



Direct calculation of ground-state electronic densities and properties of noble gas atoms through a single time-dependent hydrodynamical equation

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Abstract

Ground-state electronic densities and properties of noble gas atoms (He, Ne, Ar, Kr and Xe) have been calculated through a single time-dependent quantum fluid dynamical equation of motion. The equation has been transformed through imaginary time into a diffusion equation which is then numerically solved in order to reach a global minimum. The present results compare favourably with other available values. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Within the broad domain of density functional theory (see, e.g., Ref. [1]), the interesting problem of directly calculating the time-independent (TI) and time-dependent (TD) electron densities of atoms, molecules, clusters and solids from a single equation [2] has so far remained unsolved. A successful methodology for calculating the ab initio electron densities of such many-electron systems would considerably reduce the conceptual and computational labour in understanding the static and dynamic properties of extended systems, even though this would obscure the orbital structure of the density. Over the years, several efforts have been made to address this

problem in the case of atoms and molecules. For TI densities, beginning with the Thomas–Fermi method (see, e.g., Ref. [3]), subsequent works included a second-order differential equation (Milne equation) for atoms [4], a second-order differential equation for noble gas atoms [5–9], an algebraic (quadratic) equation for atoms and ions [10], etc. However, these equations do not yield the dynamical density.

In a parallel development, a single TD generalized nonlinear Schrödinger equation (GNLSE) of motion has been derived for studying the time-evolution of atoms and molecules under small and large perturbations [11]. The GNLSE has been based on the hydrodynamical analogy to quantum mechanics (see Ref. [12] for a comprehensive review and other references therein). It regards the collective motion of the electrons as akin to the motion of a ‘classical’ fluid, characterized by the quantum mechanical charge density and current density. The equation has been applied to study several TD processes, e.g., a He atom under intense and superintense laser fields,

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H_2 and HeH^+ molecules under an intense laser field, H^+-Ne and H^+-He collision dynamics, etc. (see Refs. [13–15]). Recently, this methodology has been applied to obtain the static (TI) ground-state electron density from a numerical solution of the TD fluid dynamical equation, by using an imaginary-time propagation technique coupled with the minimization of an expectation value [15]. Initial results for atomic (He, Be^{2+} , Ne) and molecular (H_2 , HeH^+ , He_2^{2+}) systems have been encouraging [15]. In this Letter, the method is extended to calculate the ground-state densities and properties of noble gas atoms (He, Ne, Ar, Kr and Xe), comparing the results with available literature data. The He and Ne results are slightly improved compared with the previous work.

In Section 2, a summary of the method is presented whereby the fluid dynamical GNLSE is transformed through imaginary time into a diffusion equation. Section 3 briefly describes the numerical method for solving the diffusion equation in real time. Section 4 presents the results while Section 5 makes a few concluding remarks.

2. Methodology

The methodology has been discussed elsewhere [15] in detail. Here, a summary is presented. TD quantum fluid density functional theory (QFDFT) regards all electrons in a system to be distributed over 3D space like a continuous ‘classical’ fluid. The two basic QF dynamical equations in terms of local observables, electron density $\rho(\mathbf{r}, t)$ and current density $\mathbf{j}(\mathbf{r}, t)$ are (atomic units are employed throughout unless otherwise mentioned):

(1) Continuity equation:

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0, \quad (1)$$

(2) Euler-type equation of motion:

$$\frac{\partial \chi(\mathbf{r}, t)}{\partial t} + \frac{1}{2}(\nabla \chi)^2 + \frac{\delta G[\rho]}{\delta \rho} + \frac{\delta E_{\text{el-el}}}{\delta \rho} + v(\mathbf{r}, t) = 0, \quad (2)$$

where $\mathbf{j}(\mathbf{r}, t) = \rho \nabla \chi(\mathbf{r}, t)$, χ being the velocity potential. $v(\mathbf{r}, t)$ is the TD potential including electron–nuclear attraction and interaction with the external field. $E_{\text{el-el}}$ is the interelectronic Coulomb repulsion energy while $G[\rho]$ is a universal density functional consisting of kinetic and exchange–correlation energy functionals,

$$G[\rho] = \frac{1}{8} \int \frac{|\nabla \rho|^2}{\rho} d\mathbf{r} + T_{\text{corr}}[\rho] + E_{\text{xc}}[\rho]. \quad (3)$$

