RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 35, NUMBER 1 JANUARY 1, 1987

Density-functional theory for time-dependent systems

Asish K. Dhara
Theoretical Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, India

Swapan K. Ghosh
Heavy Water Division, Bhabha Atomic Research Centre, Bombay 400 085, India

(Received 10 July 1986)

The time-dependent density-functional theory of Runge and Gross [Phys. Rev. Lett. **52**, 997 (1984)] is reexamined with regard to its limitations, and the criticisms raised by Xu and Rajagopal [Phys. Rev. A **31**, 2682 (1985)] are addressed, within the imposition of natural boundary conditions of vanishing density and potential at infinity. Also, for a single-particle system characterized by an arbitrary time-dependent potential, the uniqueness of the density-to-potential mapping is established explicitly for both bound and scattering states.

Density-functional theory (DFT)[1] for stationary systems is well established as a conceptually simple and practically useful tool[2-4] in various branches of physics and chemistry. For time-dependent (TD) problems, however, the development has been rather slow and time-dependent density-functional theory (TDDFT) had been restricted to small TD perturbations around a fixed static potential,[5,6] or to oscillating TD potentials.[7,8] An extension to include arbitrary time dependence has been provided only recently by Runge and Gross (RG),[9] who proved that the mapping between the density $\rho(\mathbf{r},t)$ and the TD potential $v(\mathbf{r},t)$ is unique. A TD Kohn-Sham-type prescription[7,8] was also suggested[9] for the calculation of $\rho(\mathbf{r},t)$ and the current density $\mathbf{j}(\mathbf{r},t)$. This work has been further broadened through the construction[10] of a Levy-type functional[11] for the TD density and also an extension to TD ensembles.[12]

In a recent work, Xu and Rajagopal (XR)[13] have, however, criticized the TD density-functional formalism of RG by attempting to cite counterexamples to disprove the validity of the RG result. They have concluded that only the mapping $v(\mathbf{r},t)\rightarrow\mathbf{j}(\mathbf{r},t)$ is invertible and it is the current density $\mathbf{j}(\mathbf{r},t)$ which plays the main role in TDDFT, as does the charge density ρ in the stationary case. Although XR have discussed a number of interesting points, some of their conclusions about the limitation of the RG work require modification. The purpose of the present work is to reply to the criticisms raised by XR while simultaneously pointing out the limitations of the RG formalism—thus presenting a more transparent view of the current status of time-dependent density-functional theory.

We first review the basic aspects of the proof RG used to establish the invertibility of the mapping $v(\mathbf{r},t)\rightarrow\rho(\mathbf{r},t)$. In the first part of their proof, they derive the relation

$$(i\partial/\partial t)^{k+1}[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0}$$
$$=i\rho(\mathbf{r},t_0)\nabla\{(i\partial/\partial t)^k[v(\mathbf{r},t)-v'(\mathbf{r},t)]\,|_{t=t_0}\}\ , \quad (1)$$

where $\mathbf{j}(\mathbf{r},t)$ and $\mathbf{j}'(\mathbf{r},t)$ are the current densities corresponding to the two external potentials $v(\mathbf{r},t)$ and $v'(\mathbf{r},t)$, which are identical at $t=t_0$, and k is the smallest integer such that the kth time derivative of the quantity $[v(\mathbf{r},t)-v'(\mathbf{r},t)]$ evaluated at an initial time $t=t_0$ is different from zero. [Here it is assumed that the Taylor expansions of $v(\mathbf{r},t)$ and $v'(\mathbf{r},t)$ around the value at $t=t_0$ exist.] Clearly, the left-hand side (lhs) of Eq. (1) is nonzero and hence $\mathbf{j}(\mathbf{r},t)$ and $\mathbf{j}'(\mathbf{r},t)$ will differ infinitesimally later than t_0. This proves the uniqueness of the mapping $v(\mathbf{r},t)\rightarrow\mathbf{j}(\mathbf{r},t)$ (Theorem I of XR).

