The Force Concept in Chemistry

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The applications, most of which have been developed in the last decade, of the Hellmann-Feynman (H–F) theorem in molecular quantum mechanics are reviewed. In general, the forces (on the nuclei of molecules) calculated with the use of this theorem provide great qualitative insight into the nature of the phenomena investigated; outstanding examples of these are in the concepts of chemical binding and molecular shapes. However, there are serious limitations in quantitative applications of the H–F theorem with approximate wave functions, since the calculated forces are extremely sensitive to small inaccuracies in the wave functions, especially near the nuclei of interest. Nevertheless, in view of the fact that it is difficult to discern general qualitative features in very accurate or *ab initio* molecular calculations, the H–F theorem is likely to be a highly useful tool for developing much needed qualitative chemical models which will be based on firm quantum mechanical foundations and will also remain open to quantitative extension, at least in principle.

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1. INTRODUCTION

In molecular quantum mechanics there are two distinct approaches, namely those of *energy* and *force*, for understanding chemical processes. The energy approach looks at a molecular system in terms of the behavior of its total energy or, where detailed insight into a chemical phenomenon is desired, in terms of the behavior of appropriately partitioned components of the total energy. The force formulation, on the other hand, views molecular processes through the net forces or, when necessary, appropriately partitioned components of the net forces on the nuclei in a molecular system (see Slater, 1963).

Of these two alternative approaches the *force concept in chemistry* has not received the attention it deserves. This is mainly because the forces are not quantum-mechanical constants of motion as they do not commute with the corresponding Hamiltonians. Consequently, during the evolution of quantum chemistry and molecular spectroscopy, forces were looked upon merely as gradients of appropriate potential energy functions rather than as quantities capable of being

derived independently. However, as we shall see below, direct consideration of the forces on the nuclei in molecules can yield outstanding qualitative chemical information; for example, a consistent pictorial understanding of molecular shapes and chemical binding. Unfortunately, however, we shall also see that the quantitative possibilities of the force concept are somewhat limited at present.

A practical way of calculating the force on a nucleus in a molecule, when the former suffers arbitrary displacements from the equilibrium position, is provided by the *Hellmann–Feynman (H–F) theorem* (Hellmann, 1937; Feynman, 1939). In this article we shall attempt to deal with the various chemical applications of this theorem, most of which have been developed in the last decade. The discussion falls into two parts: molecular structure and reactivity. The structural discussion will consist mainly of investigations on chemical binding and molecular geometry. However, there has been little application of this approach to the field of chemical reactivity, apart from some qualitative and semiquantitative discussions of intermolecular forces. Some extensions and modifications of the H–F theorem are also mentioned.

2. THE HELLMANN–FEYNMAN THEOREM AND ITS CONDITIONS OF VALIDITY FOR APPROXIMATE WAVE FUNCTIONS

The Hellmann–Feynman theorem states that *if ψ is an exact (unnormalized) eigenfunction of a Hamiltonian H, and E is the corresponding energy eigenvalue, then, if λ is any parameter occurring in H,*

$$\partial E/\partial\lambda\langle\psi\mid\psi\rangle=\langle\psi\mid\partial H/\partial\lambda\mid\psi\rangle. \qquad (1)$$

In other words, *for a normalized wave function, the first derivative of the energy with respect to a parameter is equal to the expectation value of the corresponding first derivative of the Hamiltonian.* A simple proof of this theorem will follow shortly. Depending on the physical nature of the parameter λ (e.g., it may be an internuclear distance, a semiempirical parameter in an approximate theory, a nuclear charge, a nuclear coordinate, and so on) one

can obtain much valuable information about variations in the energy of a molecular system with the help of the above theorem. If λ is taken as the x coordinate, X_p say, of the pth nucleus in a molecule then, *in the framework of the adiabatic approximation* (see Slater, 1963), the H–F theorem leads (Feynman, 1939) to the following expression for the x component, F_{px}, of the force acting on the pth nucleus

$$F_{px} = Z_p \Big[\sum_{q \neq p} (Z_q/R_{pq}^2)(\partial R_{pq}/\partial X_p)$$

$$- \int \rho(\mathbf{r})(x_p/r_p^3)\, d\tau \Big], \quad (2)$$

where Z_p is the nuclear charge of p, R_{pq} an internuclear distance, and $\rho(\mathbf{r})$ is the *total one-electron density* at the point $\mathbf{r}$; the integration in (2) is to be carried out in the one-electron space and x_p, r_p are position coordinates in space measured from the pth nucleus. In order to obtain the y and z components of the force on p, one replaces the x coordinates in Eq. (2) by the y and z coordinates, respectively.

Equation (2) has sometimes been called *the electrostatic Hellmann–Feynman theorem*. It tells us that the force acting on a nucleus in any system of nuclei and electrons can be interpreted solely in terms of classical electrostatics, *once the electronic charge density or the first-order density matrix has been obtained by a quantum mechanical procedure*. Such a force on a nucleus is simply the resultant of the classical electrostatic forces due to the other nuclei and to the surrounding electronic distribution. These nuclear forces can then be integrated, if necessary, to obtain the energy of a molecular system (relative to separated atoms) in terms of the first-order density matrix.[1] If the latter is known for various nuclear configurations of a molecule, then the corresponding forces on the nuclei may be obtained, and the equilibrium molecular geometry determined as the configuration where the net force on any nucleus vanishes. This obviously corresponds to the energy minimum. Thus, within the range of validity of the adiabatic approximation, the force and energy pictures are equivalent insofar as corresponding *stationary* properties of the latter are concerned, provided one has available the *exact* single-particle density.

Apart from being conceptually attractive, the force picture has distinct computational advantages: If one chooses to work within the adiabatic approximation, then interelectronic distances and nuclear coordinates are mutually independent; hence the troublesome interelectronic terms automatically drop out of consideration when one differentiates the energy to obtain the force.[2] Therefore, the integration in Eq. (2) involves only one-

electron operators and if a single-determinantal LCAO–MO wave function is used[3] to obtain the single-particle density $\rho(\mathbf{r})$, then no force integrals involving more than *three* centers are required. There are now *four* available methods (Deb, 1971; Flygare, *et al.*, 1966), none of which is completely satisfactory, for evaluating such 3-center force integrals numerically, seminumerically, and analytically. However, the H–F theorem which obviously holds good for an exact wave function need not be valid for an approximate solution to the wave equation. As we shall see later, this theorem is in fact very sensitive to inaccuracies in the wave function.

Various authors have examined the conditions of validity of the H–F theorem for an approximate wave function. If, for an approximate (unnormalized) wave function ψ, we write

$$E = \langle \psi \mid H \mid \psi \rangle / \langle \psi \mid \psi \rangle, \quad (3)$$

then by differentiating Eq. (3) with respect to the parameter λ and by making use of the hermiticity of H, one obtains (Hirschfelder and Coulson, 1962)

$$(\partial E/\partial \lambda)\langle \psi \mid \psi \rangle - \langle \psi \mid \partial H/\partial \lambda \mid \psi \rangle$$

$$= \langle (\partial \psi/\partial \lambda) \mid H - E \mid \psi \rangle + \langle (\partial \psi/\partial \lambda) \mid H - E \mid \psi \rangle^*. \quad (4)$$

For an exact ψ, this gives

$$(H - E)\psi = 0 \quad (5)$$

so that one obtains Eq. (1). For a diatomic molecule with internuclear separation R, let us write Eq. (1) as

$$(\partial E/\partial R)\langle \psi \mid \psi \rangle = \langle \psi \mid \partial H/\partial R \mid \psi \rangle, \quad (6)$$

with $\psi = \psi(\xi_i, \eta_i, \phi_i; \lambda_1, \lambda_2, \cdots, \lambda_n)$, where ξ_i, η_i, ϕ_i are the spheroidal coordinates for the ith electron, and the λ_i's are a set of parameters which may be functions of R. Hurley (1954, 1956) has shown that the H–F theorem is satisfied by "floating"[4] wave functions[5] obtained by requiring that all λ_i be independent of R, since by putting $\partial \psi/\partial R = 0$ in Eq. (4) we obtain Eq. (6). Following Hall (1961), one can then demonstrate that the wave functions obtained by optimizing all the above parameters λ_i will satisfy the H–F theorem: Since we have

$$\partial \psi/\partial R = \sum_i (\partial \psi/\partial \lambda_i)(d\lambda_i/dR), \quad (7)$$

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[1] It should be remembered that an accurate single-particle density includes correlation effects due to the Coulomb and Pauli repulsive forces between the electrons.

[2] In the case of vibronic coupling, the force on a nucleus has a less simple meaning since the interelectronic terms in the Hamiltonian cannot be omitted when calculating forces on nuclei [see Eq. (19)].

[3] For a single determinantal LCAO–MO wave function, we have

$$\rho(\mathbf{r}) = \sum_i \eta_i \phi_i^2(\mathbf{r}),$$

where ϕ_i is a real MO with occupation number η_i.

[4] An orbital is said to be "floating" when the distance of its centroid from a reference point is itself a parameter to be optimized.

[5] Shull and Ebbing (1958) are of the opinion that, for H_2^+ and H_2 molecules, at least, the introduction of floating orbitals provides an energy improvement too small to justify the extra computational labor involved.

Eq. (4) takes the form

$$(\partial E/\partial R)\langle \psi \mid \psi \rangle - \langle \psi \mid \partial H/\partial R \mid \psi \rangle$$
$$= \sum_i (d\lambda_i/dR)(\partial E/\partial \lambda_i)\langle \psi \mid \psi \rangle,$$

where

$$(\partial E/\partial \lambda_i)\langle \psi \mid \psi \rangle = \langle (\partial \psi/\partial \lambda_i) \mid H-E \mid \psi \rangle$$
$$+ \langle (\partial \psi/\partial \lambda_i) \mid H-E \mid \psi \rangle^*, \quad (8)^{6a}$$

assuming that the parameters λ_i do not occur explicitly in the Hamiltonian. Hence, Eq. (6) is satisfied if either $\partial E/\partial \lambda_i = 0$, or $d\lambda_i/dR = 0$; that is, if either λ_i's dependent on R are optimized at the given R, or if all λ_i are independent of R. Thus Hurley (1954, 1956, 1964), Hall (1961), and Stanton (1962)[6b] concluded that Hartree–Fock wave functions obtained by optimizing all parameters will satisfy the H–F theorem. Further, let us write

$$\partial \psi/\partial \lambda = iAW\psi + B\psi, \quad (14)$$

where A and B are functions of λ, A is real, and W is a function of coordinates and momenta. We take W to be a Hermitian operator which may or may not contain the parameter λ. Using Eq. (14) and the Hermitian character of W and H, we can write Eq. (4) as

$$(\partial E/\partial \lambda)\langle \psi \mid \psi \rangle - \langle \psi \mid \partial H/\partial \lambda \mid \psi \rangle$$
$$= iA\langle \psi \mid [H, W] \mid \psi \rangle \quad (15)$$

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[6] (a) Equations (9)–(13) are included in Footnote 6(b).

(b) The same conclusion is made by Coulson (1971) who uses Brillouin's theorem to prove the H–F theorem for a nonexact normalized wave function ψ_0. For such a wave function we can write Eq. (4) as

$$\partial E/\partial \lambda = \langle \psi_0 \mid \partial H/\partial \lambda \mid \psi_0 \rangle + \langle \partial \psi_0/\partial \lambda \mid H \mid \psi_0 \rangle$$
$$+ \langle \psi_0 \mid H \mid \partial \psi_0/\partial \lambda \rangle \quad (9)$$

so that the H–F theorem is satisfied only if

$$\langle \partial \psi_0/\partial \lambda \mid H \mid \psi_0 \rangle + \langle \psi_0 \mid H \mid \partial \psi_0/\partial \lambda \rangle = 0 \quad (10)$$

Now, let ψ_0 be a closed-shell function (real, say) represented by the single determinant

$$\psi_0 = \mid \phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \cdots \phi_n \bar{\phi}_n \mid, \quad (11)$$

where the bar denotes β spin. The set of orbitals $\phi_1, \phi_2, \cdots, \phi_n$ may be made complete by adding another set of functions ("virtual" orbitals) $x_{n+1}, x_{n+2}, \cdots$ etc. One can then show (see Coulson, 1971) that

$$\partial \psi_0/\partial \lambda = \sum_{i>0} c_i \psi_i, \quad (12)$$

where all the ψ_i's represent *singly excited configurations only*; i.e., configurations obtained by replacing *one* of the ϕ orbitals in (11) by *one* of the x orbitals. Thus, we have

$$\langle \partial \psi_0/\partial \lambda \mid H \mid \psi_0 \rangle = \sum_{i>0} c_i \langle \psi_i \mid H \mid \psi_0 \rangle$$

and

$$\langle \psi_0 \mid H \mid \partial \psi_0/\partial \lambda \rangle = \sum_{i>0} c_i \langle \psi_0 \mid H \mid \psi_i \rangle. \quad (13)$$

Now, if the original orbitals in Eq. (11) are chosen to satisfy Hartree–Fock equations, then, according to Brillouin's theorem, H has no nonvanishing matrix element between ψ_0, and any singly excited wave function. Thus, the right-hand sides of Eqs. (13) vanish, and the H–F theorem is satisfied. The above proof can be extended (Coulson, 1971) to general Hartree–Fock excited states.

