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A 'CLASSICAL' VIEW OF QUANTUM CHEMISTRY

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ABSTRACT

An attempt has been made to present a review of the recent developments towards bringing out a 'classical' picture of the quantum mechanics of many-electron systems in terms of the hydrodynamical model in three-dimensional space. Interesting new insights and information obtainable through 'local' hydrodynamical quantities like electron density, current density, force density, etc. have been outlined.

THE central problem in quantum chemistry is the prediction and interpretation of physicochemical phenomena. Although its traditional approaches, viz. the solution of the Schrodinger equation in an approximate manner followed by the evaluation of certain expectation values have been successful in yielding fairly accurate numbers for many quantities, it still fails to give full satisfaction to a chemist who would prefer to use his 'classical' concepts to understand the behaviour of the chemical world. As a result, in order to develop a physical picture, it becomes essential to interpret the quantum mechanical formalisms within the framework of classical ideas¹.

The first step in this endeavour would be to formulate quantum chemistry in three-dimensional (3-D) space². This is because "we live and perceive in a 3-D world" and hence visualization in 3-D space becomes much more transparent. Thus, instead of using the wavefunction ψ , which is a function in $3N$ -dimensional ($3N$ -D) configuration space, one has to develop concepts and interpretive formalisms in terms of 3-D quantities like electron density, current density, etc.

Although the advantages of employing the electron density as the basic quantity have been emphasized on many occasions², the question may arise whether it contains sufficient information about a system. An affirmative answer has been provided by Hohenberg

and Kohn³ who have proved a theorem according to which all information about the ground state of a system is contained in the density $\rho(\mathbf{r})$. Later, it has been extended to excited states⁴ as well as certain time-dependent cases^{5,6}. This provides a formal justification of using density as the central quantity bypassing the wavefunction and has led to the well-known density-functional theory (DFT)⁷.

Besides enabling one to build up various interpretive models², the density-based formalisms offer tremendous simplification over the usual wavefunction approach due to reduction in dimensionality. Further, the density, being a fundamental physical observable, also permits the accuracy of quantum chemical calculations to be tested directly.

In the present work, an attempt has been made to bring out a 'classical' picture⁸ of a quantum system in terms of the density functions.

We adopt what is commonly known as the hydrodynamical model⁹ of quantum mechanics where the original ψ -formalism is replaced by an alternative one using the probability density ρ and the current density \mathbf{J} (or the velocity field \mathbf{v}) as the fundamental quantities.

Expressing the wavefunction ψ in polar form

$$\psi(\mathbf{r}, t) = R(\mathbf{r}, t) \exp [i S(\mathbf{r}, t)/\hbar] \quad (1)$$

the one-particle time-dependent Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (2)$$

has been transformed into the following pair of hydrodynamical equations, viz., continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (3)$$

and Euler equation:

$$m\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = -\rho \nabla (V + V_q), \quad (4)$$

where

$$\rho = R^2, \quad \mathbf{v} = \frac{1}{m} \nabla S \text{ and } V_q = -\frac{\hbar^2 \nabla^2 R}{2m R} \quad (5)$$

The fluid-dynamical equations (3) and (4) form the basis of the hydrodynamical model of quantum mechanics or quantum fluid dynamics (QFD)¹. The equations are purely classical but for the appearance of the term V_q , interpreted as the quantum or Bohr potential¹⁰ of hidden variable theory. Thus, the picture of the electron is that of a flowing fluid of density ρ and a 'local' velocity field \mathbf{v} [or current density $\mathbf{J}(\mathbf{r}, t) = \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)$] moving under the influence of forces arising out of a quantum potential V_q in addition to that of the usual Coulomb potential V .

