Uniqueness and asymptotic behavior of the local kinetic energy

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Abstract

The exact asymptotic behavior and the uniqueness of the local kinetic energy are discussed. The physical significance of the local kinetic energy is demonstrated, and a few popular models of the local kinetic energy are surveyed and compared.

1. Introduction

In the density-Functional theory (DFT) [1-4], the total ground electronic state energy of an atom or a molecule is completely determined by its electron density \( \rho(r) \). The energy functional \( E[\rho] \) is expressed as

\[
E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho],
\]

where \( T[\rho] \), \( V_{ne}[\rho] \), and \( V_{ee}[\rho] \) are the kinetic energy, the nuclear-electron attraction, and the electron-electron repulsion functionals, respectively. Consequently, the main task of the DFT is to search and to construct these functionals exactly or approximately [3,4]. It has recently been recognized [4] that kinetic energy functional \( T[\rho] \) is the most difficult component in the total energy functional \( E[\rho] \) to be represented approximately. A great deal of effort has been made to construct \( T[\rho] \) by various approaches [3-17]. \( T[\rho] \) is usually represented in terms of the kinetic energy density (KED) and its Green-theorem equivalences. Furthermore, it is commonly believed that the KED could be defined by different formulas in which extra zero-integral terms could be added freely [14-17].

In this Letter, we will define the single-electron Schrödinger local kinetic energy (SESLKE) according to the reduced Schrödinger equation, then discuss the exact asymptotic behavior and the uniqueness of the SESLKE, and demonstrate that there is no arbitrary term can be freely chosen in the definition of the SESLKE. Finally, a few popular, competitive models of the single-electron local kinetic energy (SELKE) are surveyed and compared. Atomic units are used throughout this Letter, and we focus on the ground state of an \( N \)-electron chemical system, albeit that similar conclusions hold for excited states as well.

2. The reduced Schrödinger equation

Conventionally [3,4], the nonrelativistic electronic Hamiltonian \( \hat{H}^N \) of an \( N \)-electron chemical system is approximated by

\[
\hat{H}^N = \hat{T}^N + \hat{V}^N = \hat{T}^N + V_{ne}^N + V_{ee}^N,
\]

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where the kinetic energy, the nuclear–electron attraction, and the electron–electron repulsion operators are written as

\[ \hat{\mathcal{N}}^{N} = \sum_{i} \hat{\mathcal{N}}_{i} = \sum_{i} -\frac{1}{2} \nabla_{i}^{2}, \]

\[ \hat{\mathcal{V}}_{\text{ne}}^{N} = \sum_{i} \hat{\mathcal{V}}_{\text{ne}}(i), \]

\[ \hat{\mathcal{V}}_{\text{ee}}^{N} = \sum_{i<j} r_{ij}^{-1}. \]  

(3)

The nonrelativistic, time-independent, electronic Schrödinger equation for state \( |\Psi^{N}\rangle \) is

\[ \hat{\mathcal{H}}^{N} |\Psi^{N}\rangle = E^{N} |\Psi^{N}\rangle. \]  

(4)

Multiplying Eq. (4) from the left by \( \langle \Psi^{N} | \) and integrating over the spin and space coordinates of \( \rho \) electrons, one arrives at the \((N - p)\)th-order reduced Schrödinger equation

\[ \langle \Psi^{N} | \hat{\mathcal{H}}^{N} |\Psi^{N}\rangle_{p} = E^{N} \langle \Psi^{N} |\Psi^{N}\rangle_{p}, \]

\((p = 0, 1, \ldots, N)\).