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where $[H, W]$ is the commutator of H and W, given by $[H, W] = HW - WH$.

Hirschfelder and Coulson (1962) have used Eq. (15)[7a] to show that, for a diatomic molecule, the H–F theorem is satisfied at a given R if the set of hypervirial relations[7b] (Hirschfelder, 1960; Epstein and Hirschfelder, 1961; Coulson, 1965) corresponding to all the parameters λ_i

$$\langle \psi \mid [H, W_i] \mid \psi \rangle = 0, \quad (18)$$

where W_i is a Hermitian operator, is simultaneously satisfied. These authors discuss the possibility of calculating the potential energy curve of a diatomic molecule (relative to the separated atoms) by obtaining $\partial E/\partial R$ for a range of R, from wave functions chosen at each R (by applying the above hypervirial criterion) to satisfy the H–F theorem. Hirschfelder and Coulson's work is consistent with that of Frost and Lykos (1956) who showed that if the kinetic and the potential energy parts of the Hamiltonian of a diatomic molecule are affected differently by a variation in λ, Eq. (1) will lead to the virial theorem. Tuan (1969) has further shown that Eq. (1) is valid for multiconfiguration self-consistent-field energies and wave functions, as well as for both closed- and open-shell systems. Goddard (1968) demonstrated that the H–F theorem is also applicable to certain other wave functions which are not of Hartree–Fock type.

3. EXTENSIONS AND GENERALIZATIONS OF THE HELLMANN–FEYNMAN THEOREM

Some generalizations of the H–F theorem are worth mentioning. Kerner (1959) has extended it to outside the framework of the adiabatic approximation by assuming that the nuclei move classically while the electrons move quantum mechanically. If $x_p(t)$ represents the coordinate of the pth nucleus of mass M_p, then Eq. (2) becomes Kerner's "dynamical Feynman theorem" (see also Clinton, 1960)

$$M_p \ddot{x}_p = (\partial W_N/\partial x_p) - \int \rho(t)(\partial V/\partial x_p) \, d\tau, \quad (19)$$

where W_N is the nuclear repulsive energy, and $\partial V/\partial x_p$ represents the instantaneous electronic force on the pth nucleus due to the electronic density $\rho(t)$. Hayes and Parr (1965) have derived more general time-dependent H–F formulae of which Eq. (19) is a special case. Löwdin (1959) has also derived a general expression

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[7] (a) Equations (16)–(17) are in Footnote 7(b).

(b) *The Hypervirial Theorem*: If ψ is a bound-state eigenfunction of a Hamiltonian H, and W is a hermitian time-independent operator involving coordinates and momenta, then we have

$$\langle [H, W] \rangle \equiv \langle \psi \mid [H, W] \mid \psi \rangle = 0. \quad (16)$$

Since

$$d\langle W \rangle/dt = i/\hbar \langle [H, W] \rangle \quad (17)$$

Equation (16) means that the expectation value of W, for a stationary state ψ, is independent of the time. The hypervirial theorem Eq. (16) is so named because it can be regarded (Hirschfelder, 1960) as a generalization of the usual virial theorem.

which is a special case of the H–F theorem Eq. (1). By choosing a complete set of basis functions, $\{\phi_i\}$, one defines an arbitrary wave function ψ, the overlap matrix S, and the Hamiltonian matrix H as

$$\psi = \sum_i c_i \phi_i$$

$$S_{ij} = \langle \phi_i \mid \phi_j \rangle$$

$$H_{ij} = \langle \phi_i \mid H \mid \phi_j \rangle, \qquad (20)$$

respectively, both S and H being self-adjoint. One can then obtain (Löwdin, 1959)

$$(\partial E/\partial \lambda)\langle \psi \mid \psi \rangle = \langle \psi \mid (\partial H/\partial \lambda) - E(\partial S/\partial \lambda) \mid \psi \rangle, \quad (21)$$

a generalized H–F theorem. Levine (1968) has further extended the theorem (21) to forms involving functions of the Hamiltonian, while Epstein (1967) discusses a generalized H–F theorem in curvilinear coordinates for both exact and nonexact "floating" wave functions. Numerical applications of the above generalizations have not been made.

Recently Parr (1964, 1965) proposed an interesting method for calculating energy differences involved in isoelectronic molecular processes such as changes in molecular conformations (e.g., those due to vibrations and internal rotations), formation of molecules from atoms, dissociation of molecules into atoms or ions, molecular "transmutations" of the type $CO \rightarrow N_2$, intermolecular and scattering phenomena, x-ray spectra, and so on, embracing a wide area of chemistry. This is the so-called "integral Hellmann–Feynman theorem" (see also Kim and Parr, 1964). If ψ_A and ψ_B are the normalized wave functions of two systems, A and B, having Hamiltonians H_A and H_B, respectively, with E_A and E_B as the corresponding energy eigenvalues, then one readily obtains

$$\Delta E = E_B - E_A = S^{-1}\langle \psi_A \mid \Delta H \mid \psi_B \rangle, \qquad (22)$$

where

$$S = \langle \psi_A \mid \psi_B \rangle,$$

$$\Delta H = H_B - H_A. \qquad (23)$$

Equation (22) has been called the "integral" H–F theorem, since Eq. (1) can be looked upon as a differential form of it (Kim and Parr, 1964).

If the transition A→B is an isoelectronic process, then by adopting the adiabatic approximation, one can write (see Parr, 1965)

$$\Delta H = \Delta V_{nn} + \sum_i H'(i), \qquad (24)$$

where ΔV_{nn} is the change in nuclear repulsion energy due to the transition, and $H'(i) = V_{ne}{}^B(i) - V_{ne}{}^A(i)$ is the difference in electron–nuclear attraction energy for the ith electron. When Eq. (24) is substituted into Eq. (22), the latter reduces (Kim and Parr, 1964)

to the *one-electron form*

$$\Delta E = \Delta W_{nn} + \int \rho_{AB}(1) H'(1) \, d\tau_1, \qquad (25)$$

where ΔW_{nn} is the change in nuclear repulsion energy between B and A, $H'(1)$ is the corresponding change in the electron–nuclear attraction operator for electron 1, and $\rho_{AB}(1)$ is the normalized one-electron "transition density" between ψ_A and ψ_B, i.e.,

$$\rho_{AB}(1) = NS^{-1}\int \psi_A \psi_B \, d\tau_2 \cdots d\tau_N. \qquad (26)$$

It is clearly seen that Eq. (25), like Eq. (2), admits rigorously a classical interpretation of the energy change, within the adiabatic approximation, in terms of a nuclear–nuclear and an electron–nuclear component. Therefore, for reasons outlined previously with the H–F theorem, it is tempting to use Eq. (25) in calculating energy changes in isoelectronic processes. However, as Parr himself (1965) has cautioned, to use Eq. (25) with approximate wave functions is "fraught with danger" (see also Allen, 1969). In the various *quantitative* applications of the H–F and "integral" H–F theorems cited below, we shall see that there are important reasons for being wary. For example, Rothstein and Blinder (1967) comment on the need for modifying the "integral" H–F theorem to suit wave functions of presently available quality. However, Richardson and Pack (1964) have pointed out that with an improvement in the wave function, ΔE, obtained through Eq. (25), improves faster than does the corresponding expectation-value difference. Epstein *et al.* (1967) have given a detailed discussion of the relative merits and demerits of the types of formulae used in calculating energy changes accompanying isoelectronic processes, viz. (a) the expectation-value difference, (b) the H–F theorem and (c) the "integral" H–F theorem. These authors show that if ψ_A and ψ_B are chosen variationally from a fixed basis set, the three formulae give identical ΔE. On the other hand, if each of ψ_A and ψ_B are thus chosen from a given class of functions, as is the case when each is a Hartree–Fock wave function, (a) and (b) give the same ΔE which may be different from that calculated by (c). However, (c) may sometimes provide a better estimate of ΔE than (a) (see also Lowe and Mazziotti, 1968).

4. CHEMICAL APPLICATIONS OF THE HELLMANN–FEYNMAN THEOREM

Except for certain diatomic molecules involving first- and second-row elements or their hydrides present day molecular wave functions are insufficient for the H–F theorem since they do not usually satisfy the validity conditions mentioned above. However, in spite of its limitations with approximate wave functions, this theorem has been extensively employed in recent years to understand molecular processes in terms of the calculated forces. The inspiration to exploit the chemical potentialities of the H–F theorem was provided mainly
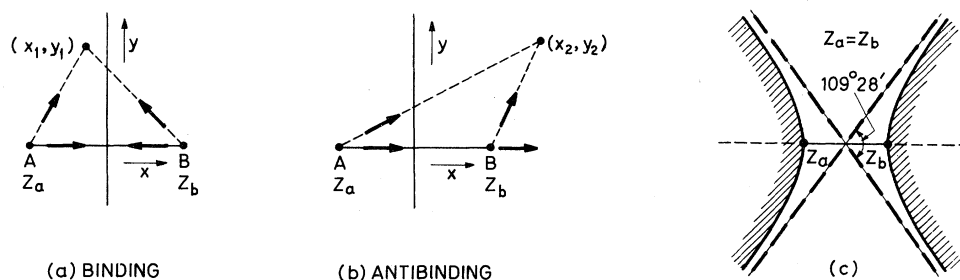
FIG. 1. Binding and antibinding regions in a diatomic molecule AB with nuclear charges Z_a and Z_b, respectively. In (a) an electronic charge at (x_1, y_1) leads to a net force of attraction between the nuclei; in (b) an electronic charge at (x_2, y_2) results in a net force of repulsion between the nuclei. In (c) are indicated coutours of the boundary surfaces separating binding and antibinding regions in a homonuclear diatomic molecule. The shaded area indicates the antibinding region, while the thick arrows indicate the directions of the electron–nuclear forces [Reproduced by permission from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), pp. 935, 936].

by the imaginative work of Berlin (1951; see also Hirschfelder, *et al.*, 1964).

A. Berlin's Work: A Physical Picture of the Chemical Bond

Berlin had divided the 3-dimensional space around a diatomic molecule AB into *binding* and *antibinding* regions. Any electronic charge in the binding region would attract both nuclei until offset by the nuclear repulsion; any charge in the antibinding region, on the other hand, would tend to pull the nuclei apart. Conversely, *removal of electronic charge from the binding region results in an increase in bond length, while charge removal from the antibinding region leads to a shortening of bond length* (see Figs. 1(a) and 1(b). The boundary surfaces separating the binding from the antibinding region are defined by the relation

$$f_{Az} = f_{Bz}, \qquad (27)$$

where z is taken along the molecular axis, and f_{Az} is the z component of the electronic force on A. For homonuclear diatomic molecules, the contours of the boundary surfaces are hyperbolas [see Fig. 1(c)] with opposite asymptotes intersecting at the tetrahedral angle, $109°28'$. With an increase in the ratio Z_A/Z_B the surface at A flattens out and approaches a plane perpendicular to AB, while the surface at B closes on to itself forming a region that approaches a point as $Z_A/Z_B \to \infty$ [see Figs. 2(a) and (b)].

