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Bounds for the exchange and correlation potentials

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Knowledge of bounds and equalities for the exact density-functional exchange-correlation potential $\delta E_{\rm xc}[n]/\delta n(\mathbf{r})$ is necessary for its accurate approximation. With this in mind, it is shown, for $\lambda\rightarrow 0$, that $\lambda^{-1}\int d^3 r n(\mathbf{r})\delta E_{\rm xc}[n_\lambda]/\delta n(\mathbf{r})\geq 2\lambda^{-1}E_{\rm xc}[n_\lambda]$ and $\int n(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}d^3 r' + \lambda^{-1}\delta E_{\rm xc}[n_\lambda]/\delta n(\mathbf{r})\geq 0$, where $n_\lambda(x,y,z)=\lambda^3 n(\lambda x,\lambda y,\lambda z)$. The local-density approximation satisfies the former inequality but violates the latter one. Moreover, with respect to the Fermi level, it is shown that the exact correlation potential $\delta E_c[n]/\delta n(\mathbf{r})$ satisfies $E_c[n]-E_c[n-\Delta n_F]\leq\int\delta E_c[n]/\delta n(\mathbf{r})\Delta n_F(\mathbf{r})d^3\mathbf{r}$, where Δn_F is the density of the highest-occupied Kohn-Sham orbital of n. The corresponding inequality for the exact exchange potential $\delta E_x[n]/\delta n(\mathbf{r})$ is in the opposite direction: $E_x[n]-E_x[n-\Delta n_F]\geq\int\delta E_x[n]/\delta n(\mathbf{r})\Delta n_F(\mathbf{r})d^3 r$. It is a difficult challenge for an approximate exchange-correlation functional to simultaneously satisfy both inequalities. For instance, the local-density approximation does *not*.

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I. INTRODUCTION AND SUMMARY

For the purpose of obtaining more accurate approximations to the exact exchange-correlation density functional $E_{\rm xc}[n]$, and the corresponding exchange-correlation potential $v_{\rm xc}([n];\mathbf{r})=\delta E_{\rm xc}[n]/\delta n(\mathbf{r})$, it is essential to continue to find conditions satisfied by $E_{\rm xc}$ and $v_{\rm xc}$. Any given approximation to $E_{\rm xc}$ or $v_{\rm xc}$ should then be modified to satisfy the conditions, if it does not already do so.

There are not a large number of relations known that involve $v_{\rm xc}$. In this paper, we focus upon $v_{\rm xc}$, as well as upon $E_{\rm xc}$, and show that

$$\lim_{\lambda\rightarrow 0}\lambda^{-1}\int d^3 r\, n(\mathbf{r})\frac{\delta E_{\rm xc}[n_\lambda]}{\delta n(\mathbf{r})}\geq 2\lim_{\lambda\rightarrow 0}\lambda^{-1}E_{\rm xc}[n_\lambda] \qquad (1)$$

and

$$\lim_{\lambda\rightarrow 0}\lambda^{-1}\frac{\delta E_{\rm xc}[n_\lambda]}{\delta n(\mathbf{r})}+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'\geq 0\ , \quad \text{for } all\ \mathbf{r}\ , \qquad (2a)$$

or

$$\lim_{\lambda\rightarrow 0}\lambda^{-1}\int d^3 r\, g(\mathbf{r})\frac{\delta E_{\rm xc}[n_\lambda]}{\delta n(\mathbf{r})} +\int\int\frac{g(\mathbf{r})n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3 r\geq 0\ , \qquad (2b)$$

with $g(\mathbf{r})\geq 0$. The scaled density $n_\lambda(\mathbf{r})$ is obtained from the original density $n(\mathbf{r})$ by uniform coordinate scaling

$$n_\lambda(x,y,z)=\lambda^3 n(\lambda x,\lambda y,\lambda z)\ .$$

[Note that constraint (2b), with $g=n$, is equivalent to Eq. (1) plus

$$2\lim_{\lambda\rightarrow 0}\lambda^{-1}\int E_{\rm xc}[n_\lambda]\geq -\int\int\frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3 r_1 d^3 r_2\ ,$$

which was previously obtained in Ref. [1].] As shown in the Appendix, the functional derivative $\delta E_{\rm xc}[n_\lambda]/\delta n(\mathbf{r})$ is equal to $v_{\rm xc}([n_\lambda];\mathbf{r}/\lambda)$, which therefore can be substituted for $\delta E_{\rm xc}[n_\lambda]/\delta n(\mathbf{r})$ in Eqs. (1) and (2).

