The role of single-particle density in chemistry*†

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The definition, properties, and applications of the single-particle (electron) density $\rho(\mathbf{r})$ are discussed in this review. Since the discovery of Hohenberg–Kohn theorem, which gave a theoretical justification for considering $\rho(\mathbf{r})$, rather than the wave function, for studying both nondegenerate and degenerate ground states of many-electron systems, $\rho(\mathbf{r})$ has been acquiring increasing attention. The quantum subspace concept of Bader *et al.* has further highlighted $\rho(\mathbf{r})$ since a rigorous decomposition of the three-dimensional (3D) space of a molecule into quantum subspaces or virial fragments is possible, the boundaries of such subspaces being defined solely in terms of $\rho(\mathbf{r})$. Further, $\rho(\mathbf{r})$ is a very useful tool for studying various chemical phenomena. The successes and drawbacks of earlier models, such as Thomas–Fermi–Dirac, incorporating $\rho(\mathbf{r})$ are examined. The applications of $\rho(\mathbf{r})$ to a host of properties—such as chemical binding, molecular geometry, chemical reactivity, transferability, and correlation energy—are reviewed. There has been a recent trend in attempting to bypass the Schrödinger equation and directly consider single-particle densities and reduced density matrices, since most information of physical and chemical interest are encoded in these quantities. This approach, although beset with problems such as N-representability, and although unsuccessful at present, is likely to yield fresh concepts as well as shed new light on earlier ideas. Since charge density in 3D space is a fundamental quantum-mechanical observable, directly obtainable from experiment, and since its use in conjunction with density-functional theory and quantum fluid dynamics would provide broadly similar approaches in nuclear physics, atomic-molecular physics, and solid-state physics, it is not unduly optimistic to say that $\rho(\mathbf{r})$ may be the unifying link between the microscopic world and our perception of it.

CONTENTS

I. INTRODUCTION: SINGLE-PARTICLE DENSITY AND CHEMISTRY IN THREE-DIMENSIONAL SPACE

Traditional studies on quantum-chemical systems are based on the time-independent Schrödinger equation

$$H\psi = E\psi \tag{1.1}$$

or some variant of it. The wave function ψ contains *all* stationary-state information about a system so that once ψ is known, any information on the system can be extracted as the expectation value of the corresponding observable A,

$$\langle A\rangle \equiv \langle\psi|A|\psi\rangle/\langle\psi|\psi\rangle\,. \tag{1.2}$$

For details, the operator A may be partitioned into physically meaningful components and the expectation value of each component obtained. For example, H may be partitioned as[1]

H = nuclear kinetic energy + electronic kinetic energy + electron-nuclear attraction + electron-electron repulsion + nuclear-nuclear repulsion + orbit-orbit interaction + electron spin-orbit coupling + electron spin-spin coupling + electron spin-nuclear spin coupling + electron orbit-nuclear spin coupling + nuclear spin-spin coupling + external electromagnetic field-dependent terms. (1.3)

Although the vast edifice of quantum chemistry is largely built in this way, there are serious reasons why chemists should not remain completely satisfied

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[1] For a more complete molecular Hamiltonian, including relativistic corrections, see Moss (1973), especially Chap. 6.

with this kind of approach. The main reasons are (i) Even with present-day techniques one can only hope for approximate solutions to (1.1) except in the special cases of one-electron atoms and one-electron *homonuclear* diatomic molecules; (ii) ψ is a function of space and spin variables in the multidimensional configuration space, being indeterminate to within a phase factor, and no physical significance can be attributed to ψ; as a result, the chemist is forced to abandon any attempt at directly visualizing what atoms and molecules are "doing", since such visualizations can only be done in the three-dimensional (3D) space; (iii) This dependence on ψ, and on the Schrödinger equation, has resulted in a curious dichotomy in quantum chemistry whereby simple *ad hoc* qualitative approaches (much used by chemists) exist side by side with rigorous or *ab initio* approaches bereft of simple concepts and pictures; and there appears hardly any hope of ever bridging the chasm between the two.

Now, most observables of interest to chemists and physicists correspond to one- and two-electron operators, and the expectation values of these operators can be evaluated once the single-particle and two-particle density matrices (Sec.II.A) are known [see, for example, Davidson (1976)]. There is a considerable economy in dealing with these density matrices, rather than the wave function ψ, since the former are functions of many fewer space and spin variables. It is thus possible to construct an alternative formulation of the quantum mechanics of many-electron systems, employing density matrices rather than the wave function; further, it is generally believed that all information of physical and chemical interest is encoded in these density matrices. Unfortunately, although the density-matrix approach began with a lot of promise, a direct determination of density matrices raises the horrendous specter of N-representability (Sec.II.C), and all hopes of solving the N-representability problem for the two-particle density matrix seem to be abandoned at present.

The single-particle (electron) density is the total particle (electron) density in 3D space and may be obtained either directly (in principle) or from the single-particle density matrix or the wave function. Since it obviously contains considerable information, it is an attractive basis for the construction of models to study chemical phenomena for several reasons: (i) Being a function in the 3D space, it can be easily visualized, since we live and perceive in a 3D world. (ii) It can be related to classical concepts. (iii) It is an observable, directly measurable by experimental methods such as diffraction and scattering. It is therefore possible to talk about *chemistry in* 3D *space*, dealing with both ground and excited states of molecules. The present article is mainly devoted to this purpose.

A question, however, arises regarding the *fundamental* significance of the single-particle density *vis-a-vis* the wave function and the density matrices. This reassurance is provided by the Hohenberg-Kohn theorem [Hohenberg and Kohn (1964)]; which states that, *for both nondegenerate and degenerate ground states of many-electron systems, the energy is a unique functional of the single-particle density*. Thus, *all* information about the *ground* states of molecules is contained in the single-particle density.[2] Further, Srebrenik and Bader (1975) have shown that a decomposition of 3D molecular space into *quantum subspaces* is possible, the boundaries of such subspaces being defined solely in terms of the properties of single-particle density (Sec. II.B.3).

These fundamental issues have been further discussed in Secs. II.A–II.G following which the significance of single-particle density regarding chemical binding, molecular geometry, intermolecular forces, chemical reactivity, and other molecular properties has been examined. The connection between $\rho(\mathbf{r})$ and the fluid-dynamical interpretation of quantum mechanics is also delineated.

II. FOUNDATIONS

A. From wave function to reduced density matrices

The wave function $\psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N)$ describes a system of N indistinguishable particles in a pure state. With fermions the wave function changes sign when the particles undergo an odd permutation and remains unchanged by an even permutation.

The N-particle density matrix associated with ψ is given by

$$D^N = \psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) . \tag{2.1}$$

In (2.1), $\mathbf{x}_i \equiv \mathbf{r}_i \cdot \mathbf{s}_i$, viz., the set of space and spin variables. Associated with any fixed N-particle function ψ there is a linear operator P_ψ, called the projector onto ψ, such that

$$P_\psi f = \langle \psi | f \rangle \psi , \tag{2.2}$$

where f is any N-particle function. Therefore

$$P_\psi = |\psi\rangle\langle\psi| . \tag{2.3}$$

If we wish to regard P_ψ as an integral operator [see Coleman (1980)], we see that the kernel is the N-particle density

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\psi^*(\mathbf{x}_1', \mathbf{x}_2', \ldots, \mathbf{x}_N') . \tag{2.4}$$

By integrating with respect to the coordinates of $(N-2)$ particles, we obtain

$$D^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = \int \psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\psi^*(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_3, \ldots, \mathbf{x}_N) d\mathbf{x}_3, \ldots, d\mathbf{x}_N . \tag{2.5}$$

Clearly, $D^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2')$ is the kernel of a two-particle

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[2] Although the Hohenberg-Kohn theorem has not been proved for excited states, implying that for such states the single-particle density may not contain *all* information, it would still be worthwhile to extract the large amount of information which $\rho(\mathbf{r})$ does contain for excited states. For a generalization of density-functional theory for excited states, see Theophilou (1979). It is also possible to argue that since $\rho(\mathbf{r})$ for the ground state fixes the Hamiltonian to within an additive constant, $\rho(\mathbf{r})$ in fact contains sufficient information to specify completely *all* the excited states of a system under a local external potential.

operator D^2 such that

$$D^2 f = D^2 f(\mathbf{x}_1, \mathbf{x}_2) = \int D^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') f(\mathbf{x}_1', \mathbf{x}_2') d\mathbf{x}_1' \, d\mathbf{x}_2' \tag{2.6}$$

is the function obtained by the action of D^2 on f. Similarly,

$$D^1(\mathbf{x}_1, \mathbf{x}_1') = \int \psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \psi^*(\mathbf{x}_1', \mathbf{x}_2, \ldots, \mathbf{x}_N) d\mathbf{x}_2, \ldots, d\mathbf{x}_N$$

$$= \int D^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2) d\mathbf{x}_2 \tag{2.7}$$

is the first-order reduced density matrix.

The normalization condition for ψ gives

$$\int D^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 \, d\mathbf{x}_2 = \int D^1(\mathbf{x}_1; \mathbf{x}_1) d\mathbf{x}_1 = 1 . \tag{2.8}$$

For a one-particle observable represented by an operator symmetric in N particles,

$$A = \sum_{i=1}^{N} A(\mathbf{x}_i) , \tag{2.9}$$

the expectation value is given by

$$\langle \psi | A | \psi \rangle = N \int [A(\mathbf{x}_1) D^1(\mathbf{x}_1; \mathbf{x}_1')]_{\mathbf{x}_1 = \mathbf{x}_1'} d\mathbf{x}_1 . \tag{2.10}$$

Similarly, for a two-particle operator

$$B = \sum_{i<j} B(\mathbf{x}_i, \mathbf{x}_j) , \tag{2.11}$$

$$\langle \psi | B | \psi \rangle = \frac{N(N-1)}{2} \int [B(\mathbf{x}_1, \mathbf{x}_2) D^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2')]_{\mathbf{x}_1 = \mathbf{x}_1', \mathbf{x}_2 = \mathbf{x}_2'} d\mathbf{x}_1 \, d\mathbf{x}_2 . \tag{2.12}$$

Thus the nonrelativistic energy depends on the first- and second-order density matrices

$$E = N \int h D^1 d\mathbf{x}_1 + \frac{N(N-1)}{2} \int g D^2 d\mathbf{x}_1 \, d\mathbf{x}_2 . \tag{2.13}$$

In (2.13), h is the kinetic energy of one electron and its attraction to the nuclei, whereas g is the electron-electron repulsion operator. Equation (2.13) highlights the importance of the first- and second-order density matrices.

Von Neumann [(1955); see also Roby (1973)] showed that in order to discuss mixtures of states on ensembles, it is convenient to specify the ensemble by means of a positive operator D^N, the Von Neumann density operator, such that the expectation value of an observable, e.g., energy, is given by

$$\mathrm{Tr}(HD^N) = \int HD^N d\mathbf{x}_1, \ldots, d\mathbf{x}_N . \tag{2.14}$$

In case the system is in a pure state,

$$D^N = P_\psi , \tag{2.15}$$

and we get the familiar expression

$$\mathrm{Tr}(HD^N) = \langle \psi | H | \psi \rangle . \tag{2.16}$$

However, if the system is an ensemble of pure states ψ_i, weighted by W_i, where

$$W_i > 0 , \tag{2.17}$$

$$\sum_i W_i = 1 , \tag{2.18}$$

then

$$D^N = \sum_i W_i P_{\psi_i} = \sum_i |\psi_i\rangle W_i \langle \psi_i | . \tag{2.19}$$

The single-particle density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = N \int \psi^* \psi \, d\mathbf{s}_1 \, d\mathbf{x}_2 \ldots d\mathbf{x}_N . \tag{2.20}$$

From (2.20) we clearly see that

$$\int \rho(\mathbf{r}) d\mathbf{r} = N . \tag{2.21}$$

Thus, given the wave function, it is a straightforward task to obtain the density matrices as well as $\rho(\mathbf{r})$. One may also conceive of a quantum mechanics formulated in terms of density matrices as primary quantities, rather than the wave function. However, the direct evaluation of density matrices is not at all simple as one faces the formidable N-representability problem (see Secs. II.D and II.E).

However, most chemical and physical observations of interest deal with structure and properties of molecules in the real 3D space. Hence, as mentioned in Sec. I, there is a strong motivation to develop models and concepts in terms of observables in 3D space, e.g., $\rho(\mathbf{r})$. The theoretical justifications for dealing with $\rho(\mathbf{r})$ are discussed below.

B. $\rho(\mathbf{r})$ as a fundamental quantity

1. The Hohenberg-Kohn theorem

In proving their theorem (see Sec. I), Hohenberg and Kohn (1964) considered a collection of an arbitrary number of electrons enclosed in a large box, moving under the influence of an external potential $v(\mathbf{r})$ and the mutual Coulomb repulsion. We outline their proof below.

In the language of second quantization, the Hamiltonian for the system is

$$H = T + V + U , \tag{2.22}$$

where

$$T \equiv \tfrac{1}{2} \int \nabla \psi^*(\mathbf{r}) \nabla \psi(\mathbf{r}) d\mathbf{r} , \tag{2.23}$$

$$V \equiv \int v(\mathbf{r}) \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} , \tag{2.24}$$

$$U \equiv \tfrac{1}{2} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi^*(\mathbf{r}) \psi^*(\mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}) d\mathbf{r} \, d\mathbf{r}' . \tag{2.25}$$

In the above expressions for kinetic and potential energy operators, ψ, ψ^* are the local field operators [see Fetter and Walecka (1971); Longuet-Higgins (1966)] expressed in terms of particle creation and annihilation operators. The electron density associated with the nondegenerate ground state ψ is given by

$$\rho(\mathbf{r}) = \langle \psi | \psi^*(\mathbf{r}) \psi(\mathbf{r}) | \psi \rangle , \tag{2.26}$$

which is clearly a functional of $v(\mathbf{r})$. Conversely, it can be shown that $v(\mathbf{r})$ is a universal functional of $\rho(\mathbf{r})$ apart from an additive constant. Assuming $v'(\mathbf{r})$ to be another potential with ground state $|\psi'\rangle$ that gives rise to the *same* density $\rho(\mathbf{r})$, we know $\psi' \neq \psi$ since they satisfy different Schrödinger equations [unless $v'(\mathbf{r}) - v(\mathbf{r}) = \text{constant}$].

By the minimal property of the ground state

$$E' = \langle\psi'|H'|\psi'\rangle < \langle\psi|H'|\psi\rangle = \langle\psi|H + V' - V|\psi\rangle , \qquad (2.27)$$

so

$$E' < E + \int [v'(\mathbf{r}) - v(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r} . \qquad (2.28)$$

Similarly,

$$E < E' + \int [v(\mathbf{r}) - v'(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r} . \qquad (2.29)$$

Addition of the last two equations leads to an inconsistent result:

$$E' + E < E' + E . \qquad (2.30)$$

Hence $v(\mathbf{r})$ is a unique functional of $\rho(\mathbf{r})$. Since $v(\mathbf{r})$ fixes H, the full many-particle state is a unique functional of $\rho(\mathbf{r})$.

Hohenberg and Kohn also show the energy functional defined by

$$E_v[\rho] \equiv \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho] , \qquad (2.31)$$

where $F[\rho]$ is a universal functional valid for any number of particles and any external potential, viz.

$$F[\rho] = \langle\psi|T + U|\psi\rangle , \qquad (2.32)$$

assumes its minimum value for the correct $\rho(\mathbf{r})$ if the admissible functions are restricted by the condition

$$N[\rho] \equiv \int \rho(\mathbf{r})d\mathbf{r} = N . \qquad (2.33)$$

It is well known that for a system of N particles, the energy functional of ψ',

$$\varepsilon_v[\psi'] \equiv \langle\psi|V|\psi'\rangle + \langle\psi'|T + U|\psi'\rangle ,$$

has a minimum at the correct ground state ψ, relative to arbitrary variations of ψ' in which the number of particles is kept constant. In particular, let ψ' be the ground state associated with a different external potential $v'(\mathbf{r})$. Then

$$\varepsilon_v[\psi'] = \int v'(\mathbf{r})\rho'(\mathbf{r})d\mathbf{r} + F[\rho']$$

is greater than

$$\varepsilon_v[\psi] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho] . \qquad (2.34)$$

Thus the minimal property of $E_v[\rho]$ is established relative to all density functions $\rho'(\mathbf{r})$ associated with some other external potential $v'(\mathbf{r})$.

If $F[\rho]$ were a known, sufficiently simple functional of ρ, the problem of determining the ground-state energy and density in a given external potential would be rather easy, since it requires the minimization of a functional of the 3D density function. However, the major part of the complexities in the many-electron system is associated with the determination of $F[\rho]$ (see Sec. 2 of Hohenberg and Kohn, 1964).

At first, the Hohenberg-Kohn theorem seems to be a rather startling result: The electron density $\rho(\mathbf{r})$ *alone* carries enough information to determine completely the ground state of a system. However, as Coleman (1980) has shown, one obtains from Kato's (1957) cusp condition,

$$\lim_{r\to 0}[\ln \bar{\rho}(r)] = -2z . \qquad (2.35)$$

In (2.35) $\bar{\rho}$ is the spherically averaged $\rho(\mathbf{r})$. The cusps at the nuclei are the only singularities of $\rho(\mathbf{r})$. Thus $\rho(\mathbf{r})$ contains a "record" of the position and strength of the nuclear charges z; moreover,

$$\int \rho(\mathbf{r})d\mathbf{r} = N . \qquad (2.36)$$

This information is sufficient to specify the ground state of the molecule.

2. The density-functional theory

The central works of this theory are the Hohenberg-Kohn theorem and subsequent reduction of the energy-density-functional variation to a set of one-electron Schrödinger-type equations by Kohn and Sham (1965). The scheme is formally analogous to the Hartree theory; however, exchange and correlation are accounted for in a local approximation.

For $\rho(\mathbf{r})$ which is slowly varying, the exchange-correlation energy of an interacting system can be written as

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r} , \qquad (2.37)$$

where ε_{xc} is the exchange-correlation energy per electron of a uniform gas of density ρ.

Since the energy

$$E = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + G[\rho] , \qquad (2.38)$$

where

$$G[\rho] = T_s[\rho] + E_{xc}[\rho] , \qquad (2.39)$$

$T_s[\rho]$ being the kinetic energy of a system of noninteracting electrons of density ρ, is stationary and

$$\int \delta\rho(\mathbf{r})d\mathbf{r} = 0 , \qquad (2.40)$$

we obtain the equation

$$\int \delta\rho(\mathbf{r})\left(\phi(\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} + \mu_{xc}[\rho(\mathbf{r})]\right) = 0 . \qquad (2.41)$$

In (2.41)

$$\phi(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} , \qquad (2.42)$$

and

$$\mu_{xc}[\rho] = \frac{d\{\rho\varepsilon_{xc}[\rho]\}}{d\rho} \qquad (2.43)$$

is the exchange and correlation contribution to the chemical potential of a uniform gas of density ρ.

For a given ϕ and μ, one obtains the $\rho(\mathbf{r})$ which satisfies these equations by solving the one-particle Schrödinger equation

$$(-\tfrac{1}{2}\nabla^2+\{\phi(\mathbf{r})+\mu_{xc}[\rho(\mathbf{r})]\})\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r}) \tag{2.44}$$

and setting

$$\rho(\mathbf{r})=\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2 . \tag{2.45}$$

Equations (2.42) to (2.45) are solved self-consistently, assuming that a $\rho(\mathbf{r})$, $\phi(\mathbf{r})$, and μ_{xc} are constructed from (2.42) and (2.43) and then the new $\rho(\mathbf{r})$ is found using the last two equations.