B. A View of Chemical Binding through the Total One-Electron Difference Density

Berlin's ideas about binding and antibinding regions in diatomic molecules have been extensively exploited by Bader and his co-workers (Bader and Henneker, 1965; Bader, *et al.*, 1967a, b; Bader and Chandra, 1968; Bader and Bandrauk, 1968a, b; Bader and Preston, 1969; Cade, *et al.*, 1969). Through their use of sophisticated

wave functions[8] (to obtain single-electron densities) for certain diatomic molecules involving first- and second-row atoms, a fairly comprehensive view of bond formation, in terms of molecular one-electron density and the one-electron difference density, has now emerged. The contours of the total one-electron density itself, while not particularly useful in discussions of chemical binding, do nevertheless provide an estimate of the bond length as well as an idea about the over-all molecular size (Bader, *et al.*, 1967a). The 0.002 contour (see Fig. 3) is useful in deciding the latter as 95 percent or more of the total charge usually resides within this
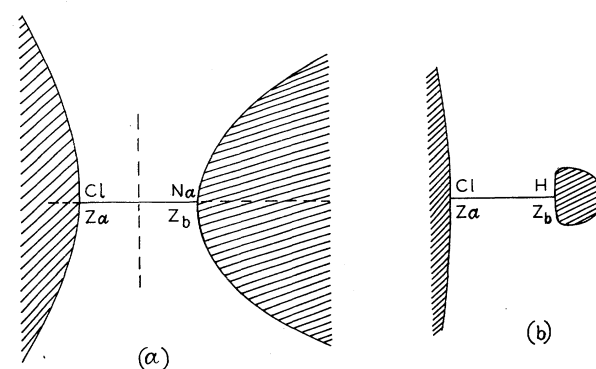

FIG. 2. Contours of the boundary surfaces separating binding from antibinding regions in heteronuclear diatomic molecules AB. (a) Sodium chloride molecule, $Z_a/Z_b = 17/11$, (b) Hydrogen chloride molecule, $Z_a/Z_b = 17$. [Reproduced by permission from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), p. 936].

[8] Figure 4 shows that, with the wave functions for H_2, at $R \leq 2.3$ a.u. the agreement between the calculated and empirical forces is very good. Clinton and Hamilton (1960) had previously proposed use of force curves, instead of potential energy curves, for discussing certain excited states of diatomic molecules. Goodisman (1963) also uses force curves, rather than potential energy curves, for evaluating the force constants in diatomic molecules.

Li₂ ¹Σ⁺ₚ

B₂ ³Σ⁻ₚ

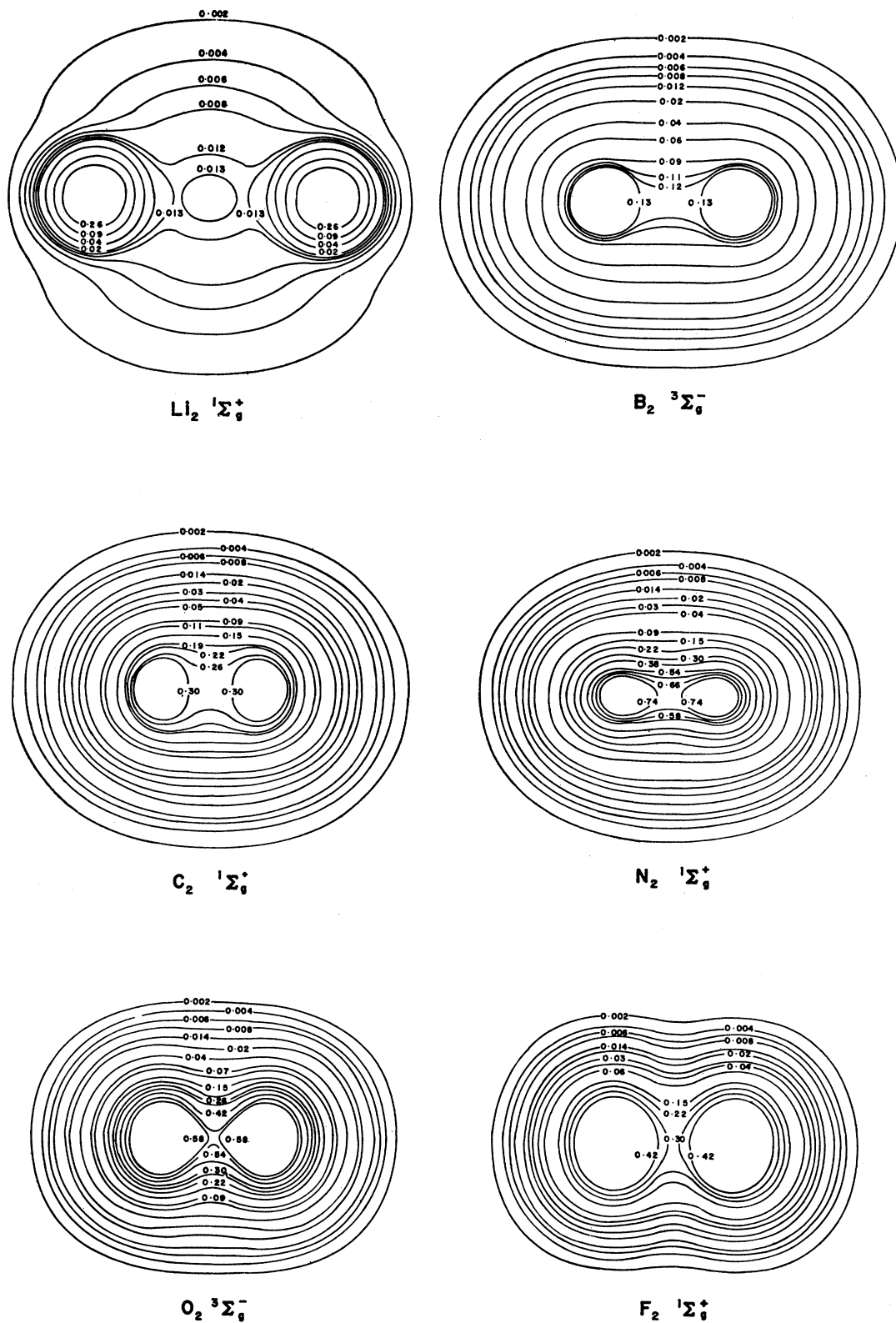C₂ ¹Σ⁺ₚ

N₂ ¹Σ⁺ₚ

O₂ ³Σ⁻ₚ

F₂ ¹Σ⁺ₚ

FIG. 3. Contours of the total molecular one-electron densities for the first-row homonuclear diatomic molecules. Values are in atomic units [Reproduced from R. F. W. Bader, W. H. Henneker, and P. E. Cade, J. Chem. Phys. **46**, 3343 (1967)].

Force Curve for H — H interaction
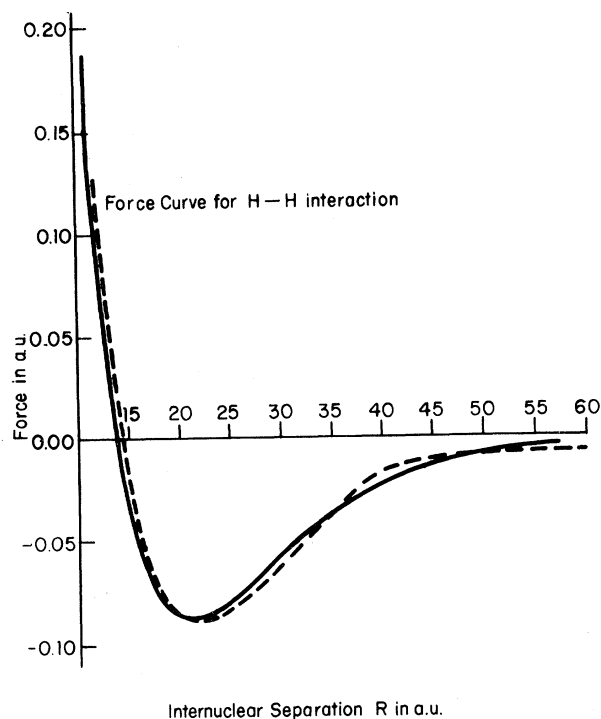
Internuclear Separation R in a.u.

FIG. 4. Theoretical (dotted line), and experimental (solid line) force curves for the H_2 molecule. [Reproduced by permission of the National Research Council of Canada, from R. F. W. Bader, and A. K. Chandra, Can. J. Chem. **46**, 955 (1968)].

contour. The difference density, on the other hand, is obtained by subtracting, from the molecular density at a given R, the superimposed individual atomic densities at the same R. The contours of this difference density reveal the redistribution of charge which accompanies the formation of a chemical bond (see subsequent figures). The usefulness of this quantity in discussing bond formation lies in the fact that, like the total single-particle density, the difference density is invariant with respect to unitary transformations of the wave functions although, for approximate wave functions, its quality depends on the nature and size of the basis set adopted.

The mere overlap of superimposed atomic densities in the binding region is not sufficient to balance the nuclear repulsion. A stable molecule must have a charge build-up in the binding region which will "cement" the two nuclei. For the first-row homonuclear diatomic molecules, more than fifty percent of the total electronic charge lies within the binding region, the most effective build-up occurring on the bond axis; for H_2 the electronic density in the binding region has a seventy percent increase over that resulting from the overlap of atomic densities. It is, however, clear that in balancing the forces of nuclear repulsion both the extent of charge buildup and its distribution are significant; for

instance, *even a little charge concentration on the axis between the nuclei is very effective in binding them.* However, the surprizing fact emerges that there is also a charge build-up *behind* the nuclei; i.e., in the anti-binding region (see Figs. 5 and 6). The reasons for this unexpected buildup, which can sometimes exceed that in the binding region (this may still be sufficient to bind the nuclei), are not clear (see also Bader and Beddall, 1972).

There are significant differences between the charge buildup distributions in H_2 and in A_2 and AH molecules,[9] where A is a first-row atom (see Fig. 7). Such differences arise from the involvement of $2p$ orbitals in bonding for A_2 and AH molecules. In such cases the charge increase in the $p\sigma$ component appears to be at the expense of the $p\pi$ component of the density as well as of the s density at nucleus A. In the equilibrium configurations for H_2 and AH molecules, the difference density plots do not indicate any depletion of charge at the position of the proton.

The difference density maps for stable molecules such as H_2 and unstable ones such as He_2 (compare Figs. 5 and 8) *reveal their differences in chemical binding to be those of degree rather than of kind.* In the case of He_2 there also occurs a charge increase in the binding region, but this is not sufficient to overcome the forces of nuclear repulsion.

A comparison of the density difference contours in LiF and in A_2 molecules helps to point out the differences in ionic and covalent binding (see Fig. 9). In ionic binding, the two nuclei are bound by the charge *localized* on one nucleus (on F in case of LiF), whereas in covalent binding the nuclei are bound by a charge build-up in the binding region which is *shared* equally between them and is sufficient to balance the nuclear repulsion.

The difference density is also likely to provide a useful qualitative insight into the nature of electron reorganization during the progress of a chemical reaction.