At the Fermi level, we then show that

$$E_{\rm xc}[n]-E_{\rm xc}[n-\Delta n_F] \leq\int\frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})}\Delta n_F(\mathbf{r})d^3 r +\tfrac{1}{2}\int\int\frac{\Delta n_F(\mathbf{r}_1)\Delta n_F(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3 r_1 d^3 r_2\ , \qquad (3)$$

where Δn_F is the density at the Fermi level. That is, Δn_F is the density of the highest occupied Kohn-Sham orbital of that noninteracting Hamiltonian whose ground-state density is n.

The functional derivative $\delta E_{\rm xc}[n]/\delta n(\mathbf{r})$ is defined only to within an additive constant if, as in this work, densities are assumed to have a fixed electron number [2–4]. In the more general theory, which allows continuously varying electron numbers, $\delta E_{\rm xc}[n]/\delta n(\mathbf{r})$ is completely defined, however, and has a derivative discontinuity at integer electron numbers [3,4]. For the densities appearing in this work, which have a fixed integer electron number, the functional derivative $\delta E_{\rm xc}[n]/\delta n(\mathbf{r})$ is completely defined as the one obtained from the more general theory if the density n is approached from the electron deficiency side [2–4]. In the same way, possible ambiguities from additive constants are removed in the functional derivatives $\delta E_x[n]/\delta n(\mathbf{r})$ and $\delta E_c[n]/\delta n(\mathbf{r})$ of the components $E_x[n]$ and $E_c[n]$ of $E_{\rm xc}[n]$. For finite

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systems with boundary conditions that require their densities to have asymptotic exponential decay [2], this means that the functional derivatives *vanish* as $|\mathbf{r}|\rightarrow\infty$. It is crucial for the validity of the result given in this work that the functional derivatives of $E_x[n]$, $E_c[n]$, and $E_{\mathrm{xc}}[n]$ be defined as described above.

Observe that in Eqs. (1) and (2), the scaled density n_λ is placed within E_{xc}, then the functional derivative is taken with respect to the unscaled density n, and finally the limit $\lambda\rightarrow 0$ is taken. If we assume that the functional E_{xc} is sufficiently well behaved, we can interchange the last two steps. Although this is by no means necessary to apply Eqs. (1) and (2), it leads to algebraic simplifications for most approximation functionals. For example, let us consider

$$\tilde{E}_{\mathrm{xc}}[n]=\int n^{4/3}d^3r+\int d^3r|\nabla n|^2n^{-4/3} + \int d^3r(n+|\nabla n|n^{-1/3})(1+n^{-1/3})^{-1} \tag{4}$$

as an approximation to $E_{\mathrm{xc}}[n]$. (The functional $\tilde{E}_{\mathrm{xc}}[n]$ is employed here for illustrative purposes only; it is a rather poor approximation.) Now substitute n_λ for n in Eq. (4) to form

$$\tilde{E}_{\mathrm{xc}}[n_\lambda]=\lambda\int n^{4/3}d^3r+\lambda\int d^3r|\nabla n|^2n^{-4/3} + \int d^3r(n+|\nabla n|n^{-1/3})(1+\lambda^{-1}n^{-1/3})^{-1}\ , \tag{5}$$

so that

$$\lim_{\lambda\rightarrow 0}\lambda^{-1}\tilde{E}_{\mathrm{xc}}[n_\lambda]=2\int n^{4/3}d^3r+\int d^3r|\nabla n|^2n^{-4/3} + \int d^3r|\nabla n| \tag{6}$$

and

$$\lim_{\lambda\rightarrow 0}\lambda^{-1}\frac{\delta\tilde{E}_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})} = \frac{\delta}{\delta n(\mathbf{r})}\left[2\int n^{4/3}d^3r+\int d^3r|\nabla n|^2n^{-4/3} + \int d^3r|\nabla n|\right] . \tag{7}$$

Alternatively, if the exchange-correlation potential $\tilde{v}_{\mathrm{xc}}([n];\mathbf{r})$ of the approximate functional $\tilde{E}_{\mathrm{xc}}[n]$ is known, then one can substitute n_λ for n and $\mathbf{r}/\lambda$ for $\mathbf{r}$ in $\tilde{v}_{\mathrm{xc}}([n];\mathbf{r})$, replace in Eqs. (1) and (2) $\delta E_{\mathrm{xc}}[n_\lambda]/\delta n(\mathbf{r})$ by the resulting $v_{\mathrm{xc}}([n_\lambda];\mathbf{r}/\lambda)$, and finally take the limit $\lambda\rightarrow 0$ (see Appendix).