In tensorial representation, the Euler equation (4) takes the form of the Navier-Stokes equation

$$m \frac{\partial}{\partial t} (\rho v_\mu) + \sum_\nu \nabla_\nu \left\{ m\rho v_\mu v_\nu + p_{\mu\nu}^{(q)} \right\} = -\rho \nabla_\mu V \quad (6)$$

where v_μ is the μ th component of velocity and ∇_ν is the ν th gradient. The term $p_{\mu\nu}^{(q)}$ given by

$$p_{\mu\nu}^{(q)} = -\frac{\hbar^2}{4m} \nabla^2 \rho \delta_{\mu\nu} + \frac{\hbar^2}{4m} \frac{(\nabla_\mu \rho)(\nabla_\nu \rho)}{\rho} \quad (7)$$

is known as the quantum stress tensor¹¹ and is of purely quantum origin—differing from ordinary hydrodynamics in that it depends on the derivatives of density rather than velocity. However, it can be interpreted as arising from the imaginary velocity field¹² defined as

$$\mathbf{v}_i = \text{Im} \frac{1}{m} \frac{\hbar \nabla \psi}{i \psi} = -\frac{\hbar}{2m} \nabla \ln \rho. \quad (8)$$

An interesting point about the quantum force ($\rho \nabla V_q$) is that the integral of the quantum force density vanishes, i.e.

$$\int \rho \nabla V_q \, d\mathbf{r} = 0 \quad (9)$$

indicating that the quantum force has no resultant and hence is purely an inner force.

Stationary states correspond to time-independent ρ and \mathbf{v} , and can be divided into two types¹³, viz. (i) the

static stationary state with zero velocity field indicating $\nabla(V + V_q) = 0$, and (ii) the dynamic stationary state with nonzero velocity field. In the case of the former, the classical electrostatic force on the electron fluid is exactly balanced by the forces of quantum origin while in the latter case, the uncompensated force maintains the stationary flow with velocity \mathbf{v} giving rise to the macroscopic kinetic energy $1/2 m v^2$. The ground state of a hydrogen atom is an example of static stationary state whereas the $2p_{\pm 1}$ states are the dynamical ones—the latter possessing non-zero angular momentum. The angular momentum arising in certain static stationary states e.g. $2p_0$ state seems to originate from the imaginary velocity field defined by (8).

The above work can easily be generalised to the case of magnetic field $\mathbf{B} (\equiv \nabla \times \mathbf{A})$ acting in addition to the electric field $\mathbf{E} (\equiv -\nabla \phi - 1/c \partial \mathbf{A} / \partial t)$ characterised by the vector potential \mathbf{A} and scalar potential ϕ respectively. The expression for velocity becomes

$$\mathbf{v} = \frac{1}{m} \left(\nabla S - \frac{e}{c} \mathbf{A} \right) \quad (10)$$

and the Euler equation (4) contains the additional Lorentz force term

$$\left(e \mathbf{E} + \frac{e}{c} \mathbf{v} \times \mathbf{B} \right).$$

Although the velocity field is irrotational in the absence of a magnetic field, in the presence of the latter there arises a non-zero vorticity $\nabla \times \mathbf{v}$ which is proportional to the applied magnetic field.

The system interacting with a magnetic field is appropriately described by the Pauli equation. However, although the Pauli equation reduces to the Schrodinger equation in the absence of a magnetic field, the corresponding expression for current density reduces to

$$\mathbf{J} = \rho \mathbf{v} + \frac{c}{e} \nabla \times \mathbf{M}, \text{ with } M_1 = M_2 = 0, M_3 = \frac{e\hbar}{2mc} \rho \quad (11)$$

which consists of an additional nonvanishing contribution. Thus, even in an s-state, there is a net current in the electron fluid—showing analogy to Bohr's theory. This is a consequence of the fact that the Schrodinger equation represents a system in a spin eigenstate¹⁴ rather than a spinless system.