The method is accurate only for the case of high-density uniform electron gas (Hedin and Lundqvist, 1969), although an approximate functional form for a slowly varying inhomogeneous electron gas has been derived (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Kleinman, 1974) and local-density theories based on this scheme have been applied to atoms and molecules with considerable success (Tong and Sham, 1966; Gunnarsson and Johansson, 1976; Gunnarsson *et al.*, 1977; Harris and Jones, 1978). For systems which have a net spin, the local-spin-density approximation is to be used (Von Barth and Hedin, 1972; Rajagopal and Callaway, 1973). Thus the extension to spin-unrestricted spin-density formalism (Gunnarsson and Lundqvist, 1976) involves the minimization of an energy functional both of charge density and the spin density. With an additional assumption, Gunnarsson and Lundqvist (1976) have modified the scheme to give the lowest energy corresponding to wave functions with a given set of quantum numbers.

Zunger and Freeman (1976) have proposed a fully self-consistent solution of the one-particle equations in a periodic solid within the local-density-functional formalism. For the correlation part of the chemical potential they use the previously suggested form of Singwi *et al.* (1970), which has yielded good results for charge densities and total ground-state energies for atoms (Tong, 1972) and molecules (Gunnarsson and Johansson, 1976). Thus they employ

$$\frac{\partial E_{xc}[\rho(\mathbf{r})]}{\partial\rho}=F_x[\rho(\mathbf{r})]+F_c[\rho(\mathbf{r})] \tag{2.46}$$

$$=-\left[\frac{3}{\pi}\rho(\mathbf{r})\right]^{1/3}+\frac{B}{\pi\alpha A}\ln(1+X^{-1}) , \tag{2.47}$$

where $X=r_s/A$, $\frac{4}{3}\pi r_s^3=\rho^{-1}$, and A, B, C, α are numerical constants. The ground-state properties such as structure factors, cohesive energies that have been computed for diamond, show good agreement with experiment. Note that both exchange and correlation energies are employed as local functionals of single-particle density.

Although the Kohn-Sham local-exchange-correlation method and local-spin-density approximation have been widely used, since they provide computational schemes that are practical, certain doubts have been raised (Elyashar and Koelling, 1977; Herman *et al.*, 1969) regarding the validity of the density-gradient expansion using only a finite number of terms for real systems in regions of high gradients, e.g., near a nucleus; the present trend is to avoid such gradient expansions as far as possible.

In molecules and solids, the external potential consists of one or more nuclei producing a very inhomogeneous electron-density distribution. Further, if one is interested in the valence electrons, viz., if the nuclei and core electrons are forming the fixed external potential, then a nonlocal external potential is to be considered. Such an extension of the Hohenberg-Kohn theorem has been done by Gilbert (1975). In this more general case, a nondegenerate ground-state wave function is a universal functional of the one-particle reduced ensemble density kernel $\mu(\mathbf{x}_1,\mathbf{x}_2)$. Gilbert has also shown that any non-negative differentiable function such that

$$\int\rho(\mathbf{r})d\mathbf{r}=N$$

is an N-representable single-particle density. Thus the problem of restricting trial density functions to those that are N-representable is simple.

Nakatsuji and Parr (1975) derived three different exact variational formulas that include only one-electron functions as variables, starting from the integrated Hellmann-Feynman (Epstein *et al.*, 1967), integral Hellmann-Feynman (Parr, 1964; Kim and Parr, 1964), and the virial (Clinton, 1960) theorems. The problem with these variational formulas is that they require correct density functions associated with an arbitrary chosen reference potential; this is, in general, impossible! Nakatsuji and Parr are of the opinion that although no such method is available at present, even an approximate method could be very useful.

A general linear screening formalism in the density-functional formalism has been developed by Ying and co-workers (Ying *et al.*, 1971, 1975; Smith *et al.*, 1973, 1974) for dealing with chemisorption on metals. The chemisorbed species can be represented by an external charge distribution perturbing the metallic surface. They assume the substrate to be a jellium model of positive charge density, and the density functional $G[\rho]$ is represented by the first two terms of the gradient expansion valid for slow variation of the density ρ. The perturbation due to the chemisorbed entity is treated in linear approximation. The theoretical results for ionic desorption energy, relative magnitude of dipole moment, resonance levels, etc., agree well with experimental measurements in the case of hydrogen chemisorbed on a tungsten surface.

Nonlocal approximations to exchange have also been recently proposed (Gunnarsson *et al.*, 1976, 1977; Alonso and Girifalco, 1977, 1978); these avoid gradient expansions but are based on conserving total exchange charge and satisfying some of the limiting conditions on the exchange charge density. Results on free atoms show improvements on the local approximation.

In passing, we mention the theorem analogous to the Hohenberg-Kohn theorem that has been derived by Epstein and Rosenthal (1976) for finite matrices. Let H be an $N\times N$ Hermitian matrix, E its lowest eigenvalue (possible degenerate), and ψ a lowest eigenvector;

the density ρ_i is defined by

$$\rho_i = \frac{|\psi_i|^2}{\sum_{j=1}^{N} |\psi_j|^2}, \quad i = 1, 2, \ldots, N. \tag{2.48}$$

Let V be a diagonal $N \times N$ Hermitian matrix "potential" and define H^0 by

$$H = H^0 + V.$$

Then the theorem states that *the quantities* $V_{ii} - E$ *for those i for which* $\psi_i \neq 0$ *are unique functions of the* ρ_j (*and* H^0). Epstein and Rosenthal have demonstrated the theorem with 2×2 Hermitian and 3×3 real symmetric matrices.

An interesting recent work of Parr *et al.* (1978) identifies the chemical potential of density-functional theory with the concept of electronegativity. Electronegativity is constant throughout an atom or molecule and constant from orbital to orbital within an atom or molecule, i.e., the electrons distribute themselves among orbitals in such a way as to equalize the chemical potential from orbital to orbital, a phenomenon analogous to the situation in macroscopic thermodynamics. They suggest modifications of the Hartee-Fock theory and a reshaping of the electronegativity concept, since the Hartree-Fock theory does not provide a model that easily accounts for equal electronegativities for all orbitals.

Parr *et al.* obtain an equation which shows that electronegativity differences determine the charge transfers occuring on bond formation. They also define an atom in a molecule in terms of *three* conditions; interestingly, the virial fragments (Sec. II.B.3) satisfy two of these conditions. Further, by assuming that for a neutral atom with atomic number Z the chemical potential is zero and the energy is $-0.6127Z^{7/3}$, Parr *et al.* (1979) have proposed a local energy density functional for the ground states of atoms and molecules,

$$E[\rho] = \tfrac{3}{5} A_0 \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \tfrac{3}{4} B_0 N^{2/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \tag{2.49}$$

where $A_0 = 6.4563$ and $B_0 = 1.0058$. The first term on the right represents the electronic kinetic energy, the second represents the interelectronic repulsion energy for N electrons, and the third is the electron-nuclear attraction energy with $v(\mathbf{r})$ as the external potential. For molecules in this local-density approximation, the contours of $v(\mathbf{r})$ are contours of $\rho(\mathbf{r})$. For an atomic species with fractional charge $q = 1 - (N/Z)$, the energy may be written as

$$-E/Z^2 N^{1/3} = 0.6343 + 0.1721\, q. \tag{2.50}$$

However, Tal *et al.* (1980) are doubtful whether such a local density approximation will closely resemble real systems. These authors have made interesting studies on the explicit correspondence between $\rho(\mathbf{r})$ and $v(\mathbf{r})$ in terms of their topographical properties (see Hohenberg-Kohn theorem).

There have been various other extensions, both fundamental and calculational, to the density-functional theory. Thus, for example, it has recently been extended to excited states (Theophilou, 1979), relativistic systems (Rajagopal, 1978; McDonald and Vosco, 1979), and certain time-dependent situations (Peuckert, 1978; Deb and Ghosh, 1981). The theory has also been applied to elucidate the transition from a low-density electron crystal (Wigner crystal) to a uniform electron gas (Shore *et al.*, 1978). The spin-density-functional theory has been employed by Rose *et al.* (1980) to study the phase transitions of electrons in a lattice of fixed point charges; the metal—insulator transition is found to be of first order, while the formation of magnetic moments at the proton sites is of second order [see also Becker (1980)]. For some recent works on calculational aspects, based on the pseudopotential formalism, see Szasz *et al.* (1975) and Zunger *et al.* (1979); see also the reviews by Gunnarsson and Jones (1980), and Rajagopal (1980).

3. The quantum subspace

Although the concept of a subspace has played a dominant role in the study of crystals, it is only recently that Srebrenik and Bader (Srebrenik and Bader, 1975; Srebrenik, 1975; Bader, 1975) have demonstrated two new principles of quantum mechanics. First, the variational principle for the energy is applicable to and, as a consequence, defines a particular class of subspaces. Second, the Hamiltonian operator of a many-electron system may be expressed as a sum of single-particle Hamiltonians through the use of a complete set of virial sharing operators leading to a definition of subspace energy.

Srebrenik (1975) had shown that the Hohenberg-Kohn theorem applies to a finite region in space for a one-electron system, provided that the region is bounded by a zero-flux surface. This was later extended (Bader, 1975) for many-electron systems.

The Schrödinger equation subject to the boundary condition is equivalent to the statement that the description of a quantum-mechanical system is obtained by extremizing

$$G(\phi) = \int \left(\sum_i \tfrac{1}{2} \nabla\phi^* \cdot \nabla\phi + (\hat{V} + \lambda)\phi^*\phi \right) d\tau, \tag{2.51}$$

where $\langle \phi | \phi \rangle$ remains constant, and V, λ are the potential energy operator and the Lagrange parameter, respectively. It can be shown that the natural boundary condition reduces to

$$\nabla_i \psi \cdot \hat{n}_i = 0 \tag{2.52}$$

for all particles i for all points on the boundary surface, $\hat{n}_i$ being the unit normal to the surface. Thus the satisfaction of (2.52) guaranteed by the vanishing of ψ (and $\nabla_i \psi$) yields the equivalence between solving the Schrödinger equation and extremizing $G(\phi)$.

It has been demonstrated (Srebrenik and Bader, 1975) that the Schrödinger equation may be solved over a subspace of the total system, the boundary condition that ensures the variational principle holds over the same subspace being

$$\rho(\mathbf{r}) \cdot \hat{n}(\mathbf{r}) = 0 \quad \forall\, \mathbf{r} \varepsilon S(\mathbf{r}), \tag{2.53}$$

where $\hat{n}(\mathbf{r})$ is the unit normal to the surface $S(\mathbf{r})$ at $\mathbf{r}$. The partitioning surfaces obtained by (2.53) are called the zero-flux surfaces; they define a collection of all gradient paths of $\rho(\mathbf{r})$ originating from and terminating at stationary points $[\nabla\rho(\mathbf{r})=0]$ in the molecular charge distribution.

Bader and Runtz (1975) had earlier shown that such a procedure divides the molecule into atom-like fragments, the surfaces intersecting the chemical bonds. Any gradient path not terminating at the internuclear stationary point terminates at one of the nuclei where the boundary condition is violated; thus the surfaces (Ω) are unique. The boundary condition defines a unit cell in a solid, a molecule in a collection of molecules, a group of atomic fragments in a molecule, and ultimately an atomic fragment. For examples of such partitioning surfaces in di- and polyatomic molecules, see Figs. 1 and 2.

The variational property of the energy and the satisfaction of the virial theorem are connected by the operation of scaling of wave function coordinates. Moreover, the scaling of electronic coordinates implies setting the variational function equal to $\mathbf{r}\cdot\nabla\psi$. By performing the scaling operation and defining the kinetic and potential energy operators for a fragment, it has been shown (Bader and Beddall, 1972; Bader *et al.*, 1973; Srebrenik and Bader, 1975) that

$$-2T(\Omega)=V_0(\Omega)=V'(\Omega)+V''(\Omega)+V_n(\Omega)\,, \tag{2.54}$$

where

$$V'(\Omega)=\int_\Omega -\sum_\alpha \frac{z_\alpha}{r_\alpha}\rho(\mathbf{r})d\mathbf{r}\,, \tag{2.55}$$

$$V''(\Omega)=\int_\Omega d\mathbf{r}_1\int d\mathbf{r}_2\frac{D^2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\,, \tag{2.56}$$

and

$$V_n=-\sum_\alpha \mathbf{R}_\alpha\cdot\mathbf{F}_\alpha(\Omega)\,, \tag{2.57}$$

$$\mathbf{F}_\alpha(\Omega)=z_\alpha\int_\Omega \rho(\mathbf{r})\frac{\mathbf{r}_\alpha}{r_\alpha^3}d\mathbf{r}\,. \tag{2.58}$$

Thus the right-hand side of (2.54) is the result obtained when the virial operator is averaged over a subspace

$$V_0(\Omega)=N\langle-\mathbf{r}_1\cdot\nabla_1\hat{V}\rangle_\Omega\,. \tag{2.59}$$

Further, the fragment energy has the additive property

$$\sum_\Omega E(\Omega)=E\,.$$

By defining the potential energy operator

$$\hat{p}_i=-\hat{r}\cdot\hat{\nabla}_i\,, \tag{2.60}$$

whose action on the potential energy $\hat{V}$ is to project out the potential energy of the ith particle

$$\sum_i \hat{p}_i\hat{V}=V\,, \tag{2.61}$$

the total Hamiltonian of a many-electron system can be reduced to a sum of one-electron contributions.

$$\hat{H}=\sum_i \hat{H}_i=\sum_i(-\tfrac{1}{2}\nabla_i^2+\hat{p}_i\hat{V})\,. \tag{2.62}$$

Srebrenik and Bader (1975) have proved that the total energy for a fixed nuclei system (Born-Oppenheimer approximation) in the absence of any external forces is purely electronic. The time-dependent subspace variational principle has been derived by Srebrenik *et al.* (1978) using a modified form of Hamilton's principle. The principle is also a variational statement of a time-dependent hypervirial theorem, generalized to systems bounded by zero-flux surfaces; a time dependence to subspace properties may thus be ascribed. In a subsequent paper Bader *et al.* (1978) use Schwinger's quantum action principle to obtain a quantum-mechanical description of a subspace. The expression for the subspace action integral operator obeys a principle of stationary action. Schwinger's quantum action principle is reexpressed as a sum of changes in the action integral operator for each subspace in the system. Thus the total change in the transformation function as given by the action principle may be expressed in terms of a sum over action changes for each atomlike fragment.

On the basis of these extensive studies, Bader *et al.* (1979) have found that the vector field of the single-particle density, $\nabla\rho(\mathbf{r})$ characterizes the universal properties of $\rho(\mathbf{r})$. The trajectories of $\nabla\rho(\mathbf{r})$, all of which terminate at particular critical points [points at which $\nabla\rho(\mathbf{r})=0$], define the atoms in a molecule in a manner consistent with the chemical concept of an atom in a molecule. Collard and Hall (1977) have put forth a formalism demonstrating the use of orthogonal trajectories and their critical points in the analysis of scalar functions. The catastrophe theory of Thom (1975) gives the discontinuous change in topological characteristics of a molecular distribution when a continuous change in its nuclear coordinates is occurring. Linking up their work with these theories, Bader *et al.* (1979b) extend their study to the dynamic case and give a precise meaning to the concepts of the making and breaking of bonds.

With this link-up, the primary concepts of chemistry find precise definitions in terms of topographical properties of molecular charge distribution, e.g., the existence of a (3,1) critical point (Bader *et al.*, 1979b) is associated with a particular chemical property, viz., the neighboring atoms are bonded to one another. Similarly, molecular structure and its stability are a result of competition between various nuclei in the molecule for the electronic charge of the system.

C. Electron correlation and *N*-representability

Wigner and Seitz (1933, 1934) coined the term "electron correlation" in the study of the electronic structure and cohesive energy of metals. Kutzelnigg (1973) has discussed the two aspects to correlation: "correlation energy" is that part of the energy one ignores when one uses a single-determinantal wave function. If we seek a definition independent of the choice of the wave function, it is appropriate to refer to the "best" Slater determinant in terms of the energy criterion, viz., the Hartree-Fock energy. Since it is necessary to distinguish between relativistic effects, one may define, following Löwdin (1959), the correlation energy as the difference between the "true" Hartree-Fock and the "true" nonrelativistic energy.

There is also a statistical correlation of electrons in space as a consequence of the exclusion principle; the effect of this "Fermi correlation" on the energy is allowed for in the energy of a Slater determinant wave function.

Long ago, Coulson (1960, p. 175) had remarked, "It has frequently been pointed out that a conventional many-electron wave function tells us more than we need to know.... There is an instinctive feeling that matters such as electron correlation should show up in the two-particle density matrix... but we still do not know the conditions that must be satisfied by the density matrix." This problem of obtaining intrinsic criteria by which to recognize when a function $D^2(x_1, x_2; x_1', x_2')$ can be expressed by (2.5), viz.,

$$D^2(x_1, x_2; x_1', x_2') = \int \psi(x_1, x_2, \ldots, x_N)\psi^*(x_1', x_2', \ldots, x_N)dx_3, \ldots, dx_N\,, \tag{2.5}$$

was termed the N-representability problem by Coleman (1963), who devised the necessary and sufficient conditions for the N-representability of the first-order density matrix. However, this has not been possible in the case of the second-order density matrix.

One might think that to obtain D^2 it would be sufficient to minimize the energy expression (2.13) subject to the normalization condition (2.8). However, D^2 also satisfies

$$D^2(x_1, x_2; x_1', x_2') = D^{2*}(x_1', x_2'; x_1, x_2)\,, \tag{2.63}$$

viz., D^2 is Hermitian. In addition,

$$\begin{aligned} D^2(x_1, x_2; x_1', x_2') &= -D^2(x_2, x_1; x_1', x_2') \\ &= -D^2(x_1, x_2; x_2', x_1')\,. \end{aligned} \tag{2.64}$$

$D^2 \geq 0$, viz., D^2 acting as an operator on the space of all antisymmetric functions of two variables has non-negative values. The variation of D^2 must be further restricted by the condition that $D^2(x_1, x_2; x_1', x_2')$ can be represented in (2.5) by an integral involving the wave function which is antisymmetric in N particles. Although a simple solution to this problem seems unlikely, even partial success could increase our understanding of correlation and other phenomena.

The problem stated above is that of pure N-representability, since $D^2(x_1, x_2; x_1', x_2')$, as given by (2.5), is represented by a pure state. Corresponding to an ensemble, one has the ensemble N-representability problem on which much research work has been focused. Over the years there have been various approaches (beset with frustration) to solve the N-representability problem. Here we shall mention only some of the concepts developed in this area. Extensive material dealing with this problem can be found in Davidson (1976), in the proceedings from two conferences at Queen's University (Coleman and Erdahl, 1968; Erdahl, 1974), as well as in the review article by Coleman (1980).

The set of N-representable or ensemble N-representable D^2 matrices form a convex[3] set and the mathematical tools constructed to study convex sets can be effectively employed. Further, in the variational method to obtain D^2, ensemble N-representability automatically ensures pure N-representability.

Coleman (1963) has obtained the following important result: A necessary and sufficient condition that D^1 be ensemble N-representable is that its eigenvalues be non-negative and less than or equal to N^{-1}. Such a simple characterization has been possible since the eigenvalues λ_i^1 of D^1 constitute a complete set of invariants under the action of the unitary group $U(r)$ of transformations of the orthonormal spin-orbital basis set.

The eigenfunctions of D^1, the natural spin orbitals, are well suited for expanding ψ; those of D^2, the natural geminals g_i, also possess similar virtues. If λ_i^2 be the eigenvalues of g_i,

$$D^2 = \sum \lambda_i^2 \,|g_i\rangle\langle g_i|\,, \tag{2.65}$$

then it can be shown that the energy E is given by the sum of contributions associated with natural geminals g_i

$$E = \frac{N}{2}\sum \lambda_i^2 \langle g_i | K^2 g_i\rangle\,, \tag{2.66}$$

where K^2 is the reduced Hamiltonian

$$K^2 = H(1) + H(2) + (N-1)H(12)\,. \tag{2.67}$$

Yang (1962) and Bloch (1965) have shown that large values of λ_i^2 can be associated with the phenomenon of superconductivity. A number of necessary conditions for N-representability of D^1 have been obtained by various workers; these are the so-called D, Q, B, G conditions (Coleman, 1980). Simons and Harriman (1970) have introduced the concept of "approximate N-representability". For further discussions of these problems, see Coleman (1978) and Levy (1979).