It shall perhaps prove convenient, when testing functionals, to express Eqs. (1) and (2) in alternative forms. One may partition E_{xc} as

$$E_{\mathrm{xc}}[n]=E_x[n]+E_c[n] \tag{8}$$

and utilize [5]

$$E_x[n_\lambda]=\lambda E_x[n] \tag{9}$$

to express Eqs. (1) and (2a) as

$$\int d^3r\,n(\mathbf{r})\left[\frac{\delta E_x[n]}{\delta n(\mathbf{r})}+\lim_{\lambda\rightarrow 0}\lambda^{-1}\frac{\delta E_c[n_\lambda]}{\delta n(\mathbf{r})}\right] \geq 2(E_x[n]+\lim_{\lambda\rightarrow 0}\lambda^{-1}E_c[n_\lambda]) \tag{10}$$

and

$$\frac{\delta E_x[n]}{\delta n(\mathbf{r})}+\lim_{\lambda\rightarrow 0}\lambda^{-1}\frac{\delta E_c[n_\lambda]}{\delta n(\mathbf{r})}+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r'\geq 0\ . \tag{11}$$

In the local-density approximation (LDA),

$$\begin{aligned}\lim_{\lambda\rightarrow 0}\lambda^{-1}E_{\mathrm{xc}}^{\mathrm{LDA}}[n_\lambda]&=\lim_{\lambda\rightarrow 0}\lambda^{-1}E_x^{\mathrm{LDA}}[n_\lambda] + \lim_{\lambda\rightarrow 0}\lambda^{-1}E_c^{\mathrm{LDA}}[n_\lambda]\\ &=a\int n^{4/3}(\mathbf{r})d^3r+b\int n^{4/3}(\mathbf{r})d^3r\\ &=c\int n^{4/3}(\mathbf{r})d^3r\ .\end{aligned} \tag{12}$$

[The term $b\int n^{4/3}(\mathbf{r})d^3r$ arises from the low-density limit for the correlation energy of a uniform electron gas [6].] Now, note that since the constant c emerging in the LDA low-density limit is negative, it follows that the local-density approximation satisfies Eq. (1). However, the local-density approximation does not satisfy Eqs. (2); it is easy to find well-behaved densities for which

$$\tfrac{4}{3}cn^{1/3}(\mathbf{r})+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r'\geq 0\ , \tag{13a}$$

which corresponds to Eq. (2a), and for which

$$\tfrac{4}{3}c\int n^{4/3}d^3r+\int\int\frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d^3r'd^3r\geq 0\ , \tag{13b}$$

which corresponds to Eq. (2b) with $g(\mathbf{r})=n(\mathbf{r})$, are *violated.*

for a quick example, consider $\mathbf{r}=0$ in expression (13a) and take $n(\mathbf{r})=de^{-\gamma r}$. This inequality is violated when $\gamma^2>3\pi d^{2/3}|c|^{-1}$. For another example, the inequality (13b) is violated if one substitutes $\lambda^2n(\lambda x,\lambda y,z)$ for an arbitrary n and takes $\lambda\rightarrow 0$. Nonlocal approximations have yet to be tested with respect to conditions (1) and (2).

With respect to the Fermi level, Eq. (3) is actually the $\lambda=1$ special case of

$$E_{\mathrm{xc}}[n_\lambda]-E_{\mathrm{xc}}[n_\lambda-\Delta n_{F,\lambda}] \leq\int\frac{\delta E_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})}\Delta n_F(\mathbf{r})d^3r +\tfrac{1}{2}\lambda\int\int\frac{\Delta n_F(\mathbf{r}_1)\Delta n_F(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\quad \text{all } \lambda\geq 0\ , \tag{14}$$

where $\Delta n_{F,\lambda}(\mathbf{r})\equiv\lambda^3\Delta n_F(\lambda x,\lambda y,\lambda z)$ with $\Delta n_F(\mathbf{r})=|\phi_F(\mathbf{r})|^2$, where $\phi_F(\mathbf{r})$ is the highest-occupied Kohn-Sham orbital of $n(\mathbf{r})$. Now, we have observed that a recently derived density-functional Koopmans's theorem [7,8] can be cast as [8]

$$E_x[n]-E_x[n-\Delta n_F]=\int\frac{\delta E_x[n]}{\delta n(\mathbf{r})}\Delta n_F(\mathbf{r})d^3r+\tfrac{1}{2}\int\int\frac{\Delta n_F(\mathbf{r}_1)\Delta n_F(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\times d^3r_1d^3r_2\ . \tag{15}$$

