\nu}-1)- \frac{1}{2} P^2_{\mu\nu}\}\gamma_{\mu\nu} \quad (1)$$

where $U_{\mu\mu}$, $\beta_{\mu\nu}$ are the Hückel parameters, $\gamma_{\mu\nu}$ are the atomic repulsion integrals and, if n_i is the occupation number of the i-th level and $c_{i\mu}$ the coefficient of atom μ in the i-th eigenfunction,

$$P_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu} \quad (2)$$

For open-shell systems, being $P^\alpha_{\mu\nu} + P^\beta_{\mu\nu} = P_{\mu\nu}$, the extension of (1) is [12]

$$E_\pi = \sum_\mu (P_{\mu\mu}U_{\mu\mu} + P^\alpha_{\mu\mu} P^\beta_{\mu\mu} \gamma_{\mu\mu}) + 2 \sum_{\mu<\nu} P_{\mu\nu}\beta_{\mu\nu} + \sum_{\mu<\nu} \{(P_{\mu\mu}-1)(P_{\nu\nu}-1)-$$

$$[(P^\alpha_{\mu\nu})^2 + (P^\beta_{\mu\nu})^2]\}\gamma_{\mu\nu} \quad (3)$$

which reduces to (1) if $P_{\mu\nu}^{\alpha} = P_{\mu\nu}^{\beta} = P_{\mu\nu}/2$.

Through (2), we have for (1) the expression of the π-energy as an explicit function of the occupation number. (1) is a particular case of the formula proposed by Dewar [4].

$$E_D = \sum_i (n_i H_{ii} + n_i^2 J_{ii}/4) + (1/4) \sum_{i \neq j} \sum_j n_i n_j (2J_{ij} - K_{ij}) \qquad (4)$$

for the "half-electron" method. H_{ii} is the core energy of an electron occupying the i-th eigenfunction: J_{ij} and K_{ij} are the Coulomb and exchange interactions between electrons in the molecular orbitals i and j. When i is a singly-occupied orbital, (4) introduces a spurious repulsion between the two half-electrons (1/4) J_{ii}.

On the other hand, Slater's expression for the average energy of all possible multiplets barycenter is [9] , in the Hyper-Hartree-Fock method

$$E_S = \sum_i (n_i H_{ii} + \frac{1}{2} n_i (n_i - 1) J_{ii}) + (1/4) \sum_{i \neq j} \sum_j n_i n_j (2J_{ij} - K_{ij}) \qquad (5)$$

where the term in J_{ii} vanishes, as it should, for $n_i = 1$.

Let us now propose an expression to be used instead of (3), written under a form similar to (4), which shows the explicit dependence on n^{α} and n^{β}.

$$E = \sum_i \left[(n_i^{\alpha} + n_i^{\beta}) H_{ii} + n_i^{\alpha} n_i^{\beta} J_{ii} \right] + (1/4) \sum_{i \neq j} \sum_j (n_i^{\alpha} + n_i^{\beta})(n_j^{\alpha} + n_j^{\beta})(2J_{ij} - K_{ij}) \qquad (6)$$

with $n_i^{\alpha} + n_i^{\beta} = n_i$. This reduces to (4) if $n_i^{\alpha} = n_i^{\beta} = n_i/2$. For $n_i = 0$

or 2, (4),(5) and (6) obviously coincide. We shall see that (6) is more appropriate than (5) for continuous n_i, for (5) as such is not differentiable although is used as if it were [13] ; on the other hand, (6) retains other desirable featu - res of (5).

We shall apply to these energy expressions the funda- mental equation of the $X\alpha$ method.

$$E_i = \partial E/\partial n_i \qquad\qquad (7)$$

(where E_i are the eigenvalues of the problem), which has been shown to hold also for the Hartree-Fock method [14] . For (4) and (5) we obtain respectively

$$E_{iD} = \partial E_D/\partial n_i = H_{ii} + (n_i/2)J_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij}) \qquad (8)$$

$$E_{iS} = \partial E_S/\partial n_i = H_{ii} + (n_i - \frac{1}{2})J_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij}) \qquad (9)$$

