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How can density functional theory be excited from the ground state?

B M DEB* and P K CHATTARAJ
Theoretical Chemistry Group, Department of Chemistry, Panjab University, Chandigarh 160 014, India

Abstract. Density functional theory (DFT) has not been applied on a large scale to time-dependent problems and problems involving excited states. Atomic and molecular collisions involving both these types of phenomena remain outside the purview of DFT. An amalgamation of quantum fluid dynamics (QFD) with DFT considerably broadens the range of applicability of traditional (ground-state) DFT. Ion-atom collisions have been studied by jointly using DFT and QFD.

Keywords. Density functional theory; quantum fluid dynamics; time-dependent phenomena; excited states; ion-atom collisions; molecular reaction dynamics.

1. Introduction

Density-based studies of many-electron systems have become popular in the last two decades due to their mathematical, physical, computational and conceptual simplicity. Two important approaches, where density is used as the basic variable instead of the many-particle wavefunction, are density functional theory (DFT) and quantum fluid dynamics (QFD) (Bamzai and Deb 1981; Ghosh and Deb 1982). The backbone of DFT is the Hohenberg-Kohn theorem (Hohenberg and Kohn 1964) which states that the ground-state energy is a unique functional of density and attains its minimum for the true ground-state density, thus providing a method for variational optimization of any arbitrary energy functional to calculate the appropriate density and energy. On the other hand, a set of two coupled equations, viz. an equation of continuity and an equation of motion (EOM), forms the basis of QFD (Deb and Ghosh 1987). By solving these two equations, one obtains the time-evolution of charge density and current density, the two basic variables in QFD. The major difference between these two approaches is that DFT cannot be applied to general dynamical situations unless the validity of a time-dependent DFT (TDDFT) is proved rigorously. In this paper we discuss the current status of DFT, emphasizing its two major drawbacks and briefly outline an approach towards their solution.

2. Two major problems of present-day DFT

Although the exact form of the energy functional is not known, due to the unknown nature of the kinetic energy (Chattaraj and Deb 1984) and exchange-correlation energy functionals, the existence of the total energy functional is guaranteed for the

*To whom correspondence should be addressed.

ground-state (Hohenberg and Kohn 1964). However, the number of attempts to apply DFT in time-dependent situations is relatively very small. Also, there has been no DFT calculation for obtaining the energy of an excited state. The present status concerning these two problems is reviewed below.

2.1 *Time-dependent situations*

The invertibility of the map between the TD potential and TD density should be established if one wishes to have a TD version of the Hohenberg-Kohn theorem. For a very restricted case, this was first proved by Peuckert (1978). He considered the Taylor expansion of the TD potential in the neighbourhood of zero. In a more general situation, Deb and Ghosh (1982), and subsequently Bartolotti (1981, 1982) developed a TD Kohn-Sham (TDKS) equation (Kohn and Sham 1965) to obtain the time-evolved density only in the case of a limited class of external potentials, viz. TD harmonic potentials, which do not allow any excitation. But this still leaves most TD problems outside the purview of DFT. The most general proof till today has been provided by Runge and Gross (1984), although the proof is valid only under certain conditions regarding the initial density and the time-evolution of the potential. The Runge-Gross proof has been criticised by Xu and Rajagopal (1985) according to whom this proof cannot be extrapolated to a uniform system under a TD perturbation. However, an invertible mapping does exist between the TD potential and the TD current density (rather than the charge density). Nevertheless, the Runge-Gross proof does remain valid provided the TD potentials are well-behaved at large distances (Dhara and Ghosh 1987). Kohl and Dreizler (1986) have extended the Runge-Gross proof through the construction of a Levy-Lieb-type functional (Levy 1979; Lieb 1983) while the extension to TD ensembles was done by Li and others (Li and Tong 1985; Li and Li 1985).

2.2 *Excited states*

Till today, DFT has been essentially a static ground-state theory. Its impressive success prompted many workers to extend DFT to excited states as well. Slater's (1974) transition state theory may be regarded as the first attempt to obtain a DFT for excited states. The subspace theory for excited states (Theophilou 1979, 1987) may be regarded as a rigorous justification of Slater's approach. It states that the composite energy quantity is a unique functional of the composite density. Katriel (1980) has interpreted Theophilou's approach as a special case of the original Hohenberg-Kohn theorem for an appropriately defined composite super-Hamiltonian. The Hohenberg-Kohn theorem has also been shown to be valid for any excited state that corresponds to the lowest state of a given symmetry (Gunnarsson and Lundqvist 1976). However, Kohn and Vashishta (1983) feel that the corresponding self-consistent equations generally do not exist. A one-to-one correspondence had also been established (Mikolas and Tomasek 1977) between the total energy of a particular state (ground or excited) and the density of the same state. Since the ground-state density fixes the Hamiltonian to within an additive constant, all the excited states of a system under a local external one-body potential would be characterized by the ground-state density. The Levy-Lieb functional (Levy 1979; Lieb 1983) encompasses a large class of excited states and provides a mathematical basis for Theophilou's idea (Hadjisavvas and Theophilou 1985). Use

