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Kinetic energy from a single Kohn-Sham orbital

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We observe that the noninteracting kinetic energy, as a functional of the electron density ρ, may be obtained from a formula that contains only a single Kohn-Sham orbital, $\varphi_i(\mathbf{r})$, where i is arbitrary. Specifically, $T_s[\rho]=(-1/4)\int\{\nabla^2\phi_i[\rho;\mathbf{r}]/\phi_i[\rho;\mathbf{r}]\}[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]d\mathbf{r}$.

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In modern density-functional theory (DFT), the noninteracting kinetic energy functional is most often evaluated exactly, through the use of the Kohn-Sham orbitals [1]. Nevertheless, research on orbital-free approximations has continued with the goal of discovering a viable pure density functional for the kinetic energy, so that large and cumbersome systems could be handled routinely. To this end, we observe that it is only necessary to know a *single* Kohn-Sham (KS) orbital as a functional of the density in order to evaluate T_s. Moreover, in this case T_s can be written as a simple and explicit functional that involves only $\rho(\mathbf{r})$ and one of the Kohn-Sham orbitals, $\varphi_i(\mathbf{r})$.

Assume that one is interested in the ground-state energy and electron density of a system of $2N$ electrons bound by an external potential $v(\mathbf{r})$, which is most often an electron-nuclear attraction potential. The variational principle of DFT states [2,3]

$$E_{g.s.}=\min_{\rho(\mathbf{r})}\left\{\int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}+T_s[\rho]+G[\rho]\right\}, \tag{1}$$

where the functional $G[\rho]$ must be approximated. $T_s[\rho]$ is the KS kinetic energy, which is the kinetic energy of the ground state of the noninteracting Hamiltonian,

$$H_s[\rho]=\sum_{i=1}^{2N}\tfrac{-1}{2}\nabla_i^2+v_s[\rho;\mathbf{r}_i]. \tag{2}$$

The Kohn-Sham potential, $v_s[\rho;\mathbf{r}]$, is local and multiplicative. The ground-state wave function of H_s is a Slater determinant composed of the Kohn-Sham orbitals $\{\phi_i\}$, so

$$T_s[\rho]=\sum_{i=1}^{2N}\langle\phi_i|\tfrac{-1}{2}\nabla^2|\phi_i\rangle. \tag{3}$$

The ϕ_i are the solutions to the Kohn-Sham equations,

$$\left[\tfrac{-1}{2}\nabla^2+v_s(\mathbf{r})\right]\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r}) \quad i=1,2,\ldots,N, \tag{4}$$

where $\varepsilon_1<\varepsilon_2<\cdots<\varepsilon_N$. (For simplicity of presentation, we are assuming that the number of electrons is even and that all $\varphi_i(\mathbf{r})$ are real and doubly occupied. It is straightforward to extend this analysis to singly-occupied orbitals and spin-unrestricted Kohn-Sham theory.)

Following is a self-contained derivation of the desired formula, Eq. (12). Since $\rho(\mathbf{r})$ is the ground-state density of H_s, it follows from the variational principle for the energy of the noninteracting system that

$$\min_{\lambda}\left\{T_s[\rho_\lambda]+\int\rho_\lambda(\mathbf{r})v_s(\mathbf{r})d\mathbf{r}\right\}=T_s[\rho]+\int v_s(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \tag{5}$$

where $\rho_\lambda(x,y,z)=\lambda^3\rho(\lambda x,\lambda y,\lambda z)$ and λ is a coordinate scaling factor. The prefactor λ^3 keeps the density normalized to $2N$ electrons for all λ. The minimization in Eq. (5) implies that

$$\left[\frac{\partial T_s[\rho_\lambda]}{\partial\lambda}+\int v_s(\mathbf{r})\frac{\partial\rho_\lambda(\mathbf{r})}{\partial\lambda}d\mathbf{r}\right]_{\lambda=1}=0, \tag{6}$$

which, with the coordinate scaling relation [4] $T_s[\rho_\lambda]=\lambda^2T_s[\rho]$, yields

$$T_s[\rho]=\frac{-1}{2}\int v_s(\mathbf{r})\left(\frac{\partial\rho_\lambda(\mathbf{r})}{\partial\lambda}\right)_{\lambda=1}d\mathbf{r}. \tag{7}$$

Equation (7) is similar to Eq. (A17) in ref. [5], but $v_s(\mathbf{r})$ is replaced by $-\delta T_s[\rho]/\delta\rho(\mathbf{r})$ there. Alternatively, inserting into Eq. (7) the identity

$$\left(\frac{\partial\rho_\lambda(\mathbf{r})}{\partial\lambda}\right)_{\lambda=1}=3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r}) \tag{8}$$

and integrating by parts gives the familiar virial form in Eq. (10) of ref. [6], where the corresponding gradient is of $v_s(\mathbf{r})$.