When we take in (6) $n_i^\alpha = 1$, $n_i^\beta = 0$, the J_{ii} term vanishes, avoiding thus the problem of the spurious repulsion appearing in (4). Let us find the α and β levels, which could be allowed to be different [15,16,17].

$$\left. \begin{aligned} E_i^\alpha &= \partial E/\partial n_i^\alpha = H_{ii} + n_i^\beta J_{ii} + \frac{1}{2} \sum_{j \neq i} (n_j^\alpha + n_j^\beta)(2J_{ij} - K_{ij}) \\[2mm] E_i^\beta &= \partial E/\partial n_i^\beta = H_{ii} + n_i^\alpha J_{ii} + \frac{1}{2} \sum_{j \neq i} (n_j^\alpha + n_j^\beta)(2J_{ij} - K_{ij}) \end{aligned} \right\} \qquad (10)$$

Here we must distinguish between two cases: a) $0 \leq n_i < 1$; b) $1 < n_i \leq 2$.

a) $0 \leq n_i < 1$; $n_i^\alpha = n_i$; $n_i^\beta = 0$

$$E_i^\alpha = H_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij}) \left. \vphantom{\begin{array}{c}1\\1\\1\end{array}} \right\} \tag{11}$$

$$E_i^\beta = H_{ii} + n_i J_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij})$$

On the other hand, writting (6)

$$E = \sum_i n_i H_{ii} + (1/4) \sum_{i \neq j} \sum_j n_i n_j (2J_{ij} - K_{ij}) \tag{12}$$

and, by (7), the restricted energy levels are:

$$E_i = \partial E / \partial n_i = H_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij}) \tag{13}$$

which are the α levels.

b) $1 < n_i \leq 2$; $n_i^\alpha = 1$; $n_i^\beta = n_i - 1$

$$E_i^\alpha = H_{ii} + (n_i - 1) J_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij}) \left. \vphantom{\begin{array}{c}1\\1\\1\end{array}} \right\} \tag{14}$$

$$E_i^\beta = H_{ii} + J_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij})$$

The analogous of (12) is

$$E = \sum_i \left[n_i H_{ii} + (n_i - 1) J_{ii} \right] + (1/4) \sum_{i \neq j} \sum_j n_i n_j (2J_{ij} - K_{ij}) \tag{15}$$

which, upon derivated, becomes

$$E_i = \partial E/\partial n_i = H_{ii} + J_{ii} + \frac{1}{2} \sum_{j \neq i} n_j (2J_{ij} - K_{ij}) \tag{16}$$

that is, the β levels.

From (8),(9),(13) and (16) we see that, aside from relaxation effects, the energy levels are linear in each n_j, the slopes being

$$\begin{aligned} \partial E_{iD}/\partial n_i &= J_{ii}/2 & \partial E_{iD}/\partial n_j &= \frac{1}{2}(2J_{ij} - K_{ij}) \\[2ex] \partial E_{iS}/\partial n_i &= J_{ii} & \partial E_{iS}/\partial n_j &= \frac{1}{2}(2J_{ij} - K_{ij}) \\[2ex] \partial E_i/\partial n_i &= 0 & \partial E_i/\partial n_j &= \frac{1}{2}(2J_{ij} - K_{ij}) \end{aligned} \right\} \tag{17}$$

However, the slope of the E_i level is different whether its own occupation number n_i, or another level's n_j, is varying. If more than one occupation number changes, the effects are additive. These second-derivative terms $\partial^2 E/\partial n_i \partial n_j$ "measure the magnitude of the decrease of the i-th eigenvalue when an electron is removed from the j-th eigenvalue..."[9] ; alternatively , $\partial E_i/\partial n_j = \partial E_j/\partial n_i$. The self-interaction $(\partial E_i/\partial n_j)_{i=j}$ differs in the three approximations, while the $i \neq j$ terms are the same.

3. SINGLE ORBITAL ATOMIC CASE

Let us illustrate all this first in an atomic case,

with a single orbital whose occupation number goes from 0 to 2. (The total energy is discussed in ref. [18]). The energy levels are shown in Fig. 1.

From (13) and (16), with $H_{ii} = -I$, the correct values -A for $n_i = 2$ and -I for $n_i = 0$ are obtained [19,13]. If the ionization energy is A for the negative ion, it must jump' to I as soon as the second electron is removed.

