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Comment on “Critique of the foundations of time-dependent density-functional theory”

A. Holas and M. Cinal
Institute of Physical Chemistry of the Polish Academy of Sciences, 44/52 Kasprzaka, 01–224 Warszawa, Poland

N. H. March
Department of Physics, University of Antwerp, Antwerp, Belgium and Oxford University, Oxford, England

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Two particular subjects tackled in the recent paper by Schirmer and Dreuw (SD) [J. Schirmer and A. Dreuw, Phys. Rev. A **75**, 022513 (2007)] are commented on by us. By providing a convincing example, we answer positively the question posed by SD whether a local operator can be reconstructed from the knowledge of its particle-hole matrix elements (when the number of particle states exceeds one). In connection with the problem of the utmost reduction of the density-functional theory (DFT) to a solution of one equation for the density amplitude—the radical Kohn-Sham (rKS) approach—used by SD as a valuable tool to investigate the time-independent and time-dependent DFT, we demonstrate that the calculational scheme implementing the rKS formulation is rather uncompetitive with the traditional KS scheme.

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In their recent paper, Schirmer and Dreuw (SD) [1] critically analyzed the foundations of the time-dependent density-functional theory (TDDFT). Since this theory is an extension of the original (time-independent) DFT, it is quite natural that some parts of it are discussed by these authors. Our Comment is connected with the last aspect of the SD paper. We feel that two particular problems tackled in [1] are worth exploring in greater depth.

SD [1] formulate and prove the theorem that a local (multiplicative) operator $v=v(\mathbf{r})$ is uniquely determined up to a constant by its *p*-*h* and *h*-*p* matrix elements with respect to a complete one-particle basis and an arbitrary partitioning of that basis into occupied (occ) [hole (h)] and unoccupied (unocc) [particle (p)] one-particle states (orbitals). But answering the question of whether it is possible to reconstruct a local operator if only its *p*-*h* matrix elements are given, they say, “it seems that this is not possible except for a special case of $n=1$” (here n is the number of occupied states). The positive answer valid for any n, supported by three different examples of reconstruction algorithms, is given by two of us in Sec. III of our paper [2]. We quote here an especially simple reconstruction formula (termed in [2] the type-B representation),

$$v(\mathbf{r}_1) = v(\mathbf{r}_2) + \sum_{s}^{\text{unocc}} \sum_{a}^{\text{occ}} \frac{\phi_s(\mathbf{r}_1) v_{sa} \phi_a^*(\mathbf{r}_2) - \phi_a(\mathbf{r}_1) v_{as} \phi_s^*(\mathbf{r}_2)}{\rho(\mathbf{r}_1;\mathbf{r}_2)}, \tag{1}$$

where

$$v_{jk} = \int \mathrm{d}^3 r \, \phi_j^*(\mathbf{r}) v(\mathbf{r}) \phi_k(\mathbf{r}), \tag{2}$$

$$\rho(\mathbf{r}_1;\mathbf{r}_2) = \sum_{a}^{\text{occ}} \phi_a(\mathbf{r}_1) \phi_a^*(\mathbf{r}_2). \tag{3}$$

After choosing arbitrarily and fixing the reference point $\mathbf{r}_2$ and the value $v(\mathbf{r}_2)$ of the potential there (which plays the role of an additive constant), the potential $v(\mathbf{r}_1)$ at the running point $\mathbf{r}_1$ is determined from Eq. (1) in terms of its *p*-*h* and *h*-*p* matrix elements and orbitals. Obviously, the type-B reconstruction, Eq. (1), is valid for such pairs of arguments $\mathbf{r}_1, \mathbf{r}_2$ that $\rho(\mathbf{r}_1;\mathbf{r}_2) \neq 0$. However, if the original potential is continuous at $\mathbf{r}_{10}$, but $\rho(\mathbf{r}_{10};\mathbf{r}_2)=0$, then $v(\mathbf{r}_{10})$ can be determined from Eq. (1) as $\lim v(\mathbf{r}_1)$ for $\mathbf{r}_1 \to \mathbf{r}_{10}$, just because Eq. (1) is an identity satisfied by an arbitrary local operator $v(\mathbf{r})$.