In conclusion, the problem of pure N-representability of D^2 is of paramount importance to molecular physicists, since D^2 is believed to contain all information of physical interest. The density matrix approach is very attractive since it can be generalized to include ensembles and grand canonical ensembles in a beautifully simple manner. Indeed D^N was introduced by Von Neumann in order to lay a proper mathematical basis for statistical mechanics.

Unfortunately, although various ingenious approaches have been employed, the pure N-representability of D^2 seems intractable. Thus *direct evaluation of* D^2 is beset with great difficulties and approximations. Nevertheless, the prize of its solution is well worth the effort, since, once the problem is solved, it will unfold an entire new area of quantum mechanics: quantum mechanics where the Schrödinger equation would no longer receive primary attention and where new concepts would unfold as well as light being shed on old ones such as electron correlation.

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[3] A subset c of a linear space is *convex* if together with any two points of c, all the points in the straight segment with these two points as end points are also contained in c. A convex set is thus determined by its *extreme* points.

However, as Gilbert (1975) has shown (Sec. II.B), the N-representability problem associated with the direct determination of $\rho(\mathbf{r})$ is much simpler. Such attempts at direct determination of $\rho(\mathbf{r})$ are discussed below.

D. The Thomas-Fermi model

Since its invention by Thomas (1926) and Fermi (1928), and subsequent modification by Dirac (1930), the Thomas-Fermi model has been useful in the study of heavy atoms and solids. Properties that are reasonably independent of the detailed structure of the outer electron shells of the atom [e.g., equation of state at high pressures (Feynman *et al.*, 1949)] are well represented. On the other hand, properties such as atomic diamagnetism, which is proportional to the mean square radius of the charge distribution in the atom, are poorly represented by this approach.

The model supposes a degenerate free electron gas for the atom. The electron gas is under the influence of a mean potential which varies from point to point in the atom. The electron interaction is ignored except for the mean screening effect of the electron cloud. This approximation holds for high-density regions (hence in the interior of atoms). Dirac improved on this by including the exchange energy of a free electron gas, thereby accounting approximately for the tendency of electrons of like spin to keep away from each other. His work related the Hartree-Fock theory and the Thomas-Fermi model. His assumption was that the distribution of electrons in phase space is the local Fermi density

$$\begin{aligned}\rho(\mathbf{r}) &= (2\pi h)^{-3} \quad \text{for } p<p_F(R) \\ &=0 \quad \text{for } p>p_F\,.\end{aligned} \tag{2.68}$$

The density is hence zero, outside some radius R, the Fermi momentum p_F being a function of R. Theis (1955) showed that this assumption was a consequence of the fact that the system was in its ground state and that D^2 is idempotent. Löwdin (1955) introduced correlation by using sums of Slater determinants, and this yields fractional occupation numbers for the single-particle states [for a review on the Thomas-Fermi model, see March (1957)].

Gell-Mann and Brueckner [(1957); see also Gell-Mann (1957)] accounted for the tendency of electrons of opposite spin to stay apart, viz., the Coulombic repulsion, and later modifications were introduced by Lewis (1958), who obtained a general equation from which the Thomas-Fermi (TF) and Thomas-Fermi-Dirac models emerged as special cases. The second error in the TF model, not unrelated to correlation, was that electrons did not interact with each other. In order to tackle this, Fermi and Amaldi (1934) simply multiplied the charge distribution each electron sees by a factor $(z-1)/z$, z being the nuclear charge.

In an interesting work, Balâzs (1967) studied the formation of stable molecules within the statistical theory of atoms. He demonstrated that no theory, however complex, can describe binding so long as (within it) the density $\rho(\mathbf{r})$ is expressed as a local function of the electric potential alone. Binding occurs if there exists a range of internuclear separations for which the forces on the nuclei are attractive. Balâzs thus concluded that the Thomas-Fermi, Thomas-Fermi-Dirac, Thomas-Fermi-Gombas (Gombas, 1949) theories cannot give rise to molecular binding. The Thomas-Fermi model with Fermi-Amaldi correction cannot give rise to molecular binding for homonuclear diatomic neutral molecules if $N \geqslant 4$.

However, the Thomas-Fermi-Weizsäcker [see Gombas (1949)] theory gives stable homonuclear diatomics. Coupled with Poisson's equation

$$\nabla^2\phi = 4\pi ne\,, \tag{2.69}$$

where $\rho(\mathbf{r}) = -ne$, n being the number density, any of the above theories invokes a relation between $\rho(\mathbf{r})$ and ϕ. For example, the Thomas-Fermi theory gives

$$f=\sigma(\phi-\phi_0)^{3/2}\,, \tag{2.70}$$

where

$$\sigma=\frac{1}{3\pi^2}\left(\frac{z}{ea_0}\right)^{3/2}, \tag{2.71}$$

a_0 being the Bohr radius. In the Thomas-Fermi-Dirac theory

$$f=\sigma[(\phi-\phi_0+\tau^2)^{1/2}+\tau]^3 \tag{2.72}$$

$$\tau=\left(\frac{1}{2\pi^2}\right)^{1/2}\left(\frac{e}{a_0}\right)^{1/2}. \tag{2.73}$$

In the formulas above, ϕ_0 is related to the chemical potential of the electrons

$$-e\phi_0=\mu\,, \tag{2.74}$$

and its value is obtained subject to

$$\int n\,dv=N\,. \tag{2.75}$$

Thus Balâzs's work shows that no binding is possible if $n=f(\phi)$, where f is an arbitrary non-negative function depending only on ϕ, and not on its derivatives or other functions.

Putting

$$n=\chi^2\,, \tag{2.76}$$

the Weizsäcker relation between ϕ and χ is

$$(e\phi+\mu)\chi=\tfrac{5}{3}\,\kappa_k\chi^{7/3}-4\kappa_i\Delta\chi\,, \tag{2.77}$$

where

$$\kappa_k=\frac{3e}{5}\sigma^{-2/3} \tag{2.78}$$

and

$$\kappa_i=\frac{e^2a_0}{32}\,. \tag{2.79}$$

In (2.77) the second term on the right is the Weizsäcker correction[4] (without which one gets back the Thomas-Fermi case). Balàzs shows that this correction indeed stabilizes the molecule.

Interestingly enough, his work sheds light on the previous calculations by Sheldon (1955), who studied the N_2 molecule formation in the Thomas-Fermi-Dirac model and concluded that the model yields unstable N_2.[5]

In passing, we also note that temperature effects were incorporated in the Thomas-Fermi model by Feynman *et al.* (1949), whereas field-theoretic formulations involving Green's function (Schwinger, 1951; Martin and Schwinger, 1959) (which resembles in some ways the time-independent formulation using N-particle density matrices) have been applied to the quantum-mechanical many-particle system; the Thomas-Fermi model can also be obtained as a special case (Baraff and Borowitz, 1961). Interesting extensions to the Thomas-Fermi model such as inclusion of relativistic effects, comparison with $X\alpha$ method, etc., have been considered [see the series of papers in Int. J. Quant. Chem. Symp. (1975), Vol. 9].

E. Determination of $\rho(\mathbf{r})$ using the force criterion

Bader and Jones (1963a) obtained the density distribution for the H_2O molecule in its equilibrium configuration by requiring that the forces exerted on the nuclei by the distribution, as calculated by the Hellmann-Feynman theorem [see Deb (1973)], balance the nuclear repulsive forces. The requirement of zero resultant force provides one with a number of constraints any proposed density function must fulfill. These constraints may be used to fix a corresponding number of parameters in the density function. For example, in H_2O three parameters in $\rho(\mathbf{r})$ may be determined by observing the requirement that the resulting forces exerted on the O nucleus along the symmetry axis and on the H nuclei along and perpendicular to the bond axes must be zero. The remaining force components give trivial conditions, as they are zero by symmetry alone.

Thus the criteria of zero resultant forces may be used to fit a relatively sophisticated density function to any nuclear framework. Bader and Jones (1963b) have also determined $\rho(\mathbf{r})$ for HF by the force criteria, as well as requiring $\rho(\mathbf{r})$ to predict the correct dipole moment. The ability of $\rho(\mathbf{r})$ to give expectation values of other one-electron operators is satisfactory.

The NH_3 molecule has also been studied (Bader and Jones, 1963a) in the same framework and the density distribution is compared with self-consistent field (SCF) calculations. In NH_3 the three forces, not balanced by symmetry considerations are F_N, $F_{\parallel}$, and $F_{\perp}$ (see Fig. 1). The most serious criticism of this work is the omission of any polarization around the H nuclei. Being limited in the number of parameters that one can employ by the number of forces to be balanced, one cannot include these polarizations and other fine details. Mukherji and Karplus (1963) suggested a constrained variational method which has been employed by Loeb and Rasiel (1970) using the zero force cri-

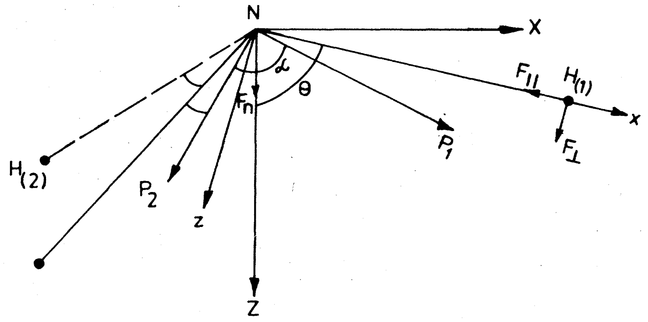

FIG. 1. F_n, $F_{\parallel}$, and $F_{\perp}$ are the three distinct forces in NH_3 that are not zero from symmetry considerations alone. Z is along the C_3 axis of the molecule. P_1, P_2 denote $2p$ orbitals, α being the angle between them, whereas $2pz$ is along the z-axis. (Reproduced from Bader and Jones, 1963c. Courtesy, R. F. W. Bader).

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[4] In terms of $\rho(\mathbf{r})$, the Weizsäcker inhomogeneity correction to the kinetic energy is commonly written as (in atomic units)

$$T_W = \tfrac{1}{8}\int \frac{(\nabla\rho)^2}{\rho}\,d\mathbf{r}\,.$$

The original Thomas-Fermi approximation assumes that particle wave functions may be replaced locally by plane waves. The Weizsäcker correction introduces an explicit account of the deviation from plane waves. This correction, whose original derivation was not satisfactory, has preoccupied many scientists. It appears as the first term in a gradient expansion for a "reasonably slowly varying" density, with or without the 1/9 factor, depending on the type of density variation (Hodges, 1973). On the other hand, Alonso and Girifalco (1978) derive this correction in a local-density approximation, without resorting to a gradient expansion. However, the major source of error in their kinetic energy formula arises from regions of rapidly varying electron density and inaccurate knowledge of the correlation factor involved. The basic trouble with all Thomas-Fermi-type methods is that kinetic energy is really a nonlocal functional (unknown) of electron density and that it depends on derivatives of the correlation factor, while the exchange energy depends on integrals of the correlation factor [for discussion, see Alonso and Girifalco (1978)].

Tal and Bader (1978) have shown that local values of the kinetic energy functional including Weizsäcker correction are incorrect. Rather than choosing a nonlocal functional of ρ, they suggest the partitioning of ρ into two terms, one rapidly varying and the other slowly varying, and use the Weizsäcker correction for both the terms. This considerably improves the local behavior and also reduces the total error. Oliver and Perdew (1979) have generalized the kinetic energy expression for the ground state of an inhomogeneous electron gas as a functional of $\rho(\mathbf{r})$, and of $\rho(\mathbf{r})$ as a functional of $v(\mathbf{r})$, to the case of two unequal spin densities (spin-up and spin-down).

[5] These works do not clearly conclude that the Weizsäcker correction is sufficient to yield the correct binding. Balàzs has not investigated the possibility of the potential curve's being so shallow that no energy level could be accommodated in it. While Sheldon demonstrates the lack of success of the Thomas-Fermi-Dirac model in the case of N_2, it is not apparent whether the Weizsäcker correction would yield total binding energy or only a fraction of it. Yonei (1971) has recently obtained good binding energies for diatomic molecules using the Thomas-Fermi-Dirac model with 1/5 Weizsäcker correction, whereas Wang and Parr (1977) suggest the use of 1/9 Weizsäcker unconstrained correction.

terion. However, there is an increase in total energy. Thus it is clear that in the method of Bader and Jones (essentially nonvariational) the sacrifice in energy must be considerable.

F. Determination of $\rho(\mathbf{r})$ via the Milne equation

Although the Thomas-Fermi model provides us a means of obtaining $\rho(\mathbf{r})$ once we know the potential and *vice versa*, it suffers from disadvantages (Sec. II.D) and attempts to correct these end up with formulas too complicated for practical use.

Starting from a single Slater determinant, Light and Yuan (1973) have obtained closed expressions for the reduced density matrices. Based on these expressions, one can directly obtain the radial density function.

Performing the Langer transformation

$$r = e^x \tag{2.80}$$

$$x = \ln r \tag{2.81}$$

on the radial part of the wave function $R_{nl}(r)$, one obtains

$$R_{nl}(r) = e^{x/2}\, U_{nl}(x)\,, \tag{2.82}$$

where

$$U_{nl}(x) = C_N w(x) \sin\int_{-\infty}^{x} w^{-2}(x) dx\,. \tag{2.83}$$

The R_{nl} is substituted in the radial equation of a Coulomb potential and it is shown that $w(x)$ satisfies the Milne equation

$$\frac{w''(x)}{w(x)} + [2Ee^{2x} + 2ze^{x} - (l+1/2)^2] - w^{-4}(x) = 0\,. \tag{2.84}$$

The radial density distribution is

$$\rho_l(r,\lambda_l) = \frac{1}{r}\left[\frac{w^{-2}(x)}{\pi} - \frac{\hbar}{\tau_0}\frac{\partial^2 w^{-2}(x)}{\partial\lambda_l^2}\,\frac{\sin\theta_N(x)}{\sin 2\pi\dfrac{\tau(x)}{\tau_0}}\right], \tag{2.85}$$

where

$$\tau(x) = \frac{\hbar\partial\theta(x)}{\partial\lambda}; \quad \theta(x) = \int_{-\infty}^{x} w^{-2} dx\,, \tag{2.86}$$

$$\tau_0 = \hbar\,\frac{\partial\phi_0}{\partial\lambda}; \quad \phi_0 = 2\int_{-\infty}^{\infty} w^{-2} dx\,, \tag{2.87}$$

$$\theta_N(x) = (N+\tfrac{1}{2})\pi \int_{-\infty}^{x} w^{-2} dx \Big/ \int_{-\infty}^{\infty} w^{-2} dx\,. \tag{2.88}$$

In (2.85), λ_l is the Fermi energy determined by

$$\int_{-\infty}^{\infty} w^{-2}(x,\lambda_l)\, dx = (N+\tfrac{1}{2})\pi \tag{2.89}$$

Using (2.84), (2.85), and (2.89), the radial density distributions for various l values of several noninteracting electrons in the Coulomb potential can be determined.

For an atom with closed-shell structure, $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \sum_l \rho_l(\mathbf{r})\,, \tag{2.90}$$

where

$$\rho_l(\mathbf{r}) = \sum_n 2(2l+1) R_{nl}^2(\mathbf{r})\,. \tag{2.91}$$

A second Milne equation, using an analytic expression for the potential for the atom is solved, subject to the quantization conditions for electron orbital energies E_{nl} and Fermi energy λ_l.

Yuan and Light (1974) have applied the formalism to the Kr atom and compared their $\rho(\mathbf{r})$ with that obtained by other methods. The authors claim that these formulas give accurate results including the shell structure (believed to be missing in the Thomas-Fermi method) through the entire r space, except for a small region around the nucleus. However, the belief that the shell structure exhibited by $\rho(\mathbf{r})$ indicates the accuracy of the results must be treated with caution for the following reason: There seems to be widespread belief that the shell structure is reflected by relative maxima in $\rho(\mathbf{r})$. This, however, is a misconception. Weinstein *et al.* (1975) have plotted $\rho(\mathbf{r})$ for *ground* states of various atoms, using SCF (near Hartree-Fock) wave functions, and their investigations definitely indicate that $\rho(\mathbf{r})$ is a monotonically decreasing function, although no general proof has been offered by them. Actually, the shell structure is revealed by a different change in slope of the density; this is seen more clearly by plotting $\log\rho(r)$ vs r for closed-shell atoms.

The method proposed by Yuan and Light appears to be promising in that there are fewer equations to be solved. If the potential $V(r)$ is known, one can directly obtain $\rho(r)$ and by an interpolation scheme, much faster than the iterative method, the eigenvalues and Fermi energies can be obtained. Kirzhnits and Shpatakovskaya (1972) follow a similar approach, except that they start with a semiclassical approximation instead of the Milne equation and obtain one formula for a closed-shell atom, in contrast to Yuan and Light's approach that yields one formula for each l state.

G. Determination of $\rho(\mathbf{r})$ via the partition function

Lawes and March (1980) have proposed an approximate differential equation for the direct calculation of electron density in closed-shell atoms and molecules. In case of one-dimensional motion, they obtain the third-order equation

$$(\mu - V)\frac{\partial\rho}{\partial x} = -\frac{1}{2}\rho\,\frac{\partial V}{\partial x} - \frac{1}{8}\frac{\partial^3\rho}{\partial x^3} \tag{2.92}$$

in a local-density approximation. Here μ is the chemical potential and V is the (one-body) external potential containing the effects of exchange and correlation subtly through ρ. Eq. (2.92) is exact for a linear harmonic oscillator and should yield better results with larger number of electrons.

For a closed-shell atom one may treat the central-field problem as a one-dimensional (1D) case. Equation (2.92) then takes the form

$$-[\mu_l - V_l]\frac{\partial}{\partial r}(r^2\rho_l) = \frac{1}{2}r^2\rho_l\frac{\partial V_l}{\partial r} + \frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2\rho_l)\,, \tag{2.93}$$

where

$$V_l(r) = V(r) + \frac{l(l+1)}{2r^2}\,, \tag{2.94}$$

$$\rho(r)=\sum_{l}(2l+1)\rho_{l}(r)\,. \tag{2.95}$$

By assuming that all μ_l's are the same and equal to μ [see Parr *et al.* (1978)], i.e., by writing

$$\mu\frac{\partial}{\partial r}(r^2\rho)\simeq\sum_{l}(2l+1)\mu_{l}\frac{\partial}{\partial r}(r^2\rho_{l})\,, \tag{2.96}$$

Eq. (2.93) may be transformed as

$$\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2\rho)+\frac{1}{2}r^2\rho\frac{\partial V}{\partial r}+(\mu-V)\frac{\partial}{\partial r}(r^2\rho)$$
$$=\sum_{l}\frac{l(l+1)(2l+1)}{2r^2}\left[r\rho_{l}+\frac{\partial}{\partial r}(r^2\rho_{l})\right]. \tag{2.97}$$

In a molecular situation, say in the 1D case, Lawes and March propose that one should first calculate the effective potential $U(x\beta)$, followed by the generalized partition function $Z(x\beta)$, and then obtain $\rho(x)$ by taking the inverse Laplace transform of Z/β. For this, define $Z(r\beta)$ as the diagonal element $C(rr\beta)$ of the canonical density matrix $C(rr'\beta)$ which is defined in terms of the external potential $V(r)$,

$$C(rr'\beta)=\sum_{i}\psi_{i}^{*}(r)\psi_{i}(r')\exp(-\beta\varepsilon_{i})\,. \tag{2.98}$$

Define also the effective potential matrix $U(rr'\beta)$ by

$$C(rr'\beta)=C_0(rr'\beta)\exp[-\beta U(rr'\beta)]\,, \tag{2.99}$$

where C_0 is the free-particle result. The diagonal element of U is the effective potential, and it satisfies the 1D nonlinear third-order differential equation

$$\tfrac{1}{2}(V'-U')+\beta\left[(U-V)U'+\frac{U'''}{8}-\frac{\partial U'}{\partial\beta}\right]$$
$$+\beta^2\left[U'\frac{\partial U}{\partial\beta}-\frac{3}{8}U'U''\right]+\frac{\beta^3}{8}U'^3=0\,. \tag{2.100}$$

The linear approximation of (2.100) is

$$\tfrac{1}{2}(V'-U_1')+\frac{\beta}{8}U_1'''-\beta\frac{\partial}{\partial\beta}U_1'=0\,, \tag{2.101}$$

and its 3D generalization yields the equation

$$\tfrac{1}{8}\beta\nabla^2U_1-\tfrac{1}{2}(U_1-V)-\beta\frac{\partial U_1}{\partial\beta}=0\,. \tag{2.102}$$

The solution of (2.102) is

$$U_1(\mathbf{r}\beta)=\int g(\mathbf{r}\mathbf{r}'\beta)V(\mathbf{r}')d\mathbf{r}'\,, \tag{2.103}$$

where

$$g(\mathbf{r}\mathbf{r}'\beta)=\frac{1}{\pi\beta|\mathbf{r}-\mathbf{r}'|}\exp\left[-\frac{2}{\beta}|\mathbf{r}-\mathbf{r}'|^2\right]. \tag{2.104}$$

However, this first-order solution should be further refined in order to obtain a better ρ. Hopefully, this approach should be applicable to the ground-state density of a molecule with arbitrarily low symmetry, with large-density gradients and low-density regions.