Observe that Eq. (4) implies that

$$v_s(\mathbf{r})=\frac{1}{2}\left(\frac{\nabla^2\phi_i(\mathbf{r})}{\phi_i(\mathbf{r})}\right)+\varepsilon_i \tag{9}$$

almost everywhere [except possibly at nodes in $\varphi_i(\mathbf{r})$]. Inserting Eq. (9) for $v_s(\mathbf{r})$ into Eq. (7) and using

$$\int\varepsilon_i\left(\frac{\partial\rho_\lambda(\mathbf{r})}{\partial\lambda}\right)d\mathbf{r}=\frac{\partial}{\partial\lambda}\int\varepsilon_i\rho_\lambda(\mathbf{r})d\mathbf{r}=\frac{\partial(2\varepsilon_iN)}{\partial\lambda}=0 \tag{10}$$

gives

$$T_s[\rho]=\frac{-1}{4}\int\frac{\nabla^2\phi_i(\mathbf{r})}{\phi_i(\mathbf{r})}\left(\frac{\partial\rho_\lambda(\mathbf{r})}{\partial\lambda}\right)_{\lambda=1}d\mathbf{r} \tag{11}$$

or, equivalently,

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$$T_s[\rho] = \frac{-1}{4}\int \frac{\nabla^2\phi_i(\mathbf{r})}{\phi_i(\mathbf{r})}[3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})]d\mathbf{r}. \qquad (12)$$

These are our key results.

At least two Kohn-Sham orbitals have special properties for analysis as functionals of $\rho(\mathbf{r})$. The lowest-occupied orbital, $\varphi_1(\mathbf{r})$, is nodeless and the highest-occupied orbital, $\varphi_N(\mathbf{r})$, has the same asymptotic decay as $\rho(\mathbf{r})$. Also any approximate functional for $\varphi_i(\mathbf{r})$ must of course satisfy $|\phi_i(\mathbf{r})|^2 \le \rho(\mathbf{r})$ for all $\mathbf{r}$. Finally, because $v_s(\mathbf{r}) = -\delta T_s[\rho]/\delta\rho(\mathbf{r})$ within a constant, and $\rho(\mathbf{r})$ is the ground-state density of H_s, we obtain a rigid constraint,

$$\frac{\delta}{\delta\rho(\mathbf{r})}\left\{\frac{-1}{4}\int \frac{\nabla^2\phi_i[\rho;\mathbf{r}]}{\phi_i[\rho;\mathbf{r}]}[3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})]d\mathbf{r}\right\} = \frac{-1}{2}\frac{\nabla^2\phi_i[\rho;\mathbf{r}]}{\phi_i[\rho;\mathbf{r}]}. \qquad (13)$$

Both Eqs. (12) and (13) are valid for any Kohn-Sham orbital and are specific to Kohn-Sham DFT: they are not valid for other orbital-based electronic structure methods, such as Hartree-Fock, where Eqs. (7) and (9) do not apply.

We present Eq. (12) as a possible paradigm shift for arriving at a good approximation to $T_s[\rho]$. While we do not know if the use of this formula, with a suitable approximation for one of the φ_i's as a functional of ρ, will in fact offer a better approach to an orbital-free $T_s[\rho]$ than those currently employed, we have displayed the formula with the hope that readers might make breakthroughs with it. At the very least, this formula provides yet another constraint that may be used to guide the development of orbital-free T_s functionals.

The key identity, Eq. (12), would also be useful if $\rho(\mathbf{r})$ could be written as a functional of a single KS orbital. For a system in which all of the orbitals are doubly occupied and for which the density is noninteracting-v-representable (so that there are no holes below the Fermi level)[7] it can be proved [8] that either the highest-occupied orbital, $\varphi_N(\mathbf{r})$, or the lowest-unoccupied orbital, $\varphi_{N+1}(\mathbf{r})$, suffices to determine the electron density. Equation (12) is thus useful for "frontier Kohn-Sham orbital" theories [8–10], where one seeks to construct the electron density and other properties of a system by solving only the KS equations for the frontier orbitals.

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