As the second subject of our Comment, we choose the problems connected with the Schrödinger equation for the density amplitude—the square root of the electron density $\rho(\mathbf{r})$,

$$\left\{-\tfrac{1}{2}\nabla^2 + \tilde{v}^{\text{eff}}[\rho](\mathbf{r})\right\}\rho^{1/2}(\mathbf{r}) = \epsilon_{\text{rKS}}\rho^{1/2}(\mathbf{r}) \tag{4}$$

(atomic units are used here and throughout the paper). This equation allows us to realize the radical Kohn-Sham (rKS) version of DFT (as it is termed by SD): when, for a given system, the effective potential $\tilde{v}^{\text{eff}}$ as a functional of ρ is known, the self-consistent solution of Eq. (4) provides the true ground-state density of the considered interacting many-electron system. It should be remembered that in the case of the traditional KS approach, one needs to find self-consistently the N lowest-energy eigensolutions of the KS equation,

$$\left\{-\tfrac{1}{2}\nabla^2 + v^{\text{eff}}[\rho](\mathbf{r})\right\}\phi_a(\mathbf{r}) = \epsilon_a \phi_a(\mathbf{r}), \tag{5}$$

to obtain the same density as $\rho(\mathbf{r})=\sum_{a=1}^{N}|\phi_a(\mathbf{r})|^2$; here N is the number of electrons. It should be noted that the potential occurring in Eq. (5) is defined by Eq. (39) of [1], and that in Eq. (4) by Eq. (50) of [1]; the latter is marked by us with a tilde to make the notation unique. The rKS formulation serves SD “as a valuable analytical tool to clarify various aspects of DFT and, in particular, TDDFT.” But SD speculate also on a practical role of this formulation, saying “it is not inconceivable that the rKS variant will have some computational potential as well.” In our view, brought out below, such an expectation seems too optimistic at present.

The Schrödinger equation for the density amplitude, like Eq. (4), was derived for the first time by Hunter [3] (see also

[4]) with the local potential $\tilde{v}^{\text{eff}}(\mathbf{r})$ calculated as the expectation value of the N-electron Hamiltonian over the conditional probability amplitude ϕ_0^N (according to Hunter's formulation introduced in [5], the N-electron ground-state function can be expressed directly as a product of ϕ_0^N and the marginal probability amplitude $[\rho(\mathbf{r})/N]^{1/2}$). The same expression for $\tilde{v}^{\text{eff}}(\mathbf{r})$ was rederived by Levy *et al.* [6]. This expression was helpful for analyzing properties of the exchange-correlation potential of DFT for two-electron spin-compensated systems. The last restriction becomes obvious when $\tilde{v}^{\text{eff}}$ is discussed in terms of the Pauli potential $v_{\text{P}}[\rho](\mathbf{r})$ (see, e.g., Levy and Görling [7] and references therein). Namely,

$$\tilde{v}^{\text{eff}}[\rho](\mathbf{r}) = v^{\text{eff}}[\rho](\mathbf{r}) + v_{\text{P}}[\rho](\mathbf{r}), \tag{6}$$

where v^{eff} is the effective potential of the traditional KS approach, see Eq. (5). Analogously to other potentials of DFT, the Pauli potential is defined as the functional derivative $v_{\text{P}}[\rho](\mathbf{r}) = \delta E_{\text{P}}[\rho]/\delta\rho(\mathbf{r})$ of the Pauli energy. The preceding is the difference of two kinetic energy (KE) functionals,

$$E_{\text{P}}[\rho] = T_{\text{s}}[\rho] - T_{\text{W}}[\rho], \tag{7}$$

namely the noninteracting-electrons KE $T_{\text{s}}[\rho]$ (defined by Levy [8] using a constrained search) and the Weizsäcker KE $T_{\text{W}}[\rho] = \frac{1}{2}\int d^3r |\boldsymbol{\nabla}[\rho^{1/2}(\mathbf{r})]|^2$. [Evidently, $E_{\text{P}}[\rho] \equiv 0$ for systems described by only one KS (spatial) orbital.] As was shown in [9] by two of us, these definitions of functionals are constructive—they lead to an algorithm allowing evaluation of $E_{\text{P}}[\rho]$ and $v_{\text{P}}[\rho](\mathbf{r})$ for any given input function $\rho(\mathbf{r})$. This means that for any choice of approximate (by necessity) functional for the exchange-correlation energy $E_{\text{xc}}[\rho]$ and, subsequently, the corresponding potential (both of which determine the practical implementation of the traditional KS scheme), one can perform also calculations with the rKS scheme and obtain the same accuracy in the results for the electron ground-state density and the total energy as calculated with the KS scheme.