C. Calculation of the Molecular One-Electron Density Using the Criterion of Electrostatic Equilibrium

From the above discussion, the total one-electron density emerges as a quantity of high significance for the discussion of the formation of bonds in terms of the nuclear forces. One might well ask if the Hartree–Fock density would be sufficient for this purpose; that is, will the neglect of electron correlation in one-electron density lead us into misinterpretations about chemical binding. Bader and Chandra (1968) have shown, in the case of H_2, that the Hartree–Fock density underestimates the charge density near the nuclei and

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[9] Bader and Beddall (1972) have said that the density distribution and the binding in H_2 and H_2^+ molecules are not typical of homonuclear diatomic molecules and that these systems are not satisfactory for a general discussion of the chemical bond.
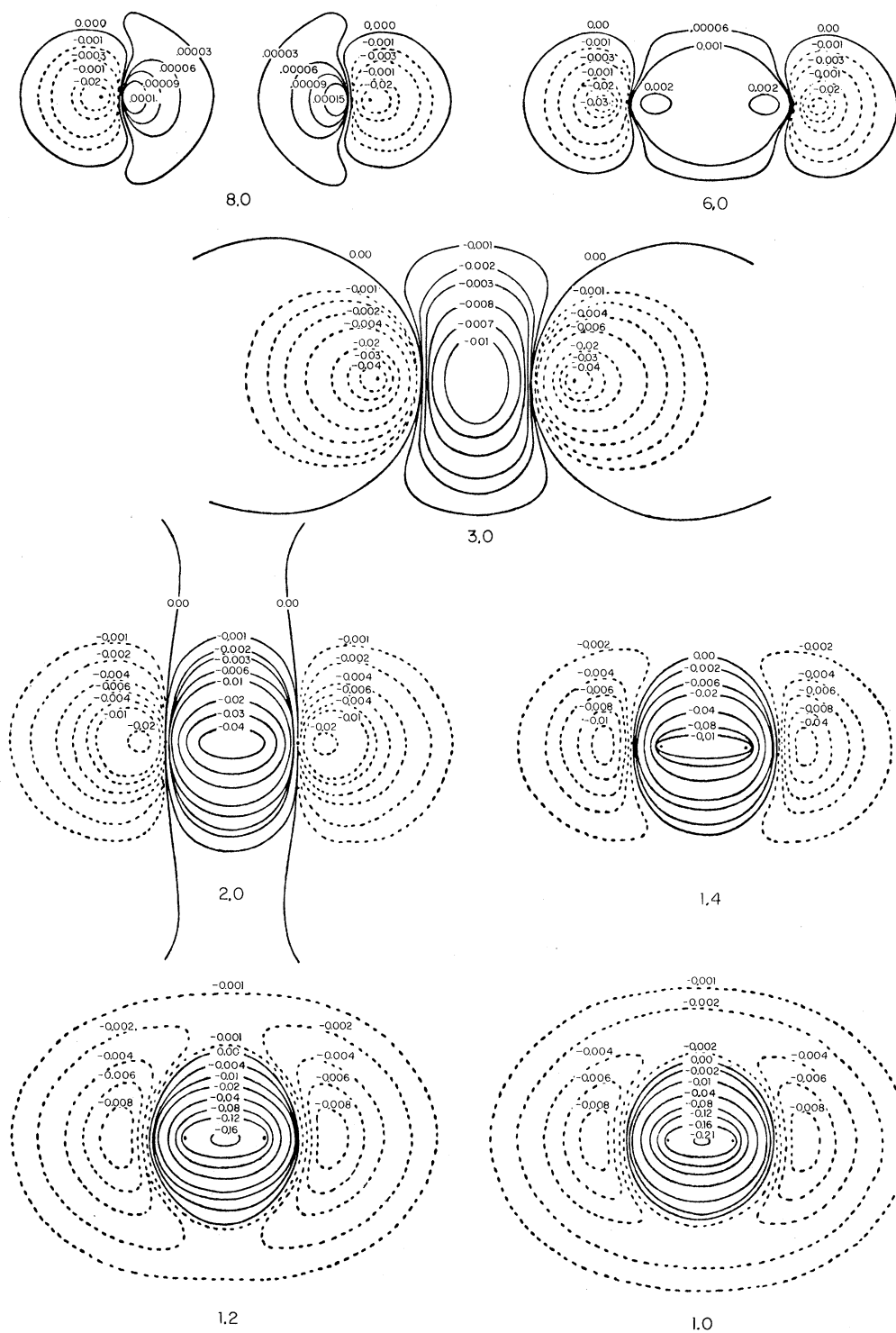
Fig. 5. Contours of the one-electron difference densities (in a.u.) for the H_2 molecule at different internuclear distances. The contour maps at $R=8.0$ and 6.0 a.u. are drawn to one-half scale relative to the others. The zero contour separates the region where charge density is increased from that where the charge density is decreased relative to the original atomic densities. [Reproduced by permission of the National Research Council of Canada, from R. F. W. Bader, and A. K. Chandra, Can. J. Chem. **46,** 956 (1968)].
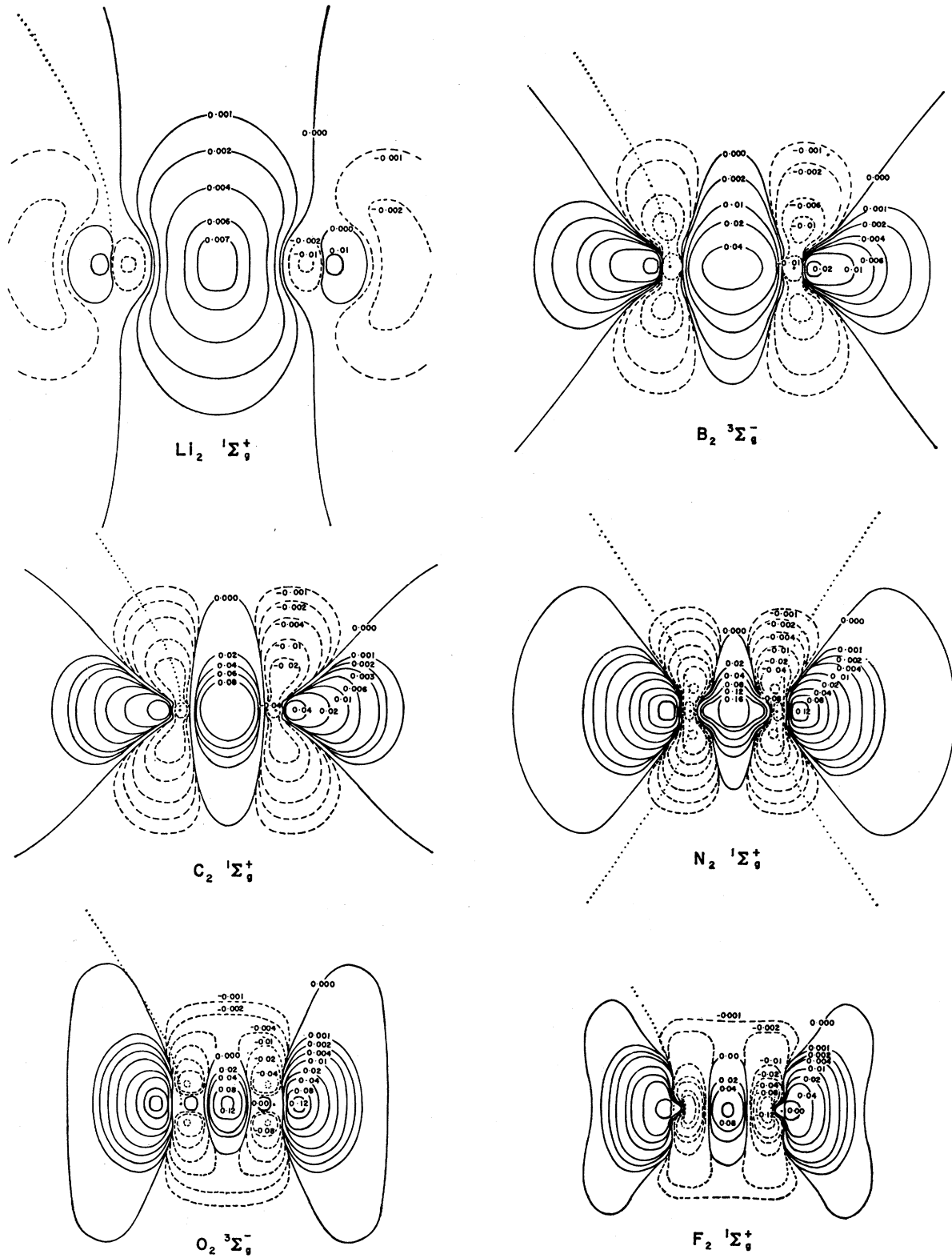
FIG. 6. Contours of the one-electron difference densities for the first-row stable homonuclear diatomic molecules. The dotted lines (shown in full for N₂) separate the binding and antibinding regions. All values are in atomic units. [Reproduced from R. F. W. Bader, W. H. Henneker, and P. E. Cade, J. Chem. Phys. **46**, 3346 (1967)].
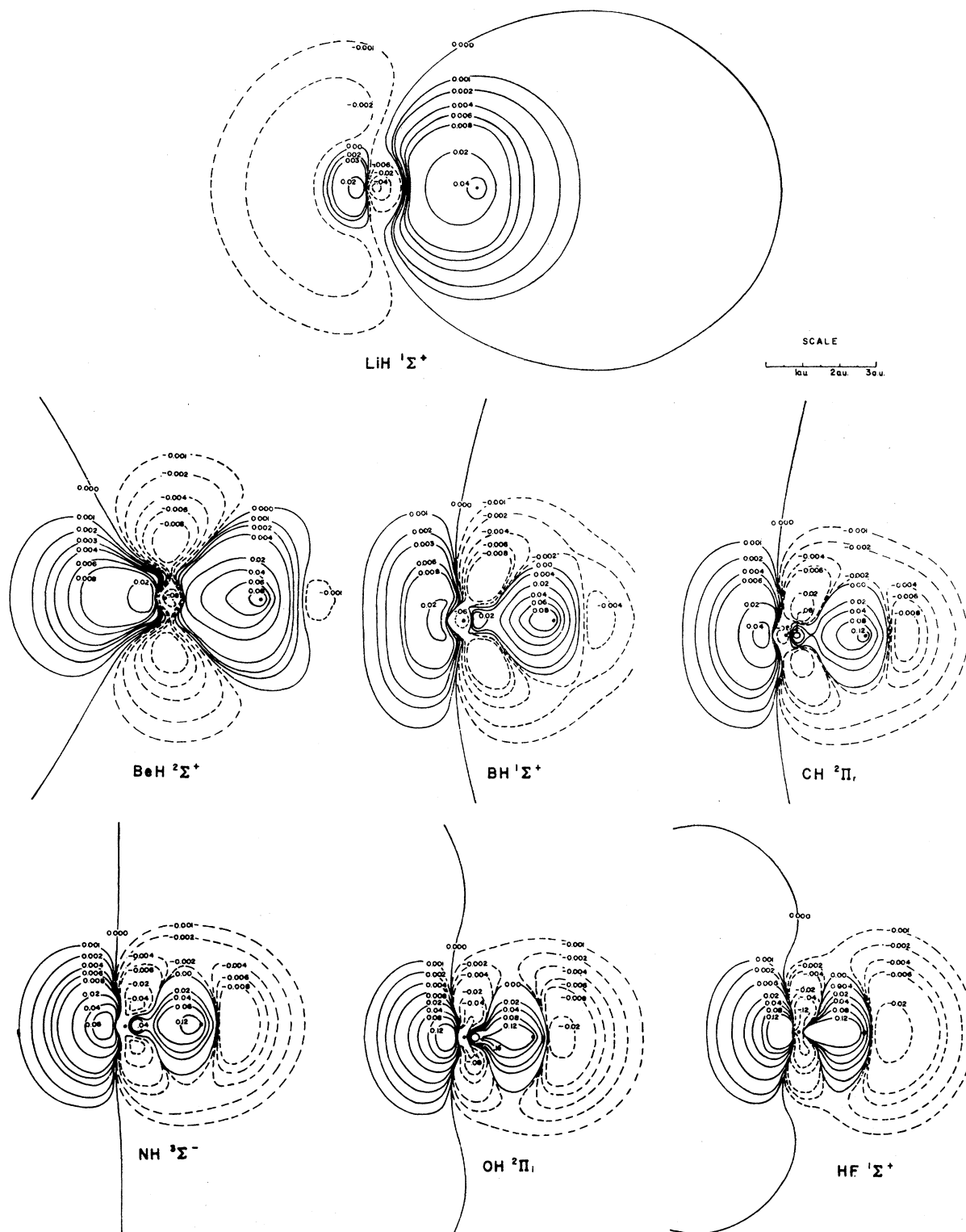
FIG. 7. Contour map of the one-electron difference density (in a.u.) for the HF molecule. [Reproduced from R. F. W. Bader, I. Keaveny, and P. E. Cade, J. Chem. Phys. **47**, 3387 (1967)].

