Binding Regions in Diatomic Molecules*

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The concept of intramolecular binding is given a precise definition in a way that relates binding to the forces acting on the nuclei in a diatomic molecule. A consequence of the definition is that the space around the nuclei may be separated into binding and antibinding regions. These regions are described and they depend on the Coulomb law of force and on the ratio of the nuclear charges: the internuclear distance is simply a scale parameter. The influence of a single electron on the binding due to other electrons is briefly discussed.

I. INTRODUCTION

A KNOWLEDGE of the electron distribution in a molecule is a fundamental requirement for the understanding of the chemical behavior of the molecule. The difficulties involved in obtaining an accurate wave function for other than the simplest molecules $(H_2)^+$ and H_2 are very great. The approximate methods which have been devised yield results which, in general, are only roughly in agreement with experiment. In this paper, the approach to the problem of binding shall be essentially qualitative.

It is the purpose of this paper to consider binding in diatomic molecules and to develop the idea of binding regions in the space around the nuclei. The word "binding" shall be defined in such a way that it relates to the *forces* acting on the nuclei in the molecule. Thus, *binding* shall be distinguished from *bonding* which is usually[1] related to the *energy* of the molecule. The bonding by a single electron is related to the energy of this electron in the molecule; in the same sense, the binding by a single electron will be related to the forces exerted by this electron on the nuclei.

In this study it is supposed that the diatomic molecule is free and, therefore, exists in stationary energy states determined by the appropriate Schrödinger Eq. (1). The charge distribution in such states is independent of the time, and it can be expected that the consideration merely of the electrostatic interaction between the nuclei and the electronic charge distribution within the molecule may be helpful for the understanding of its properties (Comm. II). Thus, it will be examined whether such a relatively simple picture can be considered as a desirable approximation.

It will be first shown on the basis of wave mechanics that the electric forces exerted on the nuclei by the molecular electron distribution can be interpreted from the electrostatic viewpoint when the molecule is in a

stationary state, even though this charge distribution is dependent on the electronic motion. A definition of binding in terms of the electric forces will then be given. Electron spin and the Pauli principle will then be taken into account, and the electrostatic viewpoint will be shown to be maintained. Some consequences of the definition, such as the separation of space into binding and antibinding regions, and the influence of a single electron on the binding due to other electrons will be discussed.

II. THE WAVE MECHANICAL FOUNDATION

In describing the electronic wave function of a diatomic molecule, the usual Born-Oppenheimer[2] approximation is assumed, that is, the nuclei are assumed to be fixed at a given internuclear distance R. The electronic wave function ψ_e and the molecular energy E_e (not including the energy arising from nuclear motion) satisfy the Schrödinger equation

$$H\psi_e = (T+V)\psi_e = E_e\psi_e, \tag{1}$$

where T, the electronic kinetic energy operator

$$= -\frac{h^2}{8\pi^2 m} \sum_{i=1}^{N} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right);$$

V, the potential energy

$$= \frac{Z_1 Z_2 e^2}{R} - \sum_{i=1}^{N} \left(\frac{Z_1 e^2}{r_{1i}} + \frac{Z_2 e^2}{r_{2i}} \right) + \sum_{i<j} \frac{e^2}{d_{ij}};$$

N is the number of electrons in the molecule; x_i, y_i, z_i are the Cartesian coordinates of the ith electron; r_{1i} is the distance of the ith electron from the nucleus of charge $+Z_1 e$; r_{2i} is the distance of the ith electron from the nucleus of charge $+Z_2 e$; and d_{ij} is the distance between the ith and jth electrons.

The internuclear distance, R, occurring in V is regarded as an external parameter. In general, E_e will be a function of R, and ψ_e will depend on R in addition to the coordinates of all the electrons. The equilibrium value of R, R_e, is that value which minimizes $E_e(R)$.