In the case of one-electron systems considered so far, the fluid-dynamical equations are automatically in 3-D space. For a many-electron system, however, although QFD can be developed following a similar approach, the fluid-dynamical equations as well as the quantities correspond¹³ to a fluid in $3N$ -D configura-

tion space. Consequently, QFD loses its physical clarity, thereby becoming essentially a device to supplement the mathematical formalism. QFD becomes appealing only when it is expressed in terms of 'local' quantities in 3-D space, viz., the electron density $\rho(\mathbf{r}, t)$ and the current density $\mathbf{J}(\mathbf{r}, t)$ which are defined in terms of the many-electron wavefunction ψ as:

$$\rho(\mathbf{r}, t) = N \int \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (12)$$

and

$$\mathbf{J}(\mathbf{r}, t) = -\frac{i\hbar N}{m} \int (\psi^* \nabla \psi - \psi \nabla \psi^*) d\mathbf{r}_2, \dots, d\mathbf{r}_N. \quad (13)$$

In view of the difficulty of direct projection¹⁵ to three-dimension, success has been achieved¹ in formulating QFD in 3-D space for many-electron systems only within the framework of one-body theories. Thus, Wong¹¹ has developed QFD using time-dependent Hartree-Fock formalism. Recently, the concept of natural orbitals (NO) corresponding to an MCSCF wavefunction has been exploited for this purpose¹³. With the help of the NO hamiltonian defined by Adams¹⁶, QFD in 3-D space has been developed¹³ for a many-electron system in the presence of external electric and magnetic fields. The continuity and the Euler-type equations viz.

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

$$m \left[\frac{\partial \mathbf{v}_k}{\partial t} + (\mathbf{v}_k \cdot \nabla) \mathbf{v}_k \right] + [e\mathbf{E} + e/c \mathbf{v}_k \times \mathbf{B}] = -\nabla (U_k + V_{\text{eff}}) \quad (15)$$

are obtained for each NO component. The fluid under consideration is thus an N -component fluid—each fluid component corresponds to an NO and moves under the action of forces arising from the effective potential V_{eff} consisting of several terms of the NO hamiltonian, the Lorentz term as well as the quantum potential $U_k (\equiv -\hbar^2/2m \nabla^2 \rho_k^{1/2} / \rho_k^{1/2})$. The net electron density and the current density are given by

$$\rho(\mathbf{r}, t) = \sum_k \eta_k \rho_k(\mathbf{r}, t), \quad (16)$$

$$\text{and } \mathbf{J}(\mathbf{r}, t) = \sum_k \eta_k \rho_k(\mathbf{r}, t) \mathbf{v}_k(\mathbf{r}, t)$$

where η_k is the occupation number of the k th NO.

Although apart from its physical content, the NO formulation seems to have promise for studying magnetic properties¹⁷, its practical applicability is, however, restricted by the difficulty¹⁸ in calculating the NO's and their occupation numbers. With a view to developing a simpler scheme, we now make use of the DFT.

Using the Hohenberg-Kohn energy density functional and the Kohn-Sham one-particle equation⁷

$$-\frac{\hbar^2}{2m} \Delta^2 \psi_k + V_{\text{coul}} + V_{\text{xc}} \psi_k = \epsilon_k \psi_k \quad (17)$$

the fluid-dynamical equations have been obtained¹² in 3-D space for the ground state of a many-electron system. This is the case of a static stationary state ($\mathbf{v}=0$) and ρ is independent of time. Thus, the continuity equation is trivially satisfied and the net force on the electron fluid consisting of quantum, classical Coulomb and exchange-correlation (XC) contributions vanishes. The equations have been expressed in tensorial form and the net quantum stress tensor is given by

$$T_{\mu\nu} = \frac{\hbar^2}{4m} \nabla^2 \rho \delta_{\mu\nu} - \frac{\hbar^2}{4m} \sum_k \frac{(\nabla_\mu \rho_k)(\nabla_\nu \rho_k)}{\rho_k} \quad (18)$$

A comprehensive stress tensor has also been defined¹² in terms of the quantum, XC and the electrostatic stress tensors. The latter can be expressed¹⁹ in terms of electric fields arising from nuclear and electronic charge distributions and have the same form as that of Maxwell's stress tensor in classical electrodynamics. The vanishing of 'local' force density provides an interesting implication of the stress tensor—it prevents a spontaneous collapse of the charge density onto the nuclei as well as a spontaneous oozing out of the charge from the system—thus explaining the stability of matter.

