9 August 1996

ELSEVIER

Chemical Physics Letters 258 (1996) 30–36

CHEMICAL
PHYSICS
LETTERS

Uniqueness and asymptotic behavior of the local kinetic energy

Zhong-Zhi Yang [a], Shubin Liu [b], Yan Alexander Wang [b,*]

[a] *Department of Chemistry, Liaoning Normal University, Dailan, Liaoning 116029, People's Republic of China*
[b] *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, USA*

Received 16 April 1996; in final form 4 June 1996

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

$$E[\rho] = T[\rho] + V_{\mathrm{ne}}[\rho] + V_{\mathrm{ee}}[\rho], \tag{1}$$

where $T[\rho]$, $V_{\mathrm{ne}}[\rho]$, and $V_{\mathrm{ee}}[\rho]$ 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

$$\hat{H}^N = \hat{T}^N + \hat{V}^N = \hat{T}^N + \hat{V}^N_{\mathrm{ne}} + \hat{V}^N_{\mathrm{ee}}, \tag{2}$$

---

[*] Corresponding author. Email: ywang@mulliken.chem.unc.edu.

PII S0009-2614(96)00624-0

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

$$\hat{T}^N = \sum_i^N \hat{t}_i = \sum_i^N -\tfrac{1}{2}\nabla_i^2 ,$$

$$\hat{V}_{\mathrm{ne}}^N = \sum_i^N \hat{v}_{\mathrm{ne}}(i) ,$$

$$\hat{V}_{\mathrm{ee}}^N = \sum_{i<j}^N r_{ij}^{-1} . \tag{3}$$

The nonrelativistic, time-independent, electronic Schrödinger equation for state $|\Psi^N\rangle$ is

$$\hat{H}^N|\Psi^N\rangle = E^N|\Psi^N\rangle . \tag{4}$$

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

$$\langle\Psi^N|\hat{H}^N|\Psi^N\rangle_p = E^N\langle\Psi^N|\Psi^N\rangle_p ,$$
$$(p = 0,1,\dots,N) . \tag{5}$$

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

$$\frac{\langle\Psi^N|\hat{T}^N|\Psi^N\rangle_p}{\langle\Psi^N|\Psi^N\rangle_p} + \frac{\langle\Psi^N|\hat{V}^N|\Psi^N\rangle_p}{\langle\Psi^N|\Psi^N\rangle_p} = E^N . \tag{6}$$

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

$$\frac{\langle\Psi^N|\hat{T}^N|\Psi^N\rangle_{N-1}}{\langle\Psi^N|\Psi^N\rangle_{N-1}} + \frac{\langle\Psi^N|\hat{V}^N|\Psi^N\rangle_{N-1}}{\langle\Psi^N|\Psi^N\rangle_{N-1}} = E^N . \tag{7}$$

Here, we define the SESLKE $k_S(r_i)$ as

$$k_S(r_i) = \frac{\langle\Psi^N|\hat{t}_i|\Psi^N\rangle_{N-1}}{\langle\Psi^N|\Psi^N\rangle_{N-1}} , \tag{8}$$

where the integration is done over the remaining $(N-1)$ electrons except for the ith electron, and $k_S(r)$ relates to the total kinetic energy $T[\rho]$ via

$$T[\rho] = \int k_S(r)\rho(r)\,\mathrm{d}r . \tag{9}$$

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,

$$\hat{H}^N(1,2,\dots,N)$$
$$= \hat{H}^{N-1}(2,\dots,N) + \hat{t}_1 + \hat{v}_{\mathrm{ne}}(1) + \hat{v}_{\mathrm{ee}}(1) ,$$
$$\hat{v}_{\mathrm{ee}}(1) = \sum_{i>1}^N r_{i1}^{-1} , \tag{10}$$

where $\hat{H}^{N-1}$ has a complete eigensystem

$$\hat{H}^{N-1}|\Psi_i^{N-1}\rangle = E_i^{N-1}|\Psi_i^{N-1}\rangle . \tag{11}$$

After defining a complete set of the Dyson orbitals $\{f_i\}$ [18] for the ground-state $|\Psi^N\rangle$

$$f_i = \langle\Psi_i^{N-1}|\Psi^N\rangle_{N-1} , \tag{12}$$

we obtain the Carlson–Keller expansion [19]

$$|\Psi^N(1,2,\dots,N)\rangle = \sum_{i=1}^{\infty} f_i(1)|\Psi_i^{N-1}(2,\dots,N)\rangle , \tag{13}$$

and the one-electron density

$$\frac{\rho(r)}{N} = \langle\Psi^N|\Psi^N\rangle_{N-1} = \sum_{i=1}^{\infty} |\langle\Psi_i^{N-1}|\Psi^N\rangle_{N-1}|^2$$
$$= \sum_{i=1}^{\infty} |f_i(r)|^2 . \tag{14}$$

