

# UPS AND DOWNS IN UPS

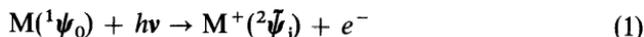
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## ABSTRACT

A few of the problems associated with UPS of medium-sized organic molecules are discussed (UPS = ultra-violet photoelectron spectroscopy). Attention is drawn to some of the pitfalls which occur, if the widely used independent electron<sup>1</sup> or the semi-empirical treatments<sup>2</sup> are taken at face value and applied without due caution.

I. The primary process investigated in UPS is the photoejection of an electron from a singlet ground state molecule M, to generate a radical cation M<sup>+</sup> in a doublet state  ${}^2\tilde{\psi}_j$ :



If the states  ${}^1\psi_0$  and  ${}^2\tilde{\psi}_j$  are written as

$${}^1\psi_0 = \mathcal{A}(\varphi_1^0 \bar{\varphi}_1^0 \dots \varphi_j^0 \bar{\varphi}_j^0 \dots \varphi_N^0 \bar{\varphi}_N^0) \quad (2)$$

and

$${}^2\tilde{\psi}_j = \begin{cases} \mathcal{A}(\varphi_1 \bar{\varphi}_1 \dots \varphi_j \dots \varphi_N \bar{\varphi}_N) \\ \mathcal{A}(\varphi_1 \bar{\varphi}_1 \dots \bar{\varphi}_j \dots \varphi_N \bar{\varphi}_N) \end{cases} \quad (3)$$

$\varphi_j^0$  and  $\varphi_j$  being the SCF canonical molecular orbitals (CMO) of M( ${}^1\psi_0$ ) and M<sup>+</sup>( ${}^2\tilde{\psi}_j$ ), respectively, then the ionization energy  $I_j$  associated with band j in the PE spectrum of M is

$$I_j = \mathcal{E}[M^+({}^2\tilde{\psi}_j)] - \mathcal{E}[M({}^1\psi_0)] \quad (4)$$

For medium-sized molecules the numerical expenditure necessary for calculating equations (3) and (4) for each j is rather formidable, even with modern computing facilities. Therefore, almost all interpretations of PE spectra use the approximation  $\varphi_j = \varphi_j^0$  (Koopmans's approximation<sup>3</sup>). If this simplification is introduced into equation (3), it is found that

$$I_j = -\varepsilon_j \quad (5)$$

where  $\varepsilon_j$  is the orbital energy of the CMO  $\varphi_j^0$  (Koopmans's theorem). This approximation neglects electron reorganization and changes of correlation in M<sup>+</sup>( ${}^2\tilde{\psi}_j$ ). Experience has shown that for molecules from first- and second-row elements the results obtained according to equation (5) are respectable,

especially if they are scaled empirically, i.e.

$$I_j = A + B\varepsilon_j \quad (6)$$

with (in general)  $A \neq 0$ ,  $B \neq -1$ . However, significant failures are sometimes encountered<sup>4</sup> which can be rationalized in terms of differences in charge redistribution depending on the state  ${}^2\psi_j$  of  $M^{+5}$ .

The main objection to the way in which Koopmans's approximation is often interpreted concerns the assumption that the 'observed' orbital energies  $\varepsilon_j = -I_j$  from equations (5) or (6) and the CMOs  $\phi_j^0$  associated with them yield a 'true' description (3) of  $M({}^1\psi_0)$ . There is, however, a great ambiguity of SCF orbitals. A unitary transformation

$$U\phi^0 = \phi' \quad (7)$$

of the set  $\phi^0$  of CMOs will yield a different set  $\phi'$  without any change in the expectation values for true observables. In particular, the transformation

$$L\phi^0 = \lambda \quad (8)$$

yields localized molecular orbitals (LMO)  $\lambda_j$  according to a preselected localization criterion: e.g. reference 6. In contrast, equations (5) and (6) are no longer applicable to a description of  $M({}^1\psi_0)$  in terms of  $\phi'$  or  $\lambda$ .

II. Semi-empirical procedures are usually calibrated to fit a particular property, e.g. CNDO/2 to reproduce *ab initio* results<sup>7</sup>, MINDO/2 to yield enthalpies of formation<sup>8</sup> or SPINDO to predict PE band positions<sup>9</sup>. To compare the different models in a chemically and heuristically useful way, one first transforms the set  $\phi^0$  of CMOs into LMOs  $\lambda$  (cf. equation 8). The matrix elements  $F_{\lambda,ij}$  of the transformed Hartree-Fock (HF) matrix  $F_\lambda = LF_\phi L^\dagger$  show a high degree of transferability from compound to compound, and their configurational and conformational dependence is similar within a given semi-empirical model. In contrast, the absolute values of the  $F_{\lambda,ij}$  differ considerably from one theoretical procedure to another<sup>10</sup>.