In order to develop a corresponding time-dependent description, one requires a time-dependent density-functional theory (TDDFT) which was not available so far. A recent formalism of TDDFT for certain oscillating time-dependent potentials provides a one-particle^{5,6} time-dependent Kohn-Sham type equation, viz.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{coul}} + V_{\text{ext}}(\mathbf{r}, t) + V_{\text{xc}} \right] \psi_k = i \hbar \frac{\partial \psi_k}{\partial t} \quad (19)$$

The QFD within this framework consists of the continuity equation

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \mathbf{v}_k) = 0,$$

and the Navier-Stokes equation

$$m \frac{\partial}{\partial t} (\rho_k \mathbf{v}_k) + \nabla (\rho_k \mathbf{v}_k \mathbf{v}_k) = -\rho_k \nabla (V_q)_k - \rho_k \nabla V_{\text{coul}} - \rho_k \nabla V_{\text{xc}} - \rho_k \nabla V_{\text{ext}} \quad (20)$$

In this case also, one encounters an N -component fluid—the net density and the current being obtained by summing over the individual orbitals, viz.

$$\rho(\mathbf{r}, t) = \sum_k \rho_k(\mathbf{r}, t),$$

$$\mathbf{J}(\mathbf{r}, t) = \sum_k \rho_k(\mathbf{r}, t) \mathbf{v}_k(\mathbf{r}, t). \quad (21)$$

The fluid-dynamical equations can also be written⁵ in terms of these mean quantities, viz.

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

$$m \frac{\partial}{\partial t} (\rho \mathbf{v}) = \nabla \cdot \mathbf{U} - \rho \nabla V_{\text{coul}} = \rho \nabla V_{\text{ext}} - \rho \nabla V_{\text{xc}}, \quad (22)$$

where the stress tensor \mathbf{U} is given by

$$U_{\mu\nu} = -m\rho v_{\mu} v_{\nu} - m \sum_k \rho_k (\mathbf{v}_k - \mathbf{v})_{\mu} (\mathbf{v}_k - \mathbf{v})_{\nu} + \frac{\hbar^2}{4m} \nabla^2 \rho \delta_{\mu\nu} - \frac{\hbar^2}{4m} \sum_k \frac{(\nabla_{\mu} \rho_k)(\nabla_{\nu} \rho_k)}{\rho_k} \quad (23)$$

The two basic quantities of importance in the hydrodynamic model are the density ρ and the current density \mathbf{J} . However, for an N -component fluid considered here, these two quantities can be obtained only through the calculation of ρ_k and \mathbf{J}_k for each component and then summing over k . Although this approach may have the advantage that it retains the orbital (or particle) picture and hence may be more useful for interpretive purposes in chemistry, it would be of interest to develop QFD in terms of the net ρ and \mathbf{J} directly.

For this purpose, we make use of the recently proposed new equation for the direct calculation of electron density in many-electron systems suggested by Deb and Ghosh²⁰. The Hartree-Fock relation between the kinetic and exchange energy density with a nonlocal approximation²¹ to the latter leads to the kinetic energy density functional as

$$t[\rho] = -\frac{\hbar^2}{4m} \nabla^2 \rho + \frac{\hbar^2}{8m} \frac{\nabla \rho \cdot \nabla \rho}{\rho} + C_k f(r) \rho^{5/3} \quad (24)$$

where

$$C_k = \frac{3}{10} (3\pi^2)^{2/3} \frac{\hbar^2}{m}$$

By incorporating this expression in the total energy-density functional of Hohenberg and Kohn, and minimizing the latter subject to N -representability conditions, one obtains an Euler-Lagrange nonlinear second order differential equation (for details, see Ref. 20)