For the second part of the proof, RG utilize the continuity equation

$$(\partial\rho/\partial t)+\nabla\cdot\mathbf{j}=0\ . \quad (2)$$

For the two densities $\rho(\mathbf{r},t)$ and $\rho'(\mathbf{r},t)$ corresponding to $\mathbf{j}(\mathbf{r},t)$ and $\mathbf{j}'(\mathbf{r},t)$, Eqs. (1) and (2) lead to the result

$$(\partial/\partial t)^{k+2}[\rho(\mathbf{r},t)-\rho'(\mathbf{r},t)]\,|_{t=t_0}$$
$$=-\nabla\cdot[\rho(\mathbf{r},t_0)\nabla\phi(\mathbf{r},t_0)]\ , \quad (3)$$

where

$$\phi(\mathbf{r},t_0)=\{(\partial/\partial t)^k[v(\mathbf{r},t)-v'(\mathbf{r},t)]\,|_{t=t_0}\}\ . \quad (4)$$

In order to prove that the right-hand side (rhs) of Eq. (3) is different from zero, RG consider the integral

$$\int d\mathbf{r}\,\phi(\mathbf{r},t_0)\nabla\cdot[\rho(\mathbf{r},t_0)\nabla\phi(\mathbf{r},t_0)]=-\int d\mathbf{r}\,\rho(\mathbf{r},t_0)\,|\nabla\phi(\mathbf{r},t_0)|^2+\tfrac{1}{2}\oint d\mathbf{S}\cdot\{\rho(\mathbf{r},t_0)[\nabla\phi^2(\mathbf{r},t_0)]\}\ , \quad (5)$$

and show that the lhs of Eq. (5) is nonvanishing since the first term on the rhs is nonzero for positive ρ unless ϕ is constant, and the second term involves a vanishing surface integral. (It may be noted that this argument has a close resemblence to that used in the well-known Dirichlet principle.[14]) Then they claim that $\nabla\cdot[\rho\nabla\phi]\not\equiv 0$ and hence ρ and ρ' will differ again infinitesimally after $t=t_0$.

On the other hand, XR reexpress the rhs of Eq. (3) as

$$\nabla\cdot[\rho(\mathbf{r},t_0)\nabla\phi(\mathbf{r},t_0)]=\nabla\rho(\mathbf{r},t_0)\cdot\nabla\phi(\mathbf{r},t_0)$$
$$+\rho(\mathbf{r},t_0)\nabla^2\phi(\mathbf{r},t_0)\ , \quad (6)$$

and argue that it can vanish, for example, if $\phi(\mathbf{r},t_0)$ is a

harmonic function ($\nabla^2\phi=0$) and is chosen such that $\nabla\phi(\mathbf{r},t_0)$ is perpendicular to $\nabla\rho(\mathbf{r},t_0)$. They, therefore, claim that the conclusion of RG regarding the uniqueness of the mapping $\rho(\mathbf{r},t)\rightarrow v(\mathbf{r},t)$ is incorrect.

It is, however, of interest, to see if such a function does really exist. For a special case of spherical symmetry of the unperturbed system, e.g., atoms with spherically symmetric $\rho(r,t_0)$, the only solution is $\phi=$const [since $\nabla\rho\cdot\nabla\phi=(\partial\rho/\partial r)(\partial\phi/\partial r)=0$ implies $(\partial\phi/\partial r)=0$ and therefore $\nabla^2\phi=0$ implies $L^2\phi=0$ leading to a constant ϕ]. For the general three-dimensional case, too, it might not be possible to have a solution not violating the conditions required in the RG proof.

The condition under which the proof of RG is valid is a positive density $\rho(\mathbf{r},t_0)$ vanishing at infinity. The restriction on ϕ is that $\nabla\phi^2$ should not increase faster than the decay of ρ at $r\rightarrow\infty$ (i.e., $\rho\nabla\phi^2\rightarrow 0$ at $r\rightarrow\infty$). The counterexample $\phi=A\exp(\lambda r)$ provided by XR, however, for a density $\rho\sim e^{-\lambda r}$ does not belong to this category and is to be excluded from the RG systems. As has been pointed out by XR, it is a limitation of the RG formalism that a condition on $\rho(\mathbf{r},t_0)$ alone is not sufficient for the RG proof.