However, the conceptual simplification of the rKS approach with respect to the traditional one is not accompanied by a gain in computational efficiency such as a reduction of costs and time of calculations. When executing the algorithm [9] for E_{P} and $v_{\text{P}}(\mathbf{r})$, one needs to determine first, as auxiliary objects, the $N-1$ lowest-energy eigensolutions $\{K_j(\mathbf{r}), \lambda_j\}_{j=2}^N$ of the second-order differential eigenequation,

$$\left\{-\tfrac{1}{2}\boldsymbol{\nabla}[1 + \ln\rho(\mathbf{r})]\cdot\boldsymbol{\nabla} + v_{\text{cpl}}(\mathbf{r})\right\}K_j(\mathbf{r}) = \lambda_j K_j(\mathbf{r}), \tag{8}$$

with the coupling (cpl) potential

$$v_{\text{cpl}}(\mathbf{r}) = \frac{1}{2}\left\{\frac{\boldsymbol{\nabla}^2 K_1(\mathbf{r})}{K_1(\mathbf{r})} + [\boldsymbol{\nabla}\ln\rho(\mathbf{r})]\cdot[\boldsymbol{\nabla}\ln K_1(\mathbf{r})]\right\}, \tag{9}$$

where K_1 is defined by $K_1^2(\mathbf{r}) = 1 - \Sigma_{j=2}^N K_j^2(\mathbf{r})$. The eigenfunctions $\{K_j(\mathbf{r})\}$ should satisfy specific boundary conditions (given in [9]). The input density enters Eqs. (8) and (9) via the vector $\boldsymbol{\nabla}\ln\rho(\mathbf{r})$ only. Since the potential v_{cpl} is a functional of $\{K_j\}_{j=2}^N$ (by means of K_1), an iterative method of solving, terminated at self-consistency, should be applied. Then

$$v_{\text{P}}(\mathbf{r}) = -v_{\text{cpl}}(\mathbf{r}), \tag{10}$$

$$E_{\text{P}} = \sum_{j=2}^{N}\lambda_j + \int d^3r\,\rho(\mathbf{r})v_{\text{P}}(\mathbf{r}). \tag{11}$$

Evidently, the effort to calculate self-consistently $N-1$ solutions of Eq. (8) and one solution of the rKS Eq. (4) is comparable with (if not greater than) the effort to calculate N solutions of the KS Eq. (5).

Of course, one may try to find an approximation for $E_{\text{P}}[\rho]$ and then have the corresponding approximate potential $v_{\text{P}} = \delta E_{\text{P}}/\delta\rho$, in analogy to the local-density approximation, the generalized-gradient approximation, etc., for $E_{\text{xc}}[\rho]$. Since T_{W} is known as the explicit functional of ρ, an approximation for $T_{\text{s}}[\rho]$ is needed, according to Eq. (7). Many such approximate *orbital-free* KE functionals have been proposed (see, e.g., Wang and Carter [10] and references therein), but, to the best of our knowledge, they are not sufficiently accurate to yield, within the variational DFT approach, a ground-state density of comparable quality to that resulting from the KS approach (e.g., showing the shell structure in the case of atoms). However, the recent investigation of Chai and Weeks [11] makes promising progress in this direction; here the kinetic potential $v_{T_{\text{s}}}[\rho](\mathbf{r}) = \delta T_{\text{s}}[\rho]/\delta\rho(\mathbf{r})$ is approximated as a basic object rather than the KE itself. Then T_{s} is evaluated from this potential by means of functional integration.

Finally, we would like to add a comment concerning terminology. The rKS Eq. (4) transformed by SD into Eq. (77) of [1], $\tilde{v}^{\text{eff}} \rightarrow w[\rho] = \boldsymbol{\nabla}^2(\rho^{1/2})/(2\rho^{1/2}) + \text{const}$, demonstrates that the shape of the effective potential for any given many-electron system can be calculated easily from its ground-state density [provided $\rho(\mathbf{r})$ is available from quantum-chemical calculations or from an experiment]. This density-dependent potential $w[\rho]$, commented on by SD as a trivial one, is studied in the recent chemistry literature under the name "*one-electron potential*." The corresponding acronym OEP should not be confused with that for the term "*optimized effective potential*," which can be spotted frequently in numerous DFT papers.

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