It is important for this study to show the validity of

* Communication VII on "The Electronic Structure of Molecules." See the previous communications: II, T. Berlin and K. Fajans, J. Chem. Phys. 10, 691 (1942); VI, K. Fajans and T. Berlin, Phys. Rev. 63, 309 (1943). See also K. Fajans, Chem. Eng. News 27, 900 (1949). These papers will be referred to as Comm. II or VI and CEN.
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[1] G. Herzberg, *Molecular Spectra and Molecular Structure I* (Prentice-Hall, Inc., New York, 1939).
[2] M. Born and R. Oppenheimer, Ann. Physik 84, 457 (1927).

the relation

$$\partial E_e/\partial R = \langle \partial V/\partial R \rangle_{Av}$$

$$\equiv \int \cdots \int \psi_e{}^*(\partial V/\partial R)\psi_e d\tau_1 d\tau_2 \cdots d\tau_N, \quad (2)$$

where $d\tau_i = dx_i dy_i dz_i$ and the integration is over all space.

Equation (2) was derived by Hellmann[3] and by Feynman,[4] but their derivations have been criticized by Coulson and Bell.[5] It will be shown, however, that Eq. (2) is valid under the conditions stated by the former authors.

Following Feynman, let us suppose that the Hamiltonian H of a system contains a parameter λ, and that the system is in a stationary state ψ. Therefore, $H\psi = E\psi$, where E is the energy of the state, and we shall assume that $\int \psi^*\psi d\tau = 1$. We then have

$$E = \int \psi^* H \psi d\tau,$$

and

$$\partial E/\partial \lambda = \int \psi^*(\partial H/\partial \lambda)\psi d\tau$$

$$+ \int (\partial \psi^*/\partial \lambda)H\psi d\tau + \int \psi^* H(\partial \psi/\partial \lambda)d\tau.$$

As H is a self-adjoint operator,

$$\int \psi^* H(\partial \psi/\partial \lambda)d\tau = \int (\partial \psi/\partial \lambda)H\psi^* d\tau.$$

Since $H\psi = E\psi$ and $H\psi^* = E\psi^*$, we have

$$\partial E/\partial \lambda = \int \psi^*(\partial H/\partial \lambda)\psi d\tau$$

$$+ E\int (\partial \psi^*/\partial \lambda)\psi d\tau + E\int \psi^*(\partial \psi/\partial \lambda)d\tau,$$

$$\partial E/\partial \lambda = \int \psi^*(\partial H/\partial \lambda)\psi d\tau$$

$$+ E(\partial/\partial \lambda)\int \psi^*\psi d\tau = \int \psi^*(\partial H/\partial \lambda)\psi d\tau,$$

because

$$(\partial/\partial \lambda)\int \psi^*\psi d\tau = (\partial/\partial \lambda)1 = 0.$$

The kinetic energy operator T is independent of λ. Hence,

$$\partial H/\partial \lambda = (\partial T/\partial \lambda) + (\partial V/\partial \lambda) = \partial V/\partial \lambda.$$

[3] H. Hellmann, *Einführing in die Quantenchemie* (Leipzig, 1937), p. 285.
[4] R. P. Feynman, Phys. Rev. **56**, 340 (1939).
[5] C. A. Coulson and R. P. Bell, Trans. Faraday Soc. **41**, 141 (1945).

Consequently,

$$\partial E/\partial \lambda = \int \psi^*(\partial V/\partial \lambda)\psi d\tau.$$

This concludes Feynman's derivation, when $\lambda = R$.

We may also consider the following derivation of Eq. (2). Let $\lambda' = \lambda + \delta\lambda$ and $H'\psi' = E'\psi'$, the primes denoting the use of λ'. If T is independent of λ, then

$$H' = T + V' = T + V + (\partial V/\partial \lambda)\delta\lambda + \cdots = H + H_1.$$

Now H_1 can be regarded as a perturbation, the unperturbed wave equation being $H\psi = E\psi$. Applying the usual perturbation theory, we find that

$$\lim_{\delta\lambda \to 0} \frac{E' - E}{\delta\lambda} = \frac{\partial E}{\partial \lambda} = \int \psi^* \frac{\partial V}{\partial \lambda}\psi d\tau,$$

assuming that ψ is normalized to unity.