When filling the α level from 0 to 1, it keeps constant. Our restricted energy level is this one. In the meantime, the β level is changing, due to the n^α dependence in formulae (10). In $n_i = 1$, E_i shifts to the β level, which remains in turn constant as it fills, while the α level changes until they rejoin at $n_i = 2$. That is, the shift in E_i for $n_i = 1$ is a consequence of the separate continuity of the α and β levels.

The Slater and Dewar energy levels coincide for $n_i = 1$ (where they are equal to the electronegativity (I+A)/2, that is the average of our two values[*]), but differ for $n_i = 0$ and 2; for these last values the Slater expression for the levels is manifestly wrong [13].

4. MOLECULAR CASE AND APPLICATION TO 1,3 TRANSBUTADIENE

In the second place, let us now explore the molecular energy level variation as a function of the occupation number treated as a continuous variable. We shall also analyse the generalization of the correction to the spurious repulsion term in Dewar's formula (4).

*It is well known that the Fourier expansion of a discontinuous function gi ves the mean value at the point where the discontinuity occurs.

We develop a standard PPP calculation, using Pariser-Parr parameters [20] for 1,3 transbutadiene applying the closed-shell energy expression (1) until self-consistency, supposing $P^{\alpha}_{\mu\nu} = P^{\beta}_{\mu\nu} = P_{\mu\nu}/2$. This gives the Dewar levels, and for 4-electron states of integral occupation numbers, bond orders coincide with the SC ones which may be obtained directly without the self-consistency process [21] . We then correct the levels with $n_i \neq 0$ or 2. As to the total π energy, the correct expression being (3) or (6), it may be easily shown that the correction which must be allowed for, with a contribution from each energy level with $n_i \neq 0$ or 2, is the removal of the spurious repulsion

$$\Delta E = \begin{cases} n_i^2 J_{ii}/4 & ; \quad 0 \leq n_i < 1 \\[2em] (1/4)n_i^2 J_{ii} - (n_i-1)J_{ii}=(2-n_i)^2 J_{ii}/4; & 1 < n_i \leq 2 \end{cases}$$

For $0 \leq n_i < 1$ the correction is the straightforward generalization of Dewar's term [4,18] $(n_i/2)^2 J_{ii}$; we suppose that the real situation is $n^{\alpha}_i=n_i$, $n^{\beta}_i=0$. Similarly, comparing a real situation $n^{\alpha}_i=1$, $n^{\beta}_i=n_i-1$ with the one $n^{\alpha}_i=n^{\beta}_i=n_i/2$, it happens as if we had an excess of electronic charge $(1-n_i/2)$ on one hand and an equal defect on the other. The corresponding spurious repulsion is then the symmetric one $(1-n_i/2)^2 J_{ii}$.

Let us underline that for $n_i=1$, according to (7), the correction of $J_{ii}/4$ in E_{π} involves a correction of $J_{ii}/2$ in the i-th level, eliminating thus the undesirable excess predicted

by Koopman's theorem in certain semiempirical approximations [6,18] (see Figs. 1 and 2).

Fig. 2 illustrates formulae (17) by showing the gradual ionization of butadiene, that is the process $(1a_u)^2(1b_g)^2 \rightarrow (1a_u)^2(1b_g)$. The slopes $\partial E_j/\partial n_{1b_g}$ are equal within 5% for $j \neq 1b_g$ (3.71, 3.83 and 3.91 β_{23}) and also equal to $2\partial E_{1b_g} D/\partial n_{1b_g}$ (3.95 β_{23}). The slope of $\partial E_{1b_g}/\partial n_{1b_g}$ is not strictly zero (0.10β_{23}) due to relaxation. Another interesting feature of the Xα method which holds here is that the difference in total energy between the final and initial states coincides with the $1b_g$ energy level of the transition state, in this case $(1a_u)^2(1b_g)^{1.5}$. This is true both for the Dewar (that is, Pople close-shell) energy, as for the corrected total energy and level.