(5)

The local \((N - p)\)th-order Schrödinger total kinetic energy and potential energy satisfy the energy conservation

\[ \frac{\langle \Psi^{N} | \hat{\mathcal{H}}^{N} |\Psi^{N}\rangle_{p}}{\langle \Psi^{N} |\Psi^{N}\rangle_{p}} + \frac{\langle \Psi^{N} | \hat{\mathcal{V}}^{N} |\Psi^{N}\rangle_{p}}{\langle \Psi^{N} |\Psi^{N}\rangle_{p}} = E^{N}. \]  

(6)

Specifically for the sake of this Letter, we only need the first-order reduced Schrödinger equation

\[ \frac{\langle \Psi^{N} | \hat{\mathcal{H}}^{N} |\Psi^{N}\rangle_{N-1}}{\langle \Psi^{N} |\Psi^{N}\rangle_{N-1}} + \frac{\langle \Psi^{N} | \hat{\mathcal{V}}^{N} |\Psi^{N}\rangle_{N-1}}{\langle \Psi^{N} |\Psi^{N}\rangle_{N-1}} = E^{N}. \]  

(7)

Here, we define the SESLKE \( k_{s}(r_{i}) \) as

\[ k_{s}(r_{i}) = \frac{\langle \Psi^{N} | \hat{\mathcal{H}}_{i} |\Psi^{N}\rangle_{N-1}}{\langle \Psi^{N} |\Psi^{N}\rangle_{N-1}}, \]

where the integration is done over the remaining \((N - 1)\) electrons except for the \(i\)th electron, and \( k_{s}(r) \) relates to the total kinetic energy \( T[\rho] \) via

\[ T[\rho] = \int k_{s}(r) \rho(r) \, dr. \]  

(9)

3. Uniqueness and asymptotic behavior of \( k_{s}(r) \)

The correct asymptotic behavior and the uniqueness of \( k_{s}(r) \) is shown by the following two theorems:

Theorem 1: For any electronic state of an atom or a molecule, its SESLKE is unique.

Proof: In Eq. (2), let us separate Electron 1 from the remaining \((N - 1)\) electrons,

\[ \hat{\mathcal{H}}^{N}(1, 2, \ldots, N) = \hat{\mathcal{H}}^{N-1}(2, \ldots, N) + \hat{\mathcal{r}}_{1} + \hat{\mathcal{d}}_{\text{ne}}(1) + \hat{\mathcal{d}}_{\text{ee}}(1), \]

\[ \hat{\mathcal{d}}_{\text{ne}}(1) = \sum_{i > 1} r_{i1}^{-1}, \]

(10)

where \( \hat{\mathcal{H}}^{N-1} \) has a complete eigensystem

\[ \hat{\mathcal{H}}^{N-1} |\Psi_{N-1}^{N-1}\rangle = E_{N-1}^{N-1} |\Psi_{N-1}^{N-1}\rangle. \]  

(11)

After defining a complete set of the Dyson orbitals \( \{f_{i}\} \) for the ground-state \( |\Psi^{N}\rangle \)

\[ f_{i} = \langle \Psi_{i}^{N-1} |\Psi^{N}\rangle_{N-1}, \]

(12)

we obtain the Carlson–Keller expansion [19]

\[ |\Psi^{N}(1, 2, \ldots, N)\rangle = \sum_{i=1}^{\infty} f_{i} |\Psi_{i}^{N-1}(2, \ldots, N)\rangle, \]

(13)

and the one-electron density

\[ \rho(r) = \frac{\langle \Psi^{N} |\Psi^{N}\rangle_{N-1}}{N} = \sum_{i=1}^{\infty} |\Psi_{i}^{N-1} |\Psi^{N}\rangle_{N-1}|^{2} \]

\[ = \sum_{i=1}^{\infty} |f_{i}(r)|^{2}. \]  

(14)

Then, Eq. (7) can be simplified as follows:

\[ \sum_{i} f_{i}^{*} \left[ (\hat{\mathcal{H}} + \mathcal{d}_{\text{ne}}) f_{i} + \langle \Psi_{i}^{N-1} |\mathcal{d}_{\text{ee}}(1) |\Psi^{N}\rangle_{N-1} \right] \]

\[ \frac{\sum_{i} |f_{i}|^{2}}{\sum_{i} |f_{i}|^{2}} + \frac{\sum_{i} E_{i}^{N-1} |f_{i}|^{2}}{\sum_{i} |f_{i}|^{2}} = E^{N}. \]  