The objection raised by Coulson and Bell to Eq. (2) is as follows. Since $E = \bar{H}$, then

$$\partial E/\partial \lambda = \partial \bar{H}/\partial \lambda = (\partial \bar{T}/\partial \lambda) + (\partial \bar{V}/\partial \lambda).$$

If $\partial E/\partial \lambda = \langle \partial V/\partial \lambda \rangle_{Av}$, then Feynman, according to Coulson and Bell, must have implied that

$$\text{(a)} \quad \partial \bar{T}/\partial \lambda = 0 \qquad \text{(b)} \quad \partial \bar{V}/\partial \lambda = \langle \partial V/\partial \lambda \rangle_{Av}. \quad (3)$$

However, as the latter point out, it can be shown that

$$\partial \bar{T}/\partial \lambda \neq 0 \quad \text{and} \quad \partial \bar{V}/\partial \lambda \neq \langle \partial V/\partial \lambda \rangle_{Av}, \quad (4)$$

and, as a consequence, Eq. (2) must be incorrect.

If we identify λ with the internuclear distance R of a diatomic molecule, then it is physically plain that the relations (4) are correct. However, the relations (3) are not implied in the derivation of Eq. (2), as Coulson and Bell assume. The following analysis, which follows Hellmann in principle, demonstrates why the relations (4) and Eq. (2) do not contradict each other. The fundamental reason for their coexistence is the assumption of a stationary state for all values of the parameter λ and the associated fact that the eigenvalue E is an extremum for a certain class of variations of the wave function ψ.

The relation $\partial E/\partial \lambda = \partial \bar{H}/\partial \lambda = \langle \partial H/\partial \lambda \rangle_{Av}$ does not imply $\partial \bar{T}/\partial \lambda = \langle \partial T/\partial \lambda \rangle_{Av}$ and $\partial \bar{V}/\partial \lambda = \langle \partial V/\partial \lambda \rangle_{Av}$. The reason for this is simply that ψ is neither an eigenfunction of the operator T nor of the operator V, whereas ψ is an eigenfunction of $H = T + V$.

The fact that E is an eigenvalue implies that if the eigenfunction ψ is varied by $\delta\psi$, then for H unvaried,

$$\delta E = \delta \int \psi^* H \psi d\tau = \int \delta\psi^* H\psi d\tau + \int \psi^* H\delta\psi d\tau = 0.$$

The relation holds when the variation function $\delta\psi$ is well behaved. Now let $\delta\psi = (\partial\psi/\partial\lambda)\delta\lambda$. We expect, in general, that $(\partial\psi/\partial\lambda)$ will be a well-behaved function and so will define a suitable $\delta\psi$. Then,

$$\int (\partial\psi^*/\partial\lambda)H\psi d\tau + \int \psi^* H(\partial\psi/\partial\lambda)d\tau = 0.$$

Since T does not depend on λ, this equation can be written as

$$(\partial \bar{T}/\partial \lambda) + \int (\partial \psi^*/\partial \lambda) V \psi d\tau$$

$$+ \int \psi^* V (\partial \psi/\partial \lambda) d\tau = 0. \quad (5)$$

Since

$$\partial \bar{V}/\partial \lambda = \langle \partial V/\partial \lambda \rangle_{Av} + \int (\partial \psi^*/\partial \lambda) V \psi d\tau$$

$$+ \int \psi^* V (\partial \psi/\partial \lambda) d\tau,$$

we are immediately led to Eq. (2).

The reason for the coexistence of Eqs. (4) and (2) is clear. The assumption of the stationary state for all λ implies that when a change $\delta \lambda$ is made, then both ψ and V are changed, and that the change in the average kinetic energy due to the change in ψ is just canceled by that part of the change of the average potential energy which is due to the change in ψ. Thus, the resulting change in E is given by the average of the change in V.

III. A DEFINITION OF BINDING

The external force, which may be purely mechanical, required to hold the nuclei fixed at the distance R is

$$F = -\partial E_e/\partial R = -\langle \partial V/\partial R \rangle_{Av}.$$

As the interelectronic distances d_{ij} are independent of R,

$$\frac{\partial V}{\partial R} = -\frac{Z_1 Z_2 e^2}{R^2} + \sum_{i=1}^{N} \left(\frac{Z_1 e^2}{r_{1i}^2} \frac{\partial r_{1i}}{\partial R} + \frac{Z_2 e^2}{r_{2i}^2} \frac{\partial r_{2i}}{\partial R} \right),$$

and

$$F = \frac{Z_1 Z_2 e^2}{R^2} - \sum_{i=1}^{N} \int \cdots \int \psi_e^*$$

$$\times \left(\frac{Z_1 e^2}{r_{1i}^2} \frac{\partial r_{1i}}{\partial R} + \frac{Z_2 e^2}{r_{2i}^2} \frac{\partial r_{2i}}{\partial R} \right) \psi_e d\tau_1 \cdots d\tau_N. \quad (6)$$