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V_{\text{coul}} + V_{\text{xc}} + V_{\text{TF}} \right] \phi = \mu \phi, \quad (25)$$

where $V_{\text{TF}} = (5/3) C_k g(r) \rho^{2/3}$ with $\rho = |\phi|^2$ and μ is Lagrange multiplier interpreted as chemical potential. The function $g(r)$ is related to $f(r)$ and $\phi(r)$ may be interpreted as a 3-D 'wave function' of a many-electron system.

As a first step to solving (25), we consider the four noble gas atoms Ne, Ar, Kr and Xe, and model the $f(r)$ and $g(r)$ functions as sums of gaussians²⁰, viz

$$f(r) = \sum_{i=1}^n A_i \exp[-\alpha_i (r - R_i)^2]$$

$$g(r) = \sum_{i=1}^n A_i \exp[-\beta_i (r - R_i)^2]$$

with $f(0) = 0$, $g(0) = 0$ and $f(\infty) = 1$, $g(\infty) = 1$, where $A_i = A_i(Z, n)$ are the peak heights; $R_i = R_i(Z, n)$ are the peak positions; Z is the nuclear charge and n is the number of shells.

With a suitable input of parameters²⁰, the density equation when solved numerically, yields not only the shell structure in radial density but also shows impressive agreement in density and energy with the corresponding Hartree-Fock values.

The simplification introduced comes from the fact that one has to solve only one equation here in contrast to N equations in the case of conventional Kohn-Sham DFT. However, although (25) is exact within the Hartree-Fock framework, at present we have introduced approximations and restrictions by modelling $f(r)$ and $g(r)$ functions as a superposition of gaussians for the closed shell atoms. *Ab initio* derivations of these functions for atomic and molecular systems would be of immense interest.

Using (25) and following the approach of our earlier work¹² within the conventional DFT, it is easy to conclude that the net 'local' force density vanishes in the present case too. The only new feature being introduced is that another term $\rho \nabla V_{\text{TF}}$ contributes to the net force.

The density equation (25) can however be generalised²² to include the effect of external oscillating time-dependent potentials⁵. The dynamic density equation becomes

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V_{\text{coul}} + V_{\text{ext}} + V_{\text{xc}} + V_{\text{TF}} \right] \phi(\mathbf{r}, t) = i \hbar \frac{\partial \phi}{\partial t} \quad (26)$$

Writing

$$\phi(\mathbf{r}, t) = R(\mathbf{r}, t) \exp [i S(\mathbf{r}, t)/\hbar]$$

the continuity and the Euler equations become

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

and

$$m \frac{\partial}{\partial t} (\rho \mathbf{v}) = \nabla \cdot \mathbf{U} - \rho \nabla (V_{\text{coul}} + V_{\text{ext}} + V_{\text{xc}} + V_{\text{TF}}) \quad (27)$$

respectively, where the stress tensor \mathbf{U} is given by

$$U_{\mu\nu} = -m\rho v_{\mu} v_{\nu} + \frac{\hbar^2}{4m} \nabla^2 \rho \delta_{\mu\nu} - \frac{\hbar^2}{4m} \frac{(\nabla_{\mu} \rho)(\nabla_{\nu} \rho)}{\rho} \quad (28)$$

These equations involve only 3-D quantities $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$. The advantage here is that one deals with only two equations in contrast to $2N$ equations in the case of an N -component fluid.

It is now clear that a many-electron system can be viewed as a fluid in 3-D space. The evolution of the system is governed by the fluid-dynamical equations which are purely classical—the quantum property enters through the appearance of the quantum force alone. The continuous nature of the electron density distribution gives it a more fluid-like character than a classical fluid. The electron density ρ and the current density \mathbf{J} can be solved for from the hydrodynamical equations and the stress tensors can be evaluated in terms of these quantities.