(15)
Consequently, due to the Katriel-Davidson equation [20] for the Dyson orbitals

\[ (\hat{t} + \hat{\lambda}_{\alpha \alpha}) f_i + \langle \Psi_{\alpha}^{N-1} | \hat{\lambda}_{\alpha \alpha} | \Psi_{\alpha}^{N} \rangle_{N-1} = -I_i f_i \]

\[ I_i = E_i^{N-1} - E_i^{N}, \]  

(16)

the SESLKE

\[ k_s(r) = \sum_i \frac{f_i^* \hat{t} f_i}{\sum_j |f_j|^2} \]  

(17)

must be unique in order to keep the energy conservation pointwise in Eq. (15) [QED].

**Theorem 2:** For the ground electronic state of an atom or a molecule, the asymptotic limit of its SESLKE is the negative of its first ionization potential.

**Proof:** It has been rigorously demonstrated by Katriel and Davidson [20] that for an N-electron atomic or molecular system, the asymptotic form of the ground electronic state wavefunction is

\[ \lim_{r \to \infty} \Psi^N(r, 2, \ldots, N) = \sqrt{A} \Psi^{N-1}(2, \ldots, N) r^\beta \exp(-\sqrt{2I} r), \]

\[ \beta = \frac{(Z - N + 1)}{\sqrt{2I}} - 1, \]  

(18)

where A, I, and Z are the normalization factor, the first ionization potential and the total nuclear charge, respectively; and \( \Psi^{N-1} \) is the ground state wavefunction of the remaining \((N-1)\) electrons. Inserting Eq. (18) into Eq. (8) and finishing the integration over the \((N-1)\) remaining electrons, one then has

\[ \lim_{r \to \infty} k_s(r) = \lim_{r \to \infty} \frac{\hat{t} \left[ r^\beta \exp(-\sqrt{2I} r) \right]}{r^\beta \exp(-\sqrt{2I} r)} = -I. \]  

(QED)  

(19)

Conceptually, when one electron is moving far away from the rest of the particles in an atomic or molecular system, the local energy of the asymptotic electron, \( E_s \), is given by

\[ E_s(r \to \infty) = E^N - E^{N-1} = -I, \]  

(20)

where \( E^{N-1} \) is the ground state energy of the \((N-1)\)-electron system. The local effective potential energy of the asymptotic electron will be zero, and its Schrödinger local kinetic energy will be \(-I\). On the other hand, Eq. (19) indicates negative kinetic energy, which is consistent with our previous understanding [21-23]; in general, for a one-dimensional case, once the asymptotic electron moves beyond the classical turning point, its Schrodinger kinetic energy will be always negative.

It should be emphasized that the asymptotic behavior does not guarantee the uniqueness of \( k_s(r) \), which will be discussed in detail in later sections. Mathematically speaking, the asymptotic behavior is just the necessary condition the correct \( k_s(r) \) should possess. Of course, the sufficient condition requires that various different forms of \( k_s(r) \) be numerically identical to Eq. (8).

### 4. Kinetic energy density

The SELKE \( k(r) \) relates with the KED \( t(r, [\rho]) \) via the following definition [3-17]

\[ t(r, [\rho]) = k(r) \rho(r). \]  

(21)

From the definitions of the kinetic energy operator \( \hat{t} \) in Eq. (3) and the SESLKE \( k_s(r) \) in Eq. (8), it is easy to work out the expression for the Schrödinger KED \( t_s(r, [\rho]) \) [3,4]

\[ t_s(r, [\rho]) = \frac{1}{2} \nabla_\rho \cdot \nabla \gamma(r, r'), \]  