The first term on the right-hand side of Eq. (3) is the Weizsäcker kinetic energy which gives the exact kinetic energy for one-electron systems and two-electron Hartree–Fock (HF) systems. Therefore, $T_{\text{corr}}[\rho]$ vanishes for such systems. However, for systems with more than two electrons, $T_{\text{corr}}[\rho]$ has to be suitably approximated (see later). This form of kinetic energy functional, retaining the Weizsäcker term as such *plus* a correction term (usually a TF-like term), ensures proper global as well as local behaviour including atomic shell structure [5].

The complex-valued hydrodynamical wave function for the entire time-evolving system is

$$\psi(\mathbf{r}, t) = \rho(\mathbf{r}, t)^{1/2} e^{i\chi(\mathbf{r}, t)}. \quad (4)$$

Now, one can obtain a diffusion-type equation similar to the random walk quantum Monte Carlo equation [16] as follows:

Writing Eqs. (1) and (2) in imaginary time τ and substituting τ by $-it$, t being the real time, one obtains

$$-\frac{1}{i} \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \nabla \chi) = 0, \quad (5)$$

$$\frac{1}{i} \frac{\partial \chi}{\partial t} = \frac{1}{2} (\nabla \chi)^2 + \frac{\delta G[\rho]}{\delta \rho} + \frac{\delta E_{\text{el-el}}}{\delta \rho} + v(\mathbf{r}, t). \quad (6)$$

Writing Eq. (4) in τ , differentiating both sides with respect to τ and substituting τ by $-it$, one obtains

$$\frac{1}{i} \frac{\partial \rho}{\partial t} = \frac{2}{i} \frac{\partial R}{\partial t} \frac{\rho}{R} - 2 \frac{\partial \chi}{\partial t} \rho. \quad (7)$$

Note that ψ in Eq. (4) has been replaced by R since they differ from each other due to the above time transformation. Expressing $\nabla \rho$ and $\nabla^2 \rho$ as

$$\nabla \rho = \rho \left[\frac{2\nabla R}{R} - 2i\nabla \chi \right], \quad (8)$$

$$\nabla^2 \rho = \rho \left[\frac{2(\nabla R)^2}{R^2} - 4(\nabla \chi)^2 - 2i\nabla^2 \chi + \frac{2\nabla^2 R}{R} - \frac{8i\nabla R \cdot \nabla \chi}{R} \right], \quad (9)$$

$\delta G[\rho]/\delta \rho$ can be written as

$$\frac{\delta G[\rho]}{\delta \rho} = -\frac{1}{2} \frac{\nabla^2 R}{R} + \frac{i\nabla R \cdot \nabla \chi}{R} + \frac{1}{2} (\nabla \chi)^2 + \frac{i}{2} \nabla^2 \chi + \frac{\delta E_{xc}[\rho]}{\delta \rho} + \frac{\delta T_{corr}[\rho]}{\delta \rho}. \quad (10)$$

Substitution of Eq. (7) into Eq. (5) leads to

$$\frac{\partial R}{\partial t} \frac{1}{R} + \frac{1}{i} \frac{\partial \chi}{\partial t} + \frac{\nabla^2 \chi}{2i} + \frac{\nabla R \cdot \nabla \chi}{iR} - (\nabla \chi)^2 = 0. \quad (11)$$

Finally, use of Eqs. (10) and (11) in Eq. (6) eliminates χ and yields the equation

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\rho; \mathbf{r}, t) \right] R(\mathbf{r}, t) = -\frac{\partial R(\mathbf{r}, t)}{\partial t} \quad (12)$$

which closely resembles a diffusion-type equation. $R(\mathbf{r}, t)$ is the diffusion function and the diffusion process is governed by $v_{\text{eff}}(\rho; \mathbf{r}, t)$. A similar elimination of $\chi(\mathbf{r}, t)$ from Eqs. (1) and (2) leads to the TD QFDFE equation of motion