We can integrate over all the electron coordinates except those of the ith electron. Therefore, let

$$\rho_i(x_i, y_i, z_i) = \int \cdots \int' \psi_e^* \psi_e d\tau_1 \cdots d\tau_N, \quad (7)$$

the prime signifying the omission of the integration over the coordinates of the ith electron. ρ_i is the probability density of the ith electron at x_i, y_i, z_i regardless of
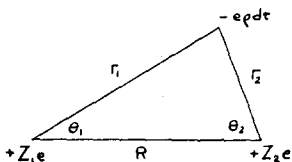

FIG. 1. The electrostatic model of a diatomic molecule.

where all the other electrons might be, and $e\rho_i d\tau_i$ is the magnitude of the charge of the ith electron in the volume element $d\tau_i$. Then,

$$F = \frac{Z_1 Z_2 e^2}{R^2} - \sum_{i=1}^{N} \int \left(\frac{Z_1 e^2}{r_{1i}^2} \frac{\partial r_{1i}}{\partial R} + \frac{Z_2 e^2}{r_{2i}^2} \frac{\partial r_{2i}}{\partial R} \right) \rho_i d\tau_i.$$

The quantity in parentheses depends only on the point in space. If we fix our attention on the point x, y, z in the volume element $d\tau$, we may write

$$F = (Z_1 Z_2 e^2/R^2) - \int [(Z_1 e^2 \partial r_1/r_1^2 \partial R)$$

$$+ (Z_2 e^2 \partial r_2/r_2^2 \partial R)] \rho d\tau, \quad (8)$$

where

$$\rho(x, y, z) = \sum_{i=1}^{N} \rho_i(x, y, z)$$

and $e\rho d\tau$ is the magnitude of the total electronic charge at the point x, y, z in the volume element $d\tau$; r_1, r_2 are the distances of the point x, y, z from Z_1, Z_2, respectively.

The electrostatic model of the molecule is shown in Fig. 1.

The derivative $\partial r_1/\partial R$ must be found when r_2 is fixed and R is changed. Thus, $\partial r_1/\partial R = \cos\theta_1$ and $\partial r_2/\partial R = 0$. In a similar way, $\partial r_1/\partial R = 0$ and $\partial r_2/\partial R = \cos\theta_2$. Adding the two resulting expressions for F and dividing by 2, we may write

$$F = (Z_1 Z_2 e^2/R^2) - \tfrac{1}{2} e^2 \int f \rho d\tau, \quad (9)$$

where

$$f = (Z_1/r_1^2) \cos\theta_1 + (Z_2/r_2^2) \cos\theta_2.$$

The quantity ef is simply the component along the internuclear axis of the total force exerted on the nuclei by a unit negative charge at x, y, z,

When F is positive, the external force prevents the nuclei from flying apart, i.e., prevents R from increasing. When F is negative, the external force prevents the nuclei from moving together, i.e., prevents R decreasing. The equilibrium value of R is to be determined by $F = 0$.

The quantity ρ is positive and never changes sign. Therefore, we can separate the integral in Eq. (9) into regions where $f > 0$ and $f < 0$.

$$F = (Z_1 Z_2 e^2/R^2) - \tfrac{1}{2} e^2 \int_{f > 0} f \rho d\tau - \tfrac{1}{2} e^2 \int_{f < 0} f \rho d\tau. \quad (10)$$

The negative charge in regions where $f > 0$ reduces the value of F, i.e., *binds* the nuclei, while negative charge in regions where $f < 0$ increases the value of F. Consequently, we may define binding in the following manner. Negative charge in a region of space where f is positive is *binding*; negative charge in a region of space where f is negative is *antibinding*. The binding region, $f > 0$, is separated from the antibinding region, $f < 0$, by the

surface of revolution $f=0$ (the internuclear axis is the axis of symmetry).

