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Molecular Orbital Method and Molecular Ionization Potentials*

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(1) Empirical evidence indicates that, other things being equal, the atomic integral α of the LCAO molecular orbital method decreases in magnitude, (*a*), with increasing interatomic distance, (*b*), with increase in the number of atoms covered by a MO.

(2) Theoretical computations give a satisfactory account of effect (*a*), and (except for the absolute values of α in many-center cases) also of effect (*b*).

(3) It is reasonable to hope that further study of theoretical approximation methods of the MO type will make possible an increasingly quantitative theoretical understanding of molecular ionization potentials and of other molecular properties.

THE electronic structure of any well-organized molecular system, e.g., an atom, a molecule, or a single crystal, can usually be indicated by specifying an electron configuration and an electronic state. To this specification corresponds a wave function, antisymmetric in the electrons, which may be a rather good approximation to the accurate eigenfunction. If the electron configuration is stated in terms of orbitals of the complete system (i.e., non-localized molecular orbitals in the case of a molecule), a wave function of the self-consistent-field type can in principle be constructed, in which the MO's (molecular orbitals) used are all mutually orthogonal.

Each MO (say ϕ_f) is then an eigenfunction of a one-electron Schrödinger equation, $h\phi = e\phi$ in which the Hamiltonian h corresponds to the proper molecular self-consistent field. The corresponding energy eigenvalue (say e_f) is of particular importance in that $-e_f$ is rather closely equal to the ionization energy I_f for removal of an electron from ϕ_f—after certain corrections in case the electron configuration is not of closed shell type. This theorem was stated by Slater in 1928 explicitly for atoms, but implicitly also for molecules. It is no longer valid (or at least is less accurate) for a molecule if the electron configuration is given in terms of localized molecular orbitals or of atomic orbitals, since such orbitals cannot be orthogonal.

TABLE I.

	I	α
CH_3 (methyl radical)	10.07	−10.07
C_2H_2 (acetylene)	11.41	−9.2
C_2H_4 (ethylene)	10.50	−8.14
C_4H_6 (1,3-butadiene)	9.07	−7.42
C_6H_6 (benzene)	9.24	−7.18
graphite	4.39	−4.39

Experimentally observed molecular ionization potentials involving removal of a single electron, after correction if necessary to the case of fixed nuclei, may then to a good approximation be set equal to the negatives of energy eigenvalues of whole-molecule, self-consistent-field MO's. On the other hand, approximate theoretical energy expressions such as

$$e_f = \alpha + b_f\beta \quad (1)$$

can be obtained by the well-known method of approximating the MO's of an m-center problem by LCAO forms ($f = 1 \cdots m$). (The symbol LCAO means "linear combination of atomic orbitals.") In the homopolar 2-center case, $m = 2$, and in Eq. (1),

$$b = \pm 1/(1 \pm S), \quad (2)$$

where S is the overlap integral $\int \chi_a \chi_b dv$ between the atomic orbitals χ_a and χ_b involved in the LCAO forms. The + and − signs in Eq. (2) correspond respectively to bonding and antibonding MO's.

The atomic integral α and the bond integral β are both negative, with $|\alpha| > |\beta|$.[1] If a and b are two adjacent-like atoms, α and β are defined by

$$\alpha = \int \chi_a h \chi_a dv,$$

and

$$\beta = \int \chi_b h \chi_a dv - S\alpha.$$

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If h in the expression for α were replaced by the Hamiltonian h_a corresponding to the self-consistent field for an isolated atom a, then α would become e_a, the atomic one-electron energy eigenvalue corresponding to the atomic orbital χ_a. Thus since h is roughly equal to h_a, α should be roughly equal to e_a. The bond integral β is roughly a measure of the strength of the chemical bond between atoms a and b.

If more than one kind of atom is involved, there is more than one α and β, and Eq. (1) is replaced by more complicated expressions. In this event, the difference in the α values of two atoms is a measure of their difference in electronegativity.

In most MO work to date, β has been determined empirically, and little attention has been paid to α.

Setting $e_f = -I_f$, an empirical α can be determined from Eq. (1) if b_f and β are known. The largest body of I data for a set of related molecules is that for the unsaturated and aromatic hydrocarbons.[1,2] The coefficient b of Eq. (1) for the most loosely bound π-type MO can be computed fairly accurately for any such molecule by solving an appropriate secular equation, while β is known from spectroscopic data to be near -3 ev for $C-C$ π-bonds.[2a,3] Using this information, it is found that $|\alpha|$ decreases with increase in the number of atoms in the conjugated system. Some examples are given in Table I (energies are in ev).

Substitution of a methyl or other alkyl group for a hydrogen atom causes a further decrease in $|\alpha|$.[1,2,3] Since the alkyl group may be regarded as part of the conjugated system (phenomenon of hyperconjugation), this effect may reasonably be considered, just as in the preceding examples, to be associated with an increase in the number of atoms in a conjugated system. The examples of Table II are illustrative. The α values for propylene and isoprene should be compared with those for ethylene and butadiene respectively. In a similar way, alkyl substitution for H atoms in CH_3 or other free radicals leads to marked decreases in I and $|\alpha|$.[1]

TABLE II.