We are now able to understand the gradual excitation process $(1a_u)^2(1b_g)^2 \rightarrow (1a_u)^2(1b_g)(2a_u)$ of Fig. 3. Here we have two levels whose occupation number changes, one in a sense, the other in the opposite sense. The result is the almost constancy of the E_{1a_u} and E_{2b_g} levels due to the addition of effects. It is worth stressing that the change of the E_{1b_g} and E_{2a_u} levels is not due to the variation of their own occupation number, but each one varies due to the modification of the other's n_i. Facing two opposite compensating effects, if only the excitation process is regarded, the effect of varying a single occupation number remains hidden [22,10] . The corrections apply opposite to one another, for n_{2a_u} increases and n_{1b_g} decreases. The slopes are therefore of equal magnitude (3.89β_{23}), as those of

the ionization process, and opposite sign; taking into account the correction, the levels cross each other. The small slopes of E_{1a_u} and of E_{2b_g} (both $|0.23 \beta_{23}|$) are due to relaxation and to the fact that the opposite additive effects do not exactly compensate. The corrected total energy shows a maximum at the level crossing point. We have verified once again that, as in the Xα method, the difference in total energy between final and initial states is equal to $E_{2a_u} - E_{1b_g}$ in the transition state $(1a_u)^2 (1b_g)^{1.5} (2a_u)^{0.5}$, both for the corrected and uncorrected eigenvalues.

The calculations and graphical representation of the negative ionization process $(1a_u)^2 (1b_g)^2 \rightarrow (1a_u)^2 (1b_g)^2 (2a_u)$ support the analysis made for Figs. 2 and 3.

Fig. 4 illustrates the gradual single population of all levels, that is $(1a_u)^0 (1b_g)^0 (2a_u)^0 (2b_g)^0 \rightarrow (1a_u)^1 \rightarrow (1a_u)^1 (1b_g)^1 \rightarrow (1a_u)^1 (1b_g)^1 (2a_u)^1 \rightarrow (1a_u)^1 (1b_g)^1 (2a_u)^1 (2b_g)^1$. The levels of the first state have a clear meaning. They are the π energy levels of the σ skeleton, which in the PPP approximation are simply the Hückel solutions [11]. At the same time as they populate, interaction is introduced. The behaviour of the energy levels is the same as before; they show a peculiar center of inversion. Both E_π curves posess a minimum, which is situated around the configuration $(1a_u)^1 (1b_g)^1 (2a_u)^{0.8}$ without correction, shifting exactly to $(1a_u)^1 (1b_g)^1 (2a_u)^1$ upon correction.

Table 1 shows numerically the effect of relaxation. It is seen to be very small (<0.1 eV) and in the correct sense. That is, the relaxed energies (corrected or not) are lower than the "frozen" ones.

Finally, we would like to mention a couple of points bearing on some concepts of MO theory. It is abundantly clear now [23,24,25,26] that inner shell excitations and ionizations and, in some cases, valence shell processes as well, change the one-electron energy sequence. These violations of Koopman's theorem are due to orbital thawing and to the fact that, as shown in equations (13) and (16), E_i is a function of n_j.

The so-called paradoxical violations of Koopman's statement [27,18] emphasize the limitations of the orbital energy diagrams and of the very concepts of bonding and antibonding orbitals. These problems will be dealt with in a forthcoming paper.

5. CONCLUSIONS

1. The correction due to the spurious repulsion appearing in the half-electron method is extended to occupation numbers varying continously from 0 to 2, with a unified interpretation.

2. The behaviour of a single occupied level whose occupation number goes from 0 to 2 is elucidated, and shown to be in agreement with the concepts of ionization potential and electron affinity.

3. The expressions found here for $\partial E_i / \partial n_j$ allow an interpretation of the energy level's behaviour of a conjugated system as a function of the occupation number of each level.

4. The results confirm that the usefulness of the transition state concept in the calculation of ionization and excitation energies is not privative of the $X\alpha$ method.

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Table 1. Corrected and uncorrected energies and Coulomb repulsion with and without relaxation, all in β_{23} units. $J_{2a_u,2a_u} = J_{1b_g,1b_g}$ for the state $(1a_u)^2(1b_g)(2a_u)$.

