

ADVANCES IN CHEMICAL PHYSICS—VOLUME VIII

I. Prigogine—Editor

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The Application of Wave  
Mechanical Methods to the  
Study of Molecular Properties

Edited by R. DAUDEL

*Centre de Mécanique Ondulatoire Appliquée, Paris*

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ADVANCES IN CHEMICAL PHYSICS  
VOLUME VIII

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## PREFACE

The present book contains some of the main papers presented at the International Summer Institute held at Menton, France (July 1-14, 1963). This institute was organized under the auspices of NATO and the patronage of Professor Louis de Broglie, Nobel Prize. The book is divided into two parts. The first is concerned with the electronic structure and the spectra of molecules and crystals. The second part is devoted to chemical and biochemical problems.

R. D.





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**PART I**  
**ELECTRONIC STRUCTURE**  
**AND SPECTRA**



# SOME RECENT DEVELOPMENTS IN THE QUANTUM THEORY OF MANY-ELECTRON SYSTEMS AND THE CORRELATION PROBLEM

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The main problem in the quantum theory of the stationary states of many-electron systems is the solution of the Schrödinger equation  $H\Psi = E\Psi$ . It is often convenient to write the Hamiltonian in the form  $H = H_0 + V$ , where  $V$  is considered as a perturbation which is not necessarily small. Following the original idea of Schrödinger, we will introduce a *single* unperturbed eigenfunction  $\varphi_0$ , satisfying the relations

$$H_0\varphi_0 = E\varphi_0, \quad \langle\varphi_0|\varphi_0\rangle = 1 \quad (1)$$

From this starting function, the exact solution is derived by means of a *wave operator*  $W$ , such that

$$\Psi = W\varphi_0, \quad \langle\Psi|\varphi_0\rangle = 1 \quad (2)$$

Combining these two relations, one obtains for the energy,

$$E = \langle\varphi_0|H\Psi\rangle = \langle\varphi_0|H_0 + V|\Psi\rangle = E_0 + \langle\varphi_0|VW|\varphi_0\rangle.$$

In this connection it is hence convenient to introduce the reaction operator  $t$  by the relation  $t = VW$ , which gives the energy shift

$$E = E_0 + \langle\varphi_0|t|\varphi_0\rangle, \quad t = VW \quad (3)$$

Formal expressions for the wave and reaction operators are easily derived by means of the partitioning technique,<sup>1</sup> which leads to the formulas

$$t = V + V \frac{P}{(E_0 - H_0) - (V - \langle\varphi_0|t|\varphi_0\rangle)} V \quad (4)$$

$$W = 1 + \frac{P}{(E_0 - H_0) - (V - \langle\varphi_0|t|\varphi_0\rangle)} V \quad (5)$$

Here  $P = 1 - |\varphi_0\rangle\langle\varphi_0|$  is the projection operator for the part of the Hilbert space which is the orthogonal complement to  $\varphi_0$ .

By using the infinite series

$$(A - B)^{-1} = A^{-1} + A^{-1}BA^{-1} + A^{-1}BA^{-1}BA^{-1} + \dots,$$

one can easily derive the basic formulas in Brillouin's and Schrödinger's perturbation theories. We note that the formulas (4) and (5) are equivalent to the results of infinite-order perturbation theory.

Most of the present development in the study of many-particle systems is devoted to efforts to find convenient forms for the wave and reaction operators. The importance of the reaction operator has been stressed particularly by Brueckner and his group. If the total Hamiltonian has symmetry properties, it is often feasible to let  $W$  contain the standard group-algebra projection operators associated with the symmetry group. The alternant molecular orbital method and the general method using "different orbitals for different spins" are both based on this idea. In other cases (Bohm and Pines and others), the wave operator has been approximated by a numerical factor expressing the correlation between the motions of the particles and particularly the collective oscillations. In connection with the self-consistent-field schemes, one has had a development based on the analogy between the energy expectation value  $\langle\varphi_0|H_0 + V|\varphi_0\rangle$ , which forms the basis for the variation principle in the standard Hartree-Fock scheme, and the exact energy value  $\langle\varphi_0|H_0 + \hat{t}|\varphi_0\rangle$ . A comparison shows that one can improve the formalism of the independent-particle model by replacing the perturbation  $V$  by the reaction  $\hat{t}$ . For further details and complete references, we will refer the reader to some other papers.<sup>2</sup>

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# CALCULATION OF TRANSITION ENERGIES FROM THE GEOMETRY OF THE SYSTEM

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In its most simple form, the calculation of transition energies for molecules with conjugated ethylenic bonds can be carried out by the method normally called LCAO MO. This type of calculation requires the introduction of a dynamic parameter, usually written  $\gamma$ , which represents the exchange integral calculated over two neighbouring atomic orbitals  $2p_z$ . The value of  $\gamma$  is usually taken from experiment. It allows us to reproduce systematically the resonance energies of the various molecules and, less satisfactorily, the transition energies as measured spectroscopically. Another method, usually known as the free-electron method, allows the calculation of the transition energies without necessitating the introduction of the dynamic parameter and taking into account only the geometry of the molecule.

The two methods have a definite relation which comes from the fact that the structure of the molecule, and particularly its dimensions, is regulated by the value of the exchange energy. We thought it possible to specify this relation by using the essential peculiarity of the free-electron model, that is, the elimination of all dynamic constants by the LCAO MO method.