As discussed earlier, the purpose behind all these works had been to find a reliable (preferably accurate) method for directly determining $\rho(\mathbf{r})$, independent of the Schrödinger equation. However, the Schrödinger equation, or its variant, generally crops up somewhere along the mathematical procedure. Indeed, it has been said that if one throws the Schrödinger equation out of the front door, it returns through the back window!

Thus far, our discussion has highlighted the important properties of $\rho(\mathbf{r})$, methods aimed at its direct determination, and the problem one faces of incorporating electron correlation in $\rho(\mathbf{r})$. Although the problems that arise in these contexts are not yet satisfactorily solved, work on them is continuing in several countries. Once we have the single-particle density at hand, the next job is to extract from it various information of physical and chemical significance. Therefore, in spite of not having satisfactorily resolved the earlier problems, we now proceed to consider the applications of $\rho(\mathbf{r})$ to the study of molecular properties. Our main object in the subsequent discussions would be to highlight the concepts, rather than the mathematical intricacies, in kinship with the spirit (McWeeny, 1976, p.28), "Perhaps we should be more adventurous once in a while, forgetting the rigours of the variation theorem, N-representability, and the like and concentrating a bit more on the physics."

III. APPLICATIONS

A. $\rho(\mathbf{r})$ and chemical binding

With brilliant insight the great physicist Sir Issac Newton had stated in his *Optics* (1704): "The parts of all homogenal hard Bodies which fully touch one another stick together very strongly. And for explaining how this may be, some have invented hooked atoms, which is begging the question... I had rather infer from their cohesion, that their particles attract one another by some force, which in immediate contact is exceedingly strong, at small distances, performs the chymical operations abovementioned and reaches not far from the particles with any sensible effect.... There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out" [quoted in Holden (1965), p.1].

Even today it is difficult to make a better statement of the problem of chemical binding which adopts a force viewpoint in contrast to an energetic one. The quantum-mechanical concept of forces[6] in molecules is introduced via the Hellmann-Feynman theorem (Hellmann, 1937; Feynman, 1939; Deb, 1973; Epstein, 1980), which states that if ψ be a normalizable eigenfunction of H with eigenvalue E, and λ be a real parameter in H,

$$\frac{\partial E}{\partial\lambda}=\frac{\left\langle\psi\left|\frac{\partial H}{\partial\lambda}\right|\psi\right\rangle}{\langle\psi|\psi\rangle}\,. \tag{3.1}$$

The force on any nucleus, considered fixed for a quantum-mechanical system of electrons and nuclei, is then given by the classical electrostatic interaction exerted on the nucleus by the other nuclei and by the electron density for all the electrons.

Chemical binding, which is the interpretative study

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[6] Based on interpretations of the Aharonov-Bohm effect, there is a controversy regarding whether the language of forces in quantum mechanics is irrelevant or not. For a discussion on this, see Erlichson (1970)

of molecule formation in terms of the forces on the nuclei, emphasizes the role of $\rho(\mathbf{r})$. Given a molecular charge distribution $\rho(\mathbf{r})$, determined either by the variational method or by an alternative method, a rationalization of binding or lack of it in a system is possible.

Within the framework of the Born-Oppenheimer (1927) approximation, the total force exerted on a nucleus α with coordinates $\mathbf{X}_\alpha$, charge z_α is given by the sum of nuclear and electronic contributions,

$$\mathfrak{F}(\mathbf{X}_\alpha) = \mathfrak{F}^n(\mathbf{X}_\alpha) + \mathfrak{F}^e(\mathbf{X}_\alpha)\,, \tag{3.2}$$

where

$$\mathfrak{F}^e(\mathbf{X}_\alpha) = z_\alpha \int d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \psi^* \sum_{i=1}^{N} \nabla_\alpha \frac{1}{|\mathbf{r}_i - \mathbf{X}_\alpha|}\psi\,. \tag{3.3}$$

Because of the equivalence of the electrons, the right-hand side of (3.3) reduces to

$$z_\alpha \int d\mathbf{r} \nabla_\alpha \frac{1}{|\mathbf{r} - \mathbf{X}_\alpha|}\rho(\mathbf{r})\,,$$

where $\rho(\mathbf{r})$ is the single-particle density,

$$\rho(\mathbf{r}) = N \int ds_1 \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_N \psi^* \psi\,, \tag{2.20}$$

where $\mathbf{x}_i$ denotes the set of space coordinate $\mathbf{r}_i$ and the spin coordinate $\mathbf{s}_i$ of the ith electron.

Berlin (1951) partitioned the space of a diatomic molecule into binding and antibinding regions by defining a quantity

$$f(\mathbf{r}) = \frac{z_\alpha}{r_\alpha^2}\cos\theta_\alpha + \frac{z_\beta}{r_\beta^2}\cos\theta_\beta\,, \tag{3.4}$$

$f(\mathbf{r})$ being the total force exerted parallel to the internuclear axis by a unit negative charge at r. Regions where $f(\mathbf{r}) > 0$ are the binding regions, whereas $f(\mathbf{r}) < 0$ defines the antibinding regions. The basis of this definition is as follows.

The electronic contribution to the force on either nucleus is

$$\mathfrak{F}_\alpha^e = \mathfrak{F}_\beta^e = \tfrac{1}{2}(\mathfrak{F}_\alpha^e + \mathfrak{F}_\beta^e) = -\tfrac{1}{2}\int f(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\,. \tag{3.5}$$

Here, a right-handed system centered on α and a left-handed one on β is assumed to ensure that the total forces exerted on nuclei are equal in sign as well as in magnitude.

Half of the total of the forces exerted on both nuclei in the system is (R being the internuclear distance)

$$\mathfrak{F} = \frac{z_\alpha z_\beta}{R^2} - \tfrac{1}{2}\int f(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\,. \tag{3.6}$$

For a system at equilibrium internuclear separation, the force $\mathfrak{F}$ equals zero. Since $\rho(\mathbf{r})$ is positive everywhere, the sign of the second term arises solely due to $f(\mathbf{r})$. Regions where $f(\mathbf{r}) > 0$ reduces $\mathfrak{F}$, thus *binding* the nuclei, and the reverse is true for $f(\mathbf{r}) < 0$.

When $\mathfrak{F} < 0$, the force exerted by the binding region is greater than the nuclear repulsion and the antibinding forces, thus drawing the nuclei closer. If $\mathfrak{F}$ is binding for all R, in the range $R_e < R < \infty$, then the resulting equilibrium corresponds to an energy minimum. At $R = R_e$, $\mathfrak{F}$ reduces to zero. Bader (1964) has extended this notion of binding and antibinding regions to polyatomic molecules by superposing the diatomic Berlin diagrams for the bonds included in a molecule, viz., a volume element is said to be binding if it exerts a binding force on *all* nuclei. Such a definition, however, does not permit a study of electron reorganizations during bending, twisting, etc., or a rationalization of the molecular geometry.

Koga *et al.* (1979) have generalized Berlin's definition to polyatomic molecules: The space around the molecule is divided into accelerating and resisting regions with respect to the process along any internal coordinate. Whereas Berlin defined $f(\mathbf{r})$ by (3.4), Koga *et al.* propose the choice of center-of-mass-of-the-nuclei coordinate system, in which internal motions of many-particle systems are more appropriately described. In this system

$$f_{\mathrm{CMN}}(\mathbf{r}) = \frac{1}{m_\alpha + m_\beta}\left(m_\beta \frac{z_\alpha \cos\theta_\alpha}{r_\alpha^2} + m_\alpha \frac{z_\beta \cos\theta_\beta}{r_\beta^2}\right). \tag{3.7}$$

The boundary surfaces for Berlin's case vary according to z_α/z_β, while for this case, the surfaces also depend on the masses. It is shown that the former is a special case of the latter.

For the polyatomic case, considering the transformation from Cartesian to internal coordinates, the internal force is given as

$$\mathfrak{F}_R = \int f_R \rho(\mathbf{r}) d\mathbf{r} + \text{nuclear part}\,, \tag{3.8}$$

where f_R is the suitably transformed electronic force operator in the internal coordinate system. The electronic part of the force is positive if $f_R > 0$ and *vice versa*. The positive force accelerates the nuclear rearrangement along R, whereas negative force resists it. Thus $f_R > 0$ are accelerating regions, whereas $f_R < 0$ are resisting regions. Koga *et al.* have applied their formalism to a nonlinear triatomic molecule AB_2. Superposing the generalized Berlin diagrams on the difference density maps (see below), the geometry of H_2O is discussed; the electron density reorganizations at nonequilibrium geometries are seen to occur in a way that facilitates the restoring of the molecule to its equilibrium geometry.

1. Difference density

Charge redistribution always accompanies the formation of a molecule, the extent of charge reorganization in any region being measured by the difference density $\Delta\rho(\mathbf{r})$,

$$\Delta\rho(\mathbf{r}) = \rho_m(\mathbf{r}) - \rho_a(\mathbf{r})\,. \tag{3.9}$$

In (3.9) $\rho_m(\mathbf{r})$ is the molecular charge density at $\mathbf{r}$, whereas $\rho_a(\mathbf{r})$ is the sum of contributions from undistorted atomic densities, the nuclei being those comprising the molecule. $\Delta\rho(\mathbf{r})$ is obviously a function of the internuclear distance R.

A simple mathematical argument using the electrostatic Gauss theorem by Hirshfeld and Rzotkiewicz (1974) shows that superposition of spherical atomic densities leads to a net repulsive force between the nuclei (arising due to their incomplete screening). Thus $\Delta\rho(\mathbf{r}) > 0$ in the binding region is a necessary (though not sufficient) condition for binding, viz., charge density is concentrated in the binding region so as to exert large attractive forces on the nuclei in order to overcome the repulsion between them.

The isodensity contours (Bader *et al.*, 1967; Bader, 1970) of $\Delta\rho(\mathbf{r})$ at various internuclear separations give a visual idea of the charge redistribution taking place. A comprehensive list and analysis of such maps have been considered by Bader (1980). The contours of $\rho(\mathbf{r})$, while not particularly useful in discussions of chemical binding, do nevertheless provide a useful estimate of the molecular size, e.g., the 0.002 contour is useful in deciding the latter, as 95% or more of $\rho(\mathbf{r})$ usually resides within this contour (Bader *et al.*, 1967).

As mentioned earlier, since we do not have satisfactory methods of obtaining $\rho(\mathbf{r})$ directly, the question naturally arises as to whether Hartree-Fock densities are sufficiently accurate for the study of chemical binding via the $\Delta\rho(\mathbf{r})$ concept, or whether a neglect of electron correlation leads to misinterpretations about chemical binding. Bader and Chandra (1968) have shown that the Hartree-Fock density for H_2 underestimates $\rho(\mathbf{r})$ near the nuclei and overestimates it in the binding region by only 1%. Moreover, electron correlation introduces a second-order correction in the density for closed-shell systems (Kern and Karplus, 1964). The magnitude and relative significance of this correction depends on the system concerned. For further discussion on this point, see Smith (1977).

Bader and Jones (1961, 1963) have also obtained $\rho(\mathbf{r})$ by an alternative method, discussed in Sec. II.E, and compared the expectation values of one-electron operators such as diamagnetic susceptibility, nuclear shielding constants, quadrupole coupling constants with those obtained from SCF wave functions. This $\rho(\mathbf{r})$ should not be used to study chemical binding, since it suffers from certain limitations, as discussed earlier.

Covalent and ionic binding exhibit different characteristics (Bader and Henneker, 1965) in the $\Delta\rho(\mathbf{r})$ maps. It is natural to characterize the bond region by the location, relative to the nuclei, of the charge increase which binds the nuclei. Thus the pure covalent bond is one for which the bond density map shows an increase in density in the binding region, which is shared equally by both nuclei. On the other hand, for ionic molecules like LiF the increase in density which binds the nuclei is localized on F. However, this localized charge is not symmetrically placed with respect to the F nucleus (this nucleus would then experience a positive electric field due to the partially descreened Li nucleus), but is polarized towards the Li nucleus. Such a polarization exerts a force on the anionic nucleus which counterbalances the net force of repulsion due to the positive electric field. Similarly, the density in the vicinity of the Li nucleus is polarized away from F, to counterbalance the net force of attraction exerted by the density transferred to F. Such polarizations are evident in the bond density maps for LiF as well as in the $\Delta\rho(\mathbf{r})$ maps (see Fig. 2). It is possible (Bader *et al.*, 1967) to decompose the total electronic force into orbital contributions by expressing $\rho(\mathbf{r})$ as the sum of orbital densities; the force due to a particular orbital density can be further reduced to a sum of atomic force (force exerted on a nucleus by its own charge population), overlap force (force exerted by the overlap density), and screening force (force exerted by the atomic charge density of the second nucleus). Thus in the covalent bond, it is the force exerted by the overlap density that binds the nuclei together. In a similar manner, the binding and antibinding character of molecular orbitals has also been studied (Cade *et al.*, 1969). Tal and Katriel (1977) relate the binding-antibinding character of an orbital to the derivative of the orbital energy

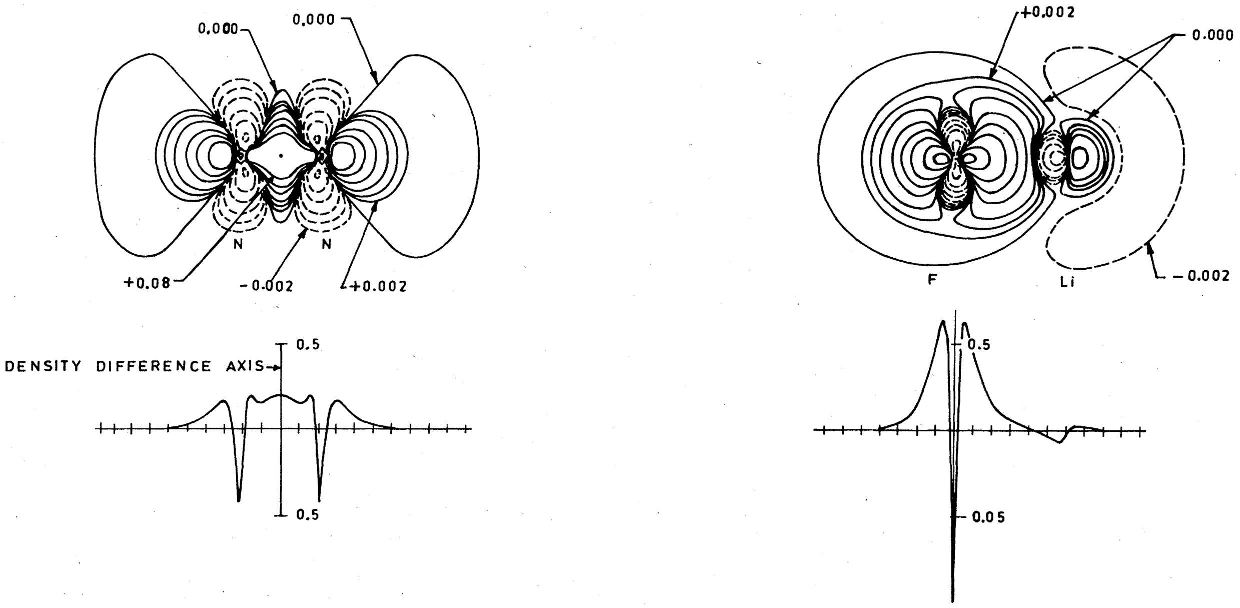

FIG. 2. Bond density (or density difference) maps and their profiles (in a.u.) along the internuclear axis for N_2 and LiF. The solid and dashed lines represent an increase and a decrease, respectively, in the molecular charge density relative to the overlapped atomic distributions. These maps contrast the two possible extremes of the manner in which the original atomic charge densities may be redistributed to form a chemical bond. (Reproduced from Bader *et al.*, 1967. Courtesy, R. F. W. Bader).

$$\frac{\partial \varepsilon_i}{\partial R} = -\frac{\partial F}{\partial n_i} . \tag{3.10}$$

In (3.10) ε_i, n_i are the orbital energy and occupation number of the ith orbital. Other workers (Chandra and Sundar, 1971; Sundar and Chandra, 1974; Hirschfeld and Rzotkiewicz, 1974; Chandra and Sebastian, 1976) have also studied chemical binding in diatomic molecules within the force framework.

2. Dissociation energies

The descreening of two nuclei that approach each other causes the charge to migrate to the region of overlap. In a covalent bond, the shared density binds the nuclei. Thus the amount of descreening taking place determines the charge migration. Bader *et al.* (1967) have concluded that there is a direct relationship between chemical bond strength (dissociation energy) and the magnitude of the electrostatic field due to charge redistribution.

Hirshfeld and Rzotkiewicz (1974) have also made a study along similar lines. They obtain a linear correlation between the net binding electrostatic force and the dissociation energy for AH and A_2 systems. They have also decomposed this field into contributions from core, σ, and π densities. The contribution of the σ valence orbitals to the field at a first-row nucleus varies regularly from binding in Li to antibinding in F. Similarly, the π orbital role is studied.

A possible criticism of this study is the fact that calculation of the penetration field has been done by assuming spherical reference atomic densities. Bader (1980), however, is of the opinion that the undistorted densities, whenever employed as reference states, must be realistically chosen; they should correspond to the appropriate spectroscopic states the atoms find themselves in after dissociation.

3. Virial theorem

The virial theorem (Slater, 1935) for a diatomic molecule states that

$$2T = -V - R\,\frac{\partial E}{\partial R} , \tag{3.11}$$

where T, V are the kinetic and potential energy of the system. At $R = R_e$, since the binding energy ΔE must be negative,

$$\Delta V < 0 , \tag{3.12}$$

$$\Delta T > 0 , \tag{3.13}$$

$$2\Delta T = -\Delta V . \tag{3.14}$$

In (3.12), (3.13), and (3.14) the symbol Δ denotes the difference in value between the molecule and the separated atoms.

The virial theorem, along with the Hellmann-Feynman theorem, provides a detailed description of the charge redistribution taking place during molecule formation in terms of the decrease in potential energy and increase in kinetic energy.

If the net force is binding, the virial theorem gives

$$\Delta T < \tfrac{1}{2}\,|\Delta V| \tag{3.15}$$

and vice versa; at equilibrium, of course, we get (3.14). If one has a complete knowledge of $\mathfrak{F}$, $d\mathfrak{F}/dR$, one may obtain further constraints on dT/dR and dV/dR.

