

Search for a density-based alternative quantum mechanics of many-electron systems

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Abstract. There are three reasons for seeking an alternative density-based quantum mechanics of many-electron systems, incorporating both interpretive and basic quantum mechanical aspects: (i) failure of popular *ad hoc* chemical concepts under *ab initio* scrutiny; (ii) failure of *ab initio* calculations to provide simple concepts; and (iii) highly attractive concepts and pictures generated by the electron density in three-dimensional space. At present the three interlinked pillars for such a density mechanics (in contrast to wave mechanics) are: (a) density functional theory; (b) quantum fluid dynamics; and (c) property densities in three-dimensional space. This article describes several studies dealing with these aspects. Although a density mechanics may well be an impossible ideal to realize, the search for it is indeed rejuvenating the whole of quantum chemistry.

Keywords. Density mechanics; electron density; densityfunctional theory; quantum hydrodynamics.

1. Introduction

The central theme in quantum chemistry is the prediction and interpretation of physicochemical phenomena. In order to understand the behaviour of the chemical world, the chemist would prefer to employ simple, attractive concepts and pictures, enabling him to visualize and discourse in a classical language, as far as possible. Through successive generations, this desire on the part of the chemist has resulted in his using a number of popular *ad hoc* ideas which have passed into the folklore of chemistry. Many of these popular ideas provide an interesting contrast between myth and reality in that they collapse when subjected to careful scrutiny through highly accurate *ab initio* calculations; several such examples are discussed in § 2. However, the *ab initio* calculations themselves have been unable to provide simple but rigorous concepts and pictures for use by all chemists. This is because it is very difficult to visualize, tabulate or interpret the many-electron wavefunction. As opposed to these dilemmas, recent years have seen the emergence of a number of highly attractive, visually delightful new insights into chemical binding, molecular geometry, molecular reactivity, etc based on the electron density (ground and excited) and associated quantities in the three-dimensional (3D) space. These insights were not accessible directly through the wavefunction. A few such examples are described in § 3.

In view of the above considerations, it appears natural to think of an 'alternative' quantum mechanics of many-electron systems, which would be based on the electron density and associated quantities rather than the wavefunction, so that the generation of simple chemical concepts and pictures with solid theoretical foundations becomes possible.

There are two *interlinked* aspects of such a density-based alternative quantum

mechanics: (i) *interpretive aspect*, i.e. given the electron density $\rho(\mathbf{r})$ in 3D space, what information of physical, chemical and biological significance can be extracted from it? (ii) *Basic, quantum mechanical aspect*, dealing with the fundamental properties of the single-particle density. Both these aspects will be briefly discussed in this article.

The scientific literature on electron density studies has been growing at a fast pace over the past ten years. In three previous articles (Bamzai and Deb 1981a; Ghosh and Deb 1982a; Deb 1984) and a book (Deb 1981a), the reader would find comprehensive discussions on various facets of the electron density. In this short article, especially in §§ 3 and 4, we constrain ourselves to describing mainly some of the new concepts and formalisms developed at our laboratory.

2. Failure of popular *ad hoc* ideas under *ab initio* scrutiny

Out of many such examples, we present only four in this section, without going into details.

2.1 *Hund's rule of maximum multiplicity*

Consider a two-electron atom. "The conventional mythical explanation of why the triplet (parallel) [state] lies lower [compared to singlet] is that, because electrons with parallel spins tend to keep apart . . . their repulsion is less than in a singlet (paired) [state]. This is not so. Detailed calculation on some cases has shown that the repulsion between the electrons is greater in triplet states than in singlets, and that the lowering of the energy is due to the modification of the electron-nucleus attraction. Thus, in a triplet atom the electron distribution contracts, and is stabilized by the improved nuclear attraction: the electron repulsion rises because the electrons are closer together, but this increase does not defeat the improvement in the nuclear attraction" (quoted from Atkins 1974).

