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Commentationes

FEMO Treatment of all Trans-Polyenes with Parametric Energy Dependences*

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The semi-empirical free electron theory with inclusion of interelectronic and electron-nuclear molecular integrals is used to examine the spectroscopic properties of the trans-polyenes. The molecular integrals were calculated at many values of Q, the free electron theory length parameter. Comparisons are made to equivalent LCAO-MO methods, especially in regard to molecular coulomb and exchange integrals, singlet-triplet separations and parametric dependence. The FET virial theorem is examined.

Mit der semiempirischen Elektronengasmethode unter Einschluß von Elektronen-Kern- und Zweielektronen-Wechselwirkungsgliedern werden die Anregungsenergien der Polyene untersucht. Die MO-Integrale werden für verschiedene Längen Q des Elektronengases bestimmt und mit den entsprechenden Größen der MO-LCAO-Methode verglichen, ebenso auch die Singulett-Triplett-Aufspaltungen und die Parameterabhängigkeiten. Das Virialtheorem wird untersucht.

Les trans-polyènes sont étudiés par la théorie de l'électron libre semi-empirique avec introduction des intégrales moléculaires interélectroniques et électron noyau. Les intégrales moléculaires ont été calculées pour de nombreuses valeurs de Q, le paramètre de longueur de la théorie de l'électron libre. Des comparaisons sont faites avec les méthodes LCAO MO équivalentes, en particulier en ce qui concerne les intégrales coulombiennes et d'échange, les séparations singulet-triplet et le rôle des paramètres. Le théorème du viriel de la théorie de l'électron libre est examiné.

Introduction

The *qualitative* ideas of the free electron theory (FET) undoubtedly lie at the heart of *much* of the general thinking about π electron systems. The first *quantitative* application of FET was made by Bayliss [1] who calculated the $\pi-\pi^*$ transition energies of the polyenes from the change in kinetic energy of an electron confined to a one-dimensional box of length Q upon excitation from the highest filled to the lowest unfilled free electron molecular orbital (FEMO). Simultaneously, Kuhn [2] applied FET to a variety of conjugated species. Simpson also contributed to the initial work in FET [3]. Later contributions are dominated by the admirable work of the Chicago group which has recently been republished [4]. Ruedenberg and Scherr [5] performed extensive FET calculations on aromatic molecules using networks of one-dimensional paths. With the introduction of interelectronic repulsion through the requisite coulomb and exchange integrals [6, 7] the theory achieved its highest level of sophistication. At this level the FET is equivalent, or superior, to the Pariser-Parr method.

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Free electron theory is the one-dimensional path theory of molecular orbitals. By generalization, when necessary, to networks of one-dimensional paths FET is applicable to a large class of conjugated molecules. Nevertheless, the usage of FET by quantum chemists has been rather limited in comparison to the LCAO-MO method, and currently it is rarely used in discussing conjugated molecules. The purpose of the present note is to demonstrate and emphasize the relevancy of certain FET results to the more popular LCAO-MO theories.

The FEMO Method

The present work will apply the version of the FET suggested by Ham and Ruedenberg [6] to the all trans-polyenes. Let

$$H=\sum_{i=1}^{N}-\frac{\hbar^2}{2m}\nabla_i^2-\sum_{K}\sum_{i=1}^{N}\frac{e^2}{|q_i-Q_K|}+\sum_{i>j}^{N}\frac{e^2}{|q_i-q_j|}+\sum_{i=1}^{N}V(q_i) \tag{1}$$

be the Hamiltonian of the $N-\pi$-electron system. It consists of kinetic energy operators, electron-nuclear potentials, interelectronic pair potentials, and an average one-electron potential, $V(q_i)$, due to the σ core. Q_K is the position of the K^{th} nucleus and q_i is the coordinate of the i^{th} electron. To proceed, the Hamiltonian of (1) is separated into a zero-order effective Hamiltonian, H_0, and an exact remainder, H_1:

$$H=H_0+H_1\,, \tag{2}$$

$$H_0=\sum_{i=1}^{N}-\frac{\hbar^2}{2m^*}\nabla_i^2\,; \tag{3}$$

m^* is the effective mass of the electron. With the usual boundary conditions the zero-order wavefunction is just a product of free electron molecular spin-orbitals:

$$H_0\Pi_0=E_0\pi_1(1)\,\pi_2(2)\cdots\pi_N(N)\,, \tag{4}$$

$$E_0=\sum_i\varepsilon_i\,,$$

$$\varepsilon_i=n^2h^2/8m^*Q^2\,, \tag{5}$$

$$\pi_i=\left(\frac{2}{Q}\right)^{\frac{1}{2}}\sin\left(\frac{n\pi}{Q}q_i\right)\cdot\begin{cases}\alpha(i)\\ \beta(i)\end{cases}; \tag{6}$$

n is the quantum number of the i^{th} orbital. The parameter, Q, arises from the boundary condition, $\pi_i(q_i=0)=\pi_i(q_i=Q)=0$.

