

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 electron¹ or the semi-empirical treatments² 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⁺ 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

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

φ_j^0 and φ_j being the SCF canonical molecular orbitals (CMO) of M(${}^1\psi_0$) and M⁺(${}^2\tilde{\psi}_j$), 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 approximation³). If this simplification is introduced into equation (3), it is found that

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

where ε_j is the orbital energy of the CMO φ_j^0 (Koopmans's theorem). This approximation neglects electron reorganization and changes of correlation in M⁺(${}^2\tilde{\psi}_j$). 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 encountered⁴ 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 ϕ_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 ϕ^0 of CMOs will yield a different set ϕ' 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) λ_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 ϕ' or λ .

II. Semi-empirical procedures are usually calibrated to fit a particular property, e.g. CNDO/2 to reproduce *ab initio* results⁷, MINDO/2 to yield enthalpies of formation⁸ or SPINDO to predict PE band positions⁹. To compare the different models in a chemically and heuristically useful way, one first transforms the set ϕ^0 of CMOs into LMOs λ (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 another¹⁰.

To take advantage of symmetry, the LMOs λ_j are transformed into symmetry-adapted (semi-) localized molecular orbitals (SLMO) ρ_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 π - π , σ - π , n - π and n - σ interactions, which leads to completely different interpretations of a given PE spectrum in terms of traditional electronic 'effects'¹⁰. 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' interactions¹¹ has become very popular (e.g. reference 12). A typical example is provided by the analysis of the PE

spectrum of 1,5-cyclooctadiyne¹³. 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 λ_i and λ_j by comparing the diagonal elements $F_{\lambda,ii}$ and $F_{\lambda,jj}$ of the HF matrix F_λ with the diagonal elements $F_{\rho,kk}$, $F_{\rho,ll}$ of the HF matrix F_ρ based on the SLMOs ρ_k , ρ_l which have been derived from λ_i , λ_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 π 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 π_a and π_b . The matrix elements $F_{\rho,kk}$ and $F_{\rho,ll}$ lie, respectively, below and above A_π (by equal absolute amounts). The difference $F_{\rho,ll} - F_{\rho,kk}$ measures the 'through-space' interaction between π_a and π_b .

An estimate of the 'through-bond' coupling between two LMOs λ_i , λ_j is obtained by the following procedure¹⁴: removal of the SLMOs ρ_k , ρ_l from the set ρ and diagonalization of the remaining F'_ρ HF matrix of order $N - 2$ yields a set ψ of 'precanonical' orbitals ψ_j . The matrix elements $F_{\psi,jk}$ and $F_{\psi,jl}$ between the precanonical orbitals ψ_j and the SLMOs ρ_k , ρ_l measure the 'through-bond' interaction. This procedure has been discussed in detail for norbornadiene¹⁴. Again it can be shown that different semi-empirical methods used to calculate the CMOs ϕ_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 treatments¹⁵, 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 ϕ_j^0 , ϕ_i^0 to the same virtual CMO ϕ_k^* . However, it follows from the well-known matrix elements of the Hamiltonian for the ground and singly excited states of M ¹⁵ 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 smaller¹⁶, equal to¹⁷ or larger¹⁸ than the difference between the corresponding excitation energies ${}^1E(i, k) - {}^1E(j, k)$ in the electronic spectrum of M.

V. To conclude, attention is drawn to the fact that the analytical potentialities of UPS are poor¹⁹ despite some isolated instances where UPS has contributed towards establishing the structure of an unknown.

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