2.2 *Electron exchange and chemical binding*

Consider the electronic Hamiltonian for the H_2 molecule

$$H(1, 2) = h(1) + h(2) + g(1, 2). \quad (1)$$

According to the Heitler–London method, the ground-state energy of the H_2 molecule is

$$E = (Q + K)/(1 + \Delta), \quad (2)$$

where $Q = \langle ab|H|ab \rangle \equiv$ 'coulomb integral', $K = \langle ab|H|ba \rangle \equiv$ 'exchange integral', $\Delta = \langle ab|ba \rangle = S_{ab}^2$ and $S_{ab} \equiv$ overlap between the hydrogenic orbitals a and b . Since K is negative, it was concluded for many years that 'exchange forces' are responsible for chemical binding. But, if the atomic orbitals are assumed to be orthogonal, K becomes positive. Since the orbitals are not orthogonal,

$$K = \langle ab|g|ba \rangle + 2S_{ab} \langle a|h|b \rangle. \quad (3)$$

true exchange	one-electron
integral (positive)	integral (negative)

Clearly, binding occurs not because of exchange (the first integral in (3)) but due to

electron-nuclear attraction which makes the second integral in (3) negative (McWeeny and Sutcliffe 1976).

2.3 Orbital hybridization and molecular geometry

A long perpetuated myth seems to be that since in H_2O , NH_3 and CH_4 the HAH angle is either tetrahedral or close to it, the hybridization of the central atom must be sp^3 or close to it. The best way to estimate the extent of hybridization is to calculate accurately the *ab initio* delocalized molecular orbitals (MOs) of the system and then unitarily transforming them into localized orbitals. From this it turns out that the bond hybrids and the lone-pair hybrids on the central atom in H_2O and NH_3 are not sp^3 . In case of H_2O , the localized bond orbitals do have considerable *s* character, but the angle between them is only slightly greater than 90° (bent or banana bond). The angle between localized lone-pair orbitals is 124° (i.e., more sp^2 than sp^3). For NH_3 , similar conclusions are valid and one again finds bent bonds (see Edmiston and Ruedenberg 1966).

In an interesting work, Jarvie *et al* (1973) examined the effects of hybridization in CH_4 by performing calculations in which the *s*-type basis functions (and four associated electrons) of the C atom were completely deleted and replaced by an appropriate effective nuclear charge. The preferred shape of the molecule was still tetrahedral. Therefore, the authors concluded that $2s \rightarrow 2p$ promotion and/or hybridization is not responsible for the tetrahedral shape of CH_4 . It appears that if there is a direct one-to-one correspondence between hybridization and molecular geometry, it is not yet known.

2.4 Ring current in aromatic hydrocarbons

Due to the pioneering works of K S Krishnan, L Pauling, F London and others, in the nineteen thirties, the anisotropic magnetic susceptibility of aromatic hydrocarbons had been attributed to the ability of the cyclic π -electron system to sustain a superconducting ring current. This also explains why proton magnetic resonance in benzene occurs at unexpectedly low field strengths. The concept of ring current was well entrenched in chemistry until the situation was upset by a strongly worded paper by Musher (1965). According to a proof of London, ring current is not possible for the σ electrons of, e.g. benzene. "This argument is fallacious—and London's proof is incorrect—as it can be shown that the susceptibility due to a 'ring current' exactly equals the sum of the susceptibilities of electrons localized in segments of a ring . . . We have demonstrated that there is no reason to single out the π -electron system of aromatic hydrocarbons for special treatment of their magnetic properties in terms of 'ring currents' . . . Any suggestion that 'aromaticity' . . . be defined in terms of the ability of . . . [the] molecule to sustain a ring current must be considered unreasonable" (quoted from Musher 1965). The controversy raised by Musher's work persists to this day.

So far, the most accurate calculations on the magnetic susceptibility of benzene have been performed by Lazzeretti *et al* (1982) who interpreted their results in a way that endorses the final departure from any ring current ideas. Nevertheless, it is quite likely that this concept may be partially rehabilitated on the basis of quantum fluid dynamics (see § 4).

The above four examples are just a few among a manifold of *ad hoc* concepts, much

used but without solid theoretical foundations, which have mesmerized generations of chemists by their qualitative elegance. As exemplified in the following section, perhaps the only way to recover or regenerate such concepts is through the electron density.