Hence, the combination of Eqs. (8), (9), (14), and (15) gives the following inequality that involves correlation alone:

$$E_c[n_\lambda]-E_c[n_\lambda-\Delta n_{F,\lambda}]\leq\int\frac{\delta E_c[n_\lambda]}{\delta n(\mathbf{r})}\Delta n_F(\mathbf{r})d^3r\ ,\quad\text{all }\lambda\geq 0\ . \tag{16}$$

For a diamagnetic two-electron system, $E_c[n_\lambda-\Delta n_{F,\lambda}]=0$ and $\Delta n_F=\frac{1}{2}n$. Equation (16) then gives

$$E_c[n_\lambda]\leq\tfrac{1}{2}\int\frac{\delta E_c[n_\lambda]}{\delta n(\mathbf{r})}n(\mathbf{r})d^3r\ .$$

At $\lambda=1$, Eq. (16) becomes

$$E_c[n]-E_c[n-\Delta n_F]\leq\int\frac{\delta E_c[n]}{\delta n(\mathbf{r})}\Delta n_F(\mathbf{r})d^3r\ . \tag{17}$$

This correlation expression contrasts with the following corresponding one for exchange alone:

$$E_x[n]-E_x[n-\Delta n_F]\geq\int\frac{\delta E_x[n]}{\delta n(\mathbf{r})}\Delta n_F(\mathbf{r})d^3r\ , \tag{18}$$

which is implied by Eq. (15). Note that the inequalities in expressions (17) and (18) are in *opposite* directions.

Observe that conditions (16) and (18) cannot be satisfied simultaneously by the LDA. For example, divide Eq. (16) by λ, let $\lambda\to 0$, and utilize $\lim_{\lambda\to 0}\lambda^{-1}E_c^{\text{LDA}}[n_\lambda]=b\int n^{4/3}(\mathbf{r})d^3r$ from expression (12) to obtain

$$\int n^{4/3}(\mathbf{r})d^3r-\int[n(\mathbf{r})-\Delta n_F(\mathbf{r})]^{4/3}d^3r\leq\tfrac{4}{3}\int n^{1/3}(\mathbf{r})\Delta n_F(\mathbf{r})d^3r\ . \tag{19}$$

Now utilize $E_x[n]=a\int n^{4/3}(\mathbf{r})d^3r$ in Eq. (18) to obtain

$$\int n^{4/3}(\mathbf{r})d^3r-\int[n(\mathbf{r})-\Delta n_F(\mathbf{r})]^{4/3}d^3r\geq\tfrac{4}{3}\int n^{1/3}(\mathbf{r})\Delta n_F(\mathbf{r})d^3r\ . \tag{20}$$

The simultaneous validity of expressions (19) and (20) requires the equality in both expressions, which is generally impossible. The situation with nonlocal approximations for exchange correlation (such as the use of gradient corrections to the LDA) has not yet been explored with respect to the simultaneous satisfaction of conditions (16) and (18). [The LDA for exchange alone clearly violates Eq. (15). Indeed, Eq. (15) is violated as well by most approximations with gradient terms. Noteworthy then is the fact that Krieger, Li, and Iafrate [7] have incorporated Eq. (15) into their recent exchange-potential approximations, which go beyond the LDA.]

II. DERIVATION OF CONSTRAINT (1)

Define $\Psi_{[n]}^{\alpha,N}(x_1,\dots,x_N)$ as that antisymmetric wave function that yields the density n and that is the ground state of $H_{[n]}^{\alpha,N}$, where, in atomic units,

$$H_{[n]}^{\alpha,N}=\sum_{i=1}^{N}-\tfrac{1}{2}\nabla_i^2+\sum_{i=1}^{N-1}\sum_{j>i}^{N}\alpha r_{ij}^{-1}+\sum_{i=1}^{N}v_\alpha([n];\mathbf{r}_i)\ ,\quad\alpha\geq 0\ . \tag{21}$$