For the representation of H_1 one uses a semi-empirical potential form,

$$H_1=\sum_{K}\sum_{i=1}^{N}G_{iK}(|q_i-Q_K|)+\sum_{i>j}^{N}G_{ij}(|q_i-q_j|)\,. \tag{7}$$

The basic FET integrals are

$$\begin{aligned}H_{ii}&=\varepsilon_i+\sum_k\langle\pi_i(i),\,G_{iK}\pi_i(i)\rangle\,,\\ J_{ij}&=\langle\pi_i(i)\,\pi_i(i),\,G_{ij}\pi_j(j)\,\pi_j(j)\rangle\,,\\ K_{ij}&=\langle\pi_i(i)\,\pi_j(i),\,G_{ij}\pi_i(j)\,\pi_j(j)\rangle\,.\end{aligned} \tag{8}$$

The state energies of the ground state, S_0, and the first excited singlet and triplet states, S_1 and T_1, are

$$E(S_0)=\sum_{i=1}^{N} H_{ii}+\sum_{i>j}^{N}(J_{ij}-K_{ij}), \tag{9}$$

$$E(S_1)=\sum_{i\neq N}^{N+1} H_{ii}+\sum_{\substack{i>j\\ i,j\neq N}}^{N+1}(J_{ij}-K_{ij}), \tag{10}$$

$$E(T_1)=E(S_1)-2K_{N+1,N-1}\,. \tag{11}$$

Having once chosen the value of m^* and the form of the semi-empirical potential G_{ab} (which is the same for G_{ij} and G_{iK}) no further parameters need be specified except Q. While m^* and G_{ab} need be specified but once, and are not changed in treating different molecules, all the integrals of (8) and the resultant energies (9—11) depend on Q, and will be studied as functions of Q.

As for G_{ab}, its form is that of a finite cusp as $|a-b|\rightarrow 0$, thereby removing the infinity from the one-dimensional coulomb potential. At larger distances ($|a-b|>2.4$ Å) G_{ab} is coulombic. Undoubtedly this form for G_{ab} and the manner of its choice [6], go very far towards reducing the role of correlation energies in these calculations. Just as the empirical choice of the one center electronic repulsion integral in Pariser-Parr theory, $\gamma_{pp}=11$ eV, is substantially lower than the purely theoretical value, 16 eV, partially because of electronic correlation.

Results and Parametric Q Dependence

The results to be compared to the experimental transition energies are summarized in Table 1.

Table 1

Molecule	Q [Å]	$E(S_1)-E(S_0)$ [eV]	$E(S_1)-E(T_1)$ [eV]
Ethylene	4 A	7.85 (7.65)	2.65 (3.0)
Butadiene	6	5.95 (5.9)	2.55 (2.8)
Hexatriene	8	5.25 (5.1)	2.40 (2.6)
Octatetraene	10	4.55 (4.1)	2.30 —

Experimental values are in parenthesis.

In Table 2 the FEMO results of Table 1 are compared to some recent Pariser-Parr LCAO-MO calculation [8].

Table 2

Molecule	$E(S_1)-E(S_0)$ [eV]			$E(T_1)-E(S_0)$ [eV]		
	LCAO-MO	FEMO	EXPTL.	LCAO-MO	FEMO	EXPTL.
Butadiene	5.85	5.95	5.9	2.22	3.4	3.22
Hexatriene	5.1	5.25	5.1	1.84	2.85	2.58

The comparison in Table 2 is to note the very reasonable singlet-triplet separations of the FEMO calculations and the comparatively poorer LCAO-MO results. In general, the accuracy of the FET is as good as the semi-empirical LCAO-MO theory. However, because of the ascendancy and generality of

LCAO-MO theory, one may only ask if the results have any pertinence to LCAO-MO calculations.