3. New concepts arising from the electron density

3.1 *The nature of chemical binding*

Perhaps the most detailed study of chemical binding in molecules has been through the examination of electron densities, difference densities, and the like, in various molecules (Bader 1981). For a diatomic molecule, the difference density is obtained by subtracting superimposed atomic densities at a particular internuclear distance (R) from the molecular density at the same R . The contours of the difference density vividly describe the extent of charge reorganization due to the interaction resulting in the formation of a chemical bond. For the H_2 molecule, when $R \simeq 8$ a.u., electron correlation causes a simultaneous generation of atomic dipoles at the two hydrogens, pointing towards each other. In other words, the centroid of each hydrogen's electron density shifts towards the other hydrogen. This is the origin of London dispersion forces. It is not the interaction of these atomic dipoles which produce the leading term ($-C_6R^{-6}$) in the dispersion series, but rather the attraction of each distorted electron density for its own nucleus that gives the R^{-7} attractive force. Note that in the familiar physical explanation of the origin of London forces, a time-dependent picture of oscillating dipoles was inconsistently grafted onto a time-independent perturbation treatment.

At the equilibrium value of R , electron density flows into the binding region between the two protons as well as behind them. Thus, the attractive part of the diatomic potential energy curve arises due to electron-nuclear attraction while the repulsive part arises due to nuclear-nuclear repulsion and electron-nuclear attraction. These and many other points have been discussed at length by Bader (1981).

3.2 *First-order static Jahn-Teller effect in VCl_4*

The electronic ground state of tetrahedral VCl_4 is doubly degenerate, 2E . This interacts with the A_1 and E vibrational modes of the molecule, where A_1 corresponds to the totally symmetric stretching mode and E corresponds to a nontotally symmetric bending mode leading to Jahn-Teller (JT) distortion. Let us take VCl_4^+ with a nondegenerate ground state as the reference molecule and let us assume that the doubly degenerate nonbonding e MOs responsible for the JT distortion in VCl_4 are composed mainly of either d_{z^2} or $d_{x^2-y^2}$ AO on the vanadium atom. By using Hellmann-Feynman theorem and schematic representations of these charge distributions, it is possible to obtain (Coulson and Deb 1969; Deb 1973), without making a computation, detailed insights into the nature of the JT distortion in the molecule, which were not obtainable before. Calculation of distortion energies then led to the conclusion that the ground state of VCl_4 is a 50:50 mixture of elongated and flattened tetrahedra. This agreed nicely with experimental findings. Earlier elaborate treatments of the problem, on the basis of degenerate perturbation theory, had yielded quite conflicting results. But, a direct use of the electron density, instead of the wavefunction, greatly simplified the problem, made it visually transparent and the solution was highly satisfying.

3.3 HOMO postulate and a force model for molecular shapes

It was popularly believed that MO theory is incapable of making sitting-at-the-desk predictions about the shapes of molecules, without doing detailed computations. That this belief is not justified was proved by developments in qualitative MO theory in which the valence MOs of a molecule using an *sp* basis were constructed, arranged in a proper energy sequence, their electron densities examined and molecular shape predictions made in ground and excited states, all done without making any computation (Deb 1974, 1975; Deb *et al* 1974, 1976). The basis for this approach was the Hellmann-Feynman force interpretation (Coulson and Deb 1971), using electron density, of Walsh's rules of molecular geometry, as well as the HOMO postulate (Deb 1974, 1975). The HOMO postulate says that molecular shapes are mainly determined by the electron-nuclear attractive forces generated by the electron density in the highest occupied MO; if the HOMO is insensitive to shapes, then the next lower MO is to be examined and so on. This model has been remarkably successful in predicting and correlating a large amount of structural information about AH_2 , AH_3 , AH_4 , AH_5 , AB_2 , AB_3 , AB_4 , AB_5 , ABC , H_2AB , HAB_2 , B_2AC , $HAAH$ and $BAAB$ molecules, where *A*, *B* and *C* are nonhydrogenic atoms. Among the interesting successes of this model is the prediction of a bond angle of about 140° (the actual value is 136°) for the ground triplet (3B_1) of carbene molecule (CH_2) and predicting the shapes of larger molecules from those of their fragments. For small and medium-size molecules, this is probably the most versatile and successful qualitative model, utilizing the considerable power and elegance of MO theory. For large molecules, application of qualitative MO theory becomes increasingly difficult. For a detailed discussion of this and another interesting density-based approach to molecular shapes (and reactivity), see Nakatsuji and Koga (1981).

