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Functional derivative of noninteracting kinetic energy density functional

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Proofs from different theoretical frameworks, namely, the Hohenbergh–Kohn theorems, the Kohn–Sham scheme, and the first-order density matrix representation, have been presented in this paper to show that the functional derivative of the noninteracting kinetic energy density functional can uniquely be expressed as the negative of the Kohn–Sham effective potential, arbitrary only to an additive orbital-independent constant. Key points leading to the current result as well as confusion about the quantity in the literature are briefly discussed.

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I. INTRODUCTION

The noninteracting kinetic energy density functional $T_S[\rho]$ has been of considerable interest recently in the literature [1–7]. In the central issue is the existence and uniqueness of the functional derivative of $T_S[\rho]$ with respect to the electron density, $\delta T_S[\rho]/\delta\rho(\mathbf{r})$. Here from three different theoretical viewpoints, i.e., the Hohenberg–Kohn theorems, the Kohn–Sham scheme, and the first-order density matrix representation, it is shown that $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ can uniquely be expressed as the negative of the Kohn–Sham effective potential, arbitrary only to an additive orbital-independent constant.

Before we start, it is important to point out that derivation of the Kohn–Sham equations does not require the knowledge of the functional derivative of $T_S[\rho]$ [22]. What Kohn and Sham [8] proposed is the use of determinantal Kohn–Sham orbitals for the noninteracting N-electron reference system described by the Hamiltonian $\hat{H}=\Sigma_i-\frac{1}{2}\nabla_i^2+\hat{\nu}_{\text{ext}}+\Sigma_{i,j}(1/r_{ij})$ (atomic units are used throughout), so that [9]

$$T_S[\rho]=T_S[\{\phi_i\}[\rho]]\equiv\sum_{i=1}^{N}\langle\phi_i|-\tfrac{1}{2}\nabla^2|\phi_i\rangle \tag{1}$$

is minimized with a given ν-representable electron density $\rho(\mathbf{r})$ defined by

$$\rho(\mathbf{r})=\sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2, \tag{2}$$

under the constraint of orbital orthonormality, namely,

$$\int\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\,d\tau=\delta_{ij}. \tag{3}$$

Using Levy's constrained-search algorithm [10], $T_S[\rho]$ defined by Eq. (1) has been proved to be convex lower semicontinuous and Gâteaux differentiable with respect to the total electron density [11,12]. The corresponding Kohn–Sham equation reads

$$[-\tfrac{1}{2}\nabla^2+\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})]\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r}), \tag{4}$$

where ε_{i} are Kohn–Sham orbital energies and the effective Kohn–Sham potential $\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})$ can be written as

$$\upsilon_{\text{eff}}^{\text{Ks}}(\mathbf{r})=\nu_{\text{ext}}(\mathbf{r})+\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\tau'+\upsilon_{\text{xc}}(\mathbf{r}), \tag{5}$$

with $\nu_{\text{ext}}(\mathbf{r})$ being the external potential, the second term on the right-hand side the classical Coulomb repulsion potential, and the exchange-correlation potential $\upsilon_{xc}(\mathbf{r})$ defined by

$$\upsilon_{xc}(\mathbf{r})=\frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}, \tag{6}$$

where $E_{xc}[\rho]$ is the unknown exchange-correlation energy density functional.

The reason that the noninteracting kinetic energy, $T_S[\{\phi_i\}[\rho]]$ in Eq. (1), is a functional of the density is because the Kohn–Sham orbitals are functionals of the density as dictated by the first Hohenberg–Kohn theorem [13], indicating that the density determines the external potential and thus everything else of the ground state. In practice, it has been shown by the Zhao–Morrison–Parr method [14] that with the total N-representable electron density given, one can numerically calculate the Kohn–Sham orbitals, the exchange-correlation potential, etc., to very good accuracy. As will be pointed out in Sec. IV, when the noninteracting kinetic energy is expressed as a functional of the first-order density matrix γ, $T_S[\gamma]$, because of the same reason, it must be a functional of the total electron density as well, i.e.,