IV. ELECTRON SPIN AND THE PAULI PRINCIPLE

The preceding analysis has neglected electron spin and the Pauli Exclusion Principle and, therefore, does not yet apply to a real molecule. Consequently, we shall reconsider the problem taking into account both spin and the Pauli principle. We shall find that the preceding results are essentially unchanged and, therefore, can be applied to real molecules.

We again assume that the appropriate Schrödinger equation is Eq. (1). This means that we are neglecting all magnetic interactions involving the electron spin, but this neglect is justified to a high degree of approximation. However, each electron is now described by four coordinates, the three positional coordinates (x_i, y_i, z_i for the ith electron) and a spin coordinate (s_i for the ith electron) which takes on the two discrete values, $\pm\frac{1}{2}$. The total electronic wave function is now Ψ_e, which must involve the spin coordinates for all the electrons as well as the positional coordinates. The requirement of the Pauli Exclusion Principle is that Ψ_e is totally antisymmetric, that is, interchanging the positional and spin coordinates of any pair of electrons changes the sign of Ψ_e. Furthermore,

$$H\Psi_e = E_e\Psi_e, \qquad (1')$$

although H does not involve the spin coordinates.

The analysis of Sec. II is entirely valid if we replace $\int d\tau_i$ by $\int_{s_i} d\tau_i$, where the latter symbol means integrating the positional coordinates of the ith electron over all space and summing over the two spin values of the ith electron, and if we assume that a change in R does not introduce any important spin interactions. The normalization of the wave function now means

$$\int_s \Psi_e{}^*\Psi_e d\tau$$

$$\equiv \int_{s_1}\int_{s_2}\cdots\int_{s_N} \Psi_e{}^*\Psi_e d\tau_1 d\tau_2\cdots d\tau_N = 1,$$

and

$$\partial E_e/\partial R = \langle \partial V/\partial R\rangle_{\mathrm{Av}}$$

$$\equiv \int_{s_1}\cdots\int_{s_N} \Psi_e{}^*(\partial V/\partial R)\Psi_e d\tau_1\cdots d\tau_N. \quad (2')$$

Continuing with Sec. III, we have

$$F = \frac{Z_1 Z_2 e^2}{R^2} - \sum_{i=1}^N \int_{s_1}\cdots\int_{s_N} \Psi_e{}^*$$

$$\times\left(\frac{Z_1 e^2}{r_{1i}{}^2}\frac{\partial r_{1i}}{\partial R} + \frac{Z_2 e^2}{r_{2i}{}^2}\frac{\partial r_{2i}}{\partial R}\right)\Psi_e d\tau_1\cdots d\tau_N. \quad (6')$$

We can integrate over the coordinates and sum over the spins of all electrons except those of the ith electron. Therefore, let

$$P_i(x_i, y_i, z_i, s_i) = \int_{s_1}\cdots\int_{s_N}' \Psi_e{}^*\Psi_e d\tau_1\cdots d\tau_N, \quad (11)$$

the prime signifying the omission of the integration over the coordinates and of the summing over the spin of the ith electron.

Since $\Psi_e{}^*\Psi_e$ is the probability density for a given spatial configuration of the electrons with a given arrangement of spins, $P_i(x_i, y_i, z_i, s_i)$ is the probability density of the ith electron at x_i, y_i, z_i with the spin s_i regardless of the spatial and spin configuration of all the other electrons.

We now write

$$F = \frac{Z_1 Z_2 e^2}{R^2} - \sum_{i=1}^N \int_{s_i}\left(\frac{Z_1 e^2}{r_{1i}{}^2}\frac{\partial r_{1i}}{\partial R} + \frac{Z_2 e^2}{r_{2i}{}^2}\frac{\partial r_{2i}}{\partial R}\right)P_i d\tau_i. \quad (12)$$

However, we can still sum over the spin s_i. Then

$$\sum_{s_i} P_i(x_i, y_i, z_i, s_i) = \rho_i(x_i, y_i, z_i), \qquad (13)$$

where $\rho_i(x_i, y_i, z_i)$ has essentially the same meaning as the ρ_i in Sec. III; i.e., ρ_i is now the probability density of the ith electron at x_i, y_i, z_i regardless of its own spin and the spatial and spin configuration of all the other electrons. The quantity $e\rho_i d\tau_i$ is the magnitude of the charge of the ith electron in the volume element $d\tau_i$. The remaining discussion in Sec. III is unchanged.