FIG. 8. Contour maps of the difference densities for the He$_2$ molecule at different internuclear distances (a.u.) [Reproduced by permission of the National Research Council of Canada, from R. F. W. Bader, and A. K. Chandra, Can. J. Chem. **46**, 960 (1968)].

overestimates it in the binding region by only about one percent. Consequently, no serious error is likely to be caused by employing the Hartree–Fock densities to obtain the difference density and corresponding forces. Further, at least for closed-shell molecules, electron correlation introduces only a second-order correction into the Hartree–Fock density (Kern and Karplus, 1964).

In a series of papers dealing with HF, H$_2$O, and NH$_3$, Bader and Jones (1961, 1963a, b, c) demonstrated that, starting from a minimum basis set of Slater-type orbitals, it is possible to obtain fairly satisfactory one-electron distributions by requiring that the resultant electron–nuclear attractive forces on the nuclei exactly balance those of nuclear repulsions (the criterion of electrostatic equilibrium). Such density distributions
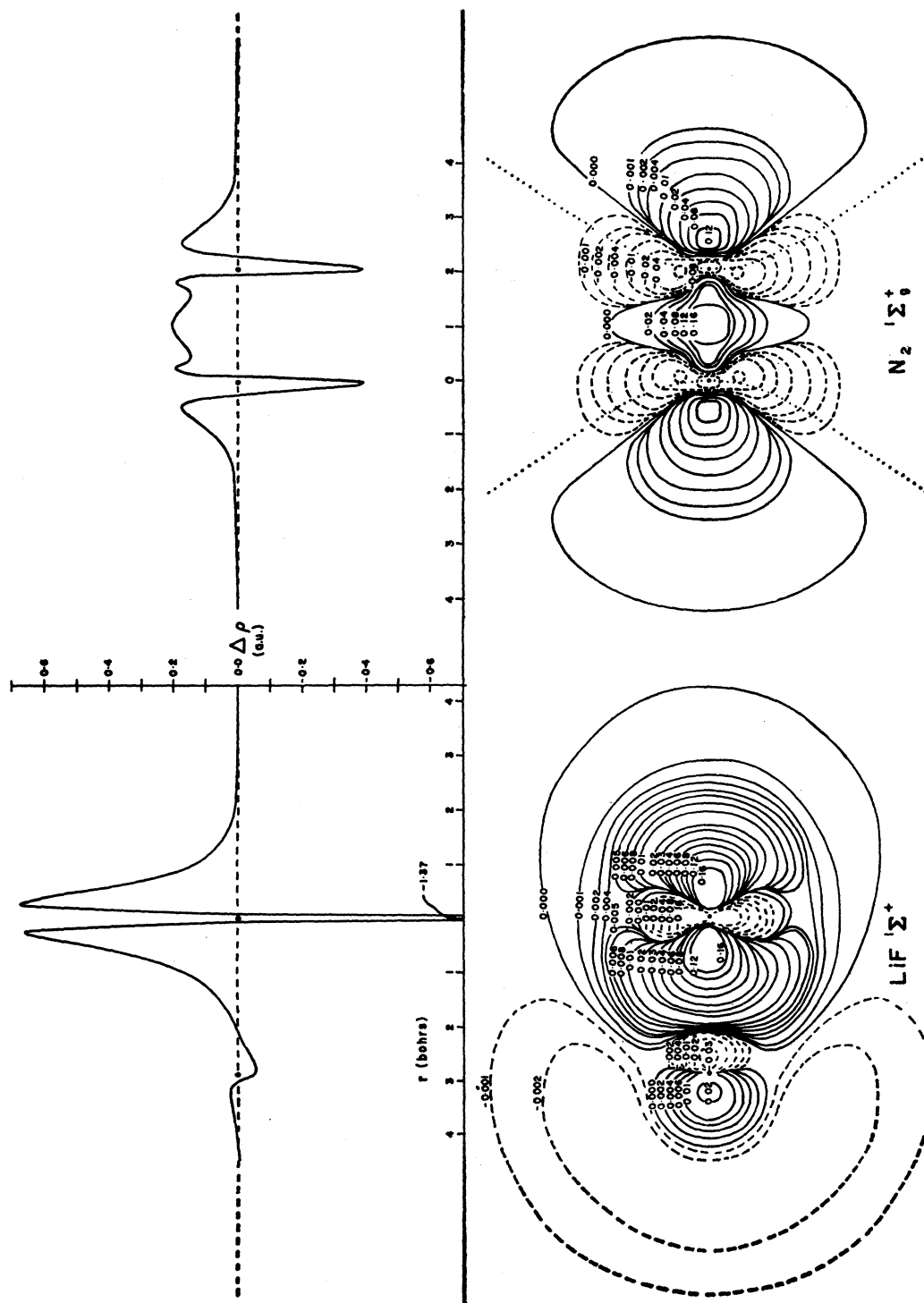
FIG. 9. Density difference contours (in a.u.) for the ionic molecule LiF. The total amount of electronic charge within the zero contour surrounding the F nucleus is 9.81. [Reproduced from R. F. W. Bader, W. H. Henneker, and P. E. Cade, J. Chem. Phys. **46**, 3360 (1967)].

can yield expectation values of certain one-electron operators such as diamagnetic susceptibility, nuclear shielding constant, nuclear quadrupole coupling constant, etc. that are in as good or better agreement with observed values than the corresponding values provided by SCF wave functions (Bader and Jones, 1963a). The criterion of electrostatic equilibrium as well as the orthogonality requirement of the MO's yields a number of constraining relations (Bader and Jones, 1963b) which determine the values of the required LCAO-coefficients. Another useful constraint for this purpose is a quantity, e.g., the observed dipole moment, which characterizes the over-all electronic distribution in a molecule. The resultant one-electron densities can then be employed, in principle, for interpretations of chemical binding as discussed above. In the future, it might also be possible to compare such calculated one-electron densities with the corresponding experimental values obtained through such studies as single-crystal x-ray diffraction measurements.

The use of nuclear forces as constraints, in order to obtain the charge density, has also been advocated by Kern and Karplus (1964), because the criterion of electrostatic equilibrium is a rather stringent condition for a molecular wave function to satisfy. These authors, however, suggest the use of Hartree–Fock, rather than Slater-type, AO's as basis functions in order to obtain more realistic charge densities. Salem and Alexander (1963) point out the highly significant role played by the atomic forces[10] (single-center) in deciding the electronic force on a nucleus. The atomic forces, especially those involving inner shells, are extremely sensitive to polarization and small density changes near the nucleus involved. Consequently, using a basis set of STO's (which do not describe adequately the electron density near the nuclei) instead of the more accurate Hartree–Fock AO's to describe the molecular wave function, is likely to result in quite unrealistic electronic forces, and *vice versa* (see Coulson and Deb, 1971). Bader (1964a) has, from the contours of the difference density for H_2O, shown that using Hartree–Fock AO's instead of STO's results only in minor variations in the difference density. Nevertheless, since such variations might easily occur in the vicinity of the nuclei, it would be better to employ Hartree–Fock AO's in the basis in future works of this kind.

D. Interpretations of Molecular Shapes: The Walsh and Jahn–Teller Effects

The gain in physical insight that results from applying the force approach to chemical problems

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[10] The atomic force on a nucleus results from a polarization of its orbitals due to molecule formation. The atomic force integral due to $1s$ polarization is usually about 2.5 times that due to $2s$ polarization.

becomes more apparent when we turn our attention to the geometry of molecules. A correct understanding of the phenomenon of molecular shapes, that is, how a number of atoms, in the course of molecule formation, arranges itself into a specific geometric pattern and not into any other, is essential if we wish to explain and correlate the various physical, chemical, and biological properties of substances. The model of molecular shapes which has been most stimulating and which has received the greatest attention from theoretical chemists is that due to Walsh (1953). Walsh expressed in an angular correlation diagram (called *the Walsh diagram*) the effect of increasing valence angle on the one-electron "binding energies" of the various MO's. Using such diagrams he demonstrated how the gross equilibrium shapes of whole classes of molecules can be predicted by simple numerical rules, depending on the number of valence electrons, for their ground and sometimes for their first excited states as well. In the last eleven years, considerable effort has been made to find a quantum-mechanical basis for Walsh's largely empirical approach so that one might understand the nature of the ordinate in a Walsh diagram [see Coulson and Deb (1971) for a critical discussion of such works; see also Takahata and Parr (1969)]. The most successful of these attempts, which retains the simple qualitative elegance of Walsh's original approach, resulted from an application of the H–F theorem (Coulson and Deb, 1971):

Consider an AH_2 molecule of HAH angle α and A–H length λ. If we imagine that the bending of the molecule is achieved by symmetric transverse motions of the hydrogen atoms, in the molecular plane, keeping λ and the atom A fixed, then the total molecular energy (E) is given as a function of α by the relation (Coulson and Deb, 1971)

$$E(\alpha) = (2\lambda)^{-1}(\csc \tfrac{1}{2}\alpha - 1) + \sum_i \eta_i w^i(\alpha),$$

$$E(180°) = 0, \quad (28)$$

where the first term arises from the proton–proton repulsive force, and the second from the electron–proton forces. The index i refers to an MO, and $w^i(\alpha)$ is given by

$$w^i(\alpha) = \lambda \int f_\perp^i \, d\alpha, \quad (29)$$

where the transverse component of the electron–nuclear force $f_\perp^i$, on a proton due to the one-electron density in an occupied MO may readily be obtained [see Eq. (2)]. The quantity $w^i(\alpha)$ represents *the work done in bending a molecule against the electron–nuclear attractive forces generated by the single-particle density in an occupied* MO and has been employed to construct a Walsh-type angular correlation diagram (Fig. 10). Similar treatments hold for NH_3 (Fig. 11), and H_2O_2
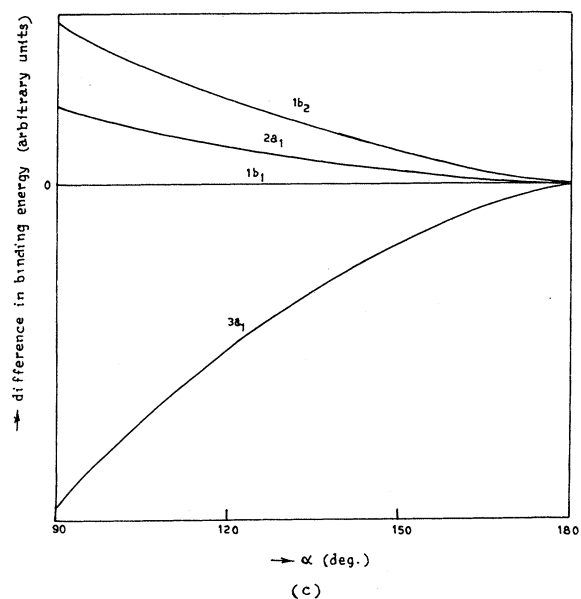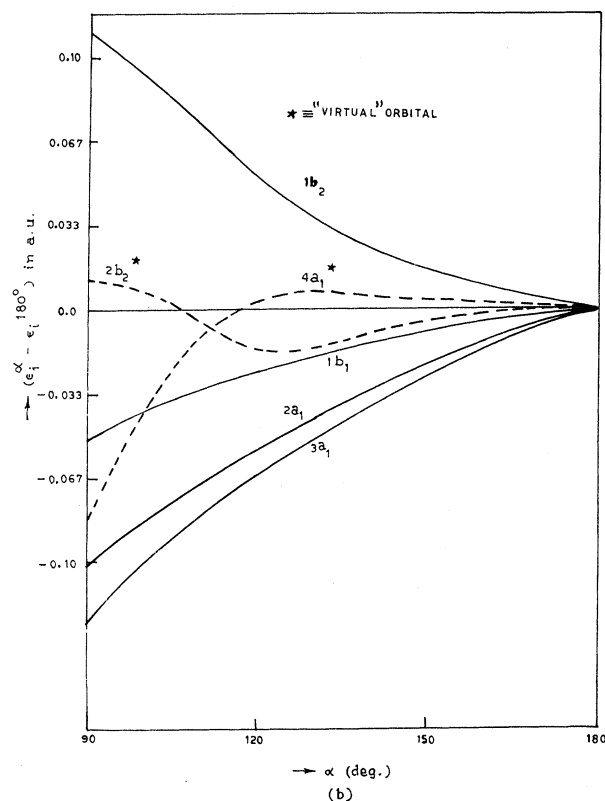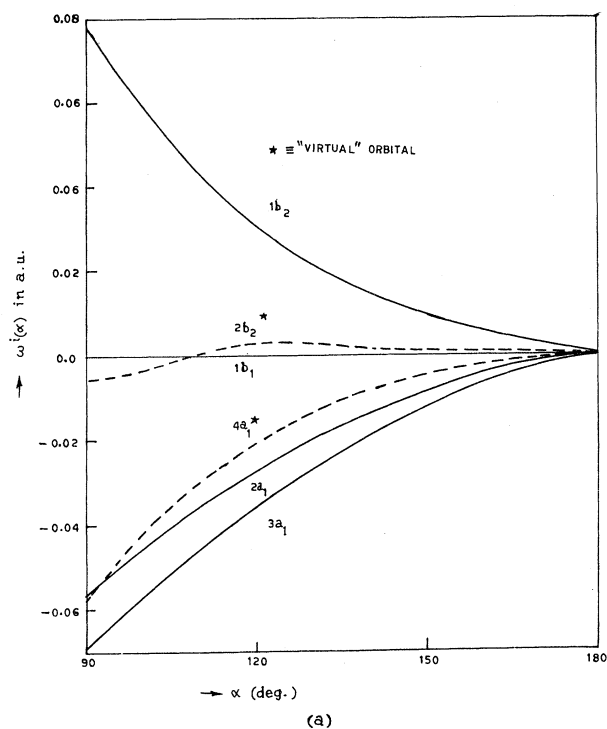
(a)

(b)

(c)

FIG. 10. Comparison of the Coulson–Deb diagram (a) for H_2O, with the corresponding "reduced" Walsh–Allen (b), and Walsh (c) diagrams. Data are taken from Coulson and Deb (1971). Here ϵ_i^{α} refers to the ith MO energy at the valence angle α.