(22)

where \( \gamma(r, r') \) is the first-order reduced density matrix. Directly employing Green's theorem yields another popular expression for \( t(r, [\rho]) \) [3,4,17]

\[ t_t(r, [\rho]) = \frac{1}{2} \nabla_\rho \cdot \nabla \gamma(r, r'), \]  

(23)

Due to the following identity

\[ \int \nabla_\rho^2 \rho(r) \, dr = 0, \]  

(24)

one can practically attach an arbitrary term to either of the above two definitions [3,4]. For instance, the following KED expression is often employed [15,16]

\[ t_2(r, [\rho]) = t_t(r, [\rho]) - \lambda \nabla^2 \rho(r), \]  

(25)

where \( \lambda \) can have any value. It has been shown [4] that \( t_s(r, [\rho]) \) relates with \( t_t(r, [\rho]) \) via

\[ t_s(r, [\rho]) = t_t(r, [\rho]) - \frac{1}{4} \nabla^2 \rho(r), \]  

(26)

although other \( \lambda \) values, including 0 [17], \( \frac{1}{8} \) [14], and so on [15,16], have been suggested as well. For-
mally, any interpolation between \( t_3(r; \rho) \) and \( t_2(r; \rho) \)
\[
t_3(r; \rho) = \alpha t_2(r; \rho) + (1 - \alpha) t_1(r; \rho)
\]
(27)
can be used as the KED as was done often in the
literature, and \( t_3(r; \rho) \) will deliver the same total kinetic energy and kinetic energy density functional derivative \( \delta T / \delta \rho \) for a given, fixed ground state density \( \rho(r) \).

5. Discussion

Equivalently, utilizing the asymptotic forms of the
first-order reduced density matrix and the ground
state density [20]
\[
\lim_{r, r' \to \infty} \gamma(r, r') = \sqrt{\rho(r)} \cdot \sqrt{\rho(r')},
\]
\[
\lim_{r \to \infty} \rho(r) = Ar^{2\beta} \exp[-2\sqrt{2I}r],
\]
(28)
with a few manipulations, we obtain the following
asymptotic equations for \( k(r) \) derived from the corre-
sponding formulas of the KED \( t(r; \rho) \) in Eqs. (22)-(27):
\[
\lim_{r \to \infty} k_3(r) = \lim_{r \to \infty} \frac{t_3(r; \rho)}{\rho(r)} = \frac{1}{2} \left( 2(1 - \alpha)(1 - 4\lambda) - 1 \right) I,
\]
\[
\lim_{r \to \infty} k_2(r) = \lim_{r \to \infty} \frac{t_2(r; \rho)}{\rho(r)} = (1 - 8\lambda) I,
\]
\[
\lim_{r \to \infty} k_1(r) = \lim_{r \to \infty} \frac{t_1(r; \rho)}{\rho(r)} = -I,
\]
(29)-(31)
From Eq. (19), in order for Eq. (32) to yield
the sole value \(-I\), we have
\[
\lim_{r \to \infty} k_3(r) = \left[ 2(1 - \alpha)(1 - 4\lambda) - 1 \right] I = -I,
\]
\[
\alpha = 1, \lambda = 1/4.
\]
(33)
Hence, only Eq. (22) and its identity, Eq. (26), are
the correct definitions of \( t_3(r; \rho) \). Furthermore, this
result vividly exemplifies that although Green’s the-
orem provides the same integral, the physical mean-
ing of the integrands cannot always be maintained
consistently throughout the integration. In the follow-
ing, further detailed discussions on the physical
meaning of various \( t(r; \rho) \) will be provided in
terms of Hermitian operators.