Consequently, Eq. (9) is still valid with $e\rho d\tau$ still interpretable as the magnitude of the total electronic charge at the point x, y, z in the volume element $d\tau$, and the results can be applied to real molecules.

It possibly might appear strange that a simple electrostatic interpretation of the force exerted on the nuclei by the electrons in a molecule is valid, even though electron spin and the Pauli principle are taken into account. The usual "exchange" terms do not appear in the analysis. Exchange does not appear because our analysis deals with the complete electronic wave function and its rigorous interpretation. Exchange terms appear when explicit form is given to Ψ_e. Nevertheless, it must be remembered that the component parts of an explicit form for Ψ_e are not rigorously interpretable in general as physically meaningful wave functions. Furthermore, the analysis illustrates the role of the Pauli principle as a restrictive principle, that is, only those solutions of Eq. (1') which are totally antisymmetric in addition to being regular, square integrable, and mutually orthogonal are to be taken as physically meaningful. It is only these wave functions which should yield a charge distribution agreeing with experiment.

It should be noted that for a stationary state of a

molecule at equilibrium the relation

$$Z_1Z_2e^2/R_e^2 = \tfrac{1}{2}e^2\int f\rho d\tau \qquad (14)$$

is formally correct, to the approximation considered here, for *any* regular, square integrable solution of Eq. (1) or (1'). However, Eq. (14) has physical content only if ρ is either the experimentally determined charge distribution of the molecule or the charge distribution computed by means of the correct wave function Ψ_e.

Once the rules for defining a physically sensible wave function have been set down, then within that framework the primary factors available for a description of molecular behavior are the forces between particles (which are mainly coulomb forces) and whatever quantum numbers are inherent in the problem.

V. BINDING AND ANTIBINDING REGIONS

At this point we shall investigate the nature of the surface separating the binding and the antibinding regions. Since the surface is one of revolution, we need only discuss the plane curve

$$f = (Z_1/r_1^2)\cos\theta_1 + (Z_2/r_2^2)\cos\theta_2 = 0.$$

A suitable coordinate system is shown in Fig. 2. Let

$$x = \tfrac{1}{2}R\xi, \quad y = \tfrac{1}{2}R\eta, \quad \alpha = Z_1/Z_2 \leqslant 1.$$

Then

$$r_1^2 = (\tfrac{1}{2}R+x)^2 + y^2 = \tfrac{1}{4}R^2[(1+\xi)^2 + \eta^2],$$
$$r_2^2 = (\tfrac{1}{2}R-x)^2 + y^2 = \tfrac{1}{4}R^2[(1-\xi)^2 + \eta^2],$$
$$r_1\cos\theta_1 = \tfrac{1}{2}R + x = \tfrac{1}{2}R(1+\xi),$$
$$r_2\cos\theta_2 = \tfrac{1}{2}R - x = \tfrac{1}{2}R(1-\xi),$$

and the equation of the curve becomes

$$\{\alpha(1+\xi)/[(1+\xi)^2 + \eta^2]^{\frac{3}{2}}\} + \{(1-\xi)/[(1-\xi)^2 + \eta^2]^{\frac{3}{2}}\} = 0.$$

The points $\xi = \pm 1$, corresponding to the position of the nuclei, shall be excluded for the moment. There is no solution for η when $-1 < \xi < +1$, as both terms of the equation are positive. Therefore, we shall first consider the range $1 < \xi < \infty$.

Let

$$0 < u = (\xi - 1)/\alpha(\xi + 1) < 1/\alpha.$$

Then, the equation of the curve may be written

$$(1 - u^{\frac{2}{3}})\eta^2 = u^{\frac{2}{3}}(\xi+1)^2 - (\xi-1)^2 = (u^{\frac{2}{3}} - \alpha^2u^2)(\xi+1)^2. \quad (15)$$

Since the right side of the equation is always positive, a solution for η is possible only for $u < 1$. As $u \to 1$, $\eta^2 \to \infty$; but $\alpha < 1$, and, therefore, $1/\alpha > 1$. Consequently, $u = 1$ is a permissible value. This equation,
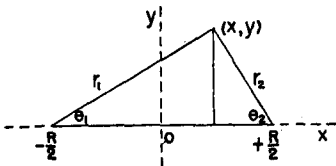

FIG. 2. The coordinate system.