(Fig. 12) molecules, taking the dihedral angle for the last molecule as its angular variable. It is clear from Figs. 10 and 11 that the resulting diagrams for H_2O and NH_3 agree, in general patterns of MO behavior, with the corresponding Walsh diagrams except that the latter predict an opposite trend of behavior for the lowest bonding valence MO. The reason for this discrepancy has been attributed to the unrealistic nature of Walsh's postulates. This work also explains why, *for many molecules, a plot of Hartree–Fock eigenvalues against a valence angle can be used for geometrical interpretations.* The above physical interpretation of the Walsh ordinate does indeed provide a basis for a new model for molecular geometry (Deb, 1972, to be
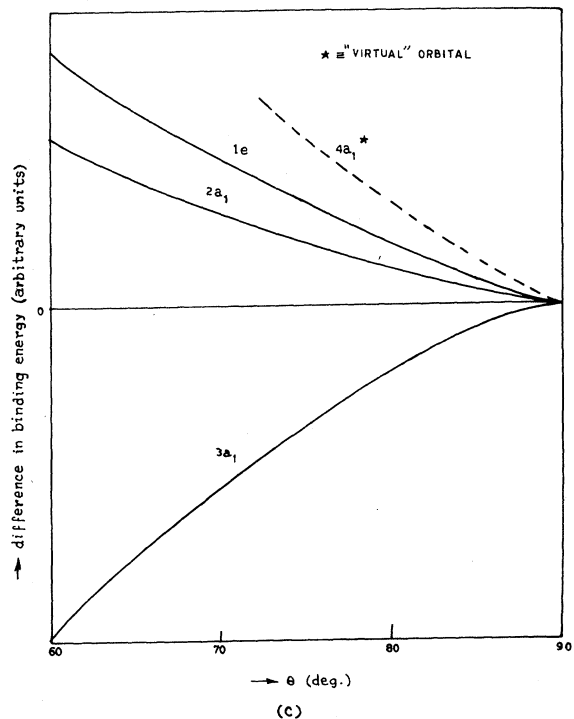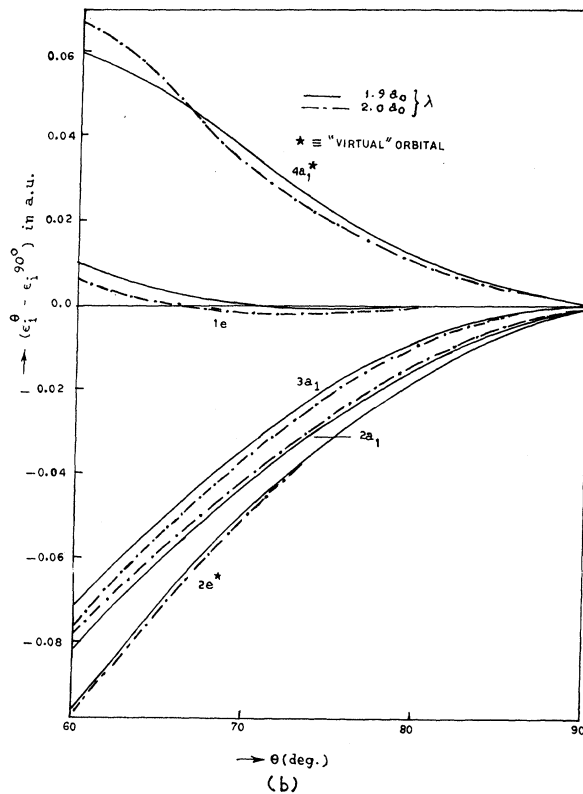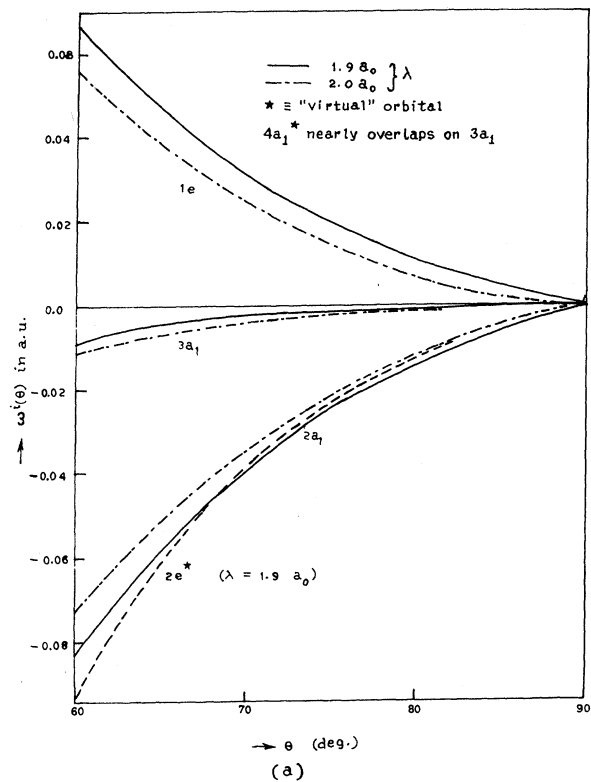
FIG. 11. Comparison of the Coulson–Deb diagram (a) for NH_3, with the corresponding "reduced" Walsh–Allen (b), and Walsh (c) diagrams. Data are taken from Coulson and Deb (1971). Here θ denotes the pyramidal angle.
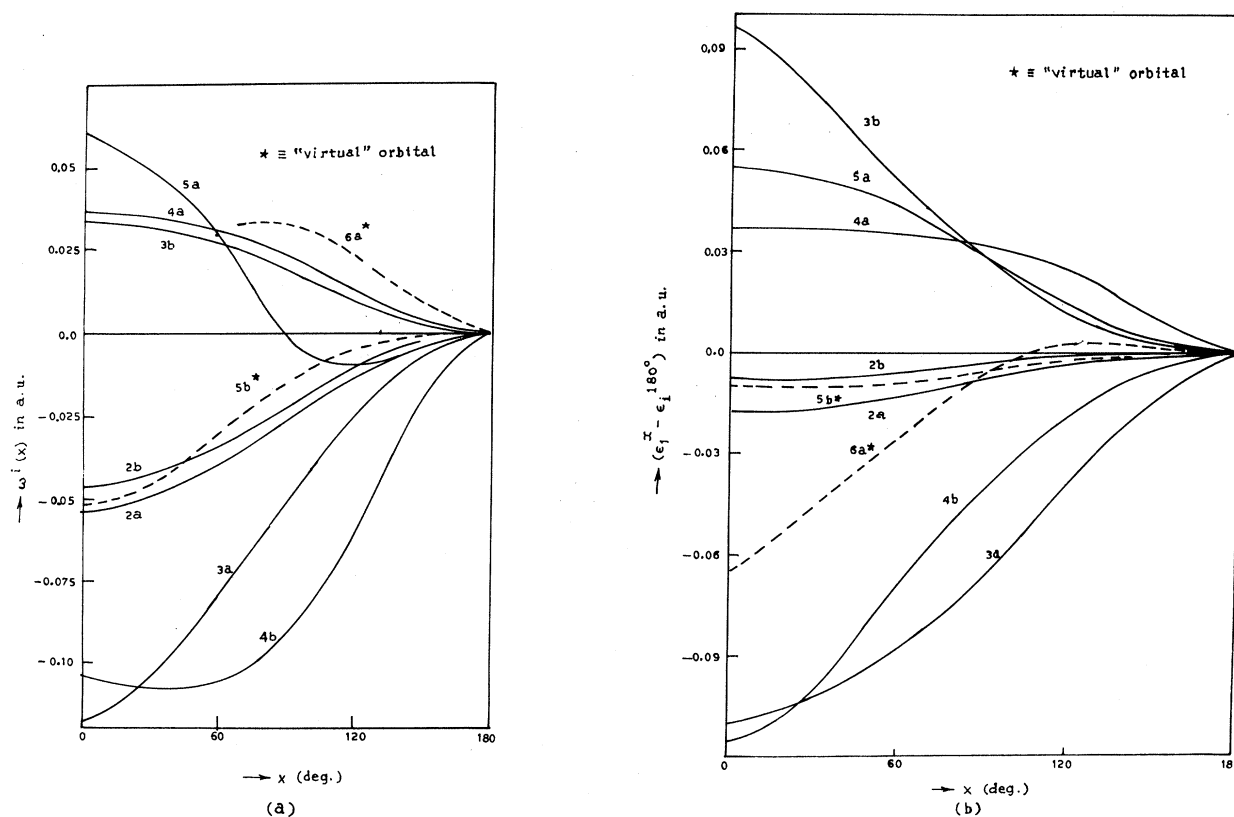
Fig. 12. Comparison of the Coulson–Deb diagram (a) for H_2O_2 with the corresponding "reduced" Walsh–Allen diagram (b). Data are taken from Coulson and Deb (1971). Here x refers to the dihedral angle.

published)[11]. The spatial disposition of the number of atoms in a molecule at the equilibrium configuration will be such as to result in a vanishing net force on the nuclei. Coulson and Luz (1968) have also employed the H–F theorem in discussing bond length changes in molecules on excitation or ionization.

A similar achievement results when one applies the H–F theorem to the problem of the static Jahn–Teller (JT) effect. This well-known theorem (Jahn and Teller, 1937; Jahn, 1938) may be stated as follows:

a polyatomic molecular configuration in which the electronic state is degenerate (either orbit or spin) cannot be stable except when (a) the configuration involved is linear, and (b) the system contains an odd number of electrons so that the degeneracy is of the twofold Kramers' type which cannot be removed by any changes in the electrostatic field but can, however, be split by a magnetic field. The polyatomic molecule will tend to distort to a lower symmetry so as to remove as much degeneracy as possible.[12] Thus, the actual equilibrium geometry (ground or excited) of such molecules may be viewed as being determined by a combined play of the Walsh and Jahn-Teller effects. For practical purposes, however, molecular distortions due to spin degeneracy may be neglected [see Salem (1966) and Ballhausen (1962) for a discussion of the JT effect in organic and inorganic molecules]. The JT theorem, therefore, provides a powerful tool for the discussion of molecular shapes provided that the occupancy of certain molecular electronic states can be specified unambiguously. However,

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[11] The main objective of this model is to provide a pictorial description of, and a physical insight into, how gross equilibrium molecular shapes come about in three-dimensional space. It postulates that molecular shapes are determined primarily by the electrostatic "pull" on the terminal nuclei by the electron-nuclear attractive forces arising from the single-particle density in the highest occupied molecular orbital (HOMO). This permits Walsh-type predictions about gross equilibrium shapes for 11 molecular classes: AH_2, AH_3, AH_4, AB_2, HAB, ABC, HAAH, BAAB, AB_3, H_2AB, and B_2AC (Deb, 1972; Deb, et al., 1972). The model can explain bond angle and bond length variations from molecule to molecule within a class, and is flexible enough to incorporate the phenomenon of internal motions as well as the distortions in molecular geometry due to the static Jahn-Teller effect (see later). It seems quite likely that the HOMO might emerge as a simple unifying theme in chemistry, linking molecular structure with molecular reactivity.