A simple model for chemical binding has earlier been developed²³ in terms of the electrostatic stress tensor. The study of the change in the total stress and force density at various points during molecule formation leads to new insights in the understanding of chemical binding. Quantum stress tensor has already been studied in problems of nuclear physics. Investigation of molecular systems through the same may yield new understanding of chemical binding, molecular shapes, chemical reactivity, etc.

This viewpoint of 'local' force density or stress in the electron fluid can be considered as a generalization of the force concept²⁴ where one considers the net forces acting on the nuclei using the Hellmann-Feynman theorem²⁵. Highly versatile models of molecular geometry²⁶⁻²⁸ have already been developed using the force concept²⁴.

The main advantage of studying a quantum system in terms of the hydrodynamical quantities, viz electron density, current density, force density, etc. is that these are all 'local' quantities and thus much finer details may be revealed¹² in contrast to the global ones. This aspect has generated further interest in studying other property density functions^{1,29} viz energy density, polarizability density, etc. These densities are defined so as to yield the corresponding global quantities, viz energy and polarizability on integration over the whole 3-D space.

Another interesting related research deals with the concept of quantum subspace. Bader³⁰ has shown how a molecule can be divided into atom-like fragments by surfaces determined by the zero flux of $\nabla\rho$. This concept of atoms in molecules³¹ which is a very important concept in chemistry has been further illustrated³² through a topological analysis of the molecular charge distribution. A similar topological analysis has begun³³ for the current density distribution also. These studies strengthen the foundation of the concept of transferability.

To summarise, we point out that the wavefunction, being complex in general, requires two real quantities for its complete specification. The treatment of QFD is consistent with this fact and involves the real quantities density and current corresponding to the amplitude

and phase parts of the wavefunction. The conventional DFT⁷ deals with only the density $\rho(\mathbf{r})$ as its basic variable for a static stationary state where the wavefunction is real. Although DFT for a completely general situation, e.g. for a many-electron system in the presence of time-dependent electric and magnetic fields, has not yet been available, it seems to involve two fundamental quantities viz the density $\rho(\mathbf{r}, t)$ and current $\mathbf{J}(\mathbf{r}, t)$. In view of this, a synthesis of the DFT and QFD as has been attempted^{1,18} here plays a role of highly vital significance in the future course of interpretive quantum chemistry.

A simple formulation of a completely general QFD in 3-D space is, however, yet to be developed (the NO scheme¹³ suffers from the drawback of complicity). It might provide a direct route to the calculation of ρ and \mathbf{J} in terms of which most of the atomic and molecular properties can be calculated. The advantages of calculating electric properties like dynamic polarizability³⁴ through the hydrodynamical approach have already been established³⁵. Recently, attention has been paid¹⁷ to the magnetic properties as well. However, the most serious drawback of the fluid dynamical approach is that the equations are highly nonlinear¹³ and rather difficult to solve.

Besides enabling one to gain considerable insight into many aspects of structure and properties of molecules, QFD seems to be attractive for developing interpretive models of various aspects of reaction dynamics. Thus, a chemical reaction can be viewed³⁶ as the collision of two liquid drops; a dissociation reaction can be considered as the splitting of a liquid drop into fragments and so on. Such models have been highly successful in understanding nuclear reactions, nuclear fission, etc. The study of quantum streamlines as well as vorticity³⁷ may again provide new information on chemical reactivity, molecular collisions, magnetic properties, etc. All these developments may have significant impact on the future progress of many areas of chemistry as well as other related disciplines.

In conclusion, it should be emphasized that the 'classical' picture of quantum chemistry developed in terms of quantum fluid dynamics in 3-D space as discussed in this work has considerable potential for applications in many areas of chemistry, physics and biology. However, much remains to be done before the hydrodynamic analogy to quantum chemistry is considered to be complete.

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