of single excited-state functionals, contrary to subspace functionals, has been introduced by Valone and Capitani (1981). The Hohenberg-Kohn theorem has also been extended to excited states (Hunter 1986) through the derivation of a Schrödinger-type equation satisfied by the square-root of the electron density. This may be regarded as an extension of a similar equation for the ground-state density (Deb and Ghosh 1983).

3. Broadening of DFT through QFD

There is a formal equivalence between DFT and QFD in 3-D space (Deb and Ghosh 1982). Since time occurs naturally in QFD, and a nonzero current density is obtained for most of the excited states by solving QFD EOMS, through QFD DFT can go into both TD situations and excited states. We have proposed (Deb and Chattaraj 1987) an amalgamation of QFD and DFT to give rise to quantum fluid density functional theory (QFDFT). The above two problems had prevented one from applying DFT on a large scale to the important area of molecular reaction dynamics. Since in atomic and molecular collisions both of the above problems, viz. TD situations and excited states, are involved, QFDFT has been applied (Deb and Chattaraj 1987) to deal with the high-energy proton-neon collision problem. Earlier, TD Thomas-Fermi theory and its variants were employed (Ludde *et al* 1979; Horbatsch and Dreizler 1981, 1982; Malzacher and Dreizler 1982; Horbatsch 1983) to study high-energy ion-atom collisions. Several nonlinear features were revealed through a numerical solution of two fluid dynamical equations. In the case of proton-argon collisions it was observed that the perturbation caused by the incoming proton to the target density is reflected through nonlinear oscillations of the latter. The oscillations dampen gradually with a different frequency for the inner and outer parts of the density. The present QFDFT method (Deb and Chattaraj 1987) can be considered as a generalization of these previous works. Considering the current status of TDDFT and excited state DFT it is quite reasonable to assume that the QFDFT approach is likely to be more promising than DFT itself. We have derived a TDKS equation in 3-D space which is a new nonlinear Schrödinger equation, by using a QFDFT approach as well as a stochastic interpretation of quantum mechanics (Nelson 1985). It has been argued that for any given Hamiltonian H and initial wavefunction $\psi(\mathbf{r}, t_0)$ there corresponds an equivalent Markov process in coordinate space such that the probability density $\rho(\mathbf{r}, t)$ of the particle (undergoing Brownian motion) being at $\mathbf{r}$ at the instant t coincides with that given by quantum mechanics, i.e. $|\psi(\mathbf{r}, t)|^2$ (Nassar 1984). This stochastic viewpoint further strengthens the use of QFD along with conventional DFT. A space-time-dependent "local molecular thermodynamics" has also been developed. This is an extension of the work of Ghosh *et al* (1984). The time-evolution of local "thermodynamic" variables can be obtained through the TDKS equation which has the following form (in atomic units):

$$i\frac{\partial\phi(\mathbf{r}, t)}{\partial t} + \frac{1}{2}\nabla^2\phi(\mathbf{r}, t) + V_{\text{eff}}(\mathbf{r}, t)\phi(\mathbf{r}, t) = 0, \tag{1}$$

where

$$V_{\text{eff}}(\mathbf{r},t) = -\frac{5}{3}C_k\rho^{2/3}+\frac{4}{3}C_x\rho^{1/3}+\frac{a(N)}{r^2}$$

$$+\frac{Q}{r}+\frac{1}{|\mathbf{R}-\mathbf{r}|}-\frac{f(\mathbf{R},N)}{N} \tag{2}$$