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\rho; \mathbf{r}, t) \right] \psi(\mathbf{r}, t) = i \frac{\partial \psi(\mathbf{r}, t)}{\partial t}. \quad (12a)$$

$v_{\text{eff}}(\rho; \mathbf{r}, t)$ contains both classical and quantum potentials,

$$v_{\text{eff}}[\rho; \mathbf{r}, t] = \frac{\delta E_{\text{el-el}}}{\delta \rho} + \frac{\delta E_{\text{nu-el}}}{\delta \rho} + \frac{\delta E_{\text{xc}}}{\delta \rho} + \frac{\delta T_{\text{corr}}}{\delta \rho} + \frac{\delta E_{\text{ext}}}{\delta \rho}. \quad (13)$$

The terms on the right-hand of Eq. (13) are as follows: the first is the interelectronic repulsion term, the second is the electron–nuclear attraction term, the third is the exchange–correlation term, the fourth

arises from a non-classical correction term added to the Weizsäcker kinetic energy while the last term arises from interaction with the external field (in the present case, this interaction is zero).

$$E_{\text{el-el}} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

$$\frac{\delta E_{\text{el-el}}}{\delta \rho} = \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (14)$$

$$E_{\text{nu-el}} = -\int \frac{Z}{r} \rho(\mathbf{r}, t) d\mathbf{r}, \quad \frac{\delta E_{\text{nu-el}}}{\delta \rho} = -\frac{Z}{r}. \quad (15)$$

Various exchange–correlation functionals are available in the literature [17–21]. We have employed the exact exchange–energy expression for He, while for other noble gas atoms a local exchange functional [22] has been used. Thus, for He,

$$E_x = -\frac{1}{4} \iint \frac{\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

$$\frac{\delta E_x}{\delta \rho} = -\frac{1}{2} \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (16)$$

For other atoms [22],

$$E_x = E_x^{\text{LDA}} - \beta \int \frac{\rho^{1/3}}{(1 + r^2 \rho^{2/3} / \alpha_x)} \rho d\mathbf{r},$$

$$E_x^{\text{LDA}} = -C_x \int \rho^{4/3} d\mathbf{r}, \quad (17)$$

$$C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}, \quad \beta = C_x, \quad \alpha_x = 0.0244,$$

and

$$\frac{\delta E_x}{\delta \rho} = \frac{\delta E_x^{\text{LDA}}}{\delta \rho} - \beta \left[\frac{\frac{4}{3} \rho^{1/3} + \frac{2}{3} \frac{r^2 \rho}{\alpha_x}}{\left(1 + \frac{r^2 \rho^{2/3}}{\alpha_x} \right)^2} \right],$$

$$\frac{\delta E_x^{\text{LDA}}}{\delta \rho} = -\frac{4}{3} C_x \rho^{1/3}. \quad (18)$$

Correlation effects have been included by using a simple, local parametrized Wigner-type functional

which yields good results even for atomic *autoionizing* states [23].

$$E_c = - \int \frac{\rho}{a + b\rho^{-1/3}} d\mathbf{r},$$

$$\frac{\delta E_c}{\delta \rho} = - \frac{a + c\rho^{-1/3}}{(a + b\rho^{-1/3})^2}, \quad (19)$$

$$a = 9.81, \quad b = 21.437, \quad c = 28.582667.$$

Section 4 shows that this somewhat unusual local exchange–correlation functional can yield very good results.