$$T_S[\gamma]\equiv T_S[\gamma[\rho]]. \tag{7}$$

Notice that to obtain Eq. (4), one has to assume orbital differentiability. From above, it is apparent that the only unknown term to be approximated in the Kohn–Sham scheme is the exchange-correlation potential $\upsilon_{xc}(\mathbf{r})$; the functional derivative of the noninteracting kinetic energy density functional $T_S[\rho]$ with respect to density, $\delta T_S[\rho]/\delta\rho(\mathbf{r})$, has not been involved in the derivation of Kohn–Sham equations. In

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what follows, we will make use of this fact and derive $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ with the help of the Kohn–Sham equations, Eq. (4).

II. HOHENBERG–KOHN THEOREMS

The first proof is straightforward and has been well documented in the literature; see, for example, Ref. [9]. It is based on the two original theorems of Hohenberg and Kohn [13]. From the first theorem of Hohenberg and Kohn, the total energy of an electronic system, expressed as a functional of the electron density, can be decomposed in the following form:

$$E[\rho] = F[\rho] + \int \rho(\mathbf{r})\nu_{\text{ext}}(\mathbf{r})d\tau, \tag{8}$$

where $F[\rho]$ is the universal energy density functional, which can further be decomposed to be

$$F[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho]. \tag{9}$$

$J[\rho]$ is the classical Coulomb repulsion,

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\tau\,d\tau', \tag{10}$$

and $E_{xc}[\rho]$ is the exchange-correlation energy density functional. According to the second theorem of Hohenberg and Kohn [13], the electron density minimizes the total electronic energy subject to the condition that the density is normalized to the total number of electrons,

$$\int \rho(\mathbf{r})\;d\tau = N. \tag{11}$$

So,

$$\frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} = \mu, \tag{12}$$

where μ is the chemical potential of the system. With Eqs. (8) and (9), one finds that the functional derivative of the kinetic energy density functional is

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = \mu - \nu_{\text{ext}}(\mathbf{r}) - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\tau' - v_{xc}(\mathbf{r}). \tag{13}$$

With Eq. (5), Eq. (13) becomes

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = \mu - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}). \tag{14}$$

III. KOHN–SHAM SCHEME

The second proof makes use of the Kohn–Sham scheme [8] for the noninteracting reference system, where the noninteracting kinetic energy is expressed via a set of Kohn–Sham orbitals,

$$T_S[\rho] = T_S[\{\phi_i[\rho]\}] \equiv \sum_{i=1}^{N}\langle\phi|\hat{T}|\phi_i\rangle = \sum_i t_i, \tag{15}$$

where t_i is the orbital kinetic energy defined as

$$t_i = \langle\phi_i| - \tfrac{1}{2}\nabla_i^2|\phi_i\rangle. \tag{16}$$

Functional differentiation of both sides of the above equation gives that

$$\delta t_i = \left\langle\delta\phi_i\middle| - \tfrac{1}{2}\nabla_i^2\middle|\phi_i\right\rangle + \left\langle\phi_i\middle| - \tfrac{1}{2}\nabla_i^2\middle|\delta\phi_i\right\rangle. \tag{17}$$

With the help of Eq. (4), there results

$$\begin{aligned}\delta t_i &= \langle\delta\phi_i|[\varepsilon_i - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})]|\phi_i\rangle + \langle\phi_i|[\varepsilon_i - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})]|\delta\phi_i\rangle\\ &= \varepsilon_i\delta\int|\phi_i|^2 d\tau - \int \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})\,\delta|\phi_i|^2\;d\tau.\end{aligned} \tag{18}$$

Since $\int|\phi_i|^2\;d\tau = 1$, the first term on the right-hand side of the last equality of Eq. (18) vanishes, yielding

$$\delta t_i = -\int \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})\,\delta|\phi_i|^2\;d\tau. \tag{19}$$