In this regard our interest centers on the parametric Q dependence of the energy integrals, which is very different from the way internuclear distances appear in the LCAO-MO theory. The singlet-triplet separations are also of great interest. While in Eqs. (8) to (11) a spin-orbital index was used, if a space orbital index is used then an important coulomb integral in FET may be written,

$$J_{11}(\mathrm{FEMO}) = \frac{1}{N^2}\left\langle \sin^2\left(\frac{\pi}{Q} q_1\right) |G_{12}| \sin^2\left(\frac{\pi}{Q} q_2\right)\right\rangle .$$

N is the normalization factor. The integration is by two electron numerical quadrature (appendix). The same integral occurs in the energy of each polyene. So, having been calculated once at each of the Q values, $J_{11}(\mathrm{FEMO})$ is transferable from one molecule to another. While the MO integrals are thus transferable in FET it's the AO integrals which are transferable in LCAO-MO theory. $J_{11}(\mathrm{FEMO})$ can be identified with the π coulomb integral of ethylene.

$$J_{11}(\text{LCAO-MO}) = \frac{1}{N^2}\left\langle (p_a(1) + p_b(1))^2 \left| \frac{1}{r_{12}} \right| (p_a(2) + p_b(2))^2 \right\rangle$$

$p_a(1)$ is a $2p_\pi$ orbital on atom a. $J_{11}(\text{LCAO-MO})$ can be given a purely theoretical evaluation over a particular AO, but in an approximate calculation this is not a very fruitful approach. Rather, analogous to the empirical choice of G_{12} in $J_{11}(\mathrm{FEMO})$, it is conventional to apply the zero differential overlap (ZDO) approximation. Empirical values for the remaining AO integrals may then be chosen.

$$J_{11}(\text{LCAO-MO-ZDO}) = \tfrac{1}{2}(\gamma_{pp} + \gamma_{pq}) ,$$

$\gamma_{pp} = \langle p_a^2 | 1/r_{12} | p_a^2 \rangle$ and $\gamma_{pq} = \langle p_a^2 | 1/r_{12} | p_b^2 \rangle$. The two center integral γ_{pq} has a parametric dependence on the internuclear distance R_{ab}.

The theoretical relation between γ_{pq} and R_{ab} is obtainable from integration over, say, STOs [9]. An empirical relation seems to be preferred, especially at small R_{ab}. Pariser and Parr [11] suggested for $R_{ab} < 2.8$ Å a short power series in R_{ab} with γ_{pp} as the leading constant term. Pullman and Schiess [12] later gave the series,

$$\gamma_{pq} = \gamma_{pp} - 3.92327\, R_{ab} + 0.69786\, R_{ab}^2 \tag{12}$$

with $\gamma_{pp} = 11.08$ eV.

The choice of parameters in the LCAO-MO-ZDO theory has been centroversial. Koutecký has discussed the various parameterizations for this theory, and recently [10] has formulated a relation between the γ_{pq} on R_{ab} dependence and the importance of configuration interaction in Pariser-Parr calculations. Nishimoto [16] has recently used a dielectric model to obtain γ_{pq} as a function of R_{ab}. His values gave rather goed singlet-triplet separations in the test calculations. Recently Hansen [17] has examined the form of γ_{pp} and γ_{pq} when "horizontal" correlation is included. He finds the R_{ab} dependence to be very different from that usually assumed. For example, γ_{pp} is itself a function of R_{ab}. The last word is a long way from being said on the subject of parameterization. The LCAO-MO method is too important and useful to be based on a set of parameters of uncertain physical significance. In the following several MO integrals in FEMO and LCAO-MO-ZDO form are compared, especially with respect to parametric dependence on Q and R_{ab}.

Figure 1 is a plot of J_{11}(FEMO) and of J_{11}(LCAO-MO-ZDO) in the Nishimoto and the Schiess-Pullman γ_{pq} on R_{ab} dependence. An initial identification of Q and R_{ab} is necessary for a meaningful comparison. The equilibrium R_{ab} of ethylene (1.35 Å) is identified with $Q = 4$ Å in consonance with the results given in Table 1. The agreement is satisfactory.

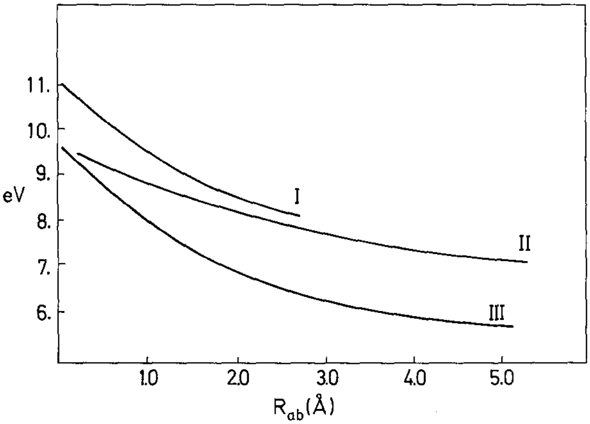

Fig. 1. The π electron coulomb integral, J_{11}. (*I*) LCAO-MO-ZDO with Schiess-Pullman parametrization of γ_{pq} on R_{ab}, (*III*) with Nishimoto parametrization. (*II*) Free electron J_{11} (see appendix for method of calculation)