The exact form of $T_{\text{corr}}[\rho]$ is unknown. However, an approximate generalized form for atoms is given by a modified Thomas–Fermi term, viz.,

$$T_{\text{corr}}[\rho] = C_k \int f(\mathbf{r}) \rho^{5/3}(\mathbf{r}) d\mathbf{r},$$

$$C_k = \frac{3}{10} (3\pi^2)^{2/3}, \quad (20)$$

where $f(\mathbf{r})$ is so chosen that

$$(\text{total kinetic energy}) = T_w[\rho] + T_{\text{corr}}[\rho].$$

$f(\mathbf{r})$ satisfies the boundary conditions $f(\mathbf{r}) \rightarrow 0$ as $r \rightarrow 0$ and $f(\mathbf{r}) \rightarrow 1$ as $r \rightarrow \infty$. The functional derivative is given by [5]

$$\frac{\delta T_{\text{corr}}[\rho]}{\delta \rho} = \frac{5}{3} C_k \rho(\mathbf{r})^{2/3} g(\mathbf{r}), \quad (21)$$

where

$$g(\mathbf{r}) = \frac{3}{5} f(\mathbf{r}) + \frac{2}{5} \rho(\mathbf{r})^{-2/3} \int \rho(\mathbf{r}') \tilde{\rho}(\mathbf{r}')^{-1/3} \times \frac{\delta \tilde{\rho}(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}', \quad (22)$$

$$\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r}) f^{3/2}(\mathbf{r}).$$

For noble gas atoms, $f(r)$ and $g(r)$ may be expressed as sums of several gaussian functions, viz.,

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

$$g(r) = \sum_{i=1}^n A_i \exp[-\beta_i (r - R_i)^2]. \quad (23)$$

Table 1
 α_i , β_i , A_i and R_i values (a.u.) for Ne, Ar, Kr and Xe

	Ne	Ar	Kr	Xe
α_1	84.35	223.65	981.70	3014.0
α_2	1.0	35.81	114.25	193.0
α_3	–	1.35	15.15	76.0
α_4	–	–	0.80	22.0
α_5	–	–	–	1.0
β_1	49.18	175.365	935.6	2850.0
β_2	1.0	10.987	57.99	123.70
β_3	–	0.6228	7.241	43.94
β_4	–	–	0.87	4.76
β_5	–	–	–	0.5
A_1	2.405	1.78	1.541	1.46
A_2	1.0	3.188	1.711	1.40
A_3	–	1.0	2.22	2.13
A_4	–	–	1.0	1.88
A_5	–	–	–	1.0
R_1	0.30	0.14647	0.06495	0.0405
R_2	2.0508	0.7429	0.2700	0.1602
R_3	–	3.016	1.020	0.47
R_4	–	–	3.42	1.35
R_5	–	–	–	4.20

The α_i , β_i , A_i and R_i values for Ne, Ar, Kr and Xe, given in Table 1, have been slightly modified from those of Ref. [5] for greater accuracy.

3. Numerical solution of the diffusion equation

Denoting the nonlinear operator within square brackets by \hat{L} , Eq. (12) can be written as

$$\hat{L}R(\mathbf{r}, t) = - \frac{\partial R(\mathbf{r}, t)}{\partial t}, \quad (24)$$

i.e., $\hat{L} = -\partial/\partial t$. The Taylor expansion of $R(\mathbf{r}, t + \Delta t)$ around $R(\mathbf{r}, t)$ is given by

$$R(\mathbf{r}, t + \Delta t) = \left[1 + \Delta t \frac{\partial}{\partial t} + \frac{1}{2} (\Delta t)^2 \frac{\partial^2}{\partial t^2} + \dots \right] R(\mathbf{r}, t),$$

$$= e^{\Delta t \partial/\partial t} R(\mathbf{r}, t) = e^{-\Delta t \hat{L}} R(\mathbf{r}, t). \quad (25)$$

Therefore, $e^{-\Delta t \hat{L}}$ is the time-propagator; it is a non-linear evolution operator propagating the diffusion function $R(\mathbf{r}, t)$ from time t to an advanced level $R(\mathbf{r}, t + \Delta t)$. Note that $e^{-\Delta t \hat{L}}$ is a real, non-unitary operator. Therefore, normalization of $R(\mathbf{r}, t)$ at a time does not guarantee normalization at an advanced time $t + dt$.