$u = 1$, defines the limiting value of ξ for $\xi > 1$, i.e.,

$$\xi = (1+\alpha)/(1-\alpha) > 1.$$

The point $\xi = +1$ offers no difficulty. Let $\xi = 1 + \epsilon$, where $\epsilon \to +0$. Then $u \simeq \epsilon/2\alpha$, and $\xi \simeq 1 + 2\alpha u$ as $u \to +0$. Therefore, $(1 - u^{\frac{2}{3}})\eta^2 \simeq \eta^2 \simeq 4u^{\frac{2}{3}}$, or $\eta \simeq \pm 2u^{\frac{1}{3}}$. Hence, $\eta \to 0$. Furthermore,

$$d\eta/d\xi \simeq \pm \tfrac{2}{3}u^{-\frac{2}{3}}du/d\xi \simeq \pm u^{-\frac{2}{3}}/3\alpha.$$

Thus, $d\eta/d\xi \to \pm\infty$, and the curve enters the point $\xi = +1$ at right angles.

For the region $-\infty < \xi < -1$, let us simply change the sign of ξ in the equation for the curve by defining $\xi = -\xi'$, and also set $\beta = 1/\alpha > 1$. Then we have

$$\{\beta(1+\xi')/[(1+\xi')^2 + \eta^2]^{\frac{3}{2}}\}$$
$$+ \{(1-\xi')/[(1-\xi')^2 + \eta^2]^{\frac{3}{2}}\} = 0.$$

Utilizing the previous analysis, let $0 < u = (\xi'-1)/\beta(\xi'+1) < 1/\beta$. Thus,

$$(1 - u^{\frac{2}{3}})\eta^2 = (u^{\frac{2}{3}} - \beta^2u^2)(\xi'+1)^2. \quad (16)$$

Since $\beta > 1$ one has $1/\beta < 1$ and the point $u = 1$ is excluded. A solution for η is possible only if $u^{\frac{2}{3}} - \beta^2u^2 \geqslant 0$. This leads to the result that

$$1 < \xi' \leqslant [(\beta)^{\frac{1}{2}}+1]/[(\beta)^{\frac{1}{2}}-1] = [1+(\alpha)^{\frac{1}{2}}]/[1-(\alpha)^{\frac{1}{2}}].$$

Consequently, η remains finite and the curve is closed. The curve enters the points

$$\xi = -1 \text{ and } \xi = -[1+(\alpha)^{\frac{1}{2}}]/[1-(\alpha)^{\frac{1}{2}}]$$

at right angles. A sketch of the curve $f = 0$ for $\alpha = \tfrac{1}{2}$ is shown in Fig. 3.

In the case of a homonuclear molecule, $\alpha = 1$, the regions are, of course, symmetrical and the curve $f = 0$ is open. The curve is shown in Fig. 4. An interesting feature is the following. The curve approaches a straight line asymptotically as $x \to \infty$. For ξ large, $u \simeq 1 - 2/\xi$. Now,

$$(1 - u^{\frac{2}{3}})\eta^2 = u^{\frac{2}{3}}(1 - u^{\frac{1}{3}})(1 + u^{\frac{1}{3}})(\xi+1)^2.$$

Therefore,

$$\eta = \pm u^{\frac{1}{3}}(1 + u^{\frac{1}{3}})^{\frac{1}{2}}(\xi+1),$$

and

$$\eta \to \pm\sqrt{2}\xi + 0(1/\xi). \quad (17)$$

The asymptotic line passes through the origin and $\tan\theta = \sqrt{2}$. Thus, 2θ equals $109°28'$, the tetrahedral angle. This result is due to the Coulomb force law, for if the force between charges varied inversely as the nth power of the distance, then $\tan\theta = (n)^{\frac{1}{2}}$.