In the case of LCAO-MO-ZDO it results that $J_{11} = J_{12} = J_{22}$. In FET these integrals differ slightly. Both J_{12} and J_{22} lie about $\frac{1}{2}$ eV below J_{11}, but follow the same Q dependence. The situation is much more serious for the MO exchange integrals, for example,

$$K_{12}(\text{FEMO}) = \frac{1}{N^2}\left\langle \sin\left(\frac{\pi}{Q}q_1\right)\sin\left(\frac{2\pi}{Q}q_1\right)|G_{12}|\sin\left(\frac{\pi}{Q}q_2\right)\sin\left(\frac{2\pi}{Q}q_2\right)\right\rangle, \quad (13)$$

$$K_{12}(\text{LCAO-MO-ZDO}) = \tfrac{1}{2}(\gamma_{pp} - \gamma_{pq}). \quad (14)$$

In a plot of K_{12} like Fig. 1 one finds that K_{12}(FEMO) hardly varies at all over this range of Q in marked contrast to the ZDO integrals. The FEMO calculations give all the other K_{ij}(FEMO) with such a slow variation with Q. Since the exchange integrals give the singlet-triplet separations, and these are predicted to within a few tenths of an eV (Tables 1 and 2) one must believe the K_{ij}(FEMO) at least at certain values of Q. Table 3 compares various calculated singlet-triplet separations, $E(S_1) - E(T_1)$, of some non-empirical LCAO-MO calculations in the π-electron approximation with FET.

The LCAO-MO-ZDO method [11] has empirical parameters chosen to give exactly the experimental result of Table 3, so the comparisons of Table 2 are more pertinent in this regard.

As a justification for little variation of K_{ij} with Q one notes that the K_{ij}(FEMO) variation with Q gives the entire $E(S_1) - E(T_1)$ separation as a function of Q, Eq. (11). Clinton and Hamilton [13] have shown that on the basis of the Hellmann-Feynman theorem the energies of S_1 and T_1 should be roughly parallel, since the force on the nuclei depends solely on the electronic density which in zero order is the same for wavefunctions with the same occupied space orbitals.

Table 3. *Singlet-triplet separation for ethylene (in eV)*

Parr-Crawford[a]	Murai[b]	Huzinaga[c]	FEMO[d]	Exptl.
8.4	6.6	2.83	2.65	3.0

[a] R. G. Parr, and B. L. Crawford: J. chem. Physics **16**, 526 (1948).
[b] T. Murai: Progr. Theoret. Phys. (Kyoto) **7**, 345 (1952).
[c] S. Huzinaga: J. chem. Physics **36**, 453 (1962).
[d] Present. Also see reference [7].

The Virial Theorem

There are at least three interpretations which one may assign to the parameter Q in FET.

1. Q is the real physical length of the free electron path. (i.e. Q is a trigonometric or multiplicative function of the known bond lengths and angles in the molecule.)
2. Q is an external constraint parameter devoid of explicit physical meaning (i.e. H_1 goes to infinity at $q=0$ and $q=Q$).
3. Q is just a scaling factor for all the electronic and internuclear distances (i.e. note that q/Q appears in the wavefunctions).

Evidently a meaning like 1. has been presumed valid in the foregoing discussions. However, regardless of the interpretation attached to Q, the virial theorem takes the same form in all cases.

$$T_{\mathrm{el}} = -\tfrac{1}{2} V_{\mathrm{el}} - \tfrac{1}{2} Q \frac{dE_{\mathrm{el}}}{dQ} \tag{15}$$

T_{el}, V_{el} and E_{el} are the electronic kinetic, potential and total energy respectively. From Eqs. (4) and (5) the total kinetic energy in the state N has the FET form, A_N/Q^2. Substituting this T_{el} in Eq. (15), the FET form of V_{el} is uniquely determined to be $V_{\mathrm{el}} = B_N/Q$. B_N is the constant of integration, both A_N and B_N are characteristic of the N^{th} state.