The variable r (the radial part in spherical polar coordinates) is discretized as

$$r_j = x_j^2, \quad x = \delta + jh, \quad j = 1, 2, \dots, N_1. \quad (26)$$

We have chosen $\delta = 10^{-6}$, $h = 0.0035$ and $N_1 = 5001$. In this discretized grid, Eq. (25) can be written as

$$R_j^{n+1} = e^{-\Delta t \hat{L}_j} R_j^n$$

or, in symmetric form,

$$e^{(\Delta t/2)\hat{L}_j} R_j^{n+1} = e^{-(\Delta t/2)\hat{L}_j} R_j^n. \quad (27)$$

Now, taking R to be a constant in θ and ϕ , \hat{L} can be written in spherical polar coordinates as

$$\begin{aligned} \hat{L} &= -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} + v_{\text{eff}}(\rho; \mathbf{r}, t) \\ &= aD^2 + bD + v_{\text{eff}}, \end{aligned} \quad (28)$$

where

$$a = -\frac{1}{8x^2}, \quad b = -\frac{3}{8x^3}, \quad D = \frac{\partial}{\partial x},$$

$$D^2 = \frac{\partial^2}{\partial x^2}.$$

Therefore, Eq. (27) can be written as

$$e^{(\Delta t/2)(aD^2 + bD + v_{\text{eff}})} R_j^{n+1} = e^{-(\Delta t/2)(aD^2 + bD + v_{\text{eff}})} R_j^n.$$

Finally, expanding the exponentials and truncating after the second term, followed by approximation of $\partial/\partial x$ and $\partial^2/\partial x^2$ by two- and three-point difference formulas respectively, a set of N_1 simultaneous equations are obtained, viz.,

$$\alpha_j R_{j-1}^{n+1} + \beta_j R_j^{n+1} + \gamma_j R_{j+1}^{n+1} = \xi_j^n, \quad (29)$$

where

$$\begin{aligned} \alpha_j &= -\frac{\Delta t}{16x_j^2 h^2} + \frac{3\Delta t}{32x_j^3 h}, \\ \beta_j &= 1 + \frac{\Delta t}{8x_j^2 h^2} + \frac{\Delta t}{2} v_{\text{eff}}, \end{aligned} \quad (30)$$

$$\gamma_j = -\frac{\Delta t}{16x_j^2 h^2} - \frac{3\Delta t}{32x_j^3 h},$$

$$\begin{aligned} \xi_j^n &= \left(\frac{\Delta t}{16x_j^2 h^2} - \frac{3\Delta t}{32x_j^3 h} \right) R_{j-1}^n \\ &+ \left(1 - \frac{\Delta t}{8x_j^2 h^2} - \frac{\Delta t}{2} v_{\text{eff}} \right) R_j^n \\ &+ \left(\frac{\Delta t}{16x_j^2 h^2} + \frac{3\Delta t}{32x_j^3 h} \right) R_{j+1}^n. \end{aligned} \quad (31)$$

Eq. (29) can be written in the following tridiagonal matrix form:

$$\begin{bmatrix} \beta_1 & \gamma_1 & & & & & \\ \alpha_2 & \beta_2 & \gamma_2 & & & & \\ & \cdot & \cdot & \cdot & & & \\ & & \cdot & \cdot & \cdot & & \\ [0] & & & \cdot & \cdot & \gamma_{N_1-1} & \\ & & & & \alpha_{N_1} & \beta_{N_1} & \end{bmatrix} \begin{bmatrix} R_1^{n+1} \\ R_2^{n+1} \\ \dots \\ R_{N_1-1}^{n+1} \\ R_{N_1}^{n+1} \end{bmatrix} = \begin{bmatrix} \xi_1^n \\ \xi_2^n \\ \dots \\ \xi_{N_1-1}^n \\ \xi_{N_1}^n \end{bmatrix}. \quad (32)$$

Eq. (32) can be solved for $\{R_j^{n+1}\}$ by using a modified Thomas algorithm [24]. After solving Eq. (25), the following steps are followed:

(1) The normalization of R_j^{n+1} to R^{n+1} (prime denotes the unnormalized function).