	I	α
$C_2H_3CH_3$ (propylene)	9.70	-7.49
$C_4H_5CH_3$ (isoprene)	8.86	-7.24

Decrease in $|\alpha|$ with increase in number of participating atoms may thus be taken as an empirically well-established phenomenon characteristic of conjugated and hyperconjugated systems. How may this be understood theoretically? A suggested explanation[1,3] in the case of alkyl substitution is that the π-electron-bearing carbon atoms become negatively charged at the expense of the alkyl groups, causing a decrease in $|\alpha|$. (It is well known that such "charge transfer" effects are important in cases such as that of H_2O, where the first I corresponds to removal of a nonbonding O atom electron but is lower than for a free O atom because of the negative charge on the O atom in H_2O.) However, charge transfer obviously cannot explain the trends in the first of the two tables above.

Recently the writer has found it possible to make approximate theoretical computations of the parameters α and β.[4] In all cases so far considered, the computed β values agree rather well with those obtained empirically from spectroscopic and other data. In the cases so far treated which involve only two-center MO's (H_2, σ MO's; C_2H_2 and C_2H_4, π MO'S), the observed and computed α values agree extremely closely (see Table III).[5] These results are very encouraging with respect to the possibility of an understanding of observed ionization potentials in diatomic

TABLE III.

	$-\alpha_{obs}$	$-\alpha_{comp}$	I_a
H_2 ($r=0.74A$)	14.68	14.86	13.60
H_2 (for $r=1.07A$)	12.7	12.10	13.60
C_2H_2 ($r=1.20A$)	9.2	8.81	10.91
C_2H_4 ($r=1.35A$)	8.25	8.33	11.28

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[1] Cf. W. C. Price, Chem. Rev. **41**, 257 (1947).

[2] R. E. Honig, J. Chem. Phys. **16**, 105 (1948).

[2a] The definition of β used here is that proposed by Mulliken and Rieke, J. Am. Chem. Soc. **63**, 1770 (1941); see Roothaan and Mulliken, J. Chem. Phys. **16**, 118 (1948) for a more explicit statement.

[3] R. S. Mulliken, Rev. Mod. Phys. **14**, 265 (1942).

[4] Reported at international colloquium on "Theory of Chemical Binding" held at Paris April 12–16, 1948. To be published in part in J. de Chimie Physique (1948).

[5] The I_a values as given for carbon are for suitable tetravalent "valence states" of the atom (cf. R. S. Mulliken, J. Chem. Phys. **2**, 792 (1934)).

and other two-center cases. In particular, the fact that the observed $-\alpha$ is *greater* than the corresponding atomic ionization potential $I_a \approx -\epsilon_a$ for closely spaced nuclei, but becomes increasingly *less* than the latter as the interatomic distance increases, is reproduced by the theoretical computation (see the last column of Table III).

Approximate theoretical formulas have also been obtained by means of which α and β values can be computed for π-type MO's extending over any number of centers. Thus far, these have been applied only to butadiene, benzene, and graphite. As in the two-center cases, they give β values in approximate agreement with experiment. For $-\alpha$, they are disappointing in that they give considerably larger values (10.83 ev for benzene, 6.29 ev for graphite) than those observed. On the other hand, they are encouraging in that the computed $|\alpha|$, like the observed $|\alpha|$ (see Table I above), diminishes with increasing molecule size.

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Quantum Theory of the Point Electron. I*

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A new treatment of the quantum theory of the electromagnetic field is discussed. The interactions between the particles and their interactions with the radiation field are treated according to the ideas of the author's classical theory. The radiation field is taken as a difference of two fields analogous to the field of the Heisenberg-Pauli electrodynamics. The commutation rules for the radiation field differ essentially from those of the Heisenberg-Pauli electrodynamics. In our formalism it is possible to avoid all the divergences by a suitable choice of the wave function of the system particles plus field. The physically relevant wave functions satisfy wave equations similar to those of systems with finite numbers of degrees of freedom, although they are also exact solutions of the Schrödinger equation of the system particles plus field which has an infinite number of degrees of freedom. There is also the possibility of getting finite non-vanishing self-energies.

I. INTRODUCTION

THE theory of point particles interacting with a field presents well-known difficulties, both in classical and quantum theories. We have shown[1-3] that it is possible to get a satisfactory classical theory of the point electron by modifying the usual ideas of the interactions between the point particles and their interactions with fields. We have also attempted a quantum generalization of our theory for the case of one electron.[4] in which there is only the interaction with the radiation field. The method we used in that paper has some basic points in common with the method we shall use in this paper (description of the radiation field by means of two fields of the Heisenberg-Pauli type) but it differs in some essential aspects, because in the present paper we shall not use anti-Hermitian operators in the description of the advanced waves.**

The essential point in our classical and quantum treatments lies in the modification of the field concepts of Faraday and Maxwell which underlie the quantum electrodynamics of Heisenberg and Pauli,[5,***] as well as more recent

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* Revised form of a paper sent to The Physical Review in February, 1947.

[1] M. Schönberg, Phys. Rev. 69, 211 (1946).

[2] M. Schönberg, Summa Brasiliensis Math. 1, 41, 77 (1946).

[3] M. Schönberg, Summa Brasiliensis Phys. 1, 51 (1947).

[4] M. Schönberg, Phys. Rev. 67, 193 (1945).

** In that paper the advanced waves give negative contributions to the energy of the field in the classical formalism. The use of anti-Hermitian operators transforms the negative energy waves into positive energy photons so that the zero-point energy of the field is not canceled (see J. Leite Lopes, Anais Acad. Brasil. Ciencias 19, 51 (1947).

[5] W. Heisenberg and W. Pauli, Zeits. f. Physik 56, 1 (1929), and 59, 168 (1930).

*** A more detailed discussion of the methods of field quantization and of the Heisenberg-Pauli electrodynamics will appear soon in the Anais da Academia Brasileirs de Ciencias.