The HOMO postulate model seems to be the only one that made geometry predictions for unknown or nonexistent molecules. In order to test these predictions, and to compare with six other current models of molecular geometry, the following molecules were synthesized quantum chemically and their structures determined by a careful application of CNDO/2 and INDO methods: $HCLi$, $HBBe$, $HBLi^-$, HCB , $HNBe$, HNB^+ , HBB^- , $NaHLi^+$, LiB_2^+ , $MgBe_2$, LiB_2^- , MgB_2 , LiH_3^+ (unstable), H_3O^- , CH_5^- , HBO_2^{2+} (unstable) and HBf_2^{2+} (unstable). The HOMO postulate is the most successful with these molecules, having only one exception ($NaHLi^+$) while the Mulliken-Walsh model stands next with three exceptions, *viz* $NaHLi^+$, HNB^+ , HBf_2^+ (Deb and Mahajan 1982; Mahajan and Deb 1982a, b).

3.4 The spatial partitioning of a molecular system: Definition of an atom in a molecule or solid

One of the major problems in chemistry has been to obtain a model-independent precise definition of an atom in a molecule or solid; in other words, how do we partition a molecule into atomic fragments. This is also linked with the unsolved problem of transferability of group or fragment properties from molecule to molecule. Using ideas from catastrophe theory, graph theory and exploiting certain quantum mechanical properties of the electron density, Bader *et al* (1980, 1981) have provided a very precise model-independent definition of the boundaries of the fragments of a molecular system. Starting from the point of minimum density between a pair of adjacent nuclei, a line in the partitioning surface follows the path of steepest descent through the electron

density $\rho(\mathbf{r})$. The definition is made quantitative by requiring that $\rho(\mathbf{r})$ be partitioned by those closed surfaces through which the flux of $\nabla\rho(\mathbf{r})$ is everywhere zero. In other words, if $S(\mathbf{r})$ is such a surface, then

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad (4)$$

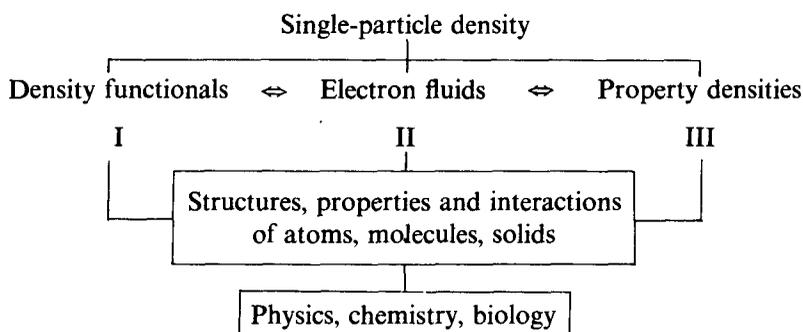
for all \mathbf{r} belonging to $S(\mathbf{r})$, where $\mathbf{n}(\mathbf{r})$ is a unit vector normal to $S(\mathbf{r})$ at \mathbf{r} . The only surfaces which satisfy this condition are those which contain stationary points in the electron density, *i.e.* points at which $\nabla\rho(\mathbf{r})$ vanishes.

A partitioning surface is thus a collection of all gradient paths which both originate (generally at infinity) and terminate (generally at a saddle point) at stationary points in the electron density (see also Bader 1981).

The above four examples are just a few of many interesting studies where the use of electron density directly leads to outstanding physical insights into the problems concerned. Although, in principle, all these informations were contained in the wavefunction, it was extremely difficult to extract them (for more examples, see Bamzai and Deb 1981a; Deb 1981a and Deb 1984). Even though this "change in emphasis from wavefunction to [electron density] . . . for interpretive purposes is rather like leaving the main road to sniff at some wayside flowers . . . who knows? – this might yet turn out to be the most exciting development in quantum chemistry" (quoted from Bamzai and Deb 1981a), *viz* the tantalizing possibility of a density-based quantum mechanics of atoms, molecules and solids.

4. Some interlinked basic quantum mechanical properties of the electron density

The following is a scheme for a density-based quantum mechanics of many-electron systems (arrows signify interlinking):



For detailed discussions on density functional theory (I), hydrodynamical (nonlinear) transcription of the wave equation (II) and property densities (III), see Bamzai and Deb (1981a), Ghosh and Deb (1982a) and Deb (1984). It is clear that the above interlinked framework would, in principle, result in unified approaches for developing very useful qualitative and quantitative models in 3D space for all branches of science. To reemphasize, the main objectives of this broad viewpoint are: (i) simplicity and enhanced visuality; (ii) 'classical' interpretations in 3D space; (iii) rigorous but transparent physics; and (iv) a drastic reduction in computational labour, exemplified later in this section through (a) direct density calculation by solving one equation, instead of N

equations ($N \equiv$ number of electrons), and (b) dynamic polarizability calculation by solving two perturbative equations instead of $2N$ equations.