Here $\alpha=\lambda^{-1}$ is a coupling constant and v_α is a local multiplicative external potential that keeps the ground-state density independent of α [9,10]. Next, by factoring $\Psi_{[n]}^{\alpha,n}$ in the manner of expression (14) in Ref. [2], as an $(N-1)$-electron part multiplied by a part involving just the Nth electron, it follows that the variational theorem dictates

$$\langle\Psi_{[n]}^{\alpha,N}|H_{[n]}^{\alpha,N-1}|\Psi_{[n]}^{\alpha,N}\rangle\geq E_{[n]}^{\alpha,N-1}\ , \tag{22}$$

where

$$H_{[n]}^{\alpha,N-1}=\sum_{i=1}^{N-1}-\tfrac{1}{2}\nabla_i^2+\sum_{i=1}^{N-2}\sum_{j>i}^{N-1}\alpha r_{ij}^{-1}+\sum_{i=1}^{N-1}v_\alpha([n];\mathbf{r}_i)\ , \tag{23}$$

or

$$H_{[n]}^{\alpha,N-1}=H_{[n]}^{\alpha,N}+\tfrac{1}{2}\nabla_N^2-\alpha\sum_{i=1}^{N-1}r_{iN}^{-1}-v_\alpha([n];\mathbf{r}_N)\ , \tag{24}$$

where $E_{[n]}^{\alpha,N-1}$ is the ground-state energy of $H_{[n]}^{\alpha,N-1}$. In other words, $H_{[n]}^{\alpha,N-1}$ is obtained by removing the Nth electron from $H_{[n]}^{\alpha,N}$. In this connection, note that the integration in Eq. (22) is defined to involve the space-spin coordinates of electrons 1 through N, even though $H_{[n]}^{\alpha,N-1}$ contains only electrons 1 through $N-1$. Also note that n is clearly not the ground-state density of $H_{[n]}^{\alpha,N-1}$; n contains N electrons and not $N-1$ electrons.

Combine Eqs. (22) and (24) to obtain

$$T^\alpha[n]+2\alpha V_{ee}^\alpha[n]+\int d^3r\,n(\mathbf{r})v_\alpha([n];\mathbf{r})+NI\leq 0\ , \tag{25}$$

where

$$T^\alpha[n]=\left\langle\Psi_{[n]}^{\alpha,N}\left|\sum_{i=1}^{N}-\tfrac{1}{2}\nabla_i^2\right|\Psi_{[n]}^{\alpha,N}\right\rangle\ , \tag{26}$$

$$V_{ee}^\alpha[n]=\left\langle\Psi_{[n]}^{\alpha,N}\left|\sum_{i=1}^{N-1}\sum_{j>i}^{N}r_{ij}^{-1}\right|\Psi_{[n]}^{\alpha,N}\right\rangle\ , \tag{27}$$

and where I, the ionization energy of $H_{[n]}^{\alpha,N}$, is given by

$$I=E_{[n]}^{\alpha,N-1}-E_{[n]}^{\alpha,N}\ . \tag{28}$$

Here $E_{[n]}^{\alpha,N}$ is the ground-state energy of $H_{[n]}^{\alpha,N}$.

Next, utilize $\lambda=\alpha^{-1}$ and in Eq. (25) utilize [1,5,11–13]

$$T^\alpha[n]=\lambda^{-2}T^1[n_\lambda]=T^0[n]+\lambda^{-2}T_{\text{xc}}[n_\lambda]\ , \tag{29}$$

$$V_{ee}^\alpha[n]=\lambda^{-1}V_{ee}^1[n_\lambda]=U[n]+\lambda^{-1}E_{\text{xc}}[n_\lambda]-\lambda^{-1}T_{\text{xc}}[n_\lambda]\ , \tag{30}$$

and [14]

$$v_\alpha([n];\mathbf{r}) = -\frac{\delta T^0[n]}{\delta n(\mathbf{r})} - \alpha \frac{\delta U[n]}{\delta n(\mathbf{r})} - \alpha^2 \frac{\delta E_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})} , \tag{31}$$

to generate

$$\int d^3r\, n(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} - T^0[n] \geq NI + 2\lambda^{-2} E_{\mathrm{xc}}[n_\lambda] - \lambda^{-2} T_{\mathrm{xc}}[n_\lambda] - \lambda^{-2} \int d^3r\, n(\mathbf{r}) \frac{\delta E_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})} , \tag{32}$$

where

$$U[n] \equiv \tfrac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r\, d^3r' , \tag{33}$$