However, the use of these theorems to study bonding and binding had been criticized by Ruedenberg (1962, 1975), and Feinberg and Ruedenberg (1971) while Bader (1980) has refuted their criticism. On the basis of extensive work notably by Bader *et al.* and by Hirschfeld and Rzotkiewicz (1974), there is hardly any doubt now that the force picture of chemical binding, though attractively simple, is nevertheless rigorous.

4. Charge equivalent of force

It is pertinent to mention here the use of the virial fragment concept (see Sec. II.B.3) to illustrate the model of ionic binding proposed by Bader *et al.* (1967). The previous arbitrariness in partitioning $\rho(\mathbf{r})$ can be removed, since the atomlike fragments partitioned by zero-flux surfaces have a sound quantum-mechanical basis.

In an ideal ionic system, the transfer of one electron to form A^+B^- takes place; the B fragment will exert a force equivalent to one negative charge (assuming a spherical symmetry for the charge distribution) on nucleus A.

$$z_B - \mathfrak{F}_A(B)\frac{R^2}{z_A} = -1 . \tag{3.16}$$

In (3.16) $\mathfrak{F}_A(B)$ is the force on nucleus A due to the charge distribution of B.

The populations $c(\Omega)$,

$$c(\Omega) = z_\Omega - N_\Omega , \tag{3.17}$$

and charge equivalents of the forces that the fragment charge distributions exert on the nuclei can be evaluated (Bader, 1980), e.g., in LiF, 0.94 excess electrons on F exert a force at Li equivalent to −0.76 charges; similarly, in LiH, 0.91 excess charge on H exerts a force at Li equivalent to −0.62 charges. Thus the charge distributions of the anionic fragments (F), (H) do not attain the idealized negatively charged ion in terms of forces on the cationic nucleus. This is because of their diffuse and polarized nature. The cationic distribution, on the other hand, is approximately spherical; hence one finds the net force on Li and the charge equivalent of the force exerted on the anionic fragment to be nearly equal. Bader (1980) has also studied the effect of nuclear repulsive potential on the fragment energy $E(\Omega)$.

5. Kinetic energy

Bader and Preston (1969) define a kinetic energy density

$$G(\mathbf{r}) = \tfrac{1}{8}\sum_i \frac{\nabla\rho_i(\mathbf{r})\cdot\nabla\rho_i(\mathbf{r})}{\rho_i(\mathbf{r})} , \tag{3.18}$$

$\rho_i(\mathbf{r})$ being the orbital density of the ith orbital,

$$\rho_i(\mathbf{r}) = \lambda_i\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) , \tag{3.19}$$

where λ_i is the occupation number of the SCF orbital ϕ_i.

$$\int G(\mathbf{r})d\mathbf{r} = T , \tag{3.20}$$

where the quantity $G(\mathbf{r})d\mathbf{r}$ is the contribution to the total kinetic energy of the system from the volume element $d\mathbf{r}$.

These authors have studied the effect of charge accumulation in the binding region on the kinetic energy of the system. Consider $T_\parallel$ and $T_\perp$ to be the parallel and perpendicular components, respectively, of the kinetic energy.

$$T_{\parallel}=\frac{1}{2}\left\langle\frac{\partial\psi}{\partial z}\middle|\frac{\partial\psi}{\partial z}\right\rangle=-\frac{1}{2}\left\langle\psi\middle|\frac{\partial^2}{\partial z^2}\middle|\psi\right\rangle, \tag{3.21}$$

$$T_{\perp}=\frac{1}{2}\left\{\left\langle\frac{\partial\psi}{\partial x}\middle|\frac{\partial\psi}{\partial x}\right\rangle+\left\langle\frac{\partial\psi}{\partial y}\middle|\frac{\partial\psi}{\partial y}\right\rangle\right\}$$

$$=-\frac{1}{2}\left\langle\psi\middle|\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\middle|\psi\right\rangle. \tag{3.22}$$

For spherical distributions

$$T_{\parallel}=\tfrac{1}{2}T_{\perp}, \tag{3.23}$$

hence

$$\frac{T_{\perp}-T_{\parallel}}{T}=\frac{1}{3}. \tag{3.24}$$

The change in the value of this quantity from its atomic value of $\frac{1}{3}$ hence provides a measure of the extent to which the molecule formation effects changes in $T_{\parallel}$ and $T_{\perp}$, thereby highlighting the role of T in the process. Detailed analyses have been considered for H_2, He_2, and extended for other diatomics.[7]

Wilson and Goddard (1970, 1972) have also devised orbital partitioning of the binding energy that places particular emphasis on changes in kinetic energy quantities. They attribute a decrease in kinetic energy, determined by an exchange-type density which must be described in terms of a set of molecular orbitals from a Geshkenbein-Ioffe (GI) type of wave function (Goddard, 1967), to be responsible for chemical binding.

In the case of H_2 and H_2^+, charge accumulation in the binding region leads to a local decrease in kinetic energy of a molecule (relative to separated atoms), and hence the increase in the kinetic energy as a result of charge accumulation in the nuclear potential field could be tolerated. However, for the more general cases, the localized decreases in kinetic energy are primarily in the antibinding region. Thus it is not certain if the localized decreases in the binding region are a necessary general requirement for chemical binding to take place.

The preceding discussion makes it clear that the single-particle density yields outstanding qualitative information on chemical binding, via useful concepts such as isodensity contours of $\rho(\mathbf{r})$, $\Delta\rho(\mathbf{r})$, the Hellmann-Feynman theorem, the virial theorem, kinetic energy density, etc. Although the numerical results depend heavily on the wave functions from which $\rho(\mathbf{r})$ is obtained [in the absence of a completely satisfactory method for the direct determination of $\rho(\mathbf{r})$], and although this is certainly a drawback of the force approach, there is no reason for dissatisfaction with the single-particle density.

The phenomenon of chemical binding is intricately linked with that of molecular geometry, viz., the shapes and sizes of molecules. As reflected in the discussion below, the broad problem of molecular geometry is mainly concerned with formulating general principles and constructing models in order to have a physical or pictorial understanding of the ground- and excited-state geometries of molecules. The use of single-particle density has greatly aided the development of such versatile concepts and models.

B. $\rho(\mathbf{r})$ and molecular geometry

The earlier models of molecular geometry were based on energetic considerations. The Mulliken-Walsh model (Mulliken, 1942; Walsh, 1953) tackled the problem by plotting correlation diagrams in which the molecular orbital (MO) energies were plotted against the valence angles and the Walsh rules were formulated to explain the correlation between the number of valence electrons and molecular shapes.

The Hartree-Fock SCF theory gives a relation between orbital energies ε_k and the total energy E of a molecule,

$$E=\sum_k \lambda_k\varepsilon_k+V_{nn}-V_{ee}, \tag{3.25}$$

λ_k being the occupation number of the kth MO. However, in the Walsh formulation to study the stabilities of alternative molecular shapes via orbital behavior, the relation

$$E\simeq\sum_k \lambda_k\varepsilon_k \tag{3.26}$$

seems to have been employed.

Recently, Politzer (1976) has obtained the relation

$$E\simeq\tfrac{3}{7}(V_{ne}+2V_{nn}). \tag{3.27}$$

Starting from (3.27) and by employing the virial theorem, Ruedenberg (1977) finds

$$E\simeq\tfrac{3}{2}\sum_k \lambda_k\varepsilon_k \tag{3.28}$$

to be approximately valid. Thus, there is a theoretical basis (see later in this section) for the Mulliken-Walsh model.

The Valence-Shell Electron-Pair Repulsion (VSEPR) model (Sidgwick and Powell, 1940; Gillespie and Nyholm, 1957; Gillespie, 1972, 1974) considers that the distribution of electrons in the valence shells of atoms in molecules is determined largely by the operation of the Pauli exclusion principle. The important physical consequence of the exclusion principle is that electrons with parallel spins have a maximum probability of being found as far apart as possible and this in turn leads to the conclusion that for a central atom, forming two or more covalent bonds, the electrons in the valence shells are localized in pairs such that the least distances between them are maximized.

However, as Bader and Preston (1966), Bills and Snow (1975), and Drago (1973) have discussed, the basic concept underlying the model appears to be fallacious; the antisymmetry requirement does not necessarily lead to repulsions between electron pairs in the 3D space. The VSEPR model is applicable only to the ground states of those molecules where one can easily identify the central atom. It cannot be applied to the internal rotation problem. However, the theoretical situation regarding VSEPR is still not completely clear,

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[7] Since we are concerned only with charge density in 3D space, we shall not discuss the calculation and interpretation of momentum densities. For a review, see Epstein (1975).

especially since Schmiedekamp *et al.* (1979) have shown, through *ab initio* calculations on a number of molecules, that the calculated relative sizes of bonds and lone pairs agree very well with the VSEPR assumptions. Also, some apparent failures of the model can be explained by examining the total angular space requirements of the bond and lone-pair orbitals, rather than restricting attention only to the bond angles.

In the Second-Order Jahn-Teller (SOJT) theory proposed by Bader (1960, 1962), Bartell (1968), and Pearson (1969–1971, 1976), the energy expression is examined when the perturbation on an *idealized* molecular configuration is a small displacement along the ith normal coordinate (Q_i),

$$E(Q_i) = E_0 + Q_i \left\langle \psi_0 \middle| \frac{\partial H}{\partial Q_i} \middle| \psi_0 \right\rangle + \frac{1}{2} Q_i^2 \left\langle \psi_0 \middle| \frac{\partial^2 H}{\partial Q_i^2} \middle| \psi_0 \right\rangle + Q_i^2 \sum_{k \neq 0} \frac{\left| \left\langle \psi_0 \middle| \frac{\partial H}{\partial Q_i} \middle| \psi_k \right\rangle \right|^2}{E_0 - E_k} . \tag{3.29}$$

In (3.29) ψ_0, ψ_k are the wave functions for the ground and kth excited states, respectively, of the undistorted molecule; E_k is the energy associated with ψ_k. The summation in the last term extends over all the excited states *including the continuum*.

Since ψ_0 for most molecules is nondegenerate and totally symmetric, and because Q_i changes the molecular shape,

$$\left\langle \psi_0 \middle| \frac{\partial H}{\partial Q_i} \middle| \psi_0 \right\rangle = 0 . \tag{3.30}$$

(3.30) is equivalent to assuming that the first-order Jahn-Teller (FOJT) (1937) distortion has already occurred. Thus the third term in (3.29) leads to a destabilization, whereas the last term which accounts for charge reorganization (since it includes ψ_k's) leads to stabilization. The net effect determines whether the idealized configuration of the molecule changes into another more (or less) stable structure by the distortion Q_i. The SOJT model then proceeds to evaluate this effect by imposing the drastic assumption that only the first low-lying excited state of appropriate symmetry has a dominant contribution to the infinite sum over the excited states. This approximation has been examined by Bamzai and Deb (1978), and a relation between the SOJT model and the highest occupied molecular orbital (HOMO) postulate (see later in this section) is indicated.

Since the SOJT theory is based on MO symmetry considerations, sometimes it is difficult to apply to molecules possessing almost no symmetry. Sometimes orbital sequence is also difficult to state precisely.[8] Although the SOJT theory can be extended to the excited states, it cannot be applied to the internal rotation about a single bond.

In case ψ_0 belongs to a degenerate energy level, the First-Order Jahn-Teller effect (FOJT) (see also Aronowitz, 1976; Englman, 1972) has to be considered. The effect is to distort such molecules into a lower symmetry. In the case of linear molecules, however, the Renner-Teller effect (Renner, 1934) takes place.

Coulson and Strauss (1962), as well as Coulson and Deb (1969) have examined the FOJT effects based on the force formulation of the effect due to Clinton and Rice [(1959); see also Clinton (1960)]. The distortion in VCl_4 has been studied, and the numerical results are in good agreement with experiment (Coulson and Deb, 1969).

Molecular geometry models based on energetics have also been formulated by Takahata *et al.* [(1971); see also Schnuelle and Parr (1972)] and Liebman (1974). Extensions to the Walsh model have been proposed by Gimarc (1970, 1971, 1979), Buenker and Peyerimhoff (1972, 1974), and Stenkamp and Davidson (1973). Coulson and Deb (1971) have provided a reinterpretation of the Walsh diagram on the basis of the Hellmann-Feynman theorem.

In the Hartree-Fock MO approximation, the Hellmann-Feynman force on nucleus A is as given by (3.2)

$$\mathfrak{F}(\mathbf{X}_A) = \mathfrak{F}^n(\mathbf{X}_A) + \mathfrak{F}^e(\mathbf{X}_A) \tag{3.2}$$

$$= -z_A \sum_{B \neq A} z_B \frac{\mathbf{R}_{AB}}{R_{AB}^3} + z_A \sum_i \lambda_i \mathfrak{F}_{Ai} , \tag{3.31}$$

where $\mathfrak{F}_{Ai}$ is the orbital contribution to the force

$$(\mathfrak{F}_{Ai} = \langle \phi_i | \mathbf{f}_A | \phi_i \rangle) .$$

Integrating $\mathfrak{F}_{Ai}$ over the displacement of the nucleus A, the electronic energy can be written as a simple sum of orbital contributions. The change in electronic energy obtained by such a procedure corresponds with that obtained directly from the Hartree-Fock method, if the exact Hartree-Fock orbitals are used throughout the displacement. Thus, the electronic part of the energy is expressible as a sum of orbital contributions, in principle. This is not the case with the conventional formula of the Hartree-Fock theory.

Coulson and Deb show that for a triatomic molecule AH_2, with apex angle α and A-H length λ, the total energy relative to linear form is

$$E(\alpha) = 2 \sum_i^{\text{occ.}} w_e^i(\alpha) + \left(\operatorname{cosec} \frac{\alpha}{2} - 1 \right) / 2 . \tag{3.32}$$

The first term in (3.32) represents the change in the electronic energy and the second term that in the nuclear-nuclear repulsion energy. $w_e^i(\alpha)$ is the work done in bending a molecule against the electron-nuclear attractive forces generated by the single-particle density in the ith occupied MO.

$$w_e^i(\alpha) = \lambda \int f_\perp^i d\alpha . \tag{3.33}$$

The correlation diagram for $w_e^i(\alpha)$ has been plotted, and agreement with the Walsh diagram is obtained. This work explains why, for many molecules, a plot of Hartree-Fock eigenvalues against a valence angle can be used for geometrical interpretations, as has been done by many workers [see, for example, Buenker and Peyerimhoff, 1974].

The highest occupied molecular orbital (HOMO) model (Deb, 1974, 1975; Deb *et al.*, 1974, 1976) considers the orbital contributions to the force acting on the terminal nuclei. The exact transverse force is

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[8] While applying the SOJT model, one takes the orbital sequence from experimental or theoretical results. Thus the success of the SOJT model seems to reflect the internal consistency of the MO formulation.

$$\mathfrak{F}_t(\mathbf{X}_A) = z_A \sum_i \lambda_i \mathfrak{F}_{Ai}^{(t)} - z_A \sum_{B=\neq A} \frac{z_B \mathbf{R}_{AB}^{(t)}}{R_{AB}^3}$$

The HOMO postulate (Deb, 1974) states that the gross equilibrium geometry is governed mainly by the behavior of the HOMO. If the HOMO is insensitive with regard to a valence angle, the angular behavior of the next lower MO, if sensitive, will determine the shape; if this MO is also insensitive, then the next lower MO is to be examined, and so on. In the case when the HOMO and the MO next to HOMO cross each other in energy and have opposite influences on the valence angle, the net effect of these MO's is to be considered. The HOMO postulate, in conjunction with Hellmann-Feynman theorem, has been remarkably successful in answering problems dealing with all *static* aspects of molecular geometry. The validity of its geometrical predictions has further been tested by intermediate neglect of differential overlap (INDO) and complete neglect of differential overlap (CNDO/2) calculations on a number of new interesting molecules (Deb *et al.*, 1977; Deb and Mahajan, 1981; Mahajan and Deb, 1981a, b). For the 17 quixotic hypothetical molecules studied by Deb and Mahajan (1981)—HCLi, HBBe, $HBLi^-$, HCB, HNBe, HNB^+, HBB^-, $NaHLi^+$, LiB_2^+, $MgBe_2$, LiB_2^-, MgB_2, LiH_3^{2+} (unstable), H_3O^-, CH_5^-, HBO_2^{2+} (unstable), HBF_2^{2+} (unstable)—seven current molecular geometry models were examined, viz., Mulliken-Walsh, VSEPR, HOMO postulate, ESF (see later), SOJT, Takahata *et al.*, and Liebman's models. The HOMO postulate was found to be the most successful, having only one exception ($NaHLi^+$), whereas the Mulliken-Walsh model stands next with only three exceptions (HNB^+, $NaHLi^+$, HBF_2^{2+}). However, the HOMO postulate has not been derived from an *a priori* quantum-mechanical basis, although some reasoning has been proposed (Deb, 1975). This reasoning in terms of electron relaxation has been tested with INDO wave functions for BeH_2, but an unequivocal answer could not be obtained (Mahajan and Deb, 1981c).

Nakatsuji (1973) has also proposed a versatile electrostatic force (ESF) theory which can be applied to a variety of molecular phenomena, such as shapes (Nakatsuji, 1973, 1974; Nakatsuji *et al.*, 1973), vibrational force constants (Nakatsuji *et al.*, 1973), chemical reactions (Nakatsuji, 1973a, 1974a; Nakatsuji *et al.*, 1973), and long-range interactions (Nakatsuji and Koga, 1974; Koga and Nakatsuji, 1976). Here we outline the essence of their work; the details may be found in a recent review by Nakatsuji and Koga (1980).

If $\{\chi_r\}$ is the atomic basis set, P_{rs} is the bond order between χ_r and χ_s, the force $\mathfrak{F}(\mathbf{X}_A)$ is rewritten as

$$\mathfrak{F}(\mathbf{X}_A) = z_A \left\{ \sum_{r,s} P_{rs} \langle \chi_r | \mathbf{f}_A | \chi_s \rangle - \sum_{B=\neq A} z_B \frac{\mathbf{R}_{AB}}{R_{AB}^3} \right\}, \tag{3.34}$$

where

$$\mathbf{f}_A = \frac{\mathbf{r}_A}{r_A^3}. \tag{3.35}$$

The single-particle density is taken as

$$\rho(\mathbf{r}) = \sum_{rs} P_{rs} \chi_r(\mathbf{r}) \chi_s(\mathbf{r}). \tag{3.36}$$

The Hellmann-Feynman force is then partitioned into three parts, similar to the earlier orbital partitioning that was proposed by Bader: The atomic dipole (AD) force comes from the one-center integrals; the exchange (EC) force comes from the net exchange force integrals [which represent the *net* attractive (or repulsive) force due to the accumulation (or depletion) of electron density in the overlap region], the extended gross charge (EGC) force which constitutes the rest of the force. Thus

$$\mathfrak{F}_A = \mathfrak{F}_A^{AD} + \mathfrak{F}_A^{EC} + \mathfrak{F}_A^{EGC}. \tag{3.37}$$

The AD, EC, and EGC forces can be written in terms of $\{\chi_r\}$, $\mathbf{f}_A$, and P_{rs}.

One may employ the point-charge approximation for the integrals in the EGC force,

$$\left\langle \chi_{sB} \left| \frac{\mathbf{r}_A}{r_A^3} \right| \chi_{sB} \right\rangle \simeq \frac{\mathbf{R}_{AB}}{R^3}, \tag{3.38}$$

and the Mulliken approximation for the three-center integrals $\langle \chi_{rB} | \mathbf{f}_A | \chi_{sC} \rangle$, where $B, C \neq A$ and $r \neq s$,

$$\langle \chi_{rB} | \mathbf{f}_A | \chi_{sC} \rangle$$
$$= \tfrac{1}{2} S_{rBsC} (\langle \chi_{rB} | \mathbf{f}_A | \chi_{rB} \rangle + \langle \chi_{sC} | \mathbf{f}_A | \chi_{sC} \rangle), \tag{3.39}$$

where S_{rBsC} is the overlap between χ_{rB} and χ_{sC}. The approximate[9] EGC force thus obtained is called the gross charge (GC) force.