The condition of vanishing density at the boundary is not met by a homogeneous electron gas and therefore the RG result is not valid as has been pointed out by XR. However, if the TD potentials are restricted so that $\phi\rightarrow 0$ at $r\rightarrow\infty$, the surface integral of Eq. (5) still vanishes and the RG proof holds good. XR argue that for a homogeneous electron gas $\nabla\rho=0$ and a harmonic function generally exists, i.e., $\nabla^2\phi=0$, thus indicating that the rhs of Eq. (3) can vanish. However, the only solution satisfying $\nabla^2\phi=0$ and also $\phi=0$ as $r\rightarrow\infty$ is the trivial one $\phi=0$ everywhere.[15] Therefore, the mapping $\rho(\mathbf{r},t)\rightarrow v(\mathbf{r},t)$ remains valid for homogeneous electron gas if the TD potentials are the ones vanishing at large distances, which most of the physical potentials satisfy.

Although the presence of point singularities in ϕ does not invalidate[16] the conclusion $\nabla\cdot[\rho\nabla\phi]\not\equiv 0$ from the nonzero integral $\int d\mathbf{r}\phi\nabla\cdot[\rho\nabla\phi]$ of Eq. (5), the Taylor expansion itself imposes restrictions on the nature of the potentials. Since none of the coefficients of the Taylor expansion are allowed to be infinite at any point, the RG formalism remains valid for "arbitrary" time dependence provided the time evolution does not alter the potential "drastically," i.e., the positions of the singularities of the original potential $v(\mathbf{r},t_0)$ are not altered or no new singularities are introduced. This limitation, however, excludes from TDDFT many important problems, e.g., molecular vibrations or chemical reactions, collisions, etc., where the movement of the nuclei are encountered.

Apart from reconsidering the proof of Runge and Gross,[9] Xu and Rajagopal[13] also present a new approach to investigate the uniqueness of the mapping among $v(\mathbf{r},t)$, $\rho(\mathbf{r},t)$, and $\mathbf{j}(\mathbf{r},t)$. They attempt an explicit construction of the potential from the current or charge densities using the equations of quantum hydrodynamics[2] for a single particle. The TD Schrödinger equation for the latter can be reformulated, with the help of the polar form of the wave function, i.e.,

$$\psi(\mathbf{r},t)=R(\mathbf{r},t)\exp[iS(\mathbf{r},t)/\hbar]\ ,$$

into the continuity equation (2): $(\partial\rho/\partial t)+\nabla\cdot\mathbf{j}=0$, and the Euler equation of motion

$$m(\partial/\partial t)(\mathbf{j}/\rho)+(m/2)\nabla(\mathbf{j}/\rho)^2=-\nabla U(\mathbf{r},t)-\nabla v(\mathbf{r},t)\ , \tag{7}$$

where $\rho=R^2$, $\mathbf{j}=(\rho\nabla S/m)$, and the quantum potential U is given by

$$U=-(\hbar^2/2m)(\nabla^2R)/R\ . \tag{8}$$

The pair of equations (2) and (7) provide a scheme for obtaining $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ for an external potential $v(\mathbf{r},t)$.