We will, first of all, briefly resume the method<sup>1, 2, 3</sup> of calculation by considering the particularly simple case of the electronic transitions of the  $\pi$  electrons of ethylene. The problem may be treated, to a first approximation at least, as a mono-electronic problem. The normal orbital  $N$  is, as is well known, described by the  $2p_z$  orbitals of the bound atoms, written  $\psi_1$  and  $\psi_2$ , and the overlap integral  $S$  by:

$$\Phi_1 = (\psi_1 + \psi_2)/\sqrt{2(1 + S)}$$

The method consists of considering all the wave functions  $\Phi_2, \Phi_3, \dots$  representing the excited levels and of representing

the function  $x\Phi_1$ , where  $x$  is the coordinate taken from the axis defined by the bound atoms, by means of the expansion

$$x\Phi_1 = x_{11}\Phi_1 + x_{21}\Phi_2 + x_{31}\Phi_3 + \dots$$

The element  $x_{11}$  is zero if the origin is taken at the centre of symmetry of the molecules. We assume, therefore, that one of the transitions is preponderant, for example,  $\Phi_1 \rightarrow \Phi_2$ . We may then represent the function  $\Phi_2$  by:

$$x_{21}\Phi_2 = x\Phi_1 \quad (1)$$

In this relation,  $x_{21}$  is defined by the normalization condition:

$$x_{21}^2 = \int x^2 \Phi_1^2 d\tau$$

which we write thus because  $\Phi_1$  is real.

The interest of Eq. (1) is that it permits the calculation of the transition energies. We have:

$$E_2 = \int \Phi_2 H \Phi_2 d\tau = \frac{1}{x_{21}^2} \int x \Phi_1 H (x \Phi_1) d\tau$$

The integral may be evaluated without having to write the expression for the Hamiltonian because we have:

$$Hx = xH - \frac{\hbar^2}{4\pi^2 m} \frac{\partial}{\partial x}$$

We obtain:

$$E_2 = E_1 + \frac{\hbar^2}{8\pi^2 m x_{21}^2}$$

The transition energy  $E_2 - E_1$  may be obtained from the structure of the molecule without the explicit use of any dynamic parameter. It is only necessary to write  $x_{21}^2$ , that is:

$$x_{21}^2 = \frac{1}{(1+S)} \int x^2 (\psi_1^2 + \psi_1 \psi_2) d\tau -$$

If  $r$  represents the length of the bond C—C, we obtain immediately

$$\int x^2 \psi_1^2 dr = \frac{r^2}{4} + \xi^2$$

where

$$\xi^2 = \int x_1^2 \psi_1^2 d\tau$$

the origin being chosen at the centre of atom 1. We also write

$$\eta^2 = \int x^2 \psi_1 \psi_2 d\tau$$

In the following calculations, we neglect the value of  $\eta$ . For  $\xi$ , we obtain, using Slater-type orbitals,

$$\xi^2 = 24a_0^2/Z^{*2}$$

where  $a_0$  is the radius of the first Bohr orbit and  $Z^*$  is the effective atomic number. We obtain:

$$\rho^2 = 4(\xi^2 + \eta^2); \quad x_{21}^2 = \frac{r^2 + \rho^2}{4(1 + S)}$$

$$E_2 - E_1 = \frac{h^2(1 + S)}{2\pi^2 m(r^2 + \rho^2)}$$

These relations are of exactly the same form as those obtained using the free-electron model taking into account the quantity which is usually called the "end" correction, and which appears here as an arbitrary factor. The value for the wavelength of the transition thus calculated is  $\lambda = 1575 \text{ \AA}$ , against  $1630 \text{ \AA}$ , the usual experimental value. This agreement is very satisfactory considering that the integral  $\eta$  is taken as zero. Taking into account the value of this integral increases the calculated value of  $\lambda$ .

From this agreement, we presume that the wave function  $x\Phi_1$  must represent the wave function of the excited state in a satisfactory manner. In the LCAO representation, the latter is given by:

$$\Phi_2 = \frac{\psi_1 - \psi_2}{\sqrt{2(1 - S)}}$$

We should therefore obtain:

$$x \frac{\psi_1 + \psi_2}{\sqrt{2(1 + S)}} = x_{21} \frac{\psi_1 - \psi_2}{\sqrt{2(1 - S)}}$$

Thus, forming the scalar product with  $\Phi_2$ :

$$x_{21} = \frac{\gamma}{2\sqrt{1-S^2}}$$

Comparing this with the value obtained above, we have:

$$S = \frac{\rho^2}{\gamma^2 + \rho^2}$$

With the above approximation ( $\eta = 0$ ), we obtain  $S = 0.22$ . It is obvious that this value is lowered in such a way that the agreement is very satisfactory.

Finally, let us study the results obtained and compare them with those obtained by the LCAO method. In this method, the energies of the two levels,  $\pi$  and  $\pi^*$ , are respectively:

$$E_1 = Q + \frac{\gamma}{1+S}; \quad E_2 = Q - \frac{\gamma}{1-S}$$

from which we obtain the bond energy of the  $\pi$  electrons,  $E_\pi = 2|\gamma|/(1+S)$ , which can be compared to that of the transition energy,  $2|\gamma|/(1-S^2)$ . Using the expression which we have just calculated for the transition energy we obtain:

$$E_\pi = \frac{h^2}{2\pi^2 m \rho^2} S(1-S^2)$$

The quantitative agreement is not good. This arises in part from the fact that  $\rho$  has been underestimated and in part also from the fact that a great number of approximations have been used. It is nonetheless true that the approximate proportionality of  $E_\pi$  and  $S$  correspond to the generally accepted result:

$$\gamma/S \approx \text{constant}$$

We have tried to apply this method to several cases, notably those of *trans*-butadiene<sup>4,5</sup> and benzene,<sup>5</sup> using antisymmetrized Slater orbitals to form the initial wave function. The function in  $\Phi_2$ , the excited state, is then supposed to be of the following form:

$$K\Phi_2 = \left(\sum_{r=1}^4 x_r\right)\Phi_1 = X\Phi_1$$