State	$(1a_u)^2(1b_g)$	$(1a_u)^2(1b_g)(2a_u)$
E_π (rel)	4.0704	0.3900
E_π	4.0118	0.3463
E_π^C (rel)	5.1086	2.4671
E_π^C	5.0586	2.4400
$J_{1b_g,1b_g}$(rel)	4.1529	4.1542
$J_{1b_g,1b_g}$	4.1873	4.1873

FIG. 1

E_i

n_i

-1

$-A$

O

1

2

E_i^β

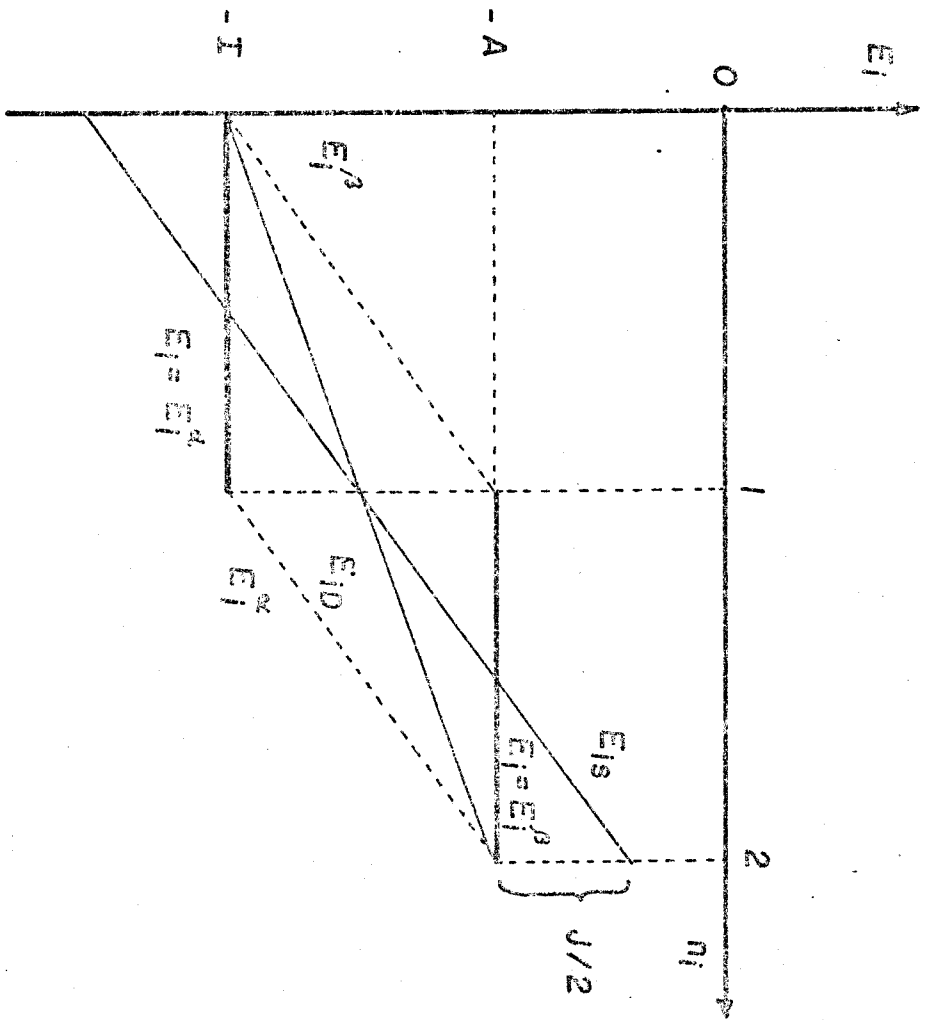$E_i = E_i^\beta$