[12] Öpik and Pryce (1957) suggest that such configurational instability may also occur with near-degeneracy (see Pearson, 1969–1970, for an application of this concept to the problem of molecular shapes.)
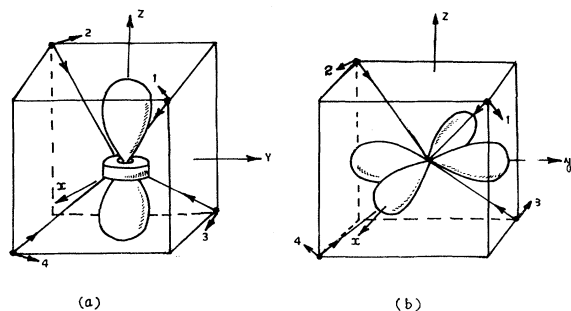
FIG. 13. The static Jahn–Teller effect in VCl_4, using (a) metal d_{z^2} AO and (b) metal $d_{x^2-y^2}$ AO. The arrows on ligand atoms indicate the directions of distortion. Arrows 1, 2 and 3, 4 lie in the planes defined by the metal z axis, and the relevant V–Cl bonds.

this theorem appears to have been used somewhat indiscriminately in the past [see Smith (1970) for a discussion of this point], applying it even to cases where no orbital degeneracy is expected [an example, ClF_3, is given by Ali (1960)].

Clinton and Rice (1959) have provided an alternative approach to the static JT effect in terms of forces. Their technique is very useful for molecules in which degeneracies may arise from excitation or ionization. The conceptual simplicity of this formulation may be demonstrated[13] with an illustrative example such as VCl_4 (Coulson and Deb, 1969). The case history of this molecule typifies the frustrating situation one usually encounters while studying the JT effect in molecules. VCl_4 differs from the hypothetical VCl_4^+, a closed-shell tetrahedral molecule, only in the presence of one electron which may be considered as occupying a nonbonding MO with e symmetry (see Coulson and Deb, 1969). The E representation is spanned by the orbitals d_{z^2} and $d_{x^2-y^2}$ of the vanadium atom (see Fig. 13). Until 1968, neither theoretical nor experimental studies could definitely establish whether the introduction of an e electron in the VCl_4^+ tetrahedral framework would result in a flattened or an elongated tetrahedron (see e.g., Ballhausen and de Heer, 1965). If we assume that the single-particle density in VCl_4 differs from that in VCl_4^+ only in the presence of the e electron (the invariant MO assumption), then[14] the resultant force on a chlorine nucleus in tetrahedral VCl_4 is given by

$$f_{Cl} = Z_{Cl} \int (\phi^* \phi \mathbf{r}_{Cl}/r_{Cl}^3) \, d\tau, \qquad (30)$$

where Z_{Cl} is the "effective" nuclear charge (see Coulson and Deb, 1969) of chlorine, $\mathbf{r}_{Cl}$ is the vector position

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[13] For more applications of the Clinton–Rice formulation see Coulson and Strauss (1962).

[14] It is, however, known that the invariant MO assumption, which is also incorporated in Koopmans' theorem, is not justified. Considerable reorganization of the remaining electrons occurs on ionization or excitation. Coulson and Deb (1969) have, nevertheless, argued in favor of Eq. (30).

from it, and ϕ is the odd-electron orbital, either d_{z^2} or $d_{x^2-y^2}$ metal AO; f_{Cl} is a linear combination of force constants, each multiplied by an appropriate linear combination of chlorine displacements. Equation (30) tells us that in passing from VCl_4^+ to VCl_4 the force on a chlorine nucleus is one of electron–nuclear attraction due to the odd electron. In view of this, an examination of Figs. 13(a) and (b) allows us to reach the following conclusions, without much difficulty: (a) The odd e electron will cause a totally symmetric decrease in the V–Cl bond lengths (relative to VCl_4^+); this, by itself, will not reduce the molecular symmetry; (b) The JT distortion, whether a flattening or an elongation of the tetrahedron, will occur only in the plane defined by the metal z-axis and the relevant V–Cl bond; this follows also from symmetry properties of the integral in Eq. (30); (c) If the odd electron is in the d_{z^2} orbital [Fig. 13(a)], then the circumscribing cube would be elongated in the z-direction (obviously, there will be three such equivalent distorted forms) whereas if it is in the $d_{x^2-y^2}$ orbital [Fig. 13(b)] the cube will be flattened; and (d) Since the two orbitals, d_{z^2} and $d_{x^2-y^2}$, lead to opposite types of distortion, the odd electron is more likely to be in either of them than in a linear combination of the two; clearly, the latter situation would result in less stabilization energy due to a JT distortion. Numerical calculations (Coulson and Deb, 1969), however, do not indicate any preference of the odd electron for one orbital or the other. This means that, according to the simple approach outlined here, both the flattened and elongated tetrahedra are equally likely for VCl_4. This conclusion agrees very well with recent esr experiments of Johannesen, et al. (1968) who interpret their results in terms of a VCl_4 ground state consisting of 58 percent flattened and 42 percent elongated forms. A similar line of reasoning may readily be applied to the case of excited or ionized benzene where, using naive Hückel MO's, one could predict the elongation or flattening of the ground hexagonal framework, depending on the occupancy of one or the other of the doubly degenerate MO's [for experimental studies on the JT effect in benzene see Asbrink, et al. (1970)].

Clinton (1960) has also tried to give a force formulation to the dynamic JT effect. However, because of the presence of vibronic coupling, the treatment becomes considerably difficult. Clinton, like Kerner (see Eq. 19), assumes that while the electrons move quantum mechanically, the nuclei move classically, and that the effect of vibronic coupling is to give rise to time-dependent perturbation terms in the electronic Hamiltonian, corresponding to a time-dependent wave function $\psi(\mathbf{r}, t)$. Considering the case of a planar D_{3h} molecule, where a doubly degenerate electronic state interacts with a doubly degenerate vibrational mode, Clinton showed that, under certain heuristic assumptions, $\psi(\mathbf{r}, t)$ may be regarded as a rotating vector in the

plane of the molecule. No further application or extension of Clinton's work seems to have been attempted in the last ten years.

E. Calculation of Energy Differences: Mechanisms of Internal Motions

A comparison of molecular energies calculated *via* the appropriate forces with those obtained by variational methods shows (Hurley, 1962) that unless the approximate wave functions satisfy the validity conditions mentioned previously, the forces will generally result in inaccurate energies. Bader (1960) had earlier shown that for certain simple systems the LCAO–MO forces can yield fairly reasonable estimates of molecular energies provided the orbital exponents are treated as functions of the internuclear separation, according to an empirical relation which duplicates very closely the optimized values for these parameters. However, as Salem and Wilson (1962) have remarked, one must exercise caution in choosing a wave function for estimating small interactions by this method since the calculated energies, because they are obtained from the forces, are generally correct to only the same order as the wave functions employed. On the other hand, if the error for variational wave functions is of the order Δ, then that for the variational energies has order Δ^2 (Brown, 1966), whereas in perturbation calculations knowledge of an nth-order wave function implies $(2n+1)$th order accuracy in the energy.[15] Therefore, except for their simplicity, the force calculations can hardly be recommended for obtaining numerical estimates of energies and energy differences. However, we shall describe below some of the efforts made in calculating certain energy differences.

Schwartz (1966) has shown that the correlation energy (E_{corr}) for D_{3h} H_3^+ at $R=1.65$ a.u. may be predicted to be in the range 0.042–0.046 a.u. by using H–F theorem and E_{corr} data for two two-electron systems, HeH$^+$ and H$_2$. This argument also yields a simple explanation of why E_{corr} in many two-electron systems happens to be in this range. Tuan (1969) has also found that "correlation energies should be nearly constant with respect to the change of any one-electron parameter, which is independent of symmetry and exclusion effects, of the zeroth order Hamiltonian."

Goodisman (1966) proposes a method for obtaining the barrier to internal rotation in a molecule by calculating the torque tending to produce internal rotation at one end of the molecule due to the other end. This approach is said to have certain advantages over the conventional method of obtaining the barrier as the energy difference of the two conformations involved,

provided one knows the required one-electron density to a high degree of accuracy. These advantages are: (a) Use of a one-electron density for only one nuclear configuration, and (b) Electron correlation is likely to play a minor role in hindered rotation since the changes in the single-electron density due to changes in nuclear configuration should provide an effect large compared to that produced by changes in electron correlation. However, unless the wave function employed takes adequate account of electron polarization around the nucleus on which one calculates the force, the resultant single-particle density is useless in calculating barrier heights due to inversion and rotation, and hence is unable to provide a detailed mechanism for such internal motions (Coulson and Deb, 1971). Ruedenberg (1964) has also employed the H–F theorem to explain why, for many ethane-like molecules, the barrier (ΔE) to internal rotation is given by

$$\Delta E \simeq 0.6\Delta V_{nn}, \tag{31}$$

where ΔV_{nn} is merely the difference in nuclear repulsion energy between the staggered and eclipsed forms.

The practical applications of the "integral" H–F theorem for calculating energy differences appear to have been made mostly in the origin of barrier to internal rotation in molecules and the mechanism of dissociation of simple diatomic molecules. Wyatt and Parr (1965, 1966) obtain the barrier in ethane as a resultant of two terms favoring opposite conformations and provide an orbital analysis of the electronic component of the barrier. Their examination of electron density maps reveals that this component arises from the noncylindrical symmetry of the electron density, in a staggered or eclipsed conformation, about the carbon–carbon axis. The barrier may be interpreted as arising mainly from regions of the "transition density" around the protons; regions near the C–C axis do not contribute significantly. For H$_2$O$_2$, the calculated barrier is inferior (Rothstein and Blinder, 1967) to that obtained by subtracting the SCF energies of the two forms involved. Musher (1965) concluded that the "integral" H–F theorem cannot be employed for calculating rotational barriers ($\sim$0.1 eV) or chemical bond strengths ($\sim$4 eV) from zeroth-order Hartree–Fock wave functions. Marron and Parr (1970) also do not advocate the use of this integral theorem as a primary computational method for calculating energy differences. Their conclusions are based on results from calculations of dissociation energies of H$_2^+$ and other simple systems (Marron, 1970). They showed that such calculated dissociation energies depend strongly on the mode of separating the atoms. Marron and Weare (1968) derive a variational principle which adds two correction terms to the integral H–F energy difference, while Lowe and Mazziotti (1968) provide an error analysis for this difference.

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[15] Yaris (1963), however, shows that in some less general cases where the parameter λ does not occur in an unperturbed Hamiltonian but appears only in the perturbation term, the nth order wave function determines the force to order $n+1$ and, in some cases, even to order $2n+1$.

Nevertheless, the qualitative usefulness of the "integral" H–F theorem should not be underestimated, although in numerical applications it generally does not offer the accuracy obtainable in variational calculations. For example, Lowe and Parr (1966; see also Lowe, 1966) have designed a semiempirical model which provides useful qualitative insight into the mechanism of the barrier to internal rotation in molecules. A look at Eq. (25) indicates that such a model should start by partitioning the change in attraction between the nuclei and the transition density into appropriate physically meaningful components. By considering that only one end of the molecule rotates while the other end remains fixed in space, and by assuming that the localized orbitals at the moving end follow perfectly the respective nuclear motions, one can neglect contributions from all fixed nuclei as well as from attractions between the moving nuclei and the transition density at the moving end. Then the only remaining term is the attraction between the moving nuclei and the transition density (ρ_{xx}) at the fixed end (x). The barrier to internal rotation is thus given by

$$\Delta E \simeq \Delta W_{nn} + \int^{\text{fixed end}} \rho_{xx}(1)H'(1)\, d\tau_1. \qquad (32)$$

For some molecules the two terms on the rhs of Eq. (32) can be combined into a single term to yield

$$\Delta E \simeq f \Delta W_{nn} \qquad (33)$$

(c.f. Eq. 31), where the proportionality constant f can be identified with an "effective" charge on each non-axial nucleus at the fixed end (see also Lowe and Parr, 1965).