Assume now that the two current densities $\mathbf{j}_1$ and $\mathbf{j}_2$, corresponding to two external potentials $v_1(\mathbf{r},t)$ and $v_2(\mathbf{r},t)$, are identical, i.e., $\mathbf{j}_1=\mathbf{j}_2$. Equation (2) then clearly suggests that $\rho_1(\mathbf{r},t)=\rho_2(\mathbf{r},t)$ if the unperturbed problem corresponding to $v_1(\mathbf{r},t_0)=v_2(\mathbf{r},t_0)$ is assumed to have been solved, i.e., $\rho_1(\mathbf{r},t_0)=\rho_2(\mathbf{r},t_0)$ and $\mathbf{j}_1(\mathbf{r},t_0)=\mathbf{j}_2(\mathbf{r},t_0)$ are known. Equation (7) then predicts that $\nabla(v_2-v_1)=0$, implying the result $(v_2-v_1)=c(t)$, a function dependent on time alone. The uniqueness of the mapping $\mathbf{j}(\mathbf{r},t)\rightarrow v(\mathbf{r},t)$ is thereby proved.

Consider, on the other hand, the case $\rho_1(\mathbf{r},t)=\rho_2(\mathbf{r},t)$, for which the continuity Eq. (2) gives $\nabla\cdot(\mathbf{j}_1-\mathbf{j}_2)=0$, i.e., $\mathbf{j}_1(\mathbf{r},t)=\mathbf{j}_2(\mathbf{r},t)+\nabla\times\mathbf{A}(\mathbf{r},t)$, where $\mathbf{A}(\mathbf{r},t)$ is an arbitrary vector. The two apparently different current densities $\mathbf{j}_1$ and $\mathbf{j}_2$ are claimed to yield, from Eq. (7), two potentials v_1 and v_2 differing by more than a simple TD function —demonstrating thereby the nonuniqueness of the mapping $\rho(\mathbf{r},t)\rightarrow v(\mathbf{r},t)$.

However, the divergencelessness of $(\mathbf{j}_1-\mathbf{j}_2)$ is equivalent to the condition $\nabla\cdot[(\rho/m)\nabla(S_2-S_1)]=0$ or $\nabla\cdot(\rho\nabla\alpha)=0$, which is not possible unless α is a constant (or merely a TD function) as can be shown by extending the arguments of RG [Eq. (5)], for the usual boundary conditions of $\rho\rightarrow 0$ at $r\rightarrow\infty$ and a current density vanishing at the boundary. The difference between the two potentials in this case is given by

$$v_2(\mathbf{r},t)-v_1(\mathbf{r},t)=-(1/2m)[(\nabla\alpha)^2+2\nabla\alpha\cdot\nabla S_1]-(\partial\alpha/\partial t)\ . \tag{9}$$

A divergenceless $(\mathbf{j}_1-\mathbf{j}_2)$ may not be possible if $\alpha(\mathbf{r},t)$ does not increase faster as $r\rightarrow\infty$ implying, thereby, a similar increase in (v_2-v_1). This case is, however, excluded from RG considerations and, therefore, such a current-density difference is not permitted.

A more elegant demonstration of the uniqueness of the mapping $\rho(\mathbf{r},t)\rightarrow v(\mathbf{r},t)$ can be given from the same pair of equations (2) and (7). Let the continuity equation (2) be rewritten as

$$\rho\nabla^2\chi+\nabla\rho\cdot\nabla\chi+(\partial\rho/\partial t)=0\ , \tag{10}$$

where $\chi=S/m$. For a particular density, if χ_1 and χ_2 are two solutions of this equation, one obtains

$$\rho\nabla^2\omega+\nabla\rho\cdot\nabla\omega=0\ , \tag{11}$$

where $\omega=(\chi_1-\chi_2)$. For a given boundary condition on χ, this elliptical equation has only the trivial solution[17] $\omega=0$. Also, the corresponding Neumann problem has a simple unique solution for given boundary conditions on the ex-