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

$$\frac{\sum_i f_i^* \left[(\hat{t} + \hat{v}_{\mathrm{ne}})f_i + \langle\Psi_i^{N-1}|\hat{v}_{\mathrm{ee}}(1)|\Psi^N\rangle_{N-1} \right]}{\sum_i |f_i|^2}$$
$$+ \frac{\sum_i E_i^{N-1}|f_i|^2}{\sum_i |f_i|^2} = E^N . \tag{15}$$

Consequently, due to the Katriel–Davidson equation [20] for the Dyson orbitals

$$\left(\hat{t}+\hat{v}_{\mathrm{ne}}\right)f_i+\langle\Psi_i^{N-1}|\hat{v}_{\mathrm{ee}}(1)|\Psi^N\rangle_{N-1}=-I_i\,f_i$$

$$I_i=E_i^{N-1}-E^N, \qquad (16)$$

the SESLKE

$$k_{\mathrm{S}}(\boldsymbol{r})=\frac{\sum\limits_i f_i^*\;\hat{t}f_i}{\sum\limits_i|f_i|^2} \qquad (17)$$

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

$$\lim_{r\to\infty}|\Psi^N(\boldsymbol{r},2,\ldots,N)\rangle$$
$$=\sqrt{A}\,|\Psi^{N-1}(2,\ldots,N)\rangle\,r^{\beta}\exp(-\sqrt{2I}\,r),$$
$$\beta=\frac{(Z-N+1)}{\sqrt{2I}}-1, \qquad (18)$$

where A, I and Z are the normalization factor, the first ionization potential and the total nuclear charge, respectively; and $|\Psi^{N-1}\rangle$ 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

$$\lim_{r\to\infty}k_{\mathrm{S}}(\boldsymbol{r})=\lim_{r\to\infty}\frac{\hat{t}\left[r^{\beta}\exp(-\sqrt{2I}r)\right]}{r^{\beta}\exp(-\sqrt{2I}r)}$$
$$=-I. \quad [\text{QED}] \qquad (19)$$

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_{e}, is given by

$$E_{\mathrm{e}}(r\to\infty)=E^N-E^{N-1}=-I, \qquad (20)$$

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 Schrödinger kinetic energy will be always negative.

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

4. Kinetic energy density

The SELKE $k(\boldsymbol{r})$ relates with the KED $t(\boldsymbol{r};[\rho])$ via the following definition [3–17]

$$t(\boldsymbol{r};[\rho])=k(\boldsymbol{r})\rho(\boldsymbol{r}). \qquad (21)$$

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

$$t_{\mathrm{S}}(\boldsymbol{r};[\rho])=-\tfrac{1}{2}\nabla_{\boldsymbol{r}}^2\,\gamma(\boldsymbol{r},\boldsymbol{r}')|_{\boldsymbol{r}'=\boldsymbol{r}}, \qquad (22)$$

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

$$t_1(\boldsymbol{r};[\rho])=\tfrac{1}{2}\nabla_{\boldsymbol{r}}\cdot\nabla_{\boldsymbol{r}'}\gamma(\boldsymbol{r},\boldsymbol{r}')|_{\boldsymbol{r}'=\boldsymbol{r}}. \qquad (23)$$

Due to the following identity

$$\int\nabla_{\boldsymbol{r}}^2\rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}=0, \qquad (24)$$

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]

$$t_2(\boldsymbol{r};[\rho])=t_1(\boldsymbol{r};[\rho])-\lambda\nabla^2\rho(\boldsymbol{r}), \qquad (25)$$

where λ can have any value. It has been shown [4] that $t_{\mathrm{S}}(\boldsymbol{r};[\rho])$ relates with $t_1(\boldsymbol{r};[\rho])$ via

$$t_{\mathrm{S}}(\boldsymbol{r};[\rho])=t_1(\boldsymbol{r};[\rho])-\tfrac{1}{4}\nabla^2\rho(\boldsymbol{r}), \qquad (26)$$

although other λ values, including 0 [17], $\frac{1}{8}$ [14], and so on [15,16], have been suggested as well. Formally, any interpolation between $t_S(r;[\rho])$ and $t_2(r;[\rho])$

$$t_3(r;[\rho]) = \alpha t_S(r;[\rho]) + (1-\alpha) t_2(r;[\rho]) \tag{27}$$

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]

$$\lim_{r,r'\to\infty} \gamma(r,r') = \sqrt{\rho(r)} \cdot \sqrt{\rho(r')}\,,$$
$$\lim_{r\to\infty} \rho(r) = A r^{2\beta} \exp\left[-2\sqrt{2I}\,r\right], \tag{28}$$

with a few manipulations, we obtain the following asymptotic equations for $k(r)$ derived from the corresponding formulas of the KED $t(r;[\rho])$ in Eqs. (22)–(27):