F. Calculation of Force Constants

The question which arises at this point is this: Although the H–F theorem does not usually result in good numerical estimates of energy differences, can it be of any use in calculating force constants? For example, Coulson and Deb (1971) demonstrate that even Ellison and Shull's (1955) relatively crude wave functions for H_2O provide a good estimate of the bending force constant. Hirschfelder and Eliason (1967) have also been able to calculate accurately the force constant for the long-range interaction of two hydrogen atoms, by employing only a second-order correction to an approximate wave function. There have been several other efforts (Brown, 1958; Phillipson, 1963, 1966; Salem, 1963; Benston and Kirtman, 1966; Schwendeman, 1966; Bader and Bandrauk, 1968a, b; Gerratt and Mills, 1968) to calculate second derivatives of the energy, starting with the H–F theorem. Benston and Kirtman (1966) demonstrate, in the case of H_2, that while the calculated forces are seriously in error the force curves do have the desired shape near the equilibrium internuclear distance. Therefore, in this region at least, the calculated force derivatives will nearly equal

the corresponding exact derivatives. It may be remembered, however, that if the H–F theorem does not hold for approximate wave functions of a diatomic molecule AB, its force constants will depend on whether the forces on nucleus A or on nucleus B were used to calculate these constants (Pulay, 1969–1971). However, from a computational point of view, this may not be as serious a drawback as might appear at first. In view of what has been said before, it will be necessary to determine whether Benston and Kirtman's conclusion remains valid for different nuclei in representative A_2, AB, and small polyatomic molecules.[16]

The magnitude of the force constant and its variation in some isoelectronic homo- and heteronuclear diatomic molecules can be interpreted in terms of a relaxation of charge density which accompanies nuclear displacements (Bader and Bandrauk, 1968b). For covalently bound molecules (see Sec. B), the charge density relaxes to facilitate the motion of the displaced nuclei. On the other hand, in a molecule with ionic binding, the relaxation of the charge distribution localized on the cation opposes the nuclear displacement while that of the charge density on the anion favors its nuclear displacement.

G. An Examination of the Pauli Repulsions Model of Molecular Shapes

Based on a discussion of electrostatic forces, Bader and Preston (1966) have provided a critical examination of the Sidgwick–Powell–Nyholm–Gillespie model of molecular shapes (Gillespie, 1967) which has been very successful from a qualitative point of view. This model considers the molecular shape to be determined primarily by Pauli repulsions between valence electron pairs around the central (heavy) atom, in the absence of bulky ligand groups. Bader and Preston point out that for a system of N electrons requiring a set of $N/2$ or $(N+1)/2$ orbitals, the Pauli principle is really an orthogonality restraint in an $N/2$ or $(N+1)/2$ dimensional space; to state that the Pauli Principle leads to repulsions between filled orbitals in three-dimensional space is not the same as requiring these orbitals to be orthogonal in the multi-dimensional space defined by the orbitals. Further, in the real space only the total one-electron density has physical significance, not the individual orbitals. By identifying Pauli repulsions between filled orbitals with shifts in the one-electron density from regions of low potential energy, these authors demonstrate that interpretations of such repulsions in terms of colliding orbitals in real space can be misleading. Also, by considering the molecules H_2O and NH_3, they show that: (a) the shifts in one-electron density arising from the Pauli principle do not

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[16] In case of Li_2, however, the theoretical and experimental force curves seem to have quite different slopes near the equilibrium bond length (Chandra and Sundar, 1971).

lead to a decrease in the "tetrahedral" bond angle in H_2O or NH_3; (b) the electron distribution in these molecules cannot be related to a tetrahedral set of orbitals; and (c) *the interactions between bonding orbitals are larger than those involving lone-pair orbitals.*

H. Intermolecular Forces

A major difficulty in applying the H–F theorem to the problem of intermolecular forces—although the theorem holds a promise of conceptual simplicity—is associated with the calculation of a reasonably good single-particle density for intermolecular systems. Such a single-particle density should contain the effects of electron correlation as the latter plays a major role in governing the nature of intermolecular forces (Hirschfelder and Meath, 1967). Bader (1964b), however, has shown that the force may still provide an insight, for example, into the nature of the hydrogen bond (Bratož, 1967) as well as into the mechanism of proton transfer reactions. Bader and Chandra (1968) and Hirschfelder and Meath (1967) have discussed the long-range interaction of two hydrogen atoms. They conclude that the origin of London dispersion forces lies in the simultaneous inward polarization of the atomic densities of both due to their interaction (see Fig. 5, $R=8.0$ a.u.). Makin (1968, 1970) has also applied the H–F theorem to: (i) the interaction of two hydrogen molecules, (ii) the three-body repulsive forces between three hydrogen and between three helium atoms, and (iii) the interaction of a helium atom and a hydrogen molecule. In the last instance the hydrogen basis AO's require some p character to be incorporated, so that the force on a helium atom is always repulsive as it approaches a hydrogen molecule along the perpendicular bisector of the H–H length.

I. Miscellaneous Other Applications of the H–F Theorem

From the preceding discussion of the applications of H–F theorem to various chemical problems it is clear that we really do need very good wave functions[17] in

order to obtain satisfactory forces. One could, therefore, turn the problem about and employ the H–F theorem to *test and analyze* calculated molecular wave functions (Bader, 1963; Kern and Karplus, 1964). The conclusions emerge that: (a) one must be careful in the selection of basis functions in large-scale molecular computations, and (b) significantly different charge distributions can result from alternative basis sets of the same size (Kern and Karplus, 1964); such density fluctuations from one basis set to another can be as large as effects of chemical binding. It is also reasonably certain that single-determinantal wave functions for a given basis, obtained by accurately evaluating all the necessary integrals, are unlikely to satisfy the criterion of electrostatic equilibrium unless this condition is employed as a pre-imposed constraint in the mathematical procedure.

A constrained variational formalism has indeed been developed by Loeb and Rasiel (1970). Their results on LiH show that the imposition of the constraint of electrostatic equilibrium, for either the proton or the Li nucleus, results in only a small increase in the over-all energy while the constrained wave functions yield improved expectation values for a number of observables.

Freed (1968) employed the H–F theorem to show that in the Hartree–Fock theory the errors in equilibrium molecular geometry and the barrier to internal rotation are of second order, like those of the one-electron properties. Coulson and Deb (1969, 1971) (a) demonstrated that Slater's rules are not adequate for molecular calculations with $3d$ AO's, and (b) reinforce the view that the closed-shell "virtual" orbitals in the Hartree–Fock procedure must be treated with caution. Bader *et al.* (1967a) suggest that, for first-row homonuclear diatomic molecules, the MO's can be classified as binding, non-binding, or antibinding, according as $f_i \gtrless 1$, respectively, where f_i is defined as the force exerted on a nucleus by the ith occupied MO, multiplied by R^2. Mulliken (1966), however, concluded that there is extremely poor correlation between the computed force exerted by an electron in an MO and its

[17] It would, of course, be very nice if one could compute an accurate single-particle density without the need to go through the wave function itself; i.e., through the Schrödinger equation. Unfortunately, this remains one of the great unsolved problems in quantum mechanics. There seems to be two possible approaches to this problem: (i) Setting up a differential or an integro-differential equation involving the first- or the second-order density matrix. [The diagonal elements of these matrices are the single-particle and two-particle densities, respectively. By integration with respect to the coordinates of one particle, the second-order matrix is reduced to the first-order matrix.] (ii) Finding out *all* the conditions which an accurate single-particle or two-particle density matrix must satisfy and then incorporating these conditions into a trial function. The prospects for either of these two approaches are bleak. No progress has been made towards (i) and, while not enough is known regarding rhe conditions in (ii) for the first-order density matrix in order to develop a variational formalism, the second-order matrix has to satisfy so many conditions that one can never incorporate all of these

into a trial function. However, as mentioned in Sec. 4.C, one can compute *approximate* single-particle densities to suit certain purposes [see Makin (1970) for the example of two interacting helium atoms]. In a recent paper, Bader and Beddall (1972) have proposed an interesting route towards obtaining the single-particle density in a molecular system. Their analysis highlights the possibility of the existence of a field relationship for the single-particle density $\rho(r)$, a relationship which might be expressed as some functional of the total virial field. This proposition is based primarily upon two observations: (a) It is possible to partition a molecular system into fragments in such a way that the same virial relationship between the average kinetic and potential energies observed for a total molecular system also holds for each individual fragment. (b) In a series of molecules having certain common fragments, the fragments which possess nearly identical $\rho(r)$ distributions also exhibit nearly identical distributions of the total virial $\nu(r)$; this suggests that $\rho(r)$ may be related to the total virial of all the forces exerted on each element of the charge density.

bonding power as judged by the so-called thermo-chemical and equilibrium criteria of bonding, neither of which, however, is infallible. In the case of a single electron moving in the joint Coulomb field of two fixed nuclei of charge Z, Cohen and McEachran (1968) show that identification of MO's as bonding or anti-bonding is not unique but depends sensitively on Z; a change in the value of Z can make bonding orbitals antibonding and *vice versa*.

Salem (1963) and Anderson, *et al.* (1969) show how one can relate a vibrational force constant, obtained by differentiating the force with respect to a nuclear coordinate, to the corresponding field gradient tensor for the electronic distribution, taking the particular nucleus as origin. By resolving the molecular one-electron density into two components, one which follows nuclear motion and another which does not, Anderson and Parr (1970) obtain a Poisson-type equation for nuclear motion

$$\nabla_\alpha{}^2 W = 4\pi Z_\alpha \rho_\beta(\alpha), \qquad (34)$$

where W is the total electronic energy, Z_α is the charge of nucleus α, and $\rho_\beta(\alpha)$ is the sum of orbital densities from all other atoms β.

There have also been several applications of the H–F theorem in which the parameter λ represents quantities other than nuclear coordinates, e.g., masses (Pais and Epstein, 1949; McKinley, 1971), nuclear charges (Wilson, 1962),[18] scale factors (Chen, 1963; Pandres, 1963), radial quantum numbers (Epstein and Epstein, 1962), etc.

5. CONCLUDING REMARKS

The theme of this article has been a realization that there are pleasures as well as heartbreaks awaiting us if we wish to employ approximate wave functions for the purposes of the H–F theorem. However, the simple concepts of chemical binding and molecular shapes provided by this little theorem, whose proof is almost trivial, have been very satisfactory and one feels unable to agree with Musher (1966) when he says that the concept of force is not a useful one. To conclude, therefore, we should do well to employ both the energy and the force formulation in our studies of molecular structure and dynamics. The former approach would generally provide more accurate numbers, while the latter should provide a simple unified basis for de-

veloping physical insights into different chemical phenomena. Chemists have a need for simple concepts and models (Coulson, 1970) for molecular shapes and chemical reactivity which can withstand a searching critical examination of their theoretical foundations and are also open to quantitative extension, at least in principle. The H–F theorem holds great promise as a useful tool for such model building, especially for explaining the mechanisms of chemical reactions.

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[18] The case where λ can be identified with a scale factor for nuclear charges has an interesting consequence. In this case, one can examine changes in e.g., total energy and MO energies, the nature of electron reorganisation etc. during molecular "transmutations" of the type $CO \rightarrow N_2$. This involves scaling "up" of the carbon nuclear charge and scaling "down" of the oxygen nuclear charge by unity. Unfortunately, at present one does not have wave functions for intermediate values for the two nuclear charges so that, apart from calculating the energy changes (see Epstein, *et al.*, 1967) involved in such isoelectronic "transmutations", one cannot at present make a detailed study of these processes.

bers can provide us with simple and useful chemical concepts; otherwise, one might as well be interested in a telephone directory.
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