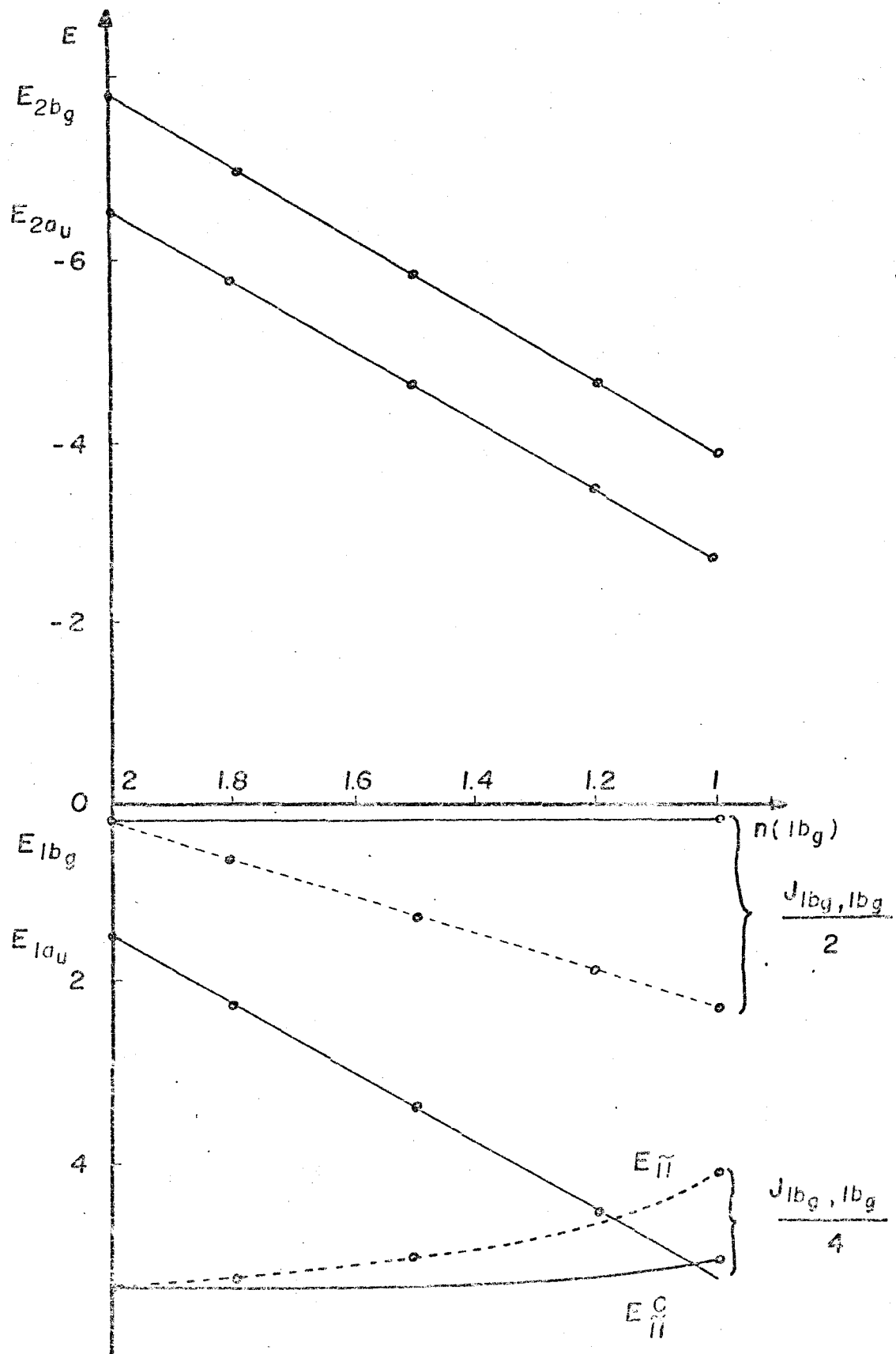
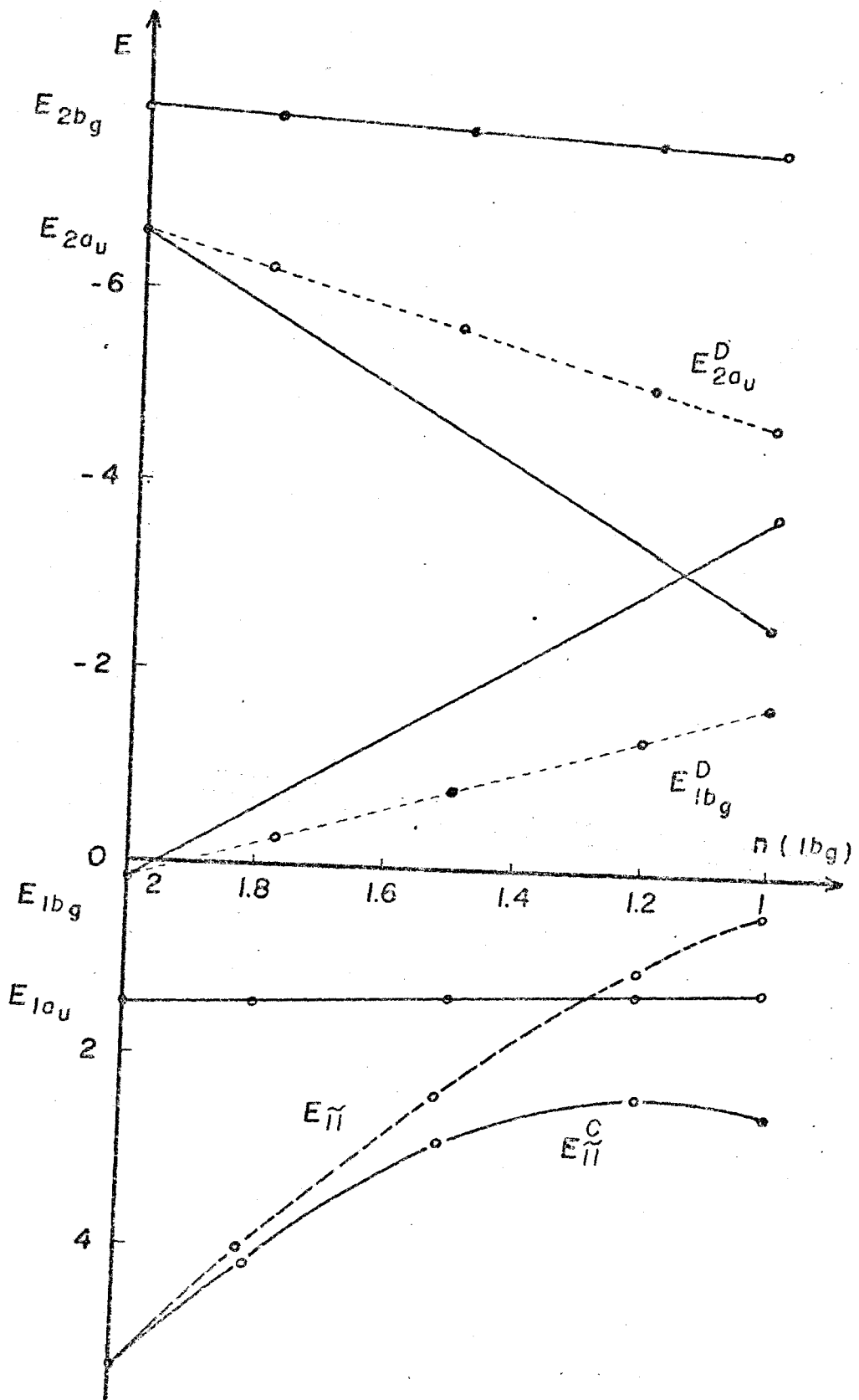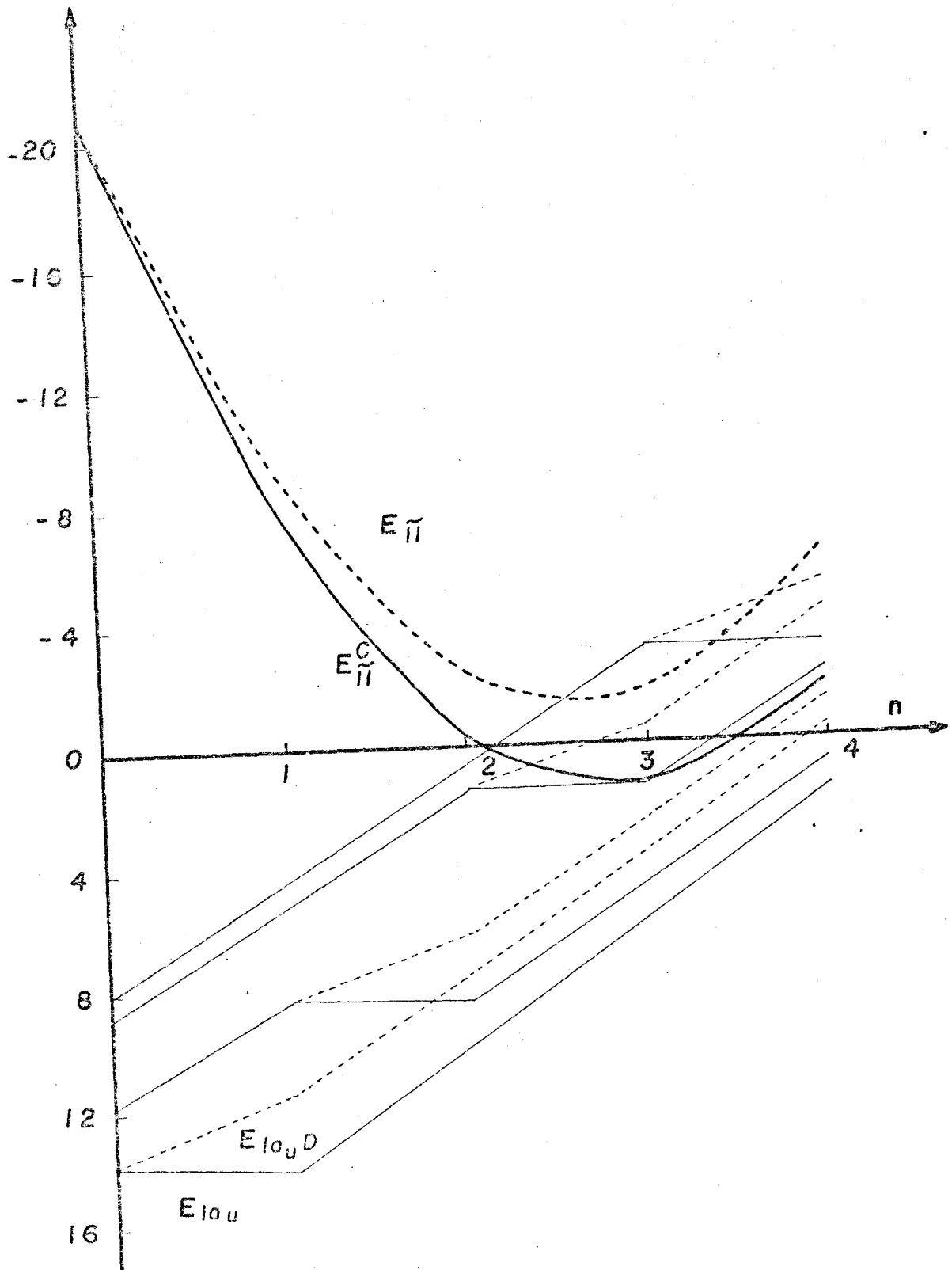$E_i^p = E_i^q$

