EVALUATION OF EMPIRICAL PARAMETERS FROM SPECTROSCOPIC DATA BY THE LEAST SQUARES METHOD*

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The previously reported method of determining the values of empirical parameters from spectral data is further extended. The method is reformulated in a way that enables us to fit the output of a semiempirical theory to experimental values in the sense of least squares. An example of application to the multiconfigurational calculation of benzene spectrum is given.

1. Introduction

In an earlier paper [1] a computational method of determining the empirical parameters in molecular orbital theories was described. The method is based on the requirement of an exact reproduction of a set of experimental data in the framework of a chosen approximate theory. This requirement leads to a set of equations for the empirical parameters to be solved iteratively. However, presumably frequently, approximations which are introduced into a theory cannot be fully compensated by any proper choice of the values of empirical parameters and, consequently, the equations derived in such a way have no solution in the physically reasonable range of parameters. In such case the values of parameters obtained at the output of the procedure have an improper physical meaning and the transferability of them to other systems is rather doubtful. A typical example of such a situation was found when the parameters were to reproduce exactly the experimental locations of the lowest electronic bands of benzene in the framework of Pariser--Parr-Pople theory with inclusion of doubly excited configurations [2, 3]. Moreover, in many cases we are rather more interested in reaching the best over-all agreement between theory and experiment than in the exact reproduction of some selected experimental data. For these reasons the use of the least squares method should be more adequate.

A general method of determining the empirical parameters based on the least squares criterion has been formulated by Brown and Taylor [4]. This method has been then used

to obtain values of parameters, occurring in the valence bond and simple molecular orbitals schemes, that yield the best fit between calculated and observed pi-electron spin densities [4]. A similar approach of Budziński [5] has been applied to a semiempirical version of SCF LCAO MO theory. However, Budziński's algorithm is a rather complicated one and using it in the case of a large configuration interaction basis is rather troublesome. In a very important special case, when the locations of the electronic bands are taken as the experimental data, a reformulation of the method given in [1] leads to a comparatively simple computational scheme. The resulting iterative process is derived in the next section. The present approach differs from that of Brown and Taylor [4] by the method of deriving the equations determining the values of empirical parameters, which is more direct here, and in the range of their applicability extended to the theory of molecular spectra.

As an example of application the optimal empirical parameters for benzene are found in the framework of Pariser-Parr-Pople theory when all configurations up to the triply-excited ones are included. The results serve, additionally, to interpret a recently observed [6] 2.55 eV transient absorption band of benzene.

2. Method

Let us consider a semiempirical theory. The empirical parameters are $p_1, p_2, ..., p_l$. The dependence of the theoretical values of experimentally observable physical quantities $e_1^T, e_2^T, ..., e_m^T$ on the empirical parameters is given as

$$G_k(p) = e_k^T, \quad k = 1, 2, ..., m \tag{1}$$

where G_k is a function defined by the theory and p is an l-dimensional vector of empirical parameters $p_1, p_2, ..., p_l$. If we denote the experimental value of e_k^T by e_k, then the condition for the best fitting of the theory and experiment, in the sense of the least squares method, can be written as

$$\sum_{k=1}^{m} (G_k(p) - e_k)^2 = \text{minimum } \{p\}. \tag{2}$$

Condition (2) can be used to determine the empirical parameters which are optimal for our theory with respect to the set of experimental quantities e_k ($k = 1, 2, ..., m$) we have chosen. In the case when $l = m$ condition (2) is equivalent to the corresponding system of equations in unknown p. This case was discussed in detail in the previous paper [1].

If the derivatives $\partial G_k / \partial p_j$ for $j = 1, 2, ..., l$ can be found, the condition (2) yields a set of equations for p_j

$$\sum_{k=1}^{m} \frac{\partial G_k(p)}{\partial p_j} (G_k(p) - e_k) = 0. \tag{3}$$

To solve equations (3) the methods presented in [1] can be used. It is, however, rather difficult to write these equations in an explicit form for the general case [5]. If we restrict

ourselves to the case of Pariser-Parr-Pople theory, treating the excitation energies of the system as observable quantities e_k, significant simplifications are possible.

