[The electron density is a very attractive starting point for the construction of models to understand the behaviour of atoms, molecules and solids. It is therefore desirable to have a reliable method for the direct calculation of electron density in such systems, bypassing the many-electron wave function and the Schrodinger equation. In this article Dr. Deb reviews briefly some recent attempts in this direction and indicates how far we are from this goal.—Ed.]

ON THE DIRECT CALCULATION OF ELECTRON DENSITY IN MANY-ELECTRON SYSTEMS

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OVER the last decade and a half, the fundamental importance of electron density in predictive and interpretive theories of chemistry has come to be well recognized[1-3]. Briefly, as compared with the wave function approach, electron density is a more attractive starting point for the construction of models to understand the behaviour of atoms, molecules and solids since these phenomena can then be visualized in the three-dimensional (3D) space enabling us to discourse in a largely classical language. In a number of instances, this yields new and deeper physical insights which are not readily extractable from the wave function[1,2]. Further, according to the Hohenberg-Kohn theorem[4], the electron density is a basic quantum-mechanical variable and, in the ground state, contains *all* information about the many-electron system. It has thus been tempting to think of an alternative formulation of the quantum mechanics of atoms, molecules and solids solely in terms of the electron density.

Clearly, the principal objective in such an alternative formulation is an *exact* method for the *direct* evaluation of electron density, bypassing the wave function and the Schrödinger equation.* It is the purpose of this article to discuss the efforts in this direction by a number of workers in different countries.

Although these efforts do not yet provide a satisfactory solution, they do provide some glimmerings of hope.

In view of the recent upsurge of interest in electron density studies, it is worthwhile to note that the density approach is almost as old as the wave function approach. Besides having paved the way to modern density-functional methods[4], the Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) models with their various modifications[5,6] continue to *interest* and *inspire* many physicists and chemists. In fact, the TFD terms (see later) still play an important role in present-day attempts to calculate the density without going through the wave function.

Ideally, what we are looking for is a differential (or an integro-differential) equation in terms of the electron density. In an earlier attempt, Yuan and Light[7] had obtained the following Milne equation for atoms through a Langer transformation, $r = e^x$, for the radial variable:

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

where Z is the nuclear charge and l is the azimuthal quantum number; the function $w(x)$ is related to the radial wave function $R_{nl}(r)$ and, therefore, to the radial density $4\pi r^2 \rho(r)$ in a roundabout manner[7]. Thus, in order to obtain the radial density for, *e.g.*, closed-shell atoms, one must first solve the above *nonlinear* second-order differential equation. For the Kr atom, the authors claimed

quite good results for the energy and density, including the shell structure (missing in the TF radial density*) over the range $0 \leqslant r \leqslant \infty$, except a small region near the nucleus.

While Eq. (1) does not directly involve the density, Lawes and March[8] have obtained approximate differential equations for atoms and molecules whose solutions would yield the corresponding densities. For closed-shell atoms, the central-field problem may be treated as a 1D case. The density equation for closed-shell atoms then turns out to be a *third-order* differential equation:

$$\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2 \rho) + \frac{1}{2}r^2 \rho \frac{\partial V}{\partial r}$$
$$+ (\mu - V)\frac{\partial}{\partial r}(r^2 \rho)$$
$$= \sum_l \frac{l(l+1)(2l+1)}{2r^2}$$
$$\times \left[r\rho_l + \frac{\partial}{\partial r}(r^2 \rho_l) \right], \qquad (3)$$

$$\rho(r) = \sum_l (2l+1)\rho_l(r), \qquad (4)$$

where the one-body external potential V contains the effects of exchange and correlation subtly through ρ. The third-order term is expected to be rather significant for light atoms but its importance is likely to diminish with much heavier atoms.

For the *molecular* situation the equation proposed by Lawes and March[8] is probably the first of its kind. For 1D motion they obtain a *nonlinear* third-order equation which does not involve $\rho(r)$ directly:

$$\frac{1}{2}(V' - U') + \beta\left[(U-V)U' + \frac{U'''}{8}\right.$$
$$\left. - \frac{\partial U'}{\partial \beta}\right] + \beta^2\left[U'\frac{\partial U}{\partial \beta} - \frac{3}{8}U'U''\right]$$
$$+ \frac{\beta^3}{8}U'^3 = 0, \qquad (5)$$

where $\beta = 1/kT$ and $U(x\beta)$ is an effective potential related to the generalized partition