To illustrate the physical meaning of different
formulas of the KED \( t(r; \rho) \) more clearly, we may
rely on their corresponding Hermitian operators.
For example, the Hermitian operator defined for
\( t_3(r; \rho) \) in Eq. (22) is
\[
\hat{t}_3(r; \rho) = \sum_{i=1}^{N} i^2 \delta(r_i - r) \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \delta(r_i - r) \frac{1}{\sqrt{2m}} \delta(r_i - r),
\]
(34)
where \( m \) is the electron mass, and \( \hat{p}_i \) is the normal
momentum operator
\[
\hat{p}_i = -i\hbar \nabla_i.
\]
(35)
A few simple manipulations can readily show the
equivalence between this new definition
\[
t_3(r; \rho) = \sum_{i=1}^{N} i^2 \delta(r_i - r) \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \delta(r_i - r) \frac{1}{\sqrt{2m}} \delta(r_i - r),
\]
(36)
and Eq. (22). Similarly, the Hermitian operator
defined for \( t_1(r; \rho) \) in Eq. (23) is
\[
\hat{t}_1(r; \rho) = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} \delta(r_i - r) \frac{1}{\sqrt{2m}} \delta(r_i - r),
\]
(37)
A general Hermitian operator defined for \( t_3(r; \rho) \)
in Eq. (27) will be a proper interpolation between
the above two definitions. Based on the physical
interpretations of the Hermitian operators, Eq. (34) sug-
jects an ideal measurement of the square of the
Schrödinger total local momentum, while Eq. (37)
indicates another ideal measurement of the square
of the module of the Schrödinger total local momentum.

In the Kohn–Sham (KS) theory [2], $k_s(r)$ is defined through the KS orbitals

$$k_{S}^{KS}(r) = \sum_{i}^{N} \frac{\phi_i^*(r)\left(-\frac{1}{2} \nabla_i^2\right)\phi_i}{\sum_{i}^{N} |\phi_i|^2} ,$$

$$(-\frac{1}{2} \nabla_i^2 + \theta_{eff}^{KS})|\phi_i\rangle = \varepsilon_i|\phi_i\rangle ,$$

$$(-I = \varepsilon_1 > \varepsilon_2 > ... > \varepsilon_N)$$

(38)

where the HOMO energy ($\varepsilon_1$) is $-I$ [24]. Asymptotically, the KS effective potential is zero [24,25]

$$\lim_{r \to \infty} \theta_{eff}^{KS} = 0 ,$$

(39)

and $k_{S}^{KS}(r)$ will take the following form:

$$\lim_{r \to \infty} k_{S}^{KS}(r) = \lim_{r \to \infty} \frac{\sum_{i}^{N} \varepsilon_i |\phi_i|^2}{\sum_{i}^{N} |\phi_i|^2} = \varepsilon_1 = -I ,$$

(40)

where we have used the fact that the KS HOMO will be the only orbital contributing to the asymptotic density. Similar relationship also holds for the Hartree–Fock (HF) theory [26,27], the natural orbital (NO) theory [28–30], and the Dyson orbital (DO) theory [18,20,31–33],

$$\lim_{r \to \infty} k_{S}^{KS}(r) = \lim_{r \to \infty} k_{S}^{NO}(r) = \lim_{r \to \infty} k_{S}^{DO}(r) = -I ,$$

$$\lim_{r \to \infty} k_{S}^{HF}(r) = \varepsilon_{HOMO}^{HF} \approx -I .$$

(41)

Here, the Koopmans theorem [26] and the asymptotic behavior of the exchange operator [27] have been applied for the HF case, and the extended Koopmans theorem [29,32] has been invoked for the NO and DO theories.

In the pursuit of finding approximate representations of the exact kinetic energy functional, several forms have been proposed [13]. So far, there are only four basic categories of the approximations based on the Thomas–Fermi (TF) theory [5,6], the full-Weizsäcker model [7–9], the Padé approximation [10], and the Conjointness conjecture [11–13]. The asymptotic behavior of typical examples of these four categories are tabulated in Table 1, and their asymptotic behaviors differ from that of the SESLKE. Since the asymptotic behavior is one of the necessary conditions of any properly approximated SESLKE, further modification on the current kinetic energy functionals may be pursued.