In the Pariser-Parr-Pople theory the energy of a system is calculated in two stages. First, by solving the SCF equations the eigenvector matrix C, which determines the set of molecular orbitals, is obtained. Next, the configuration interaction matrix H is formed. The eigenvalues of H are interpreted as the energies of the system under consideration. The dependence of the elements of eigenvector matrix C on the empirical parameters is, in general, rather complex. However, for a sufficiently large class of molecules its elements only slightly depend on the empirical parameters [1] and for the cyclic systems the elements are completely independent of them. When C is supposed to be constant, the dependence of H on the empirical parameters is given in the explicit form

$$H = \sum_{j=1}^{l} B_j p_j, \tag{4}$$

where B_j ($j = 1, 2, ..., l$) are constant matrices. If X_k are normalized to unity eigenvectors of H, the corresponding eigenvalues ω_k are given by the relation

$$\omega_k = \sum_{j=1}^{l} (X_k, B_j X_k) p_j. \tag{5}$$

According to the Hellmann-Feynman theorem

$$\frac{\partial \omega_k}{\partial p_j} = (X_k, B_j X_k). \tag{6}$$

Let us assume the matrix C to be the solution of SCF equations for the initial set of emperical parameters. Then condition (2) can be written in the form

$$\sum_{k=1}^{m} (\omega_k(p) - \omega_0(p) - e_k)^2 = \text{minimum} \{p\} \tag{7}$$

where e_k is the experimental value of the excitation energy from the ground state to the state k and ω_0 is the theoretical value of the ground state energy. When the parameters p for which condition (7) is fulfilled are found, new matrix C can be obtained. The process, if convergent, is continued up to self consistency.

The equations for parameters which realize condition (7), according to (3), (5) and (6), are

$$J^{Tr}(p) (J(p)p - e) = 0 \tag{8}$$

where e is the m-dimensional vector of $e_1, e_2, ..., e_m$, and $J(p)$ the rectangular Jacobian matrix

$$J_{kj} = (X_k, B_j X_k) - (X_0, B_j X_0), \quad k = 1, 2, ..., m, \quad j = 1, 2, ..., l. \tag{9}$$

Superscript Tr means transposition.

It is convenient to solve the equations (8) by the iterative method

$$p^{(n+1)} = [J^{Tr}(p^{(n)}) J(p^{(n)})]^{-1} J^{Tr}(p^{(n)}) e \tag{10}$$

where $p^{(n)}$ is the column vector of empirical parameters obtained in the n-th iteration. In the case $l = m$, equations (10) reduce to

$$p^{(n+1)} = J^{-1}(p^{(n)})e \qquad (11)$$

which is essentially equivalent to the quadratically convergent iterative process given by the equations (22) of Ref. [1].

3. An example of application

An an example of application, let us solve the equations (10) for the benzene molecule in the framework of the Pariser-Parr-Pople theory when all the configurations up to triply excited ones are taken into account. The excitation energies depend on the following four empirical parameters [7]: one-electron two-center core resonance integral β between neighbouring carbon atoms, and three differences of the Coulomb integrals

$$x = (11|11) - (11|22)$$

$$y = (11|22) - (11|33)$$

$$z = (11|33) - (11|44) \qquad (12)$$

where $(aa|bb)$ is the Coulomb atomic integral for the centers a and b.

The best available experimental values of Franck-Condon maxima corresponding to the electronic transitions in benzene are given by the electron impact technique [8]. Therefore, where it is possible, the electron impact values have been used for the excitation energies rather than the spectroscopical ones. From among nine experimentally known energies of the excited pi-electronic states, only seven were taken to form the equations (10). The experimental values for the two remaining ones (corresponding to 2.55 eV absorption from $^1B_{2u}$ and 4.9 eV absorption from $^3B_{1u}$) do not seem to be very reliable. In spite of some uncertainties, the assignment recently proposed by Birks [9] has been adopted here for the states used in the spectral matching procedure. The experimental values of excitation energies from the ground state, together with the assignment of the upper states are given in Table I.

A solution of the equations (10) when seven energies are fitted to experimental values is presented in Table II (parameters I). For comparison there is also given a solution of the equations (11), when only the energies of $^1B_{2u}$, $^1B_{1u}$, $^1E_{1u}$ and $^3B_{1u}$ are fitted to the experimental values (parameters II). This second case corresponds to the situation discussed in [1], where the number of parameters is equal to the number of excitation energies involved. Using the optimized empirical parameters the excitation energies of all the singlet and triplet pi-electronic states of benzene were calculated. The energies lying, in one case at least, less than 10 eV above the ground state, and the depression of the ground state caused by the configuration interaction, are given in Table III.

One can expect that in the case when the seven energies are used to determine the four parameters the probability of "statistical" cancellation of the error is rather strong.

TABLE I

Experimental energies of the excited electronic states of benzene relative to the ground state

Energy (eV)[a]	Assignment	Kind of experiment
$4.93_{I,II}$	$^1B_{2u}^-$	electron impact[b]
$6.21_{I,II}$	$^1B_{1u}^+$	electron impact[b]
$6.96_{I,II}$	$^1E_{1u}^+$	electron impact[b]
7.48	$^1E_{2g}^-$	2.55 eV absorption from $^1B_{2u}$[c]
$3.95_{I,II}$	$^3B_{1u}^+$	electron impact[d]
4.75_I	$^3E_{1u}^+$	electron impact[d]
5.60_I	$^3B_{2u}^-$	electron impact[d]
6.75_I	$^3E_{2g}^+$	2.80 eV absorption from $^3B_{1u}$[e]
8.9	$^3E_{2g}^-$	4.9 eV absorption from $^3B_{1u}$[f]

[a] The subscripts I and II indicate the energy values which were used for determining the empirical parameters I and II, respectively.