Therefore, for the total kinetic energy, we have

$$\begin{aligned}\delta T_S[\{\phi_i\}] &= \sum_i \delta t_i = -\int \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})\sum_i \delta|\phi_i|^2 d\tau\\ &= -\int \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})\,\delta\rho(\mathbf{r})d\tau,\end{aligned} \tag{20}$$

which, up to an arbitrary additive constant, const, gives that

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = \frac{\delta T_S[\{\phi_i[\rho]\}]}{\delta\rho(\mathbf{r})} = \text{const} - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}). \tag{21}$$

Indeed, it has recently been shown by Leeuwen [12] that in the noninteracting Kohn–Sham representation, the functional derivative of $T_S[\rho]$, defined in Eq. (1), at a noninteracting N- and V–representable density is given by $\delta T_s[\rho]/\delta\rho(\mathbf{r}) = -\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})$, where the potential $\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})$ generates the density $\rho(\mathbf{r})$ in a noninteracting system.

IV. FIRST-ORDER DENSITY MATRIX REPRESENTATION

Our last proof is based on the first-order density matrix representation of the noninteracting kinetic energy density functional,

$$\begin{aligned}T_S[\rho] = T_S[\gamma[\rho]] &\equiv \int t_s(\mathbf{r}_1)d\tau_1\\ &= -\frac{1}{2}\int \nabla_{\mathbf{r}_1}^2\gamma(\mathbf{r}_1,\mathbf{r}_2)\bigg|_{\mathbf{r}_1=\mathbf{r}_2} d\tau_1\\ &= -\frac{1}{2}\int \nabla_{\mathbf{r}_2}^2\gamma(\mathbf{r}_1,\mathbf{r}_2)\bigg|_{\mathbf{r}_1=\mathbf{r}_2} d\tau_2.\end{aligned} \tag{22}$$

Assuming the density-matrix differentiability, it has been known that [15,16]

$$\frac{\delta\gamma(\mathbf{r}_1,\mathbf{r}_2)}{\delta\rho(\mathbf{r})} = \int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i=1}^{\text{occ}}[\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r}_1)G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i) + \text{c.c.}]d\tau', \tag{23}$$

where G is the single-particle Green function,

$$G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i) = \sum_{j}^{\text{unocc}} \frac{\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}')}{\varepsilon_j - \varepsilon_i}, \tag{24}$$

and χ_0^{-1} is the inverse of the linear response function, with [17]

$$\chi_0(\mathbf{r}_2,\mathbf{r}') = \sum_{i}^{\text{occ}}\sum_{j}^{\text{unocc}} \frac{\phi_i^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_j - \varepsilon_i} + \text{c.c.} \tag{25}$$

Upon functional differentiation of Eq. (22), one has

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = -\frac{1}{2}\int \nabla_{\mathbf{r}_1}^2 \frac{\delta\gamma(\mathbf{r}_1,\mathbf{r}_2)}{\delta\rho(\mathbf{r})}\text{A}\Bigg|_{\mathbf{r}_1=\mathbf{r}_2} d\tau_1 = -\frac{1}{2}\int \nabla_{\mathbf{r}_2}^2 \frac{\delta\gamma(\mathbf{r}_1,\mathbf{r}_2)}{\delta\rho(\mathbf{r})}\text{A}\Bigg|_{\mathbf{r}_1=\mathbf{r}_2} d\tau_2. \tag{26}$$

Let us consider the first equality of the above equation first. Since

$$-\frac{1}{2}\nabla_{\mathbf{r}_1}^2\frac{\delta\gamma(\mathbf{r}_1,\mathbf{r}_2)}{\delta\rho(\mathbf{r})} = \int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i=1}^{\text{occ}}\left[\phi_i(\mathbf{r}') \times\left(-\frac{1}{2}\nabla_{\mathbf{r}_1}^2\right)\phi_i^*(\mathbf{r}_1)G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i) + \text{c.c.}\right] d\tau', \tag{27}$$

there results

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = -\frac{1}{2}\int \nabla_{\mathbf{r}_1}^2\frac{\delta\gamma(\mathbf{r}_1,\mathbf{r}_2)}{\delta\rho(\mathbf{r})}\text{A}\Bigg|_{\mathbf{r}_1=\mathbf{r}_2} d\tau_1 = \int\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i=1}^{\text{occ}}\left[\phi_i(\mathbf{r}')\left(-\frac{1}{2}\nabla_{\mathbf{r}_1}^2\right)\phi_i^*(\mathbf{r}_1) \times G(\mathbf{r}_1,\mathbf{r}',\varepsilon_i) + \text{c.c.}\right] d\tau_1\, d\tau'. \tag{28}$$