VI. DISCUSSION

Although the electrons cannot be strictly individualized in the many-electron molecule, it is usually a good approximation and physically fruitful to do just that. In the method of molecular orbitals the distinction of bonding and antibonding electrons is based on the criterion whether the energy level of a given electron is
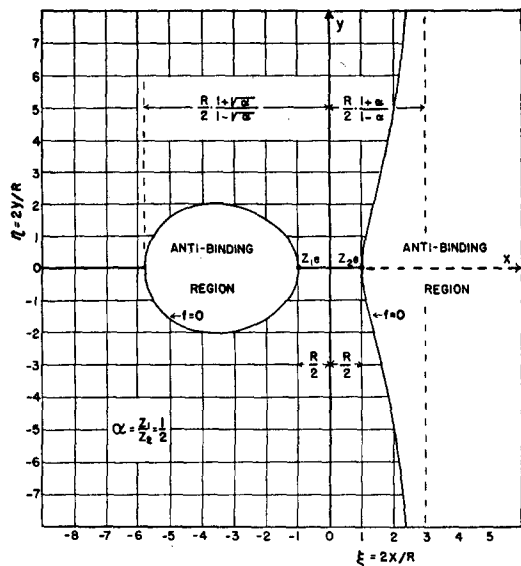
FIG. 3. Binding and antibinding regions in a heteronuclear molecule.

FIG. 4. Binding and antibinding regions in a homonuclear molecule.

lowered or raised respectively in the transition from separated atoms to the molecule. Applying the consideration of the forces exerted by an electron on the nuclei in an analogous manner, we shall say that an electron moves predominantly in the binding or antibinding region when $\int f\rho d\tau$ is positive or negative, respectively. The quantity $e\rho$, the charge density of the single electron, is a function of the internuclear distance. The sign of $\int f\rho d\tau$ gives a more exact interpretation of the expressions "binding region between the cores" and "antibinding region beyond the cores" (CEN).

It is not easy to classify generally the types of charge distribution which are binding or antibinding. Two simple distributions which give rise to a net binding effect are the following.

(a) An electron distribution which has one of the two nuclei as a center of symmetry is binding. This is so because the electron exerts no net force on the nucleus which is the center of symmetry, and the electron attracts the other nucleus. This point of view led (see CEN) to the conclusion that, e.g., in N_2 the four K electrons do contribute to the binding of the two N^{7+} nuclei because they screen the positive charge of the latter and reduce it to the charge of the cores N^{5+}.

(b) For an electron distribution which has elliptical symmetry with respect to the two nuclei as foci, it can be shown that $\int f\rho d\tau$ is also positive.

The binding behavior of a single electron has been investigated (Comm. VI) on the basis of the effect which the addition of the Nth electron to a system containing $N-1$ electrons has on the internuclear distance and the more sensitive force constant. The experi-
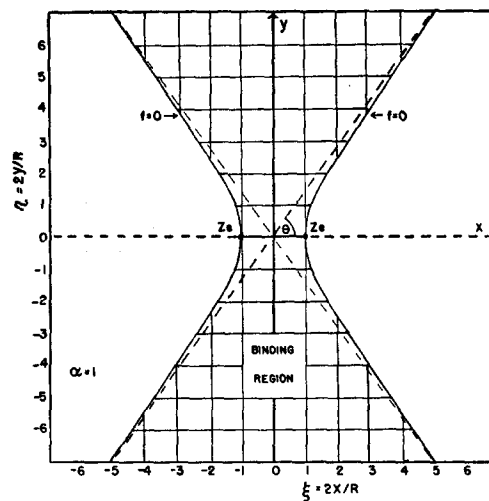
mentally determined effect is the result of two factors which are not independent of each other.

(a) The Nth electron can move predominantly either in the binding or in the antibinding region.

(b) The Nth electron always repels the remaining N-1 electrons and, in general, reduces their binding effect.

Thus, if one finds that the addition of the Nth electron strengthens the binding, this indicates that this electron moves predominantly in the binding regions and that its binding action outweighs the effect of reducing the binding of the remaining electrons. This seems to be the case, e.g., in N_2 and HCl.

However, if one finds that the addition of the Nth electron weakens the binding, there are two alternatives. Either the electron moves predominantly in the antibinding region, as seems to be the case (Comm. VI) in hydrides of the type $BeH = e^-(Be^{2+})(H^-)$, or in spite of moving predominantly in the binding region, the binding effect of the electron is outweighed by its effect of reducing the binding action exerted by the other electrons; this was concluded to be the case in CO (CEN).

In forthcoming papers the above points of view will be applied in more detail for the elucidation of the binding in various molecules.