The ESF model then proceeds to consider the role of each of these forces in determining geometry, the stable balance of these yielding equilibrium. A set of guidelines, based on the force integrals on A in A-A and A-H pairs, has been given (Nakatsuji, 1973a) in order to assess the relative importance of these forces, and the geometries of ground and excited states are rationalized (Nakatsuji and Koga, 1980) on the basis of these. The ESF model can deal with static and dynamic changes in molecular geometry, and can make both qualitative and quantitative geometry predictions.

By virtue of their use of single-particle density, the force models of molecular geometry have proved to be more useful and versatile than almost all the energetic models proposed earlier. Although the force models bring forth their own difficulties, not completely resolved at present, their enhanced visual appeal makes their theoretical foundations more transparent and sound.

The above discussions on chemical binding and molecular geometry (Secs. III.A and III.B) pave the way to a study of intermolecular forces and chemical reactivity. We shall now proceed to discuss the former as a prelude to a study of the latter. However, it should be realized that chemical binding, molecular geometry, intermolecular forces, and chemical reactivity represent merely an artificial partitioning of the broad problem of molecular interactions and that one hopes that some day we should have a unified theory that incorporates all these problems in a simple, coherent, and rigorous manner.

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[9] This approximation is not to be used for rigorous ESF calculations.

C. $\rho(\mathbf{r})$ and intermolecular forces

Because of the small changes being introduced by the interaction, until the repulsive part of the potential surface is reached, the intermolecular force problem can be effectively tackled via the perturbation method. However, in the region where the overlap of the wave functions of the two molecules is not negligible, the theory poses the following difficulty: The unperturbed Hamiltonian H_0 (this is the Hamiltonian for the separated molecules so that it considers that part of the total potential which is due to interactions of electrons with their "own" nuclei and with the other electrons in their "own" molecule) is not invariant with respect to the antisymmetrizing operator, A. Now

$$AH - HA = 0 . \tag{3.40}$$

However, from

$$H = H_0 + V , \tag{3.41}$$

$$AH_0 - H_0A = VA - AV , \tag{3.42}$$

of which neither side is zero. Thus we have an inequality between an apparently zero-order expression and an apparently first-order expression, which shows that any simple perturbation theory in which various terms are considered order by order is bound to fail. Chipman *et al.* (1973) have discussed various attempts to overcome this problem.

In the energy approach, the problem is studied by comparing the calculated energies of the two separated molecules and of the "supermolecule" comprising the two species. Ingenious methods such as the introduction of second quantization and diagrammatic perturbation theory, etc., have been discussed in a review article by Stamper (1975).

In their study of two H atoms approaching each other, Hirschfelder and Eliason (1967) verified an earlier conjecture of Feynman (1939) that the long-range van der Waals attraction arises due to a dipole-dipole force. They were able to obtain an accurate value of this force (R^{-7} term) in a perturbative treatment of the H-H interaction. Contour maps of $\Delta\rho(\mathbf{r})$ for H_2 show (Bader and Chandra, 1968) pictorially that at $R \sim 8$ a.u., the atomic distributions are inwardly polarized due to a dipole moment (of order R^{-7}) induced on each atom; each nucleus experiences a binding force due to its own distorted charge density.

A major difficulty in applying the Hellman-Feynman theorem to the study of intermolecular forces is the lack of reasonably good $\rho(\mathbf{r})$ for such systems. Since electron correlation is expected to play an important role, one should really employ electron densities of beyond Hartree-Fock accuracy. Thus, such applications have been restricted to very small systems. Interatomic forces probably "reflect the state of the art in a more candid way."

Chandra and Sebastian (1976) have partitioned ρ as

$$\rho = \rho_{\mathrm{H}} + \rho_{\mathrm{He}} + \Delta\rho \tag{3.43}$$

and have studied the $\mathrm{H} \cdots \mathrm{He}^+$ interaction leading to the lowest two states of the HeH^+ ion. The behavior of the f^{ρ}_A (charge equivalent of the electronic force along the bond on the nucleus A by charge density; see Sec. III.A.4) is studied as a function of R,[9(a)]

$$f^{\rho}_A = R^2 \int \rho(\mathbf{r}) \frac{z_A}{r_A^3} d\mathbf{r} . \tag{3.44}$$

Within the ESF framework, Nakatsuji and Koga (1974) have studied the long-range interaction between two atoms. At large R, the EC force varies as e^{-2R} and can hence be neglected in comparison to the $1/R$ varying terms. The force on A thus arises from the AD and EGC contributions,

$$\mathfrak{F}_A^{\mathrm{AD}} = z_A \int \rho_1(A) f_{A1}^{(0)} d\tau_1 , \tag{3.45}$$

$$\mathfrak{F}_A^{\mathrm{EGC}} = z_A \left\{ \int \rho_1(B) f_{A1}^{(1)} d\tau_1 - \frac{z_B}{R^2} \right\} , \tag{3.46}$$

$$\rho_1 = \rho_1(A) + \rho_1(B) .$$

In a perturbative approach, the following two results can be obtained:

$$\mathfrak{F}_A^{(n)}(\mathrm{AD}) = 0 \quad \forall\, n \quad \text{if } A \text{ is a bare nucleus} . \tag{3.47}$$

$$\mathfrak{F}_A(\mathrm{EGC}) = 0 \quad \text{at large } R \text{ if } \rho_1(B) \text{ is spherically symmetric and } B \text{ is a neutral atom} . \tag{3.48}$$

Nakatsuji and Koga (1974) have calculated the leading terms of the interaction, obtaining excellent agreement with the corresponding energy calculation. Nakatsuji *et al.* (1973) have also studied the intermediate range interaction between two initially planar methyl radicals to form ethane.

Koga and Nakatsuji (1976) have cleared an earlier paradox (Coulson and Hurley, 1962; Hirschfelder and Coulson, 1962; Steiner, 1973) concerning the application of the Hellmann-Feynman theorem to long-range forces: There were contradictions about whether certain types of wave functions satisfied the theorem or not. The authors demonstrated that the proper choice of coordinate system ensures satisfactory forces on application of the theorem. The relative (R) system (in which nuclei and electrons of each subsystem are measured from an origin fixed in each subsystem) is amenable for application of the theorem, since the nth order force is equal to the derivative of the nth order perturbation energy and wave functions and their derivatives up to order n determine the force up to order $2n+1$. Thus the force treatment of long-range interactions is as accurate as the energetic (perturbative) treatment.

In an alternative approach, Gordon and Kim (1972; Kim and Gordon, 1974) have proposed a model, involving $\rho(\mathbf{r})$, which describes satisfactorily the intermolecular potentials between closed-shell systems, at shorter distances out to the potential minima, but which fails to give an adequate description of the entire potential curve. Their calculation of energy is based on three main approximations: First, it is assumed that no rearrangement or distortion of the separate atomic densities takes place when the atoms approach each other. Thus this undistorted distribution will not describe a situation where a strong chemical bond is formed. Second, the Coulomb interaction

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[9(a)] Note that z_A within the integral sign in Eq. (3.44) denotes a coordinate, *not* a nuclear charge.

between all charges are calculated using additive electron density. The electronic kinetic energy, exchange energy, and correlation energy are evaluated using the uniform electron gas approximation. Last, atomic Hartree-Fock wave functions are used for constructing $\rho(\mathbf{r})$.

Using this model, Kim and Gordon (1974a) have evaluated the interactions of rare gas atoms with alkali and halide ions. The calculated potential curves agree well with available experimental results. However, the model fails at larger distances, since induction forces are not included. Similar calculations on ion-ion interaction potentials (Kim and Gordon, 1974b) yield molecular bond energies, bond lengths, and vibrational frequencies in agreement with experimental data.

The method works quite well for larger systems. Rae (1973) has demonstrated that an additional spurious electron self-energy term is the reason the calculation for He···He is not very satisfactory. On correction of this error and inclusion of dispersion terms, Rae has obtained potential curves for all inert gas pairs.[10] Lloyd and Pugh (1974) have improved on the Ar···Ar and Kr···Kr curves by employing the electron gas approximation to only the valence electron density.

Clugston (1978) critically discusses the assumptions in the Gordon-Kim model and assesses the relative performance of the model and its various modifications. Specifically, there are certain problems associated with writing the supermolecular density as a sum of undistorted spherical atomic densities. Davidson (1976) points out that this is not the correct zero-order formula and that the kinetic energy will therefore show erratic behavior. Kolos and Radzio (1978) have used the correct zero-order density, containing additional terms besides the superposed atomic densities, and have obtained better values for both kinetic and potential energies. However, note that classically two such atomic densities lead to intermolecular repulsion at all internuclear distances (Sec. III.A.1). The fact that the Gordon-Kim model does yield an attractive part of the intermolecular potential energy curve is due to the manner in which the model handles the exchange-correlation energy density functional. This ensures an attractive potential at large R. In fact, correlation energy contributes nearly 85% to the well depth for Ne···Ne, Ar···Ar, Kr···Kr, and Xe···Xe, while the He···He potential energy curve is made too negative with a rather deep minimum! However, this correlation energy is of the short-range type. Hence, for all other systems potential curves are too high for $R>R_e$. But the repulsive part of the potential curve is very well described. Further, the He···He results are considerably improved if the dispersion contribution is included for large R and the correlation energy for short R (Clugston, 1978).

Kim (1975) has also studied the nonadditive three-body interactions of rare gas atoms. Using again the assumption that the supermolecular density is equal to the sum of the separated atomic densities, the nonadditive interaction energies for He_3, Ne_3, Ar_3, Kr_3 at small and intermediate distances have been calculated and found to be very small (Kim, 1975a). At intermediate and large distances these energies are few percent or less than the total interaction over most internuclear separations (Kim, 1975b).

D. $\rho(\mathbf{r})$ and chemical reactivity

In order to explain the reactive properties of molecules various concepts such as atomic charges (Julg, 1975), bond orders, free valences, frontier electron densities (Fukui, 1971, 1976; Fleming 1976), and localization energies have been proposed from time to time.

In the population analysis scheme of Mulliken (1955), the atomic charges are expressed in terms of the coefficients of the linear combination of atomic orbitals (LCAO) forming the total wave function. Such descriptions have been fairly successful. However, the populations are dependent on the mathematical form of the wave function, which is obviously a drawback. Politzer and Harris (1970), as well as Bader *et al.* (1971), have proposed that the atomic charge on atom r be $(z_r - Q_r)$, where

$$Q_r = \int_r \rho(\mathbf{r})d\mathbf{r}\,. \tag{3.49}$$

In (3.49) the integration is performed over a region r associated with the rth atom. In this case, a description in a different basis set will also predict the same atomic charges. Thus by introducing $\rho(\mathbf{r})$, an earlier ambiguity is removed. However, the charge defined by (3.49) is assumed to be a point charge centered at the atom [although $\rho(\mathbf{r})$ does account for the "smeared" electron distribution].

Bonaccorsi *et al.* (1970) introduced the concept of molecular electrostatic potential, $V(\mathbf{r})$, generated in the 3D space of the molecule:

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}\,. \tag{3.50}$$

In a series of papers (Bonaccorsi *et al.*, 1970–1972, 1974, 1975; Berthier *et al.*, 1972; Petrongolo and Tomasi 1973; Scrocco and Tomasi, 1973, 1978; Ghio and Tomasi, 1973), they used this idea to study the reactive properties of several molecules, including those of pharmacological interest (Petrongolo and Tomasi, 1975; Pullman and Courriere, 1973). This has, in fact, stimulated a great deal of work by many researchers.

The first term on the right-hand side of (3.50) is the contribution to $V(\mathbf{r})$ from the nuclei, whereas the second term is the contribution from the electronic distribution to the potential at $\mathbf{r}$. $\pm QV(\mathbf{r})$ is the electrostatic interaction energy between the undistorted molecule and the charge $\pm Q$ located at $\mathbf{r}$; hence $\pm QV(\mathbf{r})$ is the first-order term in a perturbative treatment of the total interaction energy. Thus polarization, charge transfer, and exchange effects which are significant

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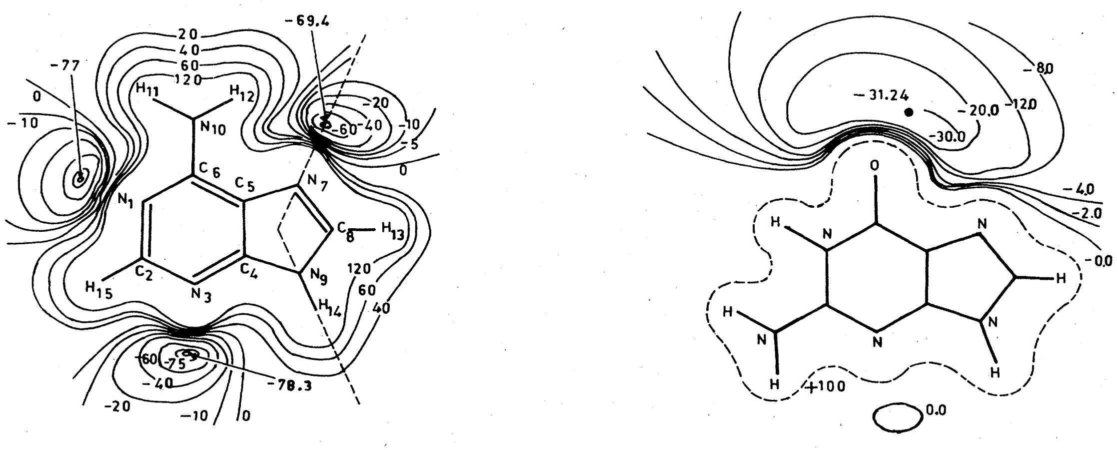
[10] Since these approaches start off with isolated neutral atoms, interesting questions such as the occurrence of the maximum in the interaction (Matsen and Scott, 1966) between He ($1s\,2s$; ^3S) and He ($1s^2$; ^1S) remain unanswered.

factors when the two distributions are fairly close are not accounted for in the $V(\mathbf{r})$ given by (3.50). Hence $V(\mathbf{r})$ is more useful for studying the earlier stages of interaction.

When isopotential contours of $V(\mathbf{r})$ are drawn for a particular molecule, the reactive properties may be studied in a *qualitative* fashion by examining regions of negative potential (possible sites of electrophilic attack) versus regions of positive potential (these may not necessarily reflect sites of nucleophilic attack since they may arise due to hydrogen atoms or high nuclear charges). The reliability of the results rests on two factors: the accuracy of $\rho(\mathbf{r})$ and the accuracy to which the integral in (3.50) is computed.

The $V(\mathbf{r})$ concept has been applied with promising results to many systems, an example being nucleic acid bases (Bonaccorsi *et al*, 1972b; Pullman and Courriere, 1973; Pullman and Pullman, 1973). Such molecules are particularly interesting since they possess more than one possible site for protonation or electrophilic attack, thus providing a good test as to whether the isopotential curves of $V(\mathbf{r})$ can distinguish among different positions of attack. Molecules with similar charge distributions on the protonating site frequently offer very different behavior, e.g., in both adenine and guanine (Fig. 3) N_7 is the most charged among the pyridine-type nitrogens; however, alkylation reactions occur preferentially at N_7 and O_6 of guanine, but at N_1 or N_3 of adenine. The isopotential maps for an approaching unit positive charge account for this, and they are the first to do so unambiguously. The map of adenine constructed by using *ab initio* wave functions shows strong attraction for an external positive charge at N_1 and N_3. The map for guanine in the CNDO/2 procedure, although less reliable, nevertheless shows the difference in behavior between the two compounds.

The effects of polarization and charge transfer have been studied by Pullman (1973) for the peptide bond with the conclusion that these effects leave the overall reactivity pattern unchanged. However, for large molecules with several competing reactive sites, it seems pertinent to investigate the effects of interaction at one site on the reactivity of another, since the interaction produces changes in the charge distribution that may affect the other fragments of the molecule. This problem has been tackled by Bartlett and Weinstein, (1975; Weinstein, 1975) via a double perturbation theory to describe the simultaneous attack of a large molecule by two or more charged species. The effects of the interaction with a neutral molecule on the reactivity of adenine were also reproduced (Weinstein, 1975) successfully by this method. Recently Chang *et al.* (1976) have formulated a multiple perturbation method for the treatment of molecular reactivity to describe the simultaneous interaction of a molecule containing several reactive sites with a second molecule and a point charge. The modification of the reactivity properties of the main molecule by electrostatic interaction, polarization, dispersion, and correlation corrections due to the presence of the second molecule is identified from the effects of these corrections on the interaction energy with the point charge. The method is applied to a simple molecule containing two reactive sites, e.g., formyl fluoride HCOF, interacting with HF at hydrogen-bond distances. The results are in agreement with the "supermolecule" LCAO SCF calculations, indicating that the electron redistribution is adequately represented by the perturbation method. These new approaches have been applied to study reactivity patterns of the tryptamines (Green *et al.*, 1976). A list of molecules for which maps of $V(\mathbf{r})$ have been characterized is given in a review by Politzer and



(a) (b)

FIG. 3. Isopotential maps (in kcal mole^{-1}) for the approach of a unit positive charge in the planes of (a) adenine (using an *ab initio* wave function), and (b) guanine (using a CNDO wave function). (Reproduced from Pullman and Pullman, 1973. Courtesy, Butterworths and Company, London).

Daiker (1980).

In an interesting work Srebrenik *et al.* (1974) have related the molecular binding energy to the electrostatic potential. Let $V(\mathbf{R},\mathbf{R}'_\alpha)$ denote the electrostatic potential generated at $\mathbf{R}'_\alpha$ due to electron density and nuclear distribution denoted by $\mathbf{R}$, viz.,

$$V(\mathbf{R},\mathbf{R}'_\alpha)=\int \frac{\rho(\mathbf{R},\mathbf{r})}{|\mathbf{r}-\mathbf{R}'_\alpha|}\,d\mathbf{r}+\sum_{\beta\neq\alpha}\frac{z_\beta}{|\mathbf{R}_\beta-\mathbf{R}'_\alpha|}\,. \tag{3.51}$$

The force exerted on nucleus α will be the gradient of this potential at $\mathbf{R}'_\alpha=\mathbf{R}_\alpha$:

$$\mathbf{F}_\alpha(\mathbf{R}_\alpha)=-z_\alpha[\nabla'_\alpha V(\mathbf{R},\mathbf{R}'_\alpha)]_{\mathbf{R}'_\alpha=\mathbf{R}_\alpha}\,. \tag{3.52}$$

The difference in energy between two configurations $\mathbf{R}_1,\mathbf{R}_2$ is the electrostatic work done in moving the nucleus α from its position in $\mathbf{R}_1$ (say $\mathbf{R}_{1\alpha}$) to its position in $\mathbf{R}_2$ (say $\mathbf{R}_{2\alpha}$), through the gradient of the electrostatic potential, itself a function of $\mathbf{R}$,

$$\Delta E=-z_\alpha\int_{R_{1\alpha}}^{R_{2\alpha}}[\nabla'_\alpha V(\mathbf{R},\mathbf{R}'_\alpha)]_{\mathbf{R}'_\alpha=\mathbf{R}_\alpha}\,d\mathbf{R}_\alpha\,. \tag{3.53}$$

Thus the electrostatic view of chemical binding provides a conceptual link between ΔE and V.

In the ESF theory proposed by Nakatsuji and coworkers it was recognized that the AD and EC forces are the dominant factors for determining molecular structure. Chemical reactivity is also tackled by similar considerations. The dynamic behavior of the electron cloud during a chemical reaction is expected to be an important factor giving rise to the internal forces that work to resist or accelerate the process. When the electron cloud precedes the nuclear motion, the system receives a force that accelerates the process and vice versa. It is possible to relate this electron reorganization to the AD, EC, and EGC forces. The electron density in the atomic region of nucleus A gives rise to the AD force on A, and that in the A-B bond region gives rise to the EC force on A. The electron density in the other regions mainly shields the other charges (EGC force) and does not have the electron preceding or following character (except in the case of ionic reactions where this character would also manifest itself in the EGC force).