From Eq. (5) we have

$$(-\tfrac{1}{2}\nabla_i^2)\phi_i(\mathbf{r}) = [\varepsilon_i - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r})]\phi_i(\mathbf{r}). \tag{29}$$

Thus

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = \int\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i=1}^{\text{occ}}[\varepsilon_i\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r}_1)G(\mathbf{r}_1,\mathbf{r}',\varepsilon_i) + \text{c.c.}]d\tau_1\, d\tau' - \int\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i=1}^{\text{occ}}[\phi_i(\mathbf{r}')\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1) \times G(\mathbf{r}_1,\mathbf{r}',\varepsilon_i) + \text{c.c.}]\, d\tau_1\, d\tau'. \tag{30}$$

The first term on the right-hand side of the above equation vanishes because all occupied orbitals $\phi_i^*(\mathbf{r}_1)$ and unoccupied orbitals $\phi_j(\mathbf{r}_1)$ are orthogonal, whereas for the second term we have

$$\sum_{i=1}^{\text{occ}}[\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r}_1)G(\mathbf{r}_1,\mathbf{r}',\varepsilon_i) + \text{c.c.}] = \chi_0(\mathbf{r}_1,\mathbf{r}'). \tag{31}$$

Hence

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = -\int\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_1)\chi_0(\mathbf{r}_1,\mathbf{r}')d\tau_1 d\tau'. \tag{32}$$

With

$$\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\chi_0(\mathbf{r}_1,\mathbf{r}')\, d\tau' = \delta(\mathbf{r}-\mathbf{r}_1), \tag{33}$$

there results

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = -\int \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_1)\delta(\mathbf{r}-\mathbf{r}_1)d\tau_1 = -\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}). \tag{34}$$

Now, let us consider the second equality of Eq. (26), where the Laplacian operator is acting on the coordinate $\mathbf{r}_2$, instead of $\mathbf{r}_1$. The integrand becomes

$$-\frac{1}{2}\nabla_{\mathbf{r}_2}^2\frac{\delta\gamma(\mathbf{r}_1,\mathbf{r}_2)}{\delta\rho(\mathbf{r})} = \int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i=1}^{\text{occ}}\left[\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r}_1) \times\left(-\frac{1}{2}\nabla_{\mathbf{r}_2}^2\right)G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i) + \text{c.c.}\right]d\tau'. \tag{35}$$

From the Appendix, it is known that

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_2}^2 + \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_2)\right]G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i) = \sum_{j}^{\text{unocc}}\frac{\varepsilon_j}{\varepsilon_j-\varepsilon_i}\phi_j(\mathbf{r}_2)\phi_j(\mathbf{r}'), \tag{36}$$

and thus

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}_2}^2\right)G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i) = \sum_{j}^{\text{unocc}}\frac{\varepsilon_j}{\varepsilon_j-\varepsilon_i}\phi_j(\mathbf{r}_2)\phi_j(\mathbf{r}') - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_2)G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i). \tag{37}$$

Therefore

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = \int\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i}\sum_{j}\left[\frac{\varepsilon_j}{\varepsilon_j-\varepsilon_i}\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r}_1) \times\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}') + \text{c.c.}\right]d\tau_1\, d\tau' - \int\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\sum_{i}[\phi_i(\mathbf{r}')\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1)$$

$$\times G(\mathbf{r}_1,\mathbf{r}',\varepsilon_i) + \text{c.c.}]d\tau_1\, d\tau'. \tag{38}$$