The vertical excitation energy is given by the virial theorem as,

$$E_{\mathrm{vertical}} = E_M - E_N = -(T_M - T_N) - Q\left(\frac{dE_M}{dQ} - \frac{dE_N}{dQ}\right). \tag{16}$$

In the simplest FET the electronic energy consists solely of kinetic energy, $E_N = T_N = A_N/Q^2$. The excitation energies are just kinetic energy differences,

$$E_{\mathrm{vertical}} = E_M - E_N = T_M - T_N, \tag{17}$$

which differs in sign from the first term in Eq. (16), but substitution of $E_N = A_N/Q^2$ and $E_M = A_M/Q^2$ in (16) gives (17). Therefore the simplest FET gives E_{vertical} in agreement with the virial theorem even though no provision is made for potential energy changes upon excitation. (Compare to reference [14] where a restricted form of virial theorem was used.)

Inclusion of potential energy has given the virial form of FET energy, $E_N = A_N/Q^2 + B_N/Q$, or a vertical excitation energy for the $S_0 \rightarrow S_1$ transition,

$$E(S_1) - E(S_0) = \Delta A/Q^2 + \Delta B/Q\,. \tag{18}$$

ΔA is known from the FET energy Eq. (5) and ΔB can be determined by fitting the singlet-singlet excitation energy at one value of Q (specifically the Q of Table 1). Eq. (18) then gives the excitation energy at all Q. As a test of the semi-empirical FET used in the present work one can plot Eq. (18) versus Q together with the transition energy from Eqs. (9) and (10) at a few values of Q. Figure 2 shows that the semi-empirical FET is fairly consistent with the virial theorem. The details of the calculations are found in the appendix.

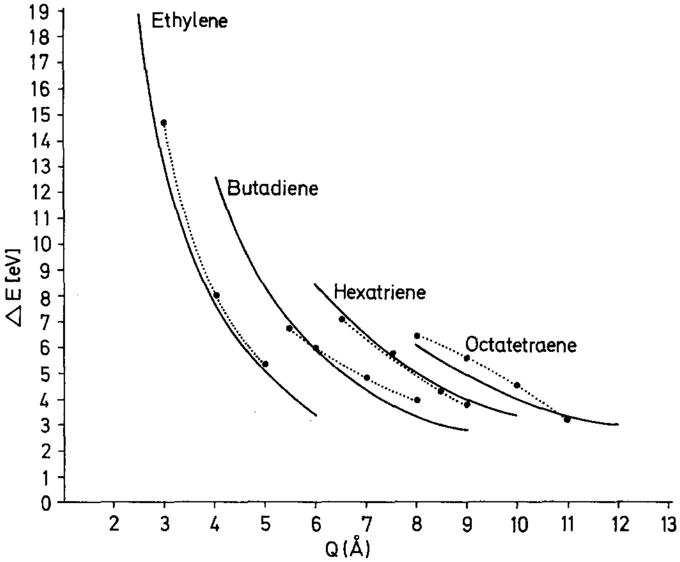

Fig. 2. Total free electron energies of excitation. Solid lines directly from the virial theorem, dots from the semi-empirical FET

Appendix

Starting from operators H_0 and H_1 as defined in Eqs. (3) and (7), the MO integrals of (8) are evaluated over the orbitals (6), at each value of Q. Expectation values of H_0 are trivially given by (5) where $m^* = 0.75$ [6]. The G_{ab} potential was obtained as a table of numerical values by interpolation of Ham and Ruedenberg's revised [15] G_j over the interparticle distance 0 to 2.5 Å. Beyond 2.5 Å the coulomb potential was used. The interelectronic integrals J_{ij} and K_{ij} were found by double Simpson's Rule integration over G_{ij} and the FEMO charge distributions on a 50 × 50 mesh from 0 to Q. Electron-nuclear integrals are found by single integration over a stationary source of charge: Simpson's Rule was again used. It was found that the same potential may be used (i.e. $G_{iK} = G_{ij}$) although we were prepared to weight this potential by a screening factor to give a better representation of an effective nuclear charge. This was found to be unnecessary nor were the results sensitive to the choice of screening.

As Q varied, the nuclear positions retained a constant fractional relation to Q: $A(K) = Q(K)/Q$, where $A(K)$ is a constant for nucleus K in a given molecule and $Q(K)$ is the actual nuclear coordinate. For example, in ethylene, $A(K) = 0.33$, meaning that the nuclei always remain at 1/3 and 2/3 of the free electron path regardless of its length. If you like, this is a linear symmetric distortion of the molecule. In general, FET dimensions are best taken from an "LCAO-MO" box, i.e. with an extension of one bond length beyond the terminal carbon at each end. The values of $A(1)$ used in these calculations for the various polyenes were, $C_2(0.33)$, $C_4(0.20)$, $C_6(0.143)$ and $C_8(0.111)$. To obtain $A(N)$ from these $A(1)$, take $A(N) = N\,A(1)$, i.e. bond alternation was not considered.

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