(2) The calculation of expectation value of \hat{L} as

$$\langle \hat{L} \rangle^{n+1} = \langle R^{n+1} | \hat{L} | R^{n+1} \rangle,$$

(3) The estimation of difference in expectation values between two successive time steps, i.e.,

$$\Delta \varepsilon = \langle \hat{L} \rangle^{n+1} - \langle \hat{L} \rangle^n.$$

(4) Until $\Delta \varepsilon$ is less than a prescribed tolerance limit (here, 10^{-7}), one proceeds with the calculation of R^{n+2} , R^{n+3} , ..., iteratively.

All the integrations are performed by a 6-point Newton–Cotes formula. Δt for He, Ne and Ar is 0.005, while for Kr and Xe, it is 0.002 and 0.0005, respectively.

3.1. The initial guess

In order to achieve faster convergence, the initial guess should satisfy the following conditions:

(1) $\int |R|^2 d\mathbf{r} = \int \rho(\mathbf{r}) d\mathbf{r} =$ (total number of electrons).

(2) The atomic shell structure is incorporated.

The combinations of Slater-type functions, chosen to launch computations for various atoms, are presented in Table 2.

4. Results and discussion

The calculated nonrelativistic ground-state energies, along with various energy components for He, Ne, Ar, Kr and Xe, are reported in Table 3. Results have been compared with the corresponding HF values and the best available results in the literature. The calculated total energy values are much improved over the HF values and compare quite favourably with the corresponding accurate values. For Kr and Xe, ‘exact’ nonrelativistic energy values are not available and therefore we have cited the values obtained by adding second-order many-body perturbation theory (MBPT) correlation energy results [28] to the HF results [25]. For all atoms, the agreement of present results with the best literature data is quite satisfactory. The exchange energies show a satisfactory agreement with HF results [18]. For He and Ne, the exchange energy is almost exact while for Ar, Kr and Xe, it is underestimated by 2.3–2.9%. In other words, the simple local functional [22] for $E_x[\rho]$ suffers in comparison with the more elaborate nonlocal, gradient-corrected function-

Table 2
Initial functions (a.u.) used in the present computation

He $\chi_1 = N_1 e^{-r}$		$\phi_{1s} = \chi_1$
Ne $\chi_1 = N_1 e^{-r}$ $\chi_2 = N_2 e^{-2r}$	$\chi_3 = N_3 r e^{-r}$ $\chi_4 = N_4 r e^{-2r}$	$\phi_{1s} = \chi_1 + \chi_2$ $\phi_{2s} = \chi_3 + \chi_4 = \phi_{2p}$
Ar $\chi_1 = N_1 e^{-r}$ $\chi_2 = N_2 e^{-2r}$ $\chi_3 = N_3 r e^{-3r}$	$\chi_4 = N_4 r^2 e^{-3r}$ $\chi_5 = N_5 r^3 e^{-4r}$	$\phi_{1s} = \chi_1 + \chi_2$ $\phi_{2s} = \chi_3 + \chi_4$ $\phi_{3s} = \chi_1 + \chi_2 + \chi_3$ $\phi_{2p} = \chi_3 + \chi_4 + \chi_5 = \phi_{3p}$
Kr $\chi_1 = N_1 e^{-r}$ $\chi_2 = N_2 r e^{-r}$ $\chi_3 = N_3 r^2 e^{-r}$ $\chi_4 = N_4 r^3 e^{-r}$ $\chi_5 = N_5 e^{-2r}$	$\chi_6 = N_6 r e^{-2r}$ $\chi_7 = N_7 r^2 e^{-2r}$ $\chi_8 = N_8 r^3 e^{-2r}$	$\phi_{1s} = \chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 = \phi_{2s}$ $\phi_{3s} = \chi_5 + \chi_6 + \chi_7 + \chi_8 = \phi_{4s}$ $\phi_{2p} = \chi_2 + \chi_3 + \chi_4$ $\phi_{3p} = \chi_6 + \chi_7 + \chi_8$ $\phi_{4p} = \chi_5 + \chi_6 + \chi_7 + \chi_8$ $\phi_{3d} = \chi_5 + \chi_6 + \chi_7 + \chi_8$
Xe $\chi_1 = N_1 e^{-r}$ $\chi_2 = N_2 r e^{-r}$ $\chi_3 = N_3 r^2 e^{-r}$ $\chi_4 = N_4 r^3 e^{-r}$ $\chi_5 = N_5 r^4 e^{-r}$; χ_6 to χ_8 are those for Kr		$\phi_{1s} = \phi_{2s} = \phi_{3s} = \phi_{4s} = \phi_{5s} = \chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5$ $\phi_{2p} = \phi_{3p} = \phi_{4p} = \phi_{5p} = \chi_5 + \chi_6 + \chi_7 + \chi_8$ $\phi_{3d} = \phi_{4d} = \chi_3 + \chi_4$