$$E_{\mathrm{xc}}[n] \equiv \left\langle \Psi^{1,N}_{[n]} \middle| \sum_{i=1}^{N} -\tfrac{1}{2}\nabla_i^2 + \sum_{i=1}^{N-1} \sum_{j>i}^{N} r_{ij}^{-1} \middle| \Psi^{1,N}_{[n]} \right\rangle - U[n] - T^0[n] , \tag{34}$$

and

$$T_{\mathrm{xc}}[n_\lambda] \equiv T^1[n_\lambda] - T^0[n_\lambda] . \tag{35}$$

(Observe that the identity [5] $T^0[n_\lambda] = \lambda^2 T^0[n]$ has been used in Eq. (29) and that the identity $U[n_\lambda] = \lambda U[n]$ has been used in Eq. (30). Also notice that $T^0[n]$ is the Kohn-Sham noninteracting kinetic energy.)

Again, $\delta E_{\mathrm{xc}}[n]/\delta n(\mathbf{r})$ is defined by the corresponding electron deficiency limit of a more general theory that allows continuously varying electron numbers. The functional derivative $\delta T^0[n]/\delta n(\mathbf{r})$ is the corresponding electron deficiency form of the functional derivative of $T^0[n]$ plus the ionization energy I. For finite systems with boundary conditions that require their densities to have asymptotic exponential decay, these definitions have the consequence that $\delta T^0[n]/\delta n(\mathbf{r})$, and subsequently also $v_\alpha([n];\mathbf{r})$, go to zero as $|\mathbf{r}| \to \infty$. As a result the ionization energy I is *independent* of α for v_α as determined by Eq. (31) and with the functional derivatives as defined in this work.

In Eq. (32), now employ [5]

$$T_{\mathrm{xc}}[n_\lambda] = -E_{\mathrm{xc}}[n_\lambda] + \frac{\lambda \partial E_{\mathrm{xc}}[n_\lambda]}{\partial \lambda} \tag{36}$$

to obtain

$$\int d^3r\, n(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} - T^0[n] \geq NI + 3\lambda^{-2} E_{\mathrm{xc}}[n_\lambda] - \lambda^{-1} \frac{\partial E_{\mathrm{xc}}[n_\lambda]}{\partial \lambda} - \lambda^{-2} \int d^3r\, n(\mathbf{r}) \frac{\delta E_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})} . \tag{37}$$

In Eq. (37), first consider $\lambda \to \infty$ and take into consideration the fact [1,15] that $E_{\mathrm{xc}}[n_\lambda] \sim -\lambda$, as $\lambda \to \infty$, to get

$$\int d^3r\, n(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} - T^0[n] \geq NI . \tag{38}$$

Finally, to arrive at Eq. (1), multiply Eq. (37) by λ, let $\lambda \to 0$, and now take into consideration the fact that for $\lambda \to 0$, $E_{\mathrm{xc}}[n_\lambda] \sim -\lambda$ [1] and therefore

$$\lim_{\lambda \to 0} \lambda^{-1} E_{\mathrm{xc}}[n_\lambda] - \lim_{\lambda \to 0} \frac{\partial E_{\mathrm{xc}}[n_\lambda]}{\partial \lambda} = 0 .$$

III. DERIVATION OF CONSTRAINT (2)

It is known that the square root of the electron density satisfies the following Schrödinger equation [2,16]:

$$\{ -\tfrac{1}{2}\nabla^2 + v_\alpha([n];\mathbf{r}) + v^\alpha_{\mathrm{eff}}([n];\mathbf{r}) \} n^{1/2}(\mathbf{r}) = -I n^{1/2}(\mathbf{r}) . \tag{39}$$

Now it has been shown [2] that

$$v^\alpha_{\mathrm{eff}}([n];\mathbf{r}) \geq 0 , \tag{40}$$

which, when combined with Eq. (39), gives

$$\tfrac{1}{2} n^{-1/2}(\mathbf{r}) \nabla^2 n^{1/2}(\mathbf{r}) - v_\alpha([n];\mathbf{r}) - I \geq 0 . \tag{41}$$

Next, employ Eq. (31) for v_α and substitute in Eq. (41) to obtain

$$\tfrac{1}{2} n^{-1/2}(\mathbf{r}) \nabla^2 n^{1/2}(\mathbf{r}) + \frac{\delta T^0[n]}{\delta n(\mathbf{r})} + \lambda^{-1} \frac{\delta U[n]}{\delta n(\mathbf{r})} + \lambda^{-2} \frac{\delta E_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})} - I \geq 0 . \tag{42}$$

Finally after multiplying by λ, in the limit $\lambda \to 0$, Eq. (42) implies Eq. (2a). Again, use has been made of the fact that $E_{\mathrm{xc}}[n_\lambda] \sim -\lambda$ as $\lambda \to 0$. Further, in the limit $\lambda \to \infty$, Eq. (42) implies

$$\tfrac{1}{2} n^{-1/2}(\mathbf{r}) \nabla^2 n^{1/2}(\mathbf{r}) + \frac{\delta T^0[n]}{\delta n(\mathbf{r})} \geq I , \tag{43}$$

which is a known result [2,17,18].