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* Recall that, according to the TF model[5], electron density is given by

$$\rho(r) = \frac{8\pi}{3h^3}(2m)^{3/2}[\mu - V(r)]^{3/2}, \qquad (2)$$

where μ is the chemical potential and $V(r)$ is the one-body external potential.

function $Z(x\beta)$. The linear approximation of Eq. (5) is

$$\frac{1}{2}(V' - U_1') + \frac{\beta}{8}U_1''' - \beta\frac{\partial U_1'}{\partial \beta} = 0. \qquad (6)$$

Generalizing Eq. (6) to 3D space gives

$$\frac{1}{8}\beta\nabla^2 U_1 - \frac{1}{2}(U_1 - V) - \beta\frac{\partial U_1}{\partial \beta} = 0, \qquad (7)$$

so that one has finally arrived at a *second-order linear* equation for a molecule. The solution of Eq. (7) is

$$U_1(r\beta) = \int g(rr'\beta) V(r')\, dr', \qquad (8)$$

where

$$g(rr'\beta) = \frac{1}{\pi\beta |r - r'|}$$
$$\times \exp\left[-\frac{2}{\beta}|r - r'|^2\right]. \qquad (9)$$

Knowledge of $U_1(r\beta)$ gives the corresponding partition function $Z(r\beta)$ and then the *approximate* $\rho(r)$ may be calculated as the inverse Laplace transform of Z/β. Actual atomic and molecular calculations following the above prescriptions do not seem to be reported so far.

An alternative density-functional approach is being developed by Deb and Ghosh[9]. Using the Hartree-Fock relation between the kinetic and exchange energy density and a nonlocal approximation to the latter[10], one can write the kinetic energy-density functional as (in atomic units)

$$t[\rho] = -\frac{1}{4}\nabla^2 \rho + \frac{1}{8}\frac{\nabla\rho \cdot \nabla\rho}{\rho}$$
$$+ Kf(r)\rho^{5/3}, \qquad (10)$$

where K is a constant and $f(r)$ is related to an average electron density over the exchange hole. By incorporating Eq. (10) in the total energy-density functional and minimizing the latter subject to N-representability conditions (see later), one obtains an Euler-Lagrange *nonlinear second-order* differential equation:

$$[-\tfrac{1}{2}\nabla^2 + v_{nuc}(r) + v_{cou}(r) + v_{xc}(r)$$
$$+ \tfrac{5}{3}Kf(r)\rho^{2/3}]\phi(r) = \epsilon\phi(r), \qquad (11)$$

where ϵ is a Lagrange multiplier, $\rho = \phi^2$ and xc denotes exchange-correlation. For atoms, the energy and the shell structure depend sensitively on $f(r)$, with the maxima in $f(r)$ corresponding to the minima in the radial

density. Note that since Eq. (11) is a Schrödinger-like equation, $\phi(r)$ has a very interesting interpretation as the 3D wave function of a many-electron system. Numerical results and other details of this work will be reported elsewhere[9].

Thus far, attempts to obtain and solve differential (or integro-differential) equations for $\rho(r)$ are complicated by the nonlinearity and higher than second-order character of the equations involved. Further, if one variationally minimizes a total energy-density functional which also includes density gradients, then one can even land with a fourth or higher order equation! To avoid these difficulties Gázquez and Parr[11] suggested the use of trial densities incorporating certain parameters that can be adjusted to make the following energy functional a minimum:

$$E[\rho] = T_0[\rho] + T_2[\rho] + T_4[\rho] + V_{ne}[\rho] + J[\rho] - K[\rho], \quad (12)$$

where T_0 is the kinetic energy of a free electron gas, T_2 is 1/9th Weizsäcker correction and T_4 is a fourth-order correction to the kinetic energy; V_{ne} is electron-nuclear attraction; J is electron cloud self-interaction and K is the exchange energy of a free electron gas. The original TF model includes only T_0, V_{ne} and J whereas the TFD model also includes $-K$. (For expressions of the separate terms in Eq. (12) see Gázquez and Parr[11].) Their suggested trial density for atoms (without the shell structure) is

$$\rho(r) = \frac{C}{(1 + \beta r)^n}, \quad \beta = \frac{a}{n}; \quad (13)$$

$$\rho(r) \to Ce^{-ar}, \text{ as } n \to \infty, \quad (14)$$

where C is a normalization constant and a and n are the variational parameters. For first-row atoms, this simple approach yields energy values within 3% error. But, for Ar, Ni and Kr, the error in energy is rather large, being 26·7, 105·6 and 235 Hartrees respectively.[*]