The first term on the right-hand side again vanishes because of orthogonality of $\phi_i^*(\mathbf{r}_1)$ and $\phi_j(\mathbf{r}_1)$, and one thus comes up with

$$\begin{aligned}\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} &= -\int\int \chi_0^{-1}(\mathbf{r},\mathbf{r}')\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_1)\chi_0(\mathbf{r}_1,\mathbf{r}')d\tau_1\, d\tau' \\ &= -\int \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}_1)\delta(\mathbf{r}-\mathbf{r}_1)d\tau_1 = -\upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}).\end{aligned} \tag{39}$$

V. DISCUSSION

Equations (14), (21), (34), and (39) are the major results of the present work. From three derivations of different theoretical frameworks, it has been shown that the functional derivative of the noninteracting kinetic energy density functional with respect to the electron density is uniquely determined to be the negative of the effective Kohn–Sham potential, arbitrary only to an additive orbital-independent constant. While Eq. (14) is well known, confirmation from the Kohn–Sham and first-order density matrix representations is not obvious. In an independent recent work, Lindgren and Salomonson [7] have proved that for a general N-electron wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$, there exists

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = \frac{E_0}{N} - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}), \tag{40}$$

where E_0 is the exact ground-state energy of the system, and for a single Slater determinant type wave function $\Phi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$, one has (for the $N=2$ case)

$$\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} = \frac{E_0}{2} - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}). \tag{41}$$

All these results verify that

$$\begin{aligned}\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})} &= \frac{\delta T_S[\gamma[\rho]]}{\delta\rho(\mathbf{r})} = \frac{\delta T_S[\{\phi_i\}[\rho]]}{\delta\rho(\mathbf{r})} = \frac{\delta T_S[\Psi[\rho]]}{\delta\rho(\mathbf{r})} \\ &= \frac{\delta T_S[\Phi[\rho]]}{\delta\rho(\mathbf{r})} = \cdots = \text{const} - \upsilon_{\text{eff}}^{\text{KS}}(\mathbf{r}),\end{aligned} \tag{42}$$

indicating that the quantity $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ does exist, is well defined, and, arbitrary only to an additive orbital-independent constant, is unique in density functional theory. The arbitrary constant cannot be determined in the present setting without extra knowledge. If asymptotic behavior or extra information such as Janak's theorem [18] is employed, it can then uniquely be ascertained.

There has been some confusion and debate about the kinetic energy density functional and its functional derivative in the literature [1–7]. The main argument, in our opinion, is related to the existence and uniqueness of $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ in the Kohn–Sham scheme. Differing from the original Thomas–Fermi and Hohenberg–Kohn cases, where everything is a functional of the electron density, the Kohn–Sham scheme introduces orbitals into the expression for the kinetic energy and thus brings in the uncertainty of whether or not variation of T_S is still a functional of the density. If not, the quantity $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ is not well defined, leading to problems in the Kohn–Sham description. Fortunately, Eq. (21) clearly shows that the answer should be positive. One can rewrite the derivation from the Kohn–Sham scheme as follows:

$$\begin{aligned}\delta T_S &= \int \sum_i \left[\delta\phi_i^*\left(-\frac{1}{2}\nabla^2\right)\phi_i + \text{c.c.}\right]d\tau \\ &= \int \sum_i [\delta\phi_i^*(\varepsilon_i - \upsilon_{\text{eff}}^{\text{KS}})\phi_i + \text{c.c.}]d\tau \\ &= \sum_i \varepsilon_i \delta \int |\phi_i|^2\, d\tau - \int \upsilon_{\text{eff}}^{\text{KS}} \delta \sum_i |\phi_i|^2\, d\tau \\ &= -\int \upsilon_{\text{eff}}^{\text{KS}} \delta\rho(\mathbf{r})d\tau.\end{aligned} \tag{43}$$

The last equality in the above derivation is a result of the orthonormality property of the Kohn–Sham orbitals.