We now consider briefly certain key elements of the above framework.

4.1 An electrostatic stress tensor

Let E_v and F_v be the v th components of internal electric fields due to the nuclear and electronic charge distributions, ρ_N and ρ respectively. Let $S_{\mu\nu}$ be an electrostatic stress tensor (cartesian) in the 3D space of a many-electron system, satisfying the force density equation

$$S_{\mu\nu,\mu} = \rho_N(E_\nu + F_\nu) + \rho(E_\nu + F_\nu). \quad (5)$$

Then, one of the solutions of (5) is

$$S_{\mu\nu} = N_{\mu\nu} + L_{\mu\nu} + P_{\mu\nu} = \frac{1}{4\pi}(G_\mu G_\nu - \frac{1}{2}\delta_{\mu\nu} \mathbf{G} \cdot \mathbf{G}), \quad (6)$$

where

$$N_{\mu\nu} = \frac{1}{4\pi}(E_\mu E_\nu - \frac{1}{2}\delta_{\mu\nu} \mathbf{E} \cdot \mathbf{E}), \quad (7)$$

$$L_{\mu\nu} = \frac{1}{4\pi}(E_\mu F_\nu + E_\nu F_\mu - \delta_{\mu\nu} \mathbf{E} \cdot \mathbf{F}), \quad (8)$$

$$P_{\mu\nu} = \frac{1}{4\pi}(F_\mu F_\nu - \frac{1}{2}\delta_{\mu\nu} \mathbf{F} \cdot \mathbf{F}), \quad (9)$$

$$\mathbf{G} = -\nabla V_{\text{mol}}, \quad (10)$$

V_{mol} being the molecular electrostatic potential (see Politzer and Daiker 1981). Thus, the electrostatic stress tensor and its three components have the same form as Maxwell's stress tensor for classical electromagnetic fields. The stress concept contains the Hellmann-Feynman viewpoint as a special case (Deb and Bamzai 1978, 1979).

The electrostatic stress tensor has been applied to obtain a local view of chemical binding in the H_2^+ and H_2 molecules (Deb and Bamzai 1979; Bamzai and Deb 1981b). For the H_2 molecule, S_{zz} (z along the internuclear axis) for a point in the antibinding region passes through a minimum near the equilibrium internuclear distance. In this viewpoint, chemical binding occurs due to the variation of electrostatic pressure from point to point in such a manner as to cause the vanishing of the total electrostatic force density or the difference force density or both at certain points on the internuclear axis.

4.2 A comprehensive stress tensor within density functional theory

The above electrostatic stress tensor is but a part of a comprehensive stress tensor which can be derived by using density functional theory (DFT) and thereby the link between DFT and quantum fluid dynamics (QFD) begins to develop. Let $\mathbf{F}(\mathbf{r})$ be the net local force density and \mathbf{U} a comprehensive stress tensor. Then, it can be shown (Deb and Ghosh 1979)

$$\mathbf{F}(\mathbf{r}) = \nabla \cdot \mathbf{U} = 0, \quad (11)$$

$$\mathbf{U} = \mathbf{T} + \mathbf{I}_{xc} + \mathbf{S}, \quad (12)$$

where $\mathbf{T} \equiv$ Bohm stress tensor (contribution from kinetic energy), $\mathbf{I}_{xc} \equiv$ Exchange-correlation stress tensor and $\mathbf{S} \equiv$ Electrostatic stress tensor. All the above stress tensors can be expressed through DFT.

Equation (11) has a fluid dynamical interpretation. It is a special case of Navier-Stokes equation

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot \mathbf{U}. \quad (13)$$

For static stationary states ($\mathbf{v} = 0$) (13) as well as the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (14)$$

are trivially satisfied. The real velocity field \mathbf{v} vanishes in this case whereas the imaginary velocity field $\mathbf{u}_i = -\frac{1}{2}\nabla \ln \rho_i$, where $\rho = \sum_i \rho_i$, gives rise to viscosity coefficients.