The number of iterations required for convergence varies from atom to atom: $\{N_i\}$ are normalization constants such that $\int \chi_i^2 d\tau = 1$. ϕ_i denotes the i th atomic orbital with occupation number n_i . $\rho(\mathbf{r}) = \sum_i n_i \phi_i^2$; $\psi = N[\rho(\mathbf{r})]^{1/2}$, where N is such that $\int |\psi|^2 d\mathbf{r} = N^2 \int \rho(\mathbf{r}) d\mathbf{r} = Z$.

Table 3
Comparison of calculated ground-state properties (a.u.) with literature data

		He	Ne	Ar	Kr	Xe
$-E$	PW	2.8973	128.9065	527.5486	2753.8809	7234.9742
	HF ^a	2.8617	128.5470	526.8174	2752.0546	7232.1302
	others	2.9037 ^{*c}	128.938 ^f *	527.604 ^d *	2753.8896 ^e	7235.0512 ^e
			128.939 ^e	527.540 ^f		
$-\langle Z/r \rangle$	PW	6.7850	311.0597	1245.5699	6533.8352	17038.2385
	HF ^b	6.7492	311.1333	1255.0504	6582.5412	17164.9821
$\langle 1/r_{12} \rangle$	PW	2.0651	65.7129	220.6552	1119.3762	2744.7642
	HF ^b	2.0516	66.1476	231.6093	1172.3372	2880.0352
$-E_x$	PW	1.0325	12.1111	29.4850	91.5847	173.9435
	exact ⁱ	1.026	12.11	30.19	93.89	179.2
$-E_c$	PW	0.0423	0.3561	0.7011	1.7529	2.8407
	others	0.042 ^{g,c} *	0.390 ^{g,f} *	0.787 ^g *	1.835 ^h	2.921 ^h
$\langle T \rangle$	PW	2.8974	128.9074	527.5523	2753.9157	7235.2844
	HF ^a	2.8617	128.5468	526.8138	2752.0481	7232.0470
T_w	PW	–	94.2068	322.0345	1377.5940	3226.9174
	HF ^b	–	90.6140	308.4206	1276.7349	2932.0548
T_{corr}	PW	–	34.7006	205.5177	1376.3217	4008.3670
	HF ^b	–	37.3886	214.4033	1465.2484	4298.9068
$-\langle T \rangle / \langle V \rangle$	PW	1.99996	1.99999	1.99999	1.99999	1.99996
	HF ^a	1.99999	2.00000	2.00001	2.00000	2.00000
Cusp	PW	3.995	19.68	35.55	71.42	107.30
	HF ^b	4.009	20.04	35.98	71.98	107.91

PW, present work. Cusp, $2Z = [1/\rho(0)][-d\rho(r)/dr]_{r=0}$; instead of $r = 0$, r is taken as 0.000049 for the cusp.

* Exact results.

^aRef. [25].

^bCalculated using HF density [25].

^cRef. [26].

^dRef. [27].

^eAdding MBPT CI result for correlation energy [28] to HF energy [25].

^fRef. [29].

^gRef. [30].

^hRef. [28], see j below.

ⁱRef. [18]. Note that other DFT exchange energies for the five atoms are: Becke's 3-parameter functional [18], 1.026, 12.16, 30.18, 93.82, 178.9; Perdew and Yue's generalized gradient approximation [17], 1.033, 12.22, 30.29, 93.8, 178.6, respectively.