$$\rho(\mathbf{r},t) = |\phi(\mathbf{r},t)|^2. \tag{3}$$

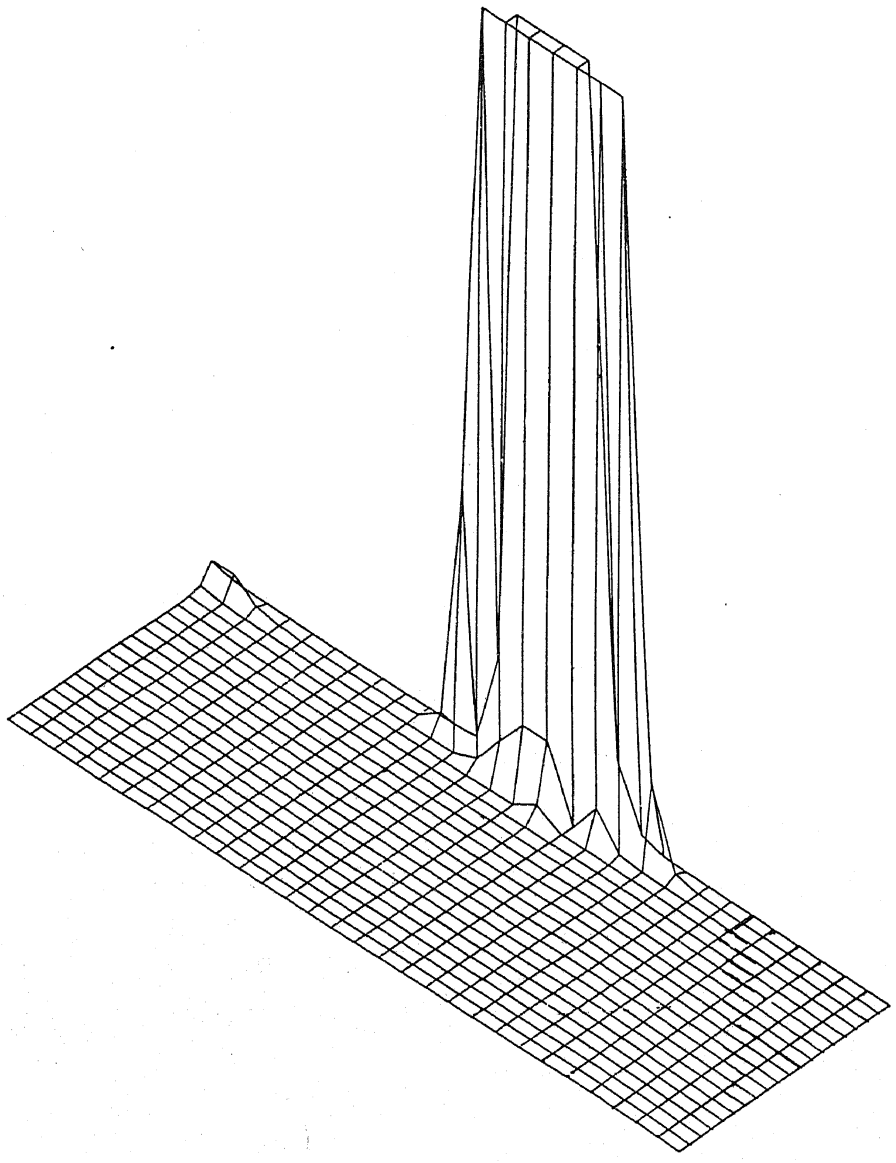

Figure 1. Perspective plot of the current density in the proton-neon colliding system, in cylindrical polar coordinates $(\tilde{\rho},z)$ at $t = 0{\cdot}08$ a.u. The basal rectangular mesh designates the $(\tilde{\rho},z)$ plane, where $0 \leqslant \tilde{\rho} \leqslant 3{\cdot}25$ and $-3 \leqslant z \leqslant +3$; the topmost line of the basal mesh corresponds to the z axis. The target neon nucleus is at $(0,0)$, i.e., at the mid-point of the topmost line in the basal mesh, and the proton is approaching from the left along this line (internuclear distance = 9·92 a.u.). The top cut-off value is 50·0 a.u.

Here C_k and C_x are the familiar Thomas-Fermi and Dirac constants, respectively, $a(N)$ depends on N (the total number of electrons), $f(R,N)$ is a function depending on both R and N, R being the internuclear distance; Q refers to a screened nuclear charge. The nonlinearity in (1) enters through the single-particle nonlocal potential V_{eff}, via nonintegral powers of ϕ as well as an integral occurring in Q. The high degree of nonlinearity in (1) causes serious problems in its solution.

However, in order to study high-energy proton-neon collisions, we have solved (1) numerically. Several nonlinear features reveal themselves. In particular, the possibility of solitary wave solutions is indicated; this requires further analysis. The time-dependent current density at $t = 0{\cdot}08$ a.u. has been depicted in figure 1. The fact that we now come across a nonzero current density implies that, due to the approach of the proton, excited states of the neon atom are mixing with its groundstate. Due to space limitations, we refrain from giving details of this work (Deb and Chattaraj 1987). We believe that this approach has the potential to monitor a time-dependent process from start to finish.

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