E_i^D

E_i^R

E_i^s

$J/2$

FIG. 2

FIG. 3

FIG. 4

FIGURE CAPTIONS

Fig. 1 - Energy levels in an atomic case with a single orbital.

Fig. 2 - Gradual ionization for butadiene: $(1a_u)^2(1b_g)^2 \rightarrow$
$\rightarrow (1a_u)^2(1b_g)$. The Fig. shows energy levels and total
π energies in β_{23} units. E_π is calculated from (1)
and E_π^C represents equation (6). The E_{1b_g} level cor_
rects the spurious repulsion of Dewar's $E_{1b_g,D}$.

Fig. 3 - Gradual excitation for butadiene: $(1a_u)^2(1b_g)^2 \rightarrow$
$\rightarrow (1a_u)^2(1b_g)(2a_u)$. The Fig. shows energy levels and
total π energies in β_{23} units. E_π is calculated from
(1) and E_π^C represents equation (6). The E_{1b_g}, E_{2a_u}
levels correct the effect of the spurious repulsion
on Dewar's $E_{1b_g,D}$, $E_{2a_u,D}$.

Fig. 4 - Gradual single population of all π levels for butadie_
ne: $(1a_u)^0(1b_g)^0(2a_u)^0(2b_g)^0 \rightarrow (1a_u)^1 \rightarrow (1a_u)^1(1b_g)^1 \rightarrow$
$\rightarrow (1a_u)^1(1b_g)^1(2a_u)^1 \rightarrow (1a_u)^1(1b_g)^1(2a_u)^1(2b_g)^1$.
$n = \sum_i n_i$