Starting from the Hellmann-Feynman and Integral Hellmann-Feynman theorems, the guiding principle obtained for chemical reactions is as follows (Nakatsuji, 1973a; Nakasuji and Koga, 1980): If the electron-cloud preceding occurs at the configuration α, the nuclear arrangement will proceed in the Q direction, but if the electron-cloud following occurs, the system will rearrange in the $-Q$ direction.[11] Further, if the energy change is known to be monotonous throughout the process between i and f, the occurrence of the electron-cloud preceding means that the configuration f is more stable than the configuration i and *vice versa*.

Thus for chemical reactions (Nakatsuji, 1973a), the interaction between reactants should cause an increase in electron density in the region between the reactive sites of the reactants and at the same time must cause a decrease in electron density in the region of the old breaking bond. Nakatsuji *et al.* (1973) have reported the study of two approaching methyl radicals to form the dimer, viz., ethane molecule. For other radical and ionic reactions, such as the formation of NH_3 and H_3^+O, see Nakatsuji *et al.* (1978) and Koga *et al.* (1979).

In passing, it is pertinent to mention that the energetic models such as the SOJT (Pearson, 1971, 1972, 1976) model, Frontier Molecular Orbital theory (Fukui, 1976; Fleming, 1976), Woodward-Hoffman rules (Woodward and Hoffmann, 1970), and earlier works of Dewar (1966) and Zimmerman (1966) have met with considerable success in the study of chemical reactions. These models are based on MO symmetry considerations for the two approaching systems. Recently McIver and co-workers (McIver and Stanton, 1972; McIver and Komornicki, 1972; McIver, 1974) have examined the role of the transition state symmetry and structure in the interpretation of chemical reactions. Thus the application of group theory provides a means of classifying geometries and normal vibrations, reduces computational labor, and sometimes even provides "selection" rules for the allowed structures of the transition states. In contrast, models such as the electrostatic potential method, as well as the ESF theory, deal with $\rho(\mathbf{r})$ and regard the changes occurring in it to be of primary importance in the study of chemical reactivity.

We shall now discuss briefly some interesting works dealing with $\rho(\mathbf{r})$ that shed light on properties such as transferability, quadrupole coupling constants, correlation energy, etc.

E. $\rho(\mathbf{r})$ and some miscellaneous properties

1. Transferability

One of the most fascinating observations in chemistry is the fact that fragments or groups of fragments in molecules have an almost fixed characteristic set of properties, e.g., dipole moment, polarizability, reactivity, etc., in differing chemical environments.[12] This retention of properties has recently been justified by the virial fragment concept, based on rigorous quantum-mechanical foundations (Sec. II.B).

It is possible to state the condition to be satisfied if a fragment is to possess an identical energy and population in two different systems in electrostatic equilibrium. The requirement that $E(\Omega)$ be the same implies that $T(\Omega)$ and $V(\Omega)$ be the same in both systems.

$$V(\Omega)=V^i(\Omega)+V^0(\Omega)\,, \tag{3.54}$$

where $V^i(\Omega)$ and $V^0(\Omega)$ are the virial of forces originating within the fragment and the virial of forces exerted on the fragment by the nuclei and charge density outside the fragment. Since the fragment is identical in all respects, the inner virial $V^i(\Omega)$ will be the same. Hence the sum of the virials of all the external forces exerted on the fragment (the individual contributions will necessarily be different) must be identical in the two systems.

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[11] The nuclear displacement coordinate of a system from initial (i) to final (f) states is designated as Q, whereas α is the intermediate nuclear configuration between i and f.

[12] For an interesting discussion on transferability of molecular shapes, see Deb (1974, 1975).

Bader and co-workers (Bader and Beddall, 1972; Bader *et al.*, 1973) have observed that kinetic and total energies of fragments remain unaltered when the fragment electronic charge remains so. Thus the extent to which fragment properties remain unchanged in different systems is determined by the extent to which $\rho(\mathbf{r})$ remains unchanged. This implies that $T(\Omega)$, $V(\Omega)$ are also conserved.

Tomasi and his co-workers (Bonaccorsi *et al.*, 1970, 1971b; Scrocco and Tomasi, 1973) have studied the contribution arising from various groups in the molecule to properties such as $\langle x\rangle$, $\langle y\rangle$, $\langle xy\rangle$, etc. The extent of variation of the terms among the set of molecules is a clue to the degree of conservation. An examination of such data shows a fair conservation of the electrostatic potential of CH_2.

Recently, Bonaccorsi *et al.* (1976,1977) have devised a method for obtaining a fairly accurate description [compared to the SCF generated $V(\mathbf{r})$] of the electrostatic potential $V(\mathbf{r})$ of a molecule which does not require a previous calculation of the molecular wave function. The molecule is considered to be composed of completely localized electron pairs, expressed in terms of LCAO models directly transferable from one molecule to another. They observe that the $V(\mathbf{r})$'s show a noticeable degree of transferability from one molecule to another.

2. Total energies, energy differences, correlation energies

Foldy (1951), Wilson (1962) and/Frost (1962) obtained expressions for the energies of atoms and molecules by visualizing a process in which $\rho(\mathbf{r})$ depends on a parameter λ which varies from 0 to 1, attaining the final value 1, as the nuclear charges get switched on from 0 to their final values; hence

$$H(\lambda)=T+\lambda^2\sum_{\alpha<\beta}\frac{z_\alpha z_\beta}{R_{\alpha\beta}}-\lambda\sum_{\alpha,i}\frac{z_\alpha}{r_{\alpha i}}+\sum_{i<j}\frac{1}{r_{ij}}, \tag{3.55}$$

$$\frac{\partial H}{\partial\lambda}=2\lambda\sum_{\alpha<\beta}\frac{z_\alpha z_\beta}{R_{\alpha\beta}}-\sum_{\alpha,i}\frac{z_\alpha}{r_{\alpha i}}. \tag{3.56}$$

Thus the electronic energy E_{el} is

$$E_{\mathrm{el}}=\sum_{\alpha<\beta}\frac{z_\alpha z_\beta}{|\mathbf{R}_\alpha-\mathbf{R}_\beta|}-\sum_\alpha z_\alpha\int_{\lambda=0}^{1}\int\frac{\rho(\mathbf{r},\lambda)}{\mathbf{r}_\alpha}d\mathbf{r}\,d\lambda. \tag{3.57}$$

The trouble with applying (3.57) to actual systems is that $\rho(\mathbf{r},\lambda)$ must be known throughout the range of integration.

Politzer and Parr (1974) prove

$$E=\frac{z^2}{2}\phi_0'-\tfrac{1}{2}\int_{z'=0}^{z}z'^2\left(\frac{\partial\phi_0'}{\partial z'}\right)_N dz', \tag{3.58}$$

where

$$\phi_0=\left(\frac{\partial\phi(\mathbf{r},z)}{dr}\right)_{r=0}=-\frac{1}{z}\int\frac{\rho(\mathbf{r}',z)d\mathbf{r}'}{\mathbf{r}'}. \tag{3.59}$$

In (3.59) $\phi(r,z)$ is the free-atom screening function which measures the screening of the nucleus by electrons in a spherically symmetric free atom of nuclear charge z,

$$\phi(r,z)=\frac{rV(r,z)}{z}, \tag{3.60}$$

where

$$V(r,z)=\frac{z}{r}-\int\frac{\rho(\mathbf{r}',z)d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}. \tag{3.61}$$

In (3.58) the path of integration for the second term is the isoelectronic series having N electrons and a nuclear charge ranging from zero to z.

For the case of molecules, the screening function ϕ_α is defined for each nucleus α, and an analogous expression for the energy of the molecule in terms of a property evaluated at its nuclei can be obtained:

$$E=\tfrac{1}{2}\sum_\alpha z_\alpha^2\phi_{\alpha,0}'-\tfrac{1}{2}\sum_\alpha\int_{z_\alpha'=0}^{z_\alpha}z_\alpha'^2\left(\frac{\partial\phi_{\alpha,0}'}{\partial z_\alpha'}\right)_N dz_\alpha'. \tag{3.62}$$

In (3.62),

$$\phi_{\alpha,0}'=\left(\frac{\partial\phi_\alpha}{\partial r_\alpha}\right)_{r_\alpha=0}, \tag{3.63}$$

where

$$\phi_\alpha(\mathbf{r}_\alpha,\lambda)=\frac{r_\alpha V(\mathbf{r}_\alpha,\lambda)}{\lambda z_\alpha}, \tag{3.64}$$

$$V(\mathbf{r}_\alpha,\lambda)=\frac{\lambda z_\alpha}{r_\alpha}+\sum_{\beta\neq\alpha}\frac{\lambda z_\beta}{|\mathbf{R}_\beta-\mathbf{r}_\alpha|}-\int\frac{\rho(\mathbf{r}',\lambda)d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}_\alpha|}. \tag{3.65}$$

Thus $V(\mathbf{r}_\alpha,\lambda)$ is the total molecular electrostatic potential evaluated at a point $\mathbf{r}_\alpha$ measured from nucleus α, and ϕ_α represents the screening of α by electrons and other nuclei.

There are three main formulas for computing energy differences:

$$\text{(i)}\quad \Delta\tilde{E}_{ed}=\frac{\langle\tilde{\psi}_B|H_B|\tilde{\psi}_B\rangle}{\langle\tilde{\psi}_B|\tilde{\psi}_B\rangle}-\frac{\langle\tilde{\psi}_A|H_A|\tilde{\psi}_A\rangle}{\langle\tilde{\psi}_A|\tilde{\psi}_A\rangle}, \tag{3.66}$$

the tilde indicating that the quantities are approximate.

$$\text{(ii)}\quad \Delta\tilde{E}_d=\int_A^B\frac{\left\langle\psi(\lambda)\left|\frac{\partial H}{\partial\lambda}\right|\psi(\lambda)\right\rangle}{\langle\psi(\lambda)|\psi(\lambda)\rangle}d\lambda. \tag{3.67}$$

Equation (3.67) is the integrated Hellmann-Feynman (Epstein *et al.*, 1967) formula; λ is some parameter, when $\lambda=A$, $\psi=\psi_A$, and when $\lambda=B$, $\psi=\psi_B$. The principal drawback in $\Delta\tilde{E}_d$ is that $\psi(\lambda)$ is required to be known for the range of integration.

$$\text{(iii)}\quad \Delta E_1=\frac{\langle\psi_B|H_B-H_A|\psi_A\rangle}{\langle\psi_B|\psi_A\rangle}. \tag{3.68}$$

Equation (3.68) is the Integral Hellmann-Feynman formula, whose utility was recognized by Parr and co-workers (Parr, 1964; Kim and Parr, 1964; Kim, 1968; Parr *et al.*, 1968; Wyatt and Parr, 1965, 1966).

Kim and Parr (1964) showed

$$\Delta E_1=\Delta V_{nn}+\int\rho_{AB}H'd\mathbf{r}, \tag{3.69}$$

where $d\mathbf{r}$ is the configuration space volume element, ΔV_{nn} is the nuclear-nuclear repulsion energy difference for the two configurations,

$$\Delta V_{nn} = \sum_{\alpha<\beta} \frac{z_\alpha z_\beta}{R^B_{\alpha\beta}} - \sum_{\alpha<\beta} \frac{z_\alpha z_\beta}{R^A_{\alpha\beta}} , \tag{3.70}$$

$$H' = \sum_\alpha \frac{z_\alpha}{r^B_\alpha} - \sum_\alpha \frac{z_\alpha}{r^A_\alpha} , \tag{3.71}$$

and ρ_{AB} is the first-order spinless electron transition density,

$$\rho_{AB} = \frac{N}{S} \int \psi_B(1,2,\ldots,N)\psi_A(1,2,\ldots,N) d\mathbf{s}_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N , \tag{3.72}$$

S being the overlap integral.

The integrated Hellmann-Feynman theorem has been applied to the barrier to the internal rotation problem, one such example being the ethane molecule, tackled by Ruedenberg (1964).

In the viewpoint of the ESF theory proposed by Nakatsuji and co-workers, the dominant origin of the internal rotation barrier arises (Nakatsuji and Koga, 1980) from the behavior of $\rho(\mathbf{r})$ during the process of internal rotation. For example, in the case of ethylene, the orbital following and the resulting resisting force are the origin of planarity of the molecule. The same holds for the coplanarity of a wide range of doubly bonded hydrocarbons. Thus the orbital following and preceding are the origin of the rotational barrier and arise from the difference in interactions (i.e., difference in overlap effects) of the $p_\perp$ and $p_\parallel$ atomic orbitals (AO's) with the electron cloud of the rotor of another side (Nakatsuji and Koga, 1980).

Regarding the correlation energy, Lie and Clementi (1974) propose that E_c be calculated semiempirically in terms of a functional of the Hartree-Fock density $\rho(\mathbf{r})$:

$$E_c = \int \rho\varepsilon[\rho] dv . \tag{3.73}$$

They defined a modified density

$$\rho_m = \sum \bar{n}_i \rho_i , \tag{3.74}$$

where

$$\bar{n}_i = e^{-0.5(2-n_i)^2} ,$$

n_i being the occupation number of the ith orbital. The empirical expression for E_c is

$$E_c = \int 0.02096(1.2 + \rho_m^{1/3})^{-1} \rho_m^{4/3} dv + \int 0.02096 \ln(1 + 2.39 \rho_m^{1/3}) \rho_m dv . \tag{3.75}$$

This form ensures that computed values of the atomic correlation energies agree with experiment, both for closed- and open-shell states.

The functional is then used to calculate E_c for first-row hydrides, as well as homonuclear diatomics of the first-row atoms. They observe an improvement with experiment in binding energies and dissociation energies, over the corresponding Hartree-Fock values when Hartree-Fock functions with proper dissociation were employed.

Kim and Gordon (1974) have calculated kinetic, exchange, correlation, and total energies for several atoms within the electron gas formalism. A comparison with values obtained from Hartree-Fock calculations shows a characteristic accuracy of 10%.

3. $X\alpha$ scattered wave method

Slater and co-workers (Slater, 1965, 1974, 1978; Johnson, 1966, 1973; Slater and Johnson, 1972; Johnson and Smith, 1972) proposed an alternative to the LCAO-MO method. Based on the scattered wave method in solids (Korringa, 1947; Kohn and Rostoker, 1954), the $X\alpha$ method aims to solve the Fock equations

$$\hat{F}\phi_i = \lambda_i \phi_i , \tag{3.76}$$

where

$$\hat{F} = T + \hat{V}_c + \hat{V}_E . \tag{3.77}$$

$\hat{V}_c$ is evaluated classically as the potential due to the nuclear charges and the electron density $\rho(\mathbf{r})$, given by the usual expression

$$\rho = \sum_i N_i \phi_i^* \phi_i ,$$

where ϕ_i is the ith occupied spin orbital and N_i equals unity.

Dividing the $\rho(\mathbf{r})$ into terms due to the up and down spins, the local exchange terms in the $X\alpha$ approximation are given by

$$\hat{V}_E \uparrow = -3\alpha \left[\frac{3}{8\pi} \rho\uparrow\right]^{1/3} \tag{3.78}$$

and a similar expression for the spin-down term.

In order to solve Eq. (3.76) numerically, the molecule is divided into a number of regions: atomic region of nonoverlapping spheres, interatomic region between the atomic spheres and an outer sphere, and extramolecular region outside the sphere.

In the first region, V_E is spherically averaged, in the second it is assumed constant (equal to the volume average), and in the third it is spherically averaged. Starting from the Herman-Skillman (1963) free-atom potentials, the spin orbitals are found by an iterative scheme. This is the so-called muffin-tin approximation; α is an adjustable parameter, of value ~ 0.7.

The total energy $E_{X\alpha}$ is obtained by the Slater statistical total energy, and it dissociates correctly to the separated atoms. The eigenvalues of the virtual orbitals are calculated for a field of $(N-1)$ electrons and are more appropriate for the description of excited states. The method gives a good description of one-electron properties and has been successfully applied to large molecules, including those of biological interest. It does, however, have its disadvantages, viz., poor prediction of molecular geometries where lone pairs are involved, a poor description of barriers to rotation for certain molecules, and inadequate description of π-electron systems. Johnson *et al.* (1973) have given a review of the method, while Slater (1973) has offered suggestions to remove the weaknesses.

While the errors due to the muffin-tin approximation can be quite large, e.g., for large planar molecules, it has been emphasized (Connolly, 1977) that these errors are not in the $X\alpha$ method itself. Various modifications have been suggested to compensate for these errors [for a discussion, see Costas and Garritz (1979)], and the exact relation between the muffin-tin approximation and non-muffin-tin corrections has been discussed by Danese and Connolly (1974; Danese, 1974). The non-muffin-tin results for H_2, C_2, N_2, and CO are considerably improved over the muffin-tin ones, although Danese (1977) pointed out that since neither the $X\alpha$ nor the local density-functional theory describes all atomic multiplets, there may be problems in describing bond-breaking processes by these methods. However, Harris and Jones (1979) have calculated the binding energy curves for low-lying states of the $3d$-dimers, K_2 to Cu_2. Overall, they obtained reasonably good agreement with spectroscopic data and attributed the discrepancies in the calculated curves to an incorrect description of s-d transfer which is inherent in the local spin-density-functional for exchange-correlation energy which these authors employed. In the case of chemisorption of oxygen on a nickel (001) surface, non-muffin-tin corrections lead to a good description of the photoemission spectrum and the interaction energy of oxygen on the metal surface (Li and Connolly, 1977).

There are ways of avoiding altogether the numerical solution of $X\alpha$ equations, thus bypassing the muffin-tin approximation. One such way is the *discrete variational method* (see Baerends and Ros, 1975, 1978; Rosen *et al*, 1979) where an LCAO-type strategy is adopted. The one-electron wave functions $\{\phi_i\}$ are expanded as linear combinations of suitably chosen analytic basis functions $\{\chi_j\}$,

$$\phi_i = \sum_j \chi_j c_{ji} \,. \tag{3.79}$$

The method requires the selection of a discrete set of appropriate sample points $\mathbf{r}_k$, with associated weights w_k, followed by minimization of the error matrix

$$\Delta_{ij} = \sum_k w_k \phi_i^*(\mathbf{r}_k)[\hat{F} - \lambda]\phi_j(\mathbf{r}_k) \,, \tag{3.80}$$

where $\hat{F}$ is the one-electron Hamiltonian. This gives the secular equation

$$|\hat{F}_{ij} - \lambda S_{ij}| = 0 \,, \tag{3.81}$$

where

$$\hat{F}_{ij} = \sum_k w_k \chi_i^*(\mathbf{r}_k)\hat{F}\chi_j(\mathbf{r}_k) \,, \tag{3.82a}$$

$$S_{ij} = \sum_k w_k \chi_i^*(\mathbf{r}_k)\chi_j(\mathbf{r}_k) \,. \tag{3.82b}$$

While Baerends and Ros used Slater-type AO's as basis functions, Sambe and Felton (1975, 1979) employed Gaussian functions in the basis. The charge density and the $X\alpha$ local exchange potential are expressed in terms of certain auxiliary fit functions f_i and g_i, centered at the nuclei,

$$\rho(\mathbf{r}) \simeq \sum_i a_i f_i(\mathbf{r}) \,, \tag{3.83a}$$

$$-3\alpha[3\rho(\mathbf{r})/8\pi]^{1/3} \simeq \sum_i b_i g_i(\mathbf{r}) \,. \tag{3.83b}$$

The Hamiltonian matrix elements are then evaluated analytically in terms of integrals involving f_i, g_i, and ϕ_i, and the coefficients a_i and b_i are fitted by a least-squares procedure. For both small and large molecules, these LCAO-type techniques lead to much improved results as compared to the earlier muffin-tin approximation, without unduly increasing computer time.