To take advantage of symmetry, the LMOs  $\lambda_j$  are transformed into symmetry-adapted (semi-) localized molecular orbitals (SLMO)  $\rho_j$ :

$$R\lambda = \rho \quad (9)$$

The resulting matrix elements  $F_{\rho,ij}$  of the blocked-out HF matrix  $F_\rho = RF_\lambda R^\dagger$  show that the models disagree with regard to the relative values of  $\pi$ - $\pi$ ,  $\sigma$ - $\pi$ ,  $n$ - $\pi$  and  $n$ - $\sigma$  interactions, which leads to completely different interpretations of a given PE spectrum in terms of traditional electronic 'effects'<sup>10</sup>. This result points to the danger of assigning PE spectra on the basis of a single preselected model, which may well be inadequate for dealing with a given type of interaction. In this context it should be emphasized that what is usually called an assignment depends both on the observed spectrum and to a large degree on the assumed model. As a consequence, UPS cannot yield answers to questions which depend heavily on the choice of a hypothetical reference system, e.g. questions concerning 'aromaticity'.

III. The discussion of PE spectra of organic compounds in terms of 'through-space' and 'through-bond' interactions<sup>11</sup> has become very popular (e.g. reference 12). A typical example is provided by the analysis of the PE

spectrum of 1,5-cyclooctadiyne<sup>13</sup>. To integrate the above concepts into a many-electron SCF model it is proposed to characterize the 'through-space' interaction between two (symmetry-related) LMOs  $\lambda_i$  and  $\lambda_j$  by comparing the diagonal elements  $F_{\lambda,ii}$  and  $F_{\lambda,jj}$  of the HF matrix  $F_\lambda$  with the diagonal elements  $F_{\rho,kk}$ ,  $F_{\rho,ll}$  of the HF matrix  $F_\rho$  based on the SLMOs  $\rho_k$ ,  $\rho_l$  which have been derived from  $\lambda_i$ ,  $\lambda_j$  according to equation (9). As an example we choose norbornadiene, in which  $\lambda_i = \pi_a$  and  $\lambda_j = \pi_b$  are the LMOs of maximum  $\pi$  character. Transformation (9) yields  $\rho_k = (\pi_a + \pi_b)/\sqrt{2}$  and  $\rho_l = (\pi_a - \pi_b)/\sqrt{2}$ . For symmetry reasons we have the degeneracy  $F_{\lambda,ii} = F_{\lambda,jj} = A_\pi$ , i.e. the basis energy of the LMO  $\pi_a$  and  $\pi_b$ . The matrix elements  $F_{\rho,kk}$  and  $F_{\rho,ll}$  lie, respectively, below and above  $A_\pi$  (by equal absolute amounts). The difference  $F_{\rho,ll} - F_{\rho,kk}$  measures the 'through-space' interaction between  $\pi_a$  and  $\pi_b$ .

An estimate of the 'through-bond' coupling between two LMOs  $\lambda_i$ ,  $\lambda_j$  is obtained by the following procedure<sup>14</sup>: removal of the SLMOs  $\rho_k$ ,  $\rho_l$  from the set  $\rho$  and diagonalization of the remaining  $F'_\rho$  HF matrix of order  $N - 2$  yields a set  $\psi$  of 'precanonical' orbitals  $\psi_j$ . The matrix elements  $F_{\psi,jk}$  and  $F_{\psi,jl}$  between the precanonical orbitals  $\psi_j$  and the SLMOs  $\rho_k$ ,  $\rho_l$  measure the 'through-bond' interaction. This procedure has been discussed in detail for norbornadiene<sup>14</sup>. Again it can be shown that different semi-empirical methods used to calculate the CMOs  $\phi_j^0$  differ considerably in their assessment of the factors which are relevant for the observed pattern of a particular PE spectrum.

IV. For the description of electronically excited states of M, i.e.  $M(1\psi_j)$  or  $M(3\psi_j)$ , one has to rely on configuration interaction treatments<sup>15</sup>, although simple orbital diagrams suggest that

$$I_j - I_i = E(j, k) - E(i, k) \quad (10)$$

where  $E(j, k)$  and  $E(i, k)$  are the one-electron excitation energies for the promotion of an electron from the CMOs  $\phi_j^0$ ,  $\phi_i^0$  to the same virtual CMO  $\phi_k^*$ . However, it follows from the well-known matrix elements of the Hamiltonian for the ground and singly excited states of  $M$ <sup>15</sup> that

$${}^1E(j, k) - {}^1E(i, k) = I_j - I_i + J_{ik} - J_{jk} + 2(K_{jk} - K_{ik}) \quad (11)$$

For the transition to triplet states the last bracket of equation (11) vanishes. Depending on the relative size of the Coulomb and exchange integrals in equation (11), the separation  $I_j - I_i$  between PE bands  $j$  and  $i$ , may be smaller<sup>16</sup>, equal to<sup>17</sup> or larger<sup>18</sup> than the difference between the corresponding excitation energies  ${}^1E(i, k) - {}^1E(i, k)$  in the electronic spectrum of  $M$ .

V. To conclude, attention is drawn to the fact that the analytical potentialities of UPS are poor<sup>19</sup> despite some isolated instances where UPS has contributed towards establishing the structure of an unknown.

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