[b] A. Skerbele, B. N. Lassettre, *J. Chem. Phys.*, **42**, 395 (1965); J. P. Doering, A. J. Williams III, *J. Chem. Phys.*, **47**, 4180 (1967).

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TABLE II

Empirical parameters obtained by fitting seven (parameters I) and four (parameters II) values of energy (compare Table I)

	Parameters I (eV)	Parameters II (eV)
x	3.203	4.465
y	1.555	1.215
z	0.737	−0.761
β	−2.623	−2.732

Indeed, in this case the values of the parameters are quite reasonable. On the contrary, if we take advantage of only four experimental excitation energies, the value of the parameter z is negative (this means that $(11|33) < (11|44)$). This strange result is well known [3], [10], [11] and it has been shown to be explainable in several different ways [10, 12, 13, 14]. One of the explanations given by the present author was based on the supposition that the assignment $^3B_{1u}$ to the lowest benzene triplet may not be correct [12, 13]. The present results enable us to conclude that the negative values of the parameter z which appear, when we want exactly reproduce the experimental separation between $^1B_{2u}$ and the lowest triplet, being assigned as $^3B_{1u}$[3, 13], cannot be an argument for supposition that the lowest benzene triplet is not $^3B_{1u}$. On the other hand, the results we have obtained seem to confirm the conclusion of de Bruijn [10], who places the responsibility for these difficulties on the intrinsic properties of the $^3B_{1u}$ state (hypothetical distortion of the

TABLE III

Excitation energies of benzene (relative to the groind state) calculated using the parameters of Table II

State	Energy (eV)[a]		Number of configurations
	Parameters I	Parameters II	
$^1B_{2u}^-$	**4.79**	**4.93**	7
$^1B_{1u}^+$	**6.22**	**6.21**	10
$^1E_{1u}^+$	**6.95**	**6.96**	11
$^1E_{2g}^-$	7.66	7.60	11
$^1E_{2g}^+$	8.67	10.30	10
$^3B_{1u}^+$	**4.10**	**3.95**	11
$^3E_{1u}^+$	**4.76**	4.87	13
$^3B_{2u}^-$	**5.64**	6.29	9
$^3E_{2g}^+$	**6.71**	6.53	11
$^3E_{2g}^-$	8.98	8.90	12
$^3B_{1u}^+$	9.98	9.79	11
$^1A_{1g}^{-\ b}$	−0.51	−0.74	10

[a] The values of energy fitted to the experimental ones are bold faced.
[b] The depression of the ground state caused by configuration interaction.

benzene ring). It is characteristic that in the case when seven energies are fitted to the experimental values there is a relatively large discrepancy only for the $^1A_{1g} - {}^3B_{1u}$ transition, as compared with the other six transitions. However, in the opinion of the present author, the influence of the rearrangements of sigma-electrons induced by pi-excitations probably leads to errors of comparable order of magnitude and, therefore, it would be premature to draw far-reaching conclusions from this fact.

The second noteworthy result is that in both of the case considered above the calculated energy of $^1E_{2g}^-$ is lower than that of $^1E_{2g}^+$, which is opposite to the assignment of Birks [9]. Theorder of these levels is changed owing to the extension of the configuration interaction b asis. Therefore, we may conclude that the 2.5 eV absorption from $^1B_{2u}$ observed by Bonneau et al. [6] corresponds to the transition to the $^1E_{2g}^-$ state rather than to the $^1E_{2g}^+$ state.

Moreover, these results may be useful for determining the assignment of the 6.21 eV absorpton band. The recent experimental data concerning the vibrational structure [15] and poilarization of the corresponding transition in paradimetoxibenzene [16] indicate that at least a predominate part of 6.21 eV absorption is due to the $^1A_{1g} - {}^1B_{1u}$ transition. On the other hand, the electron impact results [17] seem to indicate the presence of two different electronic transitions in this spectral region. As results from the energy level calculations this second transition can only be $^1A_{1g} - {}^1E_{2g}$. In the present calculation the location of the $^1B_{1u}$ level has been presupposed at 6.21 eV. However, no assumptions

have been made about $^1E_{2g}$ levels. The results of the present calculations, which locate the lowest $^1E_{2g}$ level at 7.60 eV, *i. e.* in the region corresponding to the absorption observed by Bonneau *et al.* [6], support the assignment of the 6.21 eV band to a single electronic transition.

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