In this viewpoint, the picture of the many-electron system is that of a nonuniform continuous fluid subjected to classical (coulomb) and quantum (kinetic + xc) forces. The system is stable due to the balance of these forces. Illustrative calculations were reported for the H_2^+ molecule (Deb and Ghosh 1979). Subsequently, the concept of a stress tensor has been used by Bader (1980) as well as Bader and Nguyen-Dang (1981) to derive the mechanics of an atom in a molecule, and by Parr *et al* to derive a microscopic thermodynamics (see Parr 1983).

4.3 QFD of many-electron systems in 3D space in presence of external electric and magnetic fields

Since a QFD equation of motion in 3D space in terms of $\rho(\mathbf{r}, t)$ could not be obtained by earlier workers, we employed an orbital partitioning of $\rho(\mathbf{r}, t)$ to achieve this objective, *via* natural orbitals (NOs). The starting point is the Adams-Hirschfelder equation

$$\hat{F} \phi_k = i\hbar \partial \phi_k / \partial t, \quad (15)$$

where \hat{F} is the NO Hamiltonian and the time-dependent NO ϕ_k is written as

$$\phi_k = \rho_k^{1/2} \exp [iS_k/\hbar]. \quad (16)$$

For each NO, this yields a continuity equation and a Navier-Stokes equation. In the latter, the net force density arises from the Lorentz force of the electric and magnetic fields, the body force and the tensorial force. The last has contributions from a viscous and a turbulence stress tensor. The picture of the N -electron fluid is as follows (Ghosh and Deb 1982b):

- (i) It consists of individual fluid components (NO) with density ρ_k and current density \mathbf{J}_k , in 3D space.
- (ii) The motion of each component is governed by the Bohm force, the Coulomb force, the xc force and the Lorentz force.
- (iii) In the absence of a magnetic field, each component velocity is irrotational; but, the net velocity field is rotational.
- (iv) The irrotational character of each fluid component is destroyed by molecular rotation (a Coriolis force comes in).
- (v) Electron spin introduces another term in \mathbf{J}_k .
- (vi) The motion of the entire electron fluid or each fluid component can be followed *via* quantum streamlines, obtained by integrating the velocity field.

(vii) Physical observables for the fluid are:

$$\text{Charge density, } \rho = \sum_k \eta_k \rho_k$$

$$\text{Current density, } \mathbf{J} = \sum_k \eta_k \mathbf{J}_k,$$

where η_k is an NO occupation number. The net velocity cannot be obtained by such summation and is not an observable. Note that the concept of ring current (§ 2.4) can be soundly reformulated by means of the current density.

4.4 A time-dependent DFT and its QFD analogue: A close subtle link between DFT and QFD

Consider a time-dependent (TD) external potential consisting of a harmonic electric perturbation. In this case, by utilizing a variational principle for quasiperiodic solutions to the TD wave equation, it is possible to prove Hohenberg-Kohn theorem for a nondegenerate quasiperiodic ground state of the many-electron system (Deb and Ghosh 1982). This results in another type of orbital partitioning of $\rho(\mathbf{r}, t)$ in terms of DFT orbitals. The entire analysis of § 4.3 can be carried over to this case.

The TD analogue of Kohn-Sham one-particle equation is obtained through the following sequence of steps:

- (i) Define a Lagrangian density for the N -electron fluid by writing the TD energy density as a sum of macroscopic kinetic energy density of the fluid, an intrinsic energy density (the Hohenberg-Kohn functional) and a correction term (neglected for small perturbations).
- (ii) Using this Lagrangian density, minimize the corresponding action integral with respect to variations in the densities and velocities of the fluid components, using the equation of continuity as a constraint.

For details see Deb and Ghosh (1982). A more general TDDFT has recently been suggested by Runge and Gross (1984).

In a recent work, Ghosh and Deb (1984) have extended the link between DFT and QFD to the relativistic domain.