IV. DERIVATION OF EQ. (3)

First express $E^{\alpha,N}_{[n]}$ in terms of the density functionals. To accomplish this, note that

$$E^{\alpha,N}_{[n]} = \langle \Psi^{\alpha,N}_{[n]} | H^{\alpha,N}_{[n]} | \Psi^{\alpha,N}_{[n]} \rangle . \tag{44}$$

Thus, from expressions (21), (26), and (27), we have

$$E^{\alpha,N}_{[n]} = T^\alpha[n] + \alpha V^\alpha_{ee}[n] + \int v_\alpha([n];\mathbf{r}) n(\mathbf{r}) d^3r . \tag{45}$$

Next, by relations (29) through (31), Eq. (45) becomes

$$E^{\alpha,N}_{[n]} = T^0[n] + \alpha U[n] + \alpha^2 E_{\mathrm{xc}}[n_\lambda] - \int d^3r\, n(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} - \alpha \int d^3r\, n(\mathbf{r}) \frac{\delta U[n]}{\delta n(\mathbf{r})} - \alpha^2 \int d^3r\, n(\mathbf{r}) \frac{\delta E_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})} . \tag{46}$$

Now define $\Psi^{\alpha,N-1}_{[\rho]}$ as that wave function that yields the density $\rho = n - \Delta n_F$ and minimizes the expectation value of $\sum_{i=1}^{N-1} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \alpha r_{ij}^{-1}$. (Equivalently, $\Psi^{\alpha,N-1}_{[\rho]}$ is that wave function that yields ρ and minimizes the expectation value of $H^{\alpha,N-1}_{[\rho]}$.) Clearly, employment of Eq. (23) then yields

$$\langle \Psi_{[\rho]}^{\alpha,N-1} | H_{[n]}^{\alpha,N-1} | \Psi_{[\rho]}^{\alpha,N-1} \rangle = T^{\alpha}[\rho] + \alpha V_{ee}^{\alpha}[\rho] + \int v_{\alpha}([n];\mathbf{r})\rho(\mathbf{r}) d^3r \ , \tag{47}$$

which implies

$$E_{[n]}^{\alpha,N-1} \le T^{\alpha}[\rho] + \alpha V_{ee}^{\alpha}[\rho] + \int v_{\alpha}([n];\mathbf{r})\rho(\mathbf{r}) d^3r \ , \tag{48}$$

because, of course,

$$E_{[n]}^{\alpha,N-1} \le \langle \Psi_{[\rho]}^{\alpha,N-1} | H_{[n]}^{\alpha,N-1} | \Psi_{[\rho]}^{\alpha,N-1} \rangle \tag{49}$$

by the variational theorem. [Note that the *strict* inequality applies in Eq. (49), except for $\alpha = 0$, because there are relaxation effects in the density when Δn_F is removed from n, for $\alpha > 0$. Only when $\alpha = 0$ is ρ the ground-state density of $H_{[n]}^{\alpha,N-1}$. For $\alpha > 0$, ρ is not the ground-state density of $H_{[n]}^{\alpha,N-1}$, but ρ is generally close enough to the ground-state density so that the bound in Eq. (49) is reasonably tight and thus meaningful.] Next, utilize (29)–(31) with ρ in place of n, and utilize Eq. (48) to yield

$$\begin{aligned} E_{[n]}^{\alpha,N-1} \le {} & T^0[\rho] + \alpha U[\rho] + \alpha^2 E_{\mathrm{xc}}[\rho_\lambda] \\ & - \int d^3r \, \rho(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} - \alpha \int d^3r \, \rho(\mathbf{r}) \frac{\delta U[n]}{\delta n(\mathbf{r})} \\ & - \alpha^2 \int d^3r \, \rho(\mathbf{r}) \frac{\delta E_{\mathrm{xc}}[n_\lambda]}{\delta n(\mathbf{r})} \ . \end{aligned} \tag{50}$$