terior normal derivative of the form $(d\omega/dn)=$const. If ω is a solution, then the maximum principle implies that it assumes its maximum or minimum at points of the boundary. At these points, as has been shown by Courant and Hilbert,[18] $(d\omega/dn)$ is positive or negative, respectively, unless ω is identically constant. But $(d\omega/dn)$ is a constant at the boundary and hence it follows[18] that in fact $\omega=$const. Therefore, χ_1 and χ_2 can differ only by an additive constant implying $\nabla\chi_1=\nabla\chi_2$. In real physical situations, ρ, $\mathbf{j}$, and $\nabla\chi$ vanish (for bound states) or assume constant values (for scattering states) at the boundary, i.e., at infinity, and therefore the velocity field $\nabla\chi$ and hence the current density $\mathbf{j}(\mathbf{r},t)$ is uniquely determined from Eq. (10) for a given density $\rho(\mathbf{r},t)$. Equation (7) then clearly yields a unique solution for $v(\mathbf{r},t)$. Therefore, the existence of different current densities $\mathbf{j}_1$, $\mathbf{j}_2$, etc., satisfying $\nabla\cdot(\mathbf{j}_1-\mathbf{j}_2)=0$ is ruled out in view of the definition of current density as $\mathbf{j}=\rho\nabla\chi$ and also by the fact that the current density $\mathbf{j}$ and the velocity field $\nabla\chi$ vanish or attain constant values at infinity.

Therefore, the RG proof of TDDFT regarding a unique invertibility of the mappings $v(\mathbf{r},t)\rightarrow\rho(\mathbf{r},t)$ and $v(\mathbf{r},t)\rightarrow\mathbf{j}(\mathbf{r},t)$ hold good and the criticisms of XR do not stand provided the TD potentials are such that they are well behaved at large distances, e.g., they do not increase faster than the fall off of the density. In other words, the TD potentials are required to vanish at the boundary.

Thus, an explicit unique construction of $v(\mathbf{r},t)$ is possible for a single particle system from either the current density or the charge density with the imposition of suitable boundary conditions on these quantities—which is possible for physical situations. An analogous demonstration for a many-electron system, although of much interest, is not yet available.

In general, the wave function is complex and two real quantities $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ are needed for a complete specification of the system. Nevertheless, anyone of them is sufficient, as has been demonstrated here, to determine the other within the restrictions already discussed, if both are known at an initial time $t=t_0$. The conclusion, therefore, is that the RG work provides a valid generalization of the TDDFT to "arbitrary" TD potentials which are required to satisfy suitable boundary conditions and also for which the Taylor expansion in time coordinate is permissible. We have further demonstrated that the mapping $\rho(\mathbf{r},t)\rightarrow v(\mathbf{r},t)$ is unique even for any arbitrary time dependence, at least for a single particle system for both bound and scattering states.

[1]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
[2]S. K. Ghosh and B. M. Deb, Phys. Rep. **92**, 1 (1982).
[3]R. G. Parr, Annu. Rev. Phys. Chem. **34**, 631 (1983).
[4]*Density Functional Methods in Physics,* edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).
[5]V. Peuckert, J. Phys. C **11**, 4945 (1978).
[6]S. Chakravarty, M. B. Fogel, and W. Kohn, Phys. Rev. Lett. **43**, 775 (1979).
[7]B. M. Deb and S. K. Ghosh, J. Chem. Phys. **77**, 342 (1982).
[8]L. J. Bartolotti, Phys. Rev. A **24**, 1661 (1981); **26**, 2243 (1982).
[9]E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[10]H. Kohl and R. M. Dreizler, Phys. Rev. Lett. **56**, 1991 (1986).
[11]M. Levy, Proc. Nat. Acad. Sci. U.S.A. **76**, 6062 (1979).
[12]T. Li and P. Tong, Phys. Rev. A **31**, 1950 (1985).
[13]B. X. Xu and A. K. Rajagopal, Phys. Rev. A **31**, 2682 (1985).
[14]S. Bergman and M. Schiffer, *Kernel Functions and Elliptic Differential Equations in Mathematical Physics* (Academic, New York, 1953), p. 17.
[15]I. Stakgold, *Boundary Value Problems of Mathematical Physics* (McMillan, New York, 1971), Vol. II, p. 102.
[16]G. Temple, *The Structure of Lebesgue Integration Theory* (Clarendon, Oxford, 1971), p. 130.
[17]R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Wiley, New York, 1962), Vol. II, p. 323.
[18]See Ref. 17, p. 329.