4.5 A differential equation for the direct calculation of electron density

The key equation in DFT is

$$\delta E[\rho]/\delta \rho - \mu = 0, \quad (17)$$

where μ is the chemical potential, and the unknown energy functional

$$E[\rho] = T[\rho] + V[\rho] + E_{xc}[\rho], \quad (18)$$

T being the kinetic energy. The crux of the problem in DFT is to develop a good kinetic energy-density functional with proper local behaviour (Chattaraj and Deb 1984). Such a functional was obtained by Deb and Ghosh (1983) as

$$t[\rho] = -\frac{1}{4} \nabla^2 \rho + \frac{1}{8} \frac{\nabla \rho \cdot \nabla \rho}{\rho} + C_k f(\mathbf{r}) \rho^{5/3}, \quad (19)$$

where C_k is the Thomas-Fermi constant and $f(\mathbf{r})$ is an unknown function. The

Table 1. Atomic kinetic energies (a.u.).

Atom	Equation (21)	Hartree-Fock value
He	2.860	2.862
Ne	128.133	128.546
Ar	526.575	526.812
Kr	2749.439	2752.026
Xe	7228.187	7231.961

N -representability criteria were satisfied by taking $\rho(\mathbf{r}) = |\phi(\mathbf{r})|^2$. Equation (17) then leads to the new nonlinear DFT equation (Deb and Ghosh 1983)

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}\right]\phi = \mu\phi. \quad (20)$$

Equation (20) was solved numerically for Ne, Ar, Kr and Xe, by using model potentials. This gave $\rho(\mathbf{r})$ and E , in good agreement with Hartree-Fock results.

Another expression for the kinetic energy density functional is (Haq *et al* 1984)

$$t[\rho] = C_k \rho^{5/3} - \frac{1}{40} \frac{\mathbf{r} \cdot \nabla \rho}{r^2}. \quad (21)$$

Using Hartree-Fock atomic densities (Clementi and Roetti 1974), (21) gives the following values of the kinetic energy. The agreement is better than any other similar prescription in the literature.

4.6 Frequency-dependent multipole polarizabilities

Using the formalisms in §§ 4.4 and 4.5, one can derive two perturbative equations for the 2^L -pole polarizability ($L = 1, 2, \dots$), instead of the usual $2N$ equations (Ghosh and Deb 1983a). The equations can be solved variationally (much faster, Ghosh and Deb 1982c, 1983b) or numerically (more accurate, Ghosh and Deb 1983a). The results are new and cannot be compared with any other results at present. However, the static polarizability values, obtained by using the Hartree-Fock density as unperturbed function, agree with coupled-Hartree-Fock and experimental values better than many-body perturbation-theoretic and other density-functional values. For details, see Ghosh and Deb (1983a).

4.7 Z -dependence of ground-state energies of neutral atoms

This is a vintage problem in atomic physics. Recently, Chattaraj *et al* (1984) have suggested that the Hartree-Fock energy of neutral atoms may be simulated as

$$-E(Z) = Z^{7/3}(C_7 + C_6 Z^{-1/3} + C_5 Z^{-2/3} + C_4 Z^{-1} + C_3 Z^{-4/3}), \quad (22)$$

where the C 's are universal constants and Z is the nuclear charge. C_7 is the Thomas-Fermi value, C_6 is the Scott (1952) value and C_5 the Schwinger (1980, 1981) value. In (22) all the C 's are *derived*, and *not adjusted*, parameters and their *physical significance is completely clear*. The following table gives the energy values. Again, the agreement is better than that obtained previously, the He atom being the worst case.

Table 2. Comparison of $E(Z)$ values with Hartree-Fock energies (a.u.).

Z	$-E(Z)$	$-E_{\text{HF}}$
2	2.766	2.862
10	128.4	128.5
34	2398.7	2399.8
80	18405.0	18409.0

5. Conclusion

The present article has only pointed out certain constructional elements necessary to develop a quantum mechanics of atoms, molecules and solids based on the single-particle density. There is a very long way to go for developing a complete alternative to the usual wavefunction-based quantum mechanics, in the sense that density has not yet penetrated significantly into many areas dominated by the wavefunction, *e.g.* atomic/molecular collisions and symmetry. Until then, and until a first-principles direct accurate calculation of electron density becomes possible, density mechanics will remain complementary to wave mechanics. There is also a feeling that the density objectives of transparent simplicity, enhanced visuality and mathematical rigour are too idealistic to be ever achieved. Whatever be the final outcome of this search for an alternative density-based quantum mechanics, there is no doubt that the coming years promise great excitement.

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