$$\lim_{r\to\infty} k_S(r) = \lim_{r\to\infty} \frac{t_S(r;[\rho])}{\rho(r)} = -I, \tag{29}$$

$$\lim_{r\to\infty} k_1(r) = \lim_{r\to\infty} \frac{t_1(r;[\rho])}{\rho(r)} = I, \tag{30}$$

$$\lim_{r\to\infty} k_2(r) = \lim_{r\to\infty} \frac{t_2(r;[\rho])}{\rho(r)} = (1-8\lambda)\, I, \tag{31}$$

$$\lim_{r\to\infty} k_3(r) = \lim_{r\to\infty} \frac{t_3(r;[\rho])}{\rho(r)} = [2(1-\alpha)(1-4\lambda) - 1]\, I. \tag{32}$$

From Eq. (19), in order for Eq. (32) to yield the sole value $-I$, we have

$$\lim_{r\to\infty} k_3(r) = [2(1-\alpha)(1-4\lambda) - 1]\, I = -I,$$
$$\alpha = 1\,,\ \lambda = 1/4. \tag{33}$$

Hence, only Eq. (22) and its identity, Eq. (26), are the correct definitions of $t_S(r;[\rho])$. Furthermore, this result vividly exemplifies that although Green's theorem provides the same integral, the physical meaning of the integrands cannot always be maintained consistently throughout the integration. In the following, 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 $t_S(r;[\rho])$ in Eq. (22) is

$$\hat{t}_S(r;[\rho]) = \sum_{i=1}^{N} \hat{t}_S^i(r;[\rho]),$$
$$\hat{t}_S^i(r;[\rho]) = \frac{1}{2}\left[\delta(r_i - r)(\hat{p}_i^2/2m) + (\hat{p}_i^2/2m)\delta(r_i - r)\right], \tag{34}$$

where m is the electron mass, and $\hat{p}_i$ is the normal momentum operator

$$\hat{p}_i = -\mathrm{i}\hbar\nabla_i. \tag{35}$$

A few simple manipulations can readily show the equivalence between this new definition

$$t_S(r;[\rho]) = \sum_{i=1}^{N} t_S^i(r;[\rho]),$$
$$t_S^i(r;[\rho]) = \langle\Psi^N(1,2,\ldots,N)|\hat{t}_S^i(r;[\rho]) \times|\Psi^N(1,2,\ldots,N)\rangle, \tag{36}$$

and Eq. (22). Similarly, the Hermitian operator defined for $t_1(r;[\rho])$ in Eq. (23) is

$$\hat{t}_1(r;[\rho]) = \sum_{i=1}^{N} \hat{t}_1^i(r;[\rho]),$$
$$\hat{t}_1^i(r;[\rho]) = \left(\hat{p}_i/\sqrt{2m}\right)\delta(r_i - r)\left(\hat{p}_i/\sqrt{2m}\right). \tag{37}$$

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) suggests 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

$$k_S^{KS}(r) = \frac{\sum_i^N \phi_i^*\left(-\frac{1}{2}\nabla_i^2\right)\phi_i}{\sum_i^N |\phi_i|^2},$$

$$\left(-\tfrac{1}{2}\nabla_i^2 + \hat{v}_{\text{eff}}^{KS}\right)|\phi_i\rangle = \varepsilon_i|\phi_i\rangle,$$

$$(-I = \varepsilon_1 > \varepsilon_2 > \ldots > \varepsilon_N) \tag{38}$$

where the HOMO energy (ε_1) is $-I$ [24]. Asymptotically, the KS effective potential is zero [24,25]

$$\lim_{r\to\infty} \hat{v}_{\text{eff}}^{KS} = 0, \tag{39}$$

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

$$\lim_{r\to\infty} k_S^{KS}(r) = \lim_{r\to\infty} \frac{\sum_i^N \varepsilon_i|\phi_i|^2}{\sum_i^N |\phi_i|^2} = \varepsilon_1 = -I, \tag{40}$$

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],

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

$$\lim_{r\to\infty} k_S^{HF}(r) = \varepsilon_{\text{HOMO}}^{\text{HF}} \approx -I. \tag{41}$$

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

$$\lim_{r\to\infty} \frac{\nabla^2\rho(r)}{\rho(r)} = 8\,I \tag{42}$$

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

$$t_{\text{one}}(r;[\rho]) = C_{\text{TF}}\rho(r)^{5/3} - \tfrac{1}{8}\nabla^2\rho(r), \tag{43}$$

and for the second category,

$$t_{\text{two}}(r;[\rho]) = C(N)\rho(r)^{5/3} + \frac{1}{8}\frac{|\nabla\rho(r)|^2}{\rho(r)} - \frac{1}{4}\nabla^2\rho(r), \tag{44}$$

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

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

[a] $f(I)$ and $g(I)$ are complicated functions of I, 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.