Finally, we arrive at Eq. (14) by subtracting Eq. (46) from Eq. (50) and by using the fact that the highest-occupied Kohn-Sham orbital energy of the system with ground-state density n is the negative of the exact ionization energy [2] of $H_{[n]}^{\alpha,N}$. Namely,

$$\begin{aligned} -I = E_{[n]}^{\alpha,N} - E_{[n]}^{\alpha,N-1} = {} & \int \phi_F(\mathbf{r})^* (-\tfrac{1}{2}\nabla^2) \phi_F(\mathbf{r}) d^3r \\ & - \int d^3r \, \Delta n_F(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} \end{aligned} \tag{51}$$

or

$$\begin{aligned} E_{[n]}^{\alpha,N-1} - E_{[n]}^{\alpha,N} = {} & T^0[\rho] - T^0[n] - \int d^3r \, \rho(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} \\ & + \int d^3r \, n(\mathbf{r}) \frac{\delta T^0[n]}{\delta n(\mathbf{r})} \ , \end{aligned} \tag{52}$$

where ϕ_F is the highest-occupied Kohn-Sham orbital of $-\frac{1}{2}\nabla^2 - \delta T^0[n]/\delta n(\mathbf{r})$. (Note that I is independent of α.)

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APPENDIX: BEHAVIOR OF FUNCTIONAL DERIVATIVES UNDER COORDINATE SCALING

In this Appendix the relation

$$\frac{\delta F[n_\lambda]}{\delta n(\mathbf{r})} = v([n_\lambda];\mathbf{r}/\lambda) \tag{A1}$$

is derived (see in this context also Ref. [19]). (The functional derivative of $F[n]$, which in this appendix shall be an arbitrary functional of the arbitrary function $n(\mathbf{r})$, is defined here by $v([n];\mathbf{r})$.) Next the uniformly scaled function $n_\lambda(\mathbf{r})$ is interpreted as a functional $n_\lambda([n];\mathbf{r})$ of $n(\mathbf{r})$:

$$n_\lambda([n];\mathbf{r}') = n_\lambda(\mathbf{r}') = \lambda^3 n(\lambda \mathbf{r}') \ , \tag{A2}$$

with the functional derivative

$$\frac{\delta n_\lambda([n];\mathbf{r}')}{\delta n(\mathbf{r})} = \lambda^3 \delta(\mathbf{r} - \lambda \mathbf{r}') \ . \tag{A3}$$

Equation (A3) follows from the relation

$$\delta n_\lambda(\mathbf{r}') = \lambda^3 \delta n(\lambda \mathbf{r}') = \int d^3r \, \lambda^3 \delta(\mathbf{r} - \lambda \mathbf{r}') \delta n(\mathbf{r}) \tag{A4}$$

for infinitesimal changes δn and δn_λ of n and n_λ, respectively.

The functional derivative $\delta F[n_\lambda]/\delta n(\mathbf{r})$ is now evaluated as

$$\begin{aligned} \frac{\delta F[n_\lambda]}{\delta n(\mathbf{r})} = \frac{\delta F[n_\lambda[n]]}{\delta n(\mathbf{r})} & = \int d\mathbf{r}' \frac{\delta F[n_\lambda[n]]}{\delta n_\lambda([n];\mathbf{r}')} \frac{\delta n_\lambda([n];\mathbf{r}')}{\delta n(\mathbf{r})} \\ & = \int d\mathbf{r}' v([n_\lambda[n]];\mathbf{r}') \lambda^3 \delta(\mathbf{r} - \lambda \mathbf{r}') = \int dr'' v([n_\lambda[n]];\mathbf{r}''/\lambda) \delta(\mathbf{r} - \mathbf{r}'') \\ & = v([n_\lambda[n]];\mathbf{r}/\lambda) = v([n_\lambda];\mathbf{r}/\lambda) \ . \end{aligned} \tag{A5}$$

In a similar way one obtains for nonuniform scaling

$$\frac{\delta F[n_{\alpha\beta\gamma}^{xyz}]}{\delta n(\mathbf{r})} = v([n_{\alpha\beta\gamma}^{xyz}];x/\alpha,y/\beta,z/\gamma) \tag{A6}$$

with the nonuniformly scaled density $n_{\alpha\beta\gamma}^{xyz}(\mathbf{r})$ defined as

$$n_{\alpha\beta\gamma}^{xyz}(\mathbf{r}) = \alpha\beta\gamma \, n(\alpha x, \beta y, \gamma z) \ . \tag{A7}$$

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