Three points are essential in the above derivation as well as in deriving Eqs. (34) and (39), respectively, from the first-order density matrix theory. First, as we have addressed in the Introduction, knowledge of $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ is not required in deriving the Kohn–Sham equations, implying that we can make use of the Kohn–Sham equations to obtain the expression for $\delta T_S[\rho]/\delta\rho(\mathbf{r})$. Otherwise, there would exist circular logic problem in derivation of $\delta T_S[\rho]/\delta\rho(\mathbf{r})$. Second, all terms associated with Lagrange multipliers ε_i vanish in the derivation because of orthonormality of the Kohn–Sham orbitals. This second point is extremely important to ensure that $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ is not orbital dependent. Finally, the treatment here is restricted to $\nu_{\text{eff}}^{\text{KS}}$-representable densities (densities that are associated with the ground state of a noninteracting system of electrons). For densities that are not the ground state for any noninteracting system, $\nu_{\text{eff}}^{\text{KS}}$ does not exist and the present proof does not apply. In fact, $\delta T_S[\rho]/\delta\rho(\mathbf{r})$ is not defined for densities that are not $\nu_{\text{eff}}^{\text{KS}}$-representable; this can be shown by setting the strength of the electron-electron interaction to be zero in the treatment of Englisch and Englisch [19–21]. These three points are also key in deriving Eqs. (40) and (41) in Ref. [7]. Negligence or omission of any of these points is likely to be the root of the confusion in the literature.

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APPENDIX: DERIVATION OF EQ. (36)

For the unoccupied eigenstate $\phi_j(\mathbf{r}_2)$, the Kohn–Sham equation reads

$$[-\tfrac{1}{2}\nabla^2_{\mathbf{r}_2}+v^{\mathrm{KS}}_{\mathrm{eff}}(\mathbf{r}_2)]\phi_j(\mathbf{r}_2)=\varepsilon_j\phi_j(\mathbf{r}_2). \tag{A1}$$

Multiplying both sides by $\phi_j^*(\mathbf{r}')$ and then adding $\varepsilon_i\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}')$ (with $\varepsilon_i \neq \varepsilon_j$) give

$$\begin{aligned}&[-\tfrac{1}{2}\nabla^2_{\mathbf{r}_2}+v^{\mathrm{KS}}_{\mathrm{eff}}(\mathbf{r}_2)]\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}')-\varepsilon_i\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}')\\&\quad=(\varepsilon_j-\varepsilon_i)\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}').\end{aligned} \tag{A2}$$

Dividing both sides by $\varepsilon_j-\varepsilon_i$, one has

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_2}+v^{\mathrm{KS}}_{\mathrm{eff}}(\mathbf{r}_2)\right]\frac{\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}')}{(\varepsilon_j-\varepsilon_i)}=\frac{\varepsilon_j}{(\varepsilon_j-\varepsilon_i)}{}_i\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}'). \tag{A3}$$

Upon summation over all $j's$, there results

$$\begin{aligned}&\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_2}+v^{\mathrm{KS}}_{\mathrm{eff}}(\mathbf{r}_2)\right]\sum_j^{\mathrm{unocc}}\frac{\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}')}{(\varepsilon_j-\varepsilon_i)}\\&\quad=\sum_j^{\mathrm{unocc}}\frac{\varepsilon_j}{(\varepsilon_j-\varepsilon_i)}\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}').\end{aligned} \tag{A4}$$

Given that

$$G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i)=\sum_j^{\mathrm{unocc}}\frac{\phi_j(\mathbf{r}_2)\phi_j(\mathbf{r}')}{\varepsilon_j-\varepsilon_i}, \tag{A5}$$

therefore

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_2}+v^{\mathrm{KS}}_{\mathrm{eff}}(\mathbf{r}_2)\right]G(\mathbf{r}_2,\mathbf{r}',\varepsilon_i)=\sum_j^{\mathrm{unocc}}\frac{\varepsilon_j}{\varepsilon_j-\varepsilon_i}\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}'). \tag{A6}$$

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