Noting that

$$\lim_{r \to \infty} \frac{\nabla \rho(r)}{\rho(r)} = 8 I$$

(42)

from Eq. (28), one can modify the first two categories easily by enforcing their long range behaviors like $-I$. For example, for the first category, one may have

$$t_{one}(\rho; [\rho]) = C_{TF} \rho(r)^{5/3} - \frac{1}{8} \nabla^2 \rho(r) ,$$

(43)

and for the second category,

$$t_{two}(\rho; [\rho]) = C(N) \rho(r)^{5/3} + \frac{1}{8} \frac{[\nabla \rho(r)]^2}{\rho(r)} - \frac{1}{4} \nabla^2 \rho(r) ,$$

(44)

Table 1
Asymptotic behaviors of the exact and approximated single-electron local kinetic energy

<table>
<thead>
<tr>
<th>Category</th>
<th>Typical example</th>
<th>Asymptotic behavior</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thomas–Fermi</td>
<td>$C_{TF} \rho(r)^{5/3}$</td>
<td>0</td>
<td>[5,6]</td>
</tr>
<tr>
<td>Full-Weizsäcker</td>
<td>$C(N) \rho(r)^{5/3} + \frac{1}{8} \frac{[\nabla \rho(r)]^2}{\rho(r)^2}$</td>
<td>$+I$</td>
<td>[7–9]</td>
</tr>
<tr>
<td>Padé approximation</td>
<td>DePristo–Kress</td>
<td>$f(l)^a$</td>
<td>[10]</td>
</tr>
<tr>
<td>Conjointness conjecture</td>
<td>Becke86, Becke88</td>
<td>$g(l)^a$</td>
<td>[11–13]</td>
</tr>
<tr>
<td>modified</td>
<td>Eq. (43), Eq. (44)</td>
<td>$-I$</td>
<td>this work</td>
</tr>
<tr>
<td>exact</td>
<td>Eq. (8)</td>
<td>$-I$</td>
<td>this work</td>
</tr>
</tbody>
</table>

$a$ $f(l)$ and $g(l)$ are complicated functions of $l$, which in general do not yield $-I$. 

where \( C(N) \) [7–9] is a function of \( N \), the total number of electrons within a system. Their asymptotic behaviors are coincident with that of Eq. (19), but their local behaviors are all different pointwise except for the intersections (Fig. 1). It should be noted that the added terms have no net effect on the total kinetic energy and the kinetic energy density functional derivative for a fixed, given density.

As an illustration, the accurate HF wavefunction [34] of Ne atom will be employed. Fig. 1 shows the local behaviors of the SELKE for Ne atom, defined through Eqs. (22), (23) and (44). It can be seen that the SELKEs of Eqs. (22) and Eq. (44) show the long range behavior of \(-I\), while the local behavior of the SELKE of Eq. (23) is positive everywhere and goes to \( +I \) as \( r \) approaches infinity [17]. In the short range, Fig. 1a indicates that the SELKE of Eq. (23) resembles a step function [35], with a finite value at the nucleus, where the SELKEs of Eq. (22) and Eq. (44) both diverge. More interestingly, only the SESLKE defined via Eq. (22) keeps the energy conservation point-to-point in the Schrödinger equation as shown in Eq. (15). For comparison, the radial distribution function, \( D(r) \), is plotted in Fig. 2 against various SELKE curves. However, Fig. 2 does not show any obvious correlation between the extrema of the SELKE and the radial distribution function.

6. Conclusion

The asymptotic behavior and the uniqueness of the single-electron local kinetic energy are proposed in this Letter. From both physical and theoretical points of view, it is found that the single-electron Schrödinger local kinetic energy goes to \(-I\) at infinity, where \( I \) is the first ionization potential of the system. For the sake of convenience in the calculation of the total kinetic energy, all possible definitions in Eq. (27) can be used if the density is fixed and given. However, it should be noted that although Green’s theorem provides the same integral value, the physical meanings of the integrands cannot always be maintained consistently throughout the integral transformation.

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