Lima and Ferreira[12] have, however, claimed greater accuracy than Gázquez and Parr

through a trial density which is a sum of two Yukawa terms :

$$\rho(r) = \frac{1}{4\pi r}(N_1 \partial_1^2 e^{-\delta_1 r} + N_2 \partial_2^2 e^{-\delta_2 r}), \quad (15)$$

where three of the four parameters, N_1, N_2 and ∂_1, are fixed by TF theory and the fourth (∂_2) is varied to make the energy a minimum. Thus, Eq. (15) gives essentially a one-parameter function and is apparently a more attractive alternative to Gázquez and Parr. However, Deb et al.[13] prefer the Gázquez-Parr approach since the Lima–Ferreira function has a singularity at the nucleus and involves an inherent ambiguity because of its use of TF approximation; further, they employ both the wave function and a one-electron Schrödinger equation. Hence, to improve upon the Gázquez-Parr results, Deb et al[13] suggest the inclusion of a correlation functional in Eq. (12) and the use of a two-parameter (structureless) trial density

$$\rho(r) = Ae^{-ar} e^{-\beta r^2}. \quad (16)$$

Numerical results and other details of this work will be reported elsewhere[13]. It is, however, clear that the accuracy in energy obtainable with such trial densities will not be high, and unless one employs a set of piecewise continuous (e.g., exponential) functions[14] or a linear combination of functions[9,15,16] the shell structure in the atomic radial density will not be obtained.

In an interesting work, Hall and Martin[16] have suggested the calculation of approximate electron density from a linear combination of expansion functions by minimizing the total energy of the error-field (the difference between the true and approximate electric fields). This approach is closely related to the Dirichlet minimum-energy theorem in electrostatics and provides a good approximation to the total Coulomb energy of the electrons.

Finally, the hydrodynamical analogy to quantum mechanics also promises to yield solvable differential equations for the electron density. In this approach, the Schrödinger equation in the multidimensional configuration space is replaced by two hydrodynamical equations in 3D space, viz., a continuity equation

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[*] 1 Hartree is 27·211 eV.

and an Euler or a Navier-Stokes equation of motion, involving the (electron) fluid density and fluid velocity. The hydrodynamical analogy, its connection with density-functional theory and the concept of a molecular stress tensor have received considerable recent attention (see, e.g., Refs. 17-20 and other references therein). However, here also one faces the problem of having a *nonlinear* differential equation for the density and no illustrative density calculation using this approach has been reported so far.

While substantial progress along the aforementioned three lines of attack are expected in future, it is necessary to remind ourselves that the direct calculation of electron density must satisfy certain conditions (ignored by several reported calculations), associated with the antisymmetric nature of the N-electron wave function as well as the latter's short-range and long-range behaviour. These conditions may be stated as (see, e.g., Ref. 21):

(*a*) *N-representability*[22, 23]

   (i) $\rho(r)$ *finite, nonnegative and differentiable* everywhere.

   (ii) $\int \rho(r) \, dr = N.$ (17)

(*b*) *Cusp condition*

$$\underset{r_a \to 0}{\text{Lim}} \left(\frac{\partial}{\partial r_a} + 2Z_a \right) \rho_{0a}(r_a) = 0, \quad (18)$$

where r_a is the distance from the nucleus of charge Z_a and $\rho_{0a}(r_a)$ is the spherically averaged charge density.

(*c*) *Asymptotic condition*: The long-range electron density satisfies the condition

$$\rho(r) \sim \exp\left[- 2(- 2\mu_{max})^{1/2} r\right], \quad (19)$$

where μ_{max} is the least negative eigenvalue of a matrix $\hat{\mu}$ which is a functional of the one-electron and two-electron reduced density matrices[21, 24]; its magnitude is not less than the first ionization energy. Use of cusp and aymptotic conditions is likely to reduce the number of adjustable parameters in variational calculations with trial density functions.

In conclusion, this brief article has highlighted the main problems associated with recent attempts to directly evaluate the electron density in many-electron systems. Although a satisfactory solution to this problem is not

yet in sight, considerable progress toward this is expected in future. This should profoundly influence the future growth of the quantum mechanics of atoms, molecules and solids, and therefore should have a marked impact on large areas in physical, chemical and biological sciences.

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