^jPerdew's [31] parameterized correlation energy functional involving the density gradient gave the following results: He, 0.044; Ne, 0.39; Ar, 0.80; Kr, 2.01; Xe, 3.31. See also Refs. [21,32] for more accurate DFT results.

als of Perdew–Yue [17] and Becke [18] which show a closer agreement with HF exchange energies. The 'exact' correlation energies for He to Ar are cited from Ref. [30]; these are not available for Kr and Xe, and therefore the best results [28] are cited. Except He, where the correlation energy is nearly exact, it is underestimated from Ne to Xe by 2.7–10.9%. Compared with the Wigner-type local functional em-

ployed here, Perdew's [31] parameterized, gradient-corrected correlation functional gives better results for Ne and Ar but worse results for He, Kr and Xe. However, the LYP [21] gradient-corrected, nonlocal correlation energy functional gives better results.

The radial densities for all the atoms show the expected shell structure and closely resemble the HF densities. The results in Table 3 indicate that, except

Table 4
Expectation values (a.u.) for He, Ne, Ar, Kr, and Xe

		$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
He	PW	6.0337	1.6962	0.9207	1.1664
	HF ^a	5.9955	1.6873	0.9273	1.1848
Ne	PW	42.6756	3.1106	0.7945	0.9620
	HF ^a	41.4890	3.1113	0.7891	0.9372
Ar	PW	84.0323	3.8443	0.9699	1.7323
	HF ^a	81.3908	3.8736	0.8928	1.4464
Kr	PW	185.3479	5.0415	0.7611	1.1722
	HF ^a	175.8599	5.0792	0.7289	1.0981
Xe	PW	293.0501	5.8430	0.7429	1.2311
	HF ^a	274.4421	5.8866	0.7233	1.1602

PW, present work. The density has been normalized to unity.

^aRef. [33].

for He, the HF density concentrates more electron density near the nucleus for Ne, Ar, Kr and Xe, compared with the present density. Since this concentration leads to increased interelectronic repulsion, the net effect is that the HF energy goes up compared with the present energy. For He, in the present work, the gain from electron–nuclear attraction energy more than offsets the loss due to increased electron–electron repulsion. Note that the Weizsäcker correction is 45–73% of the total energy while T_{corr} is 27–55% of the total energy. A greater concentration of electron density near the nucleus leads to greater T_{corr} which is always positive. The virial theorem and the cusp condition are well satisfied for all the atoms.

In Table 4, results are presented for the expectation values of single-particle operators r^{-2} , r^{-1} , r and r^2 . These expectation values determine the size of the atom and are related to various atomic properties such as diamagnetic susceptibility ($\langle r^{-2} \rangle$), nuclear magnetic shielding ($\langle r^{-1} \rangle$), etc. As a consequence of the fact that the operator r^{-1} appears in \hat{L} , its expectation value as calculated from the diffusion function is quite good. Literature results are taken from Fischer's HF calculations [33].

It may be noted that instead of choosing good functions (e.g., the HF function), we have also taken wild guesses for initial functions in order to test the efficiency of the method. In such cases, the number of iterations taken to achieve the desired conver-

gence limit is larger than that required for better trial functions.

5. Conclusions

By exploiting an imaginary-time evolution technique, electron densities, energies and other ground-state electronic properties of noble gas atoms have been calculated by directly solving a single, TD hydrodynamical equation. The calculated results are quite satisfactory. Such a single equation which can directly offer both TI and TD electron densities of an interacting many-electron system, may be of interest for larger molecules, clusters, solids, etc., as a practical approximation to the TD Schrödinger equation. The calculations demonstrate that the single TD QFD equation of motion (Eq. (12a)), whose diffusion form is Eq. (12), is quite accurate. Future extension of the present method would depend on the availability of accurate kinetic and exchange–correlation energy functionals. Once they are designed, the method should work well for large systems. It may be mentioned that although the imaginary-time Schrödinger equation for ground-state calculation has been employed earlier [34–36], viz., random walk or diffusion quantum Monte Carlo method which involves the transformation of TD Schrödinger equation into the form of a diffusion-type equation in imaginary time (applied to CH_4 , H_3^+ , H_2^+P , Be^1S , etc.), the present method works in terms of the 3D density rather than the wavefunction.

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