4. Force constants, quadrupole coupling constants

If λ', λ'' are parameters specifying nuclear positions, one obtains, on differentiating the Hellmann-Feynman formula,

$$K_{\lambda'\lambda''} = \frac{\partial^2 E_{el}}{\partial\lambda'\partial\lambda''} = \int \psi^* \frac{\partial^2 H}{\partial\lambda'\partial\lambda''}\psi\, d\tau + \int \psi^* \frac{\partial H}{\partial\lambda'}\frac{\partial\psi}{\partial\lambda''}\, d\tau + \int \frac{\partial\psi^*}{\partial\lambda''}\frac{\partial H}{\partial\lambda'}\psi\, d\tau \,. \tag{3.84}$$

Byers Brown (1959) termed the last two terms in (3.79) as nonclassical, since the first term gives the force constant in a classical electrostatic picture in which the nuclei move through a fixed charge density due to the electrons and the other nuclei, whereas the last two terms involve the transition densities when the perturbation theory expression is written.

Salem (1963), while discussing formulas for force constants, wrote $\partial^2 E_{el}/\partial R^2$ for a diatomic molecule as

$$K = z_A\left[q_A + \frac{4\pi}{3}\rho(A) - \int \frac{\partial\rho}{\partial X_A}\frac{\cos\theta_A}{r_A^2}d\mathbf{r}\right] \,, \tag{3.85}$$

where

$$q_A = \frac{2z_B}{R^3} - \int \frac{\rho(3\cos^2\theta_A - 1)}{r_A^3}\, d\mathbf{r} \tag{3.86}$$

is the electrostatic field gradient at nucleus A due to nucleus B and the electrons; q_A also appears in the quadrupole coupling constant expression, eq_AQ_A, Q_A being the quadrupole moment of nucleus A.

In a related work Anderson and Parr (1970) expressed the molecular electron density for a diatomic molecule as

$$\rho = \rho_A + \rho_B + \rho_{NPF} \,, \tag{3.87}$$

where NPF means "not perfectly following." The force constant can then be written as

$$\nabla_A^2 E_{el} = 4\pi z_A\rho(A) - z_A \int \nabla_A\rho \cdot \nabla_A \frac{1}{|\mathbf{r} - \mathbf{R}_A|}\, d\tau \,.$$

The part of the electron density that moves rigidly with A gives no contribution to $\nabla_A^2 E_{el}$. Hence ρ_A does not enter. Further, $\nabla_A\rho_B = 0$ (nucleus B is fixed while A moves). Thus

$$\begin{aligned}\nabla_A^2 E_{el} &= \frac{\partial^2 E_{el}}{\partial R^2} + \frac{2}{R}\frac{\partial E_{el}}{\partial R} \\ &= 4\pi z_A\rho_B(A) \\ &\quad + \left(4\pi z_A\rho_{NPF}(A) - z_A\left\langle\nabla_A\rho_{NPF} \cdot \nabla_A\frac{1}{|\mathbf{r} - \mathbf{R}_A|}\right\rangle\right) .\end{aligned} \tag{3.88}$$

(3.88) is an exact expression.

If we assume $\rho_{\mathrm{NPF}}(A)$ to be negligible compared to $\rho_B(A)$, we obtain

$$K \simeq \nabla_A^2 E_{\mathrm{el}} \simeq [4\pi z_A \rho_B(A)]_{R_e}. \tag{3.89}$$

A detailed review of expressions for force constants is given by Goodisman (1980).

We shall conclude this article with a brief discussion on two recent interrelated concepts which are likely to find quite interesting applications in the near future. These are respectively concerned with internal stresses in molecules and the fluid-dynamical interpretation of quantum mechanics.

F. $\rho(\mathbf{r})$ and internal stresses in molecules

As an extension of the force concept, following the suggestion of Feynman (1939a), Deb and Bamzai (1978, 1979) have presented a stress formalism: Associated with each point in the 3D space of a molecule, a stress tensor S_ν^μ can be defined in terms of internal fields arising due to the nuclear and electronic distribution. The index ν refers to the direction of the local force and μ refers to the direction of the positive outward normal to the area on which the force acts. The single-particle density $\rho(\mathbf{r})$ is sufficient to construct S_ν^μ, whose components have the same form as Maxwell's stress tensor for classical electromagnetic fields.

For many-electron systems the covariant derivative of S_ν^μ yields the local electrostatic force density,

$$S^\mu_{\nu,\mu} = \rho_N(E_\nu + F_\nu) + \rho(E_\nu + F_\nu). \tag{3.90}$$

In (3.90) E_ν is a component of the field arising due to nuclear charge distribution ρ_N (related by Poisson's equation $E^\mu_{,\mu} = 4\pi\rho_N$), whereas F_ν is the field arising due to electronic distribution ρ. It has been shown that

$$S_\nu^\mu = \frac{1}{4\pi}\left[G^\mu G_\nu - \tfrac{1}{2}\delta_\nu^\mu \mathbf{G}\cdot\mathbf{G}\right] \tag{3.91}$$

satisfies (3.90), where

$$\mathbf{G} = \mathbf{E} + \mathbf{F} = -\nabla V_{\mathrm{mol}}, \tag{3.92}$$

V_{mol} being the molecular electrostatic potential, Eq. (3.50).

A simple model for chemical binding may be constructed (Deb and Bamzai, 1979) starting from the stress tensors $S_\nu^\mu(I)$, $S_\nu^\mu(II)$ as those for the initial undistorted systems to form $S_\nu^\mu(I+II)$, viz., the stress tensor for the final system, after a charge migration $\Delta\rho$ has taken place.

$$S_\nu^\mu(I+II) = S_\nu^\mu(I) + S_\nu^\mu(II) + S_\nu^\mu(I,II) + S_\nu^\mu(\text{interaction}). \tag{3.93}$$

It can be readily shown

$$\begin{aligned} S_\nu^\mu(\text{interaction}) = {} & \frac{1}{4\pi}\left[G(I)^\mu J_\nu + J^\mu G(I)_\nu - \delta_\nu^\mu \mathbf{G}(I)\cdot\mathbf{J}\right] \\ & + \frac{1}{4\pi}\left[G(II)^\mu J_\nu + J^\mu G(II)_\nu - \delta_\nu^\mu \mathbf{G}(II)\cdot\mathbf{J}\right] \\ & + \frac{1}{4\pi}\left[J^\mu J_\nu - \tfrac{1}{2}\delta_\nu^\mu \mathbf{J}\cdot\mathbf{J}\right]. \end{aligned} \tag{3.94}$$

In (3.94) $\mathbf{J}$ is related to $\Delta\rho$,

$$J^\mu_{,\mu} = 4\pi\Delta\rho. \tag{3.95}$$

The interaction between systems I and II can be studied by monitoring the changes in total stress, electrostatic force density, and interaction stress. The chemical binding in the H_2 molecule has been studied using this approach and certain interesting features have been obtained; e.g., for a point in the antibinding region, the total stress and third interaction stress [last term in Eq. (3.94)] were studied for various R and found to pass through a minimum at an R value close to R_e. These detailed local variations can be rationalized by means of classical electrostatic arguments. A similar study has also been carried out for H_2^+ (Bamzai and Deb, 1981).

The stress formalism by virtue of its information content and retention of classical ideas seems to be a promising alternative approach for studying molecular behavior. It is likely that fresh insights into transferability [the integration of (3.90) is a characteristic property of a virial fragment] and reactivity will be obtained by studies on other diatomics.

While the above work is an electrostatic viewpoint, Deb and Ghosh (1979) have proposed a comprehensive stress tensor for a many-electron polyatomic system, consisting of contributions from kinetic energy, Coulomb energy, and exchange-correlation energy. Starting from the local density-functional theory (Sec. II.B), the "local" force density is obtained as the covariant derivative of the stress tensor, consisting of classical (Coulomb) and quantum force densities, where the quantum force density is derived from the Bohm (1952) potential for each electron together with the exchange-correlation potential. A stationary state arises due to a balance between classical and quantum forces.[13]

The works of Wong [(1976) and also Wong *et al.* (1975)] also deal with applications of a quantum stress tensor to complicated motions of nuclear systems, as well as density oscillations in many-fermion systems in their ground states. The kinetic energy density tensor of Deb and Ghosh has the same form as the "quantum stress tensor" defined by Takabayashi (1952), Pauli (1958), Rosen (1974), Epstein (1975), and Wong (1976).

The condition for the vanishing of the local force density has been shown to be a special case of the Euler or Navier-Stokes equation in fluid dynamics (Deb and Ghosh, 1979). A zero local force density everywhere prevents a spontaneous collapse of electronic charge onto the nuclei as well as a spontaneous oozing out of electronic charge from the system.

Bartolotti and Parr (1980) have also examined the concept of pressure within density-functional theory. They define a stress tensor σ whose divergence, the corresponding force density, contains kinetic and exchange-correlation contributions, but not the electro-

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[13] It must be emphasized, however, that in such "local" studies one has to choose very accurate $\rho(\mathbf{r})$ in contrast to the case of "global" studies, where a cancellation of errors associated with densities from various regions of space may occur. Thus a judicious selection of points of interest (Deb and Bamzai, 1979) and proper densities should yield new insights and finer details than were hitherto possible with global studies.

static one. The scalar pressure P is then defined as

$$P=-\tfrac{1}{3}\,\mathrm{tr}\,\sigma\,,$$

and a Gibbs-Duhem equation involving this pressure is derived.

G. $\rho(\mathbf{r})$ and quantum fluid dynamics

Madelung (1926) and Takabayashi (1952) had suggested that the motion of a Schrödinger fluid can be represented by an irrotational flow of a compressible perfect fluid having a stress tensor associated with it. Thus the time-dependent wave equation for N particles, masses m_ν, $\nu=1,2,\ldots,N$ moving under the influence of a potential given by

$$\left(-\frac{\hbar^2}{2}\sum_{\nu=1}^{N}\frac{\nabla_\nu^2}{m_\nu}+V-i\hbar\frac{\partial}{\partial t}\right)\psi=0 \tag{3.96}$$

can be transformed into a system of hydrodynamical equations in a $3N$-dimensional space. In (3.96) $\psi\equiv\psi(\mathbf{r},t)$ and $\nabla_\nu\equiv\partial/\partial\mathbf{r}_\nu$, $\mathbf{r}$ being a vector $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N$ with $3N$ components that are position vectors of the N particles.

Writing $\psi=Re^{iS}$, where $R(\mathbf{r},t)$, $S(\mathbf{r},t)$ are two real functions, (3.96) reduces to (in atomic units)

$$\sum_{\nu=1}^{N}\mathrm{div}_\nu(\rho\bar{v}_\nu)+\frac{\partial\rho}{\partial t}=0\,, \tag{3.97}$$

$$m_\nu\frac{\partial\bar{v}_\nu}{\partial t}=-\mathrm{grad}_\nu(Q+K+V)\,, \tag{3.98}$$

where

$$\rho_p=\rho(\mathbf{r},t)=R^2\,, \tag{3.99}$$

$$\bar{v}_\nu=\frac{\hbar}{m}\,\mathrm{grad}_\nu S\,, \tag{3.100}$$

$$Q=-\hbar^2\sum_{\mu=1}^{N}\frac{\nabla_\mu^2\rho^{1/2}}{m_\mu\rho^{1/2}}\,, \tag{3.101}$$

$$K=\tfrac{1}{2}\sum_{\mu=1}^{N}m_\mu v_\mu^2\,. \tag{3.102}$$

When $N=1$, the equations are identical to hydrodynamical equations of motion. The fluid-dynamical aspects of matter flow have been formulated and explored recently by a number of workers, notably Kan and Griffin [(1977); see also Griffin and Kan (1976)], who consider a single quantal particle moving in a time-dependent external potential. Various fluidic models for nuclei can be encompassed in this framework. The basic generalizations for extension of the treatment to the many-body Schrödinger fluid are also set forth by them.

When $N>1$, the hydrodynamical equations are in $3N$-dimensional space, having no direct physical meaning, since our space of observation is 3D. Therefore the following question has been posed by Janossy (1973, 1974, 1976): Is it possible to replace ρ_p and v by other variables that depend on one coordinate vector each, viz., can the system be characterized by densities in 3D space?

The quantities depending on one position vector only can be introduced by averaging the original quantities over $(N-1)$ position vectors, e.g., the 3D projection of the density of the nth particle is

$$\rho_n(\mathbf{r})=\left[\int\rho(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N)d\mathbf{r}_1\cdots d\mathbf{r}_{n-1}d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N\right]_{\mathbf{r}_n=\mathbf{r}} \tag{3.103}$$

Janossy (1976) has shown that the projected current and charge densities obey continuity equation. However, the projections of the hydrodynamical variables in 3D space do not obey strict equations of motion. If one could succeed in formulating equations of motion containing projected densities only, a "classical" picture of the N-body system could be built up in the 3D space (see later in this section).

Hirschfelder and co-workers have also contributed several works pertaining to the hydrodynamical aspects of quantum mechanics. The problem of reflection and transmission of a beam of particles hitting a two-dimensional square potential barrier has been considered by them (Hirschfelder *et al.*, 1974a); the two sets[14] of streamlines correspond to the real streamlines $\mathbf{r}(t,\mathbf{r}_0)$ obtained by integrating

$$\frac{d\mathbf{r}}{dt}=\mathbf{v}=\frac{1}{m}\nabla S \tag{3.104}$$

and the imaginary streamlines $\mathbf{r}(t_i,\mathbf{r}_0)$ obtained by integrating

$$\frac{d\mathbf{r}}{dt_i}=\mathbf{v}_i=-\frac{\hbar}{2m}\nabla\ln\rho\,. \tag{3.105}$$

Quantized vortices occurring around nodes of wave functions have been discussed by Hirschfelder *et al.* (1974b), while Hirschfelder and Tang (1976a) have provided computer simulation of the streamlines, density contours, and surfaces of constant phase for an atom-diatomic molecule collision considering an idealized potential energy surface. These enable one to see *how* the system goes from its initial to final configuration, thus giving a more detailed understanding of the mechanism of the collision. The elastic scattering of two particles interacting with a spherically symmetric square potential

$$\begin{aligned} V(r)&=0, \quad r>a\\ &=C, \quad r<a \end{aligned} \tag{3.106}$$

has also been dealt with (Hirschfelder and Tang, 1976b); the distortion of the streamlines provide a visual explanation of the collisional cross sections.

In another work, Hirschfelder (1977) has enunciated two types of quantum vortices: axial vortices that have angular momentum dipole moments and toroidal vortices that have orbital angular momentum quadrupole moments. The equations of motion of wave function nodal points and vortices as the result of either time or perturbations have also been developed. The analysis for spin-free systems has recently been extended (Hirschfelder, 1978) using Breit-Pauli type Hamiltonians involving particle spins, as well. The equa-

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[14] The fluid-dynamical picture of quantum mechanics suffers from an unresolved paradox: the "real" velocity ($\propto\nabla S$) appears in the continuity equation, whereas the "imaginary" velocity ($\propto\nabla\ln\rho$, $\rho=R^2$) appears additionally in the equations of motion.

tions of change for the property $\chi^+\theta\psi$ are derived where χ, ψ are wave functions satisfying the same time-dependent Schrödinger equation and θ is an arbitrary operator. Equations of change are obtained for the following subobservables $\mathrm{Re}\{\psi^+\theta\psi\}$:

(i) $\theta = 1$, one obtains the equation of continuity,

(ii) $\theta = p/m$, one obtains the equation of motion,

(iii) $\theta = \mathbf{L} = \mathbf{r} \times \mathbf{p}$, one obtains the equation of change of angular momentum density,

(iv) $\theta = p^2/2m$, one obtains the equation of change of kinetic energy density.

Reduction of the configuration space of a bound-state system to three dimensions results in projecting the properties onto 3D space.

$$D_1(\chi^+\theta\psi) = \int \cdots \int \chi^+\theta\psi d\mathbf{r}_2 \ldots d\mathbf{r}_N\,, \tag{3.107}$$

where D_1 is the desired projector. In terms of the natural spin orbitals ϕ_a's with occupation number n_a's Hirschfelder obtains

$$D_1(\chi^+\theta\psi) = \sum_a n_a(\phi_a^+\theta_1\phi_a)\,, \tag{3.108}$$

where

$$\theta(\mathbf{r}, \mathbf{s}, t) = \sum_{i=1}^{N} \theta_1(\mathbf{r}_i, \mathbf{s}_i, t)\,. \tag{3.109}$$

Thus the N-particle quantum-mechanical system may be viewed as a fluid mixture with each natural spin orbital as a component. However, one is confronted with the same problem as before; the limitation of this description in terms of spin orbitals is that one does not obtain a useful description of equations of change (ii) to (iv). Thus it remains to be seen whether the natural-orbital way of studying equations of change would be useful for properties other than the probability density. However, one advantage of natural orbitals is that in terms of these it is possible to derive the Euler and Navier-Stokes equations of fluid motion in the 3D space (Ghosh and Deb, 1981a) by recognizing that it is *not* the individual velocities associated with the natural orbitals, but rather the individual current densities, which sum together to give the corresponding quantity in 3D space.

Following an earlier work by Ying (1974), Deb and Ghosh (1981) have recently explored the connection between density-functional theory and quantum fluid dynamics, through a dynamical extension of the former [see also Peuckert (1978)]. The Hohenberg-Kohn theorem has been proved for a time-dependent harmonic perturbation with a sufficiently low frequency to avoid transitions from the ground state into excited states. The corresponding time-dependent one-particle Schrödinger equation [see Eq. (2.44)] can then be variationally derived in a local density approximation by using a fluid-dynamical Lagrangian density. The advantage of such a wedding between density-functional theory and quantum fluid dynamics is that it preserves the "particle" description of the system in the sense that the N-electron fluid has N components, each of which is an independent-particle Schrödinger fluid characterized by a density function $\rho_i(\mathbf{r})$ and an irrotational velocity field $\mathbf{u}_i(\mathbf{r})$, $i=1,\ldots,N$. Note, however, that the mean velocity $\mathbf{u}(\mathbf{r})$ of the N-electron fluid is *not* irrotational, in general, contrary to the basic assumption of Ying (1974).

The above fluid-dynamical interpretations in both configuration space and 3D space have led to studies on dynamic polarizabilities of atoms and molecules (Askar and Demiralp, 1974; Bartolotti and Tyrell, 1978; Bartolotti and Epstein, 1979; Ghosh and Deb, 1981b).

IV. CONCLUDING REMARKS

The wide range of molecular properties discussed in this article convincingly demonstrates that the single-particle density $\rho(\mathbf{r})$ is a very attractive starting point for the construction of models to understand molecular behavior. Indeed, one need not be a starry-eyed optimist to say that $\rho(\mathbf{r})$ may well be the unifying link in our perception of various facets of the molecular world. This is because the enhanced visuality of $\rho(\mathbf{r})$, in contrast to the wave function, enables one to employ classical concepts like potential, force, and stress in a quantum-mechanical framework and reveals information on a system in a much more transparent manner. In a number of instances, as discussed in this article, the use of $\rho(\mathbf{r})$ yields new and deeper physical insights than similar studies based on the wave function; thus, the latter studies are complemented and strengthened by the former. Further, formalisms based on $\rho(\mathbf{r})$ as a basic variable, such as the density-functional theory and quantum fluid dynamics, are likely to find more and more applications in nuclear, solid-state, atomic, and molecular physics, so that one has broadly similar approaches to attack diverse microscopic problems. Although, at present, in the absence of any really satisfactory method for its direct evaluation, $\rho(\mathbf{r})$ hangs on the apron strings of the wave function for all practical purposes, one hopes that "there will be radically new and better schemes. . . . Perhaps an accurate functional giving the energy in terms of the electron density will be found so that densities will be obtained directly, thus bypassing wave functions for many purposes. That really could be revolutionary. . ." (Wilson, 1976, p. 47). For the chemist this change in emphasis from wave function to $\rho(\mathbf{r})$ for interpretative purposes is rather like leaving the main road to sniff at some wayside flowers and—who knows?—this might yet turn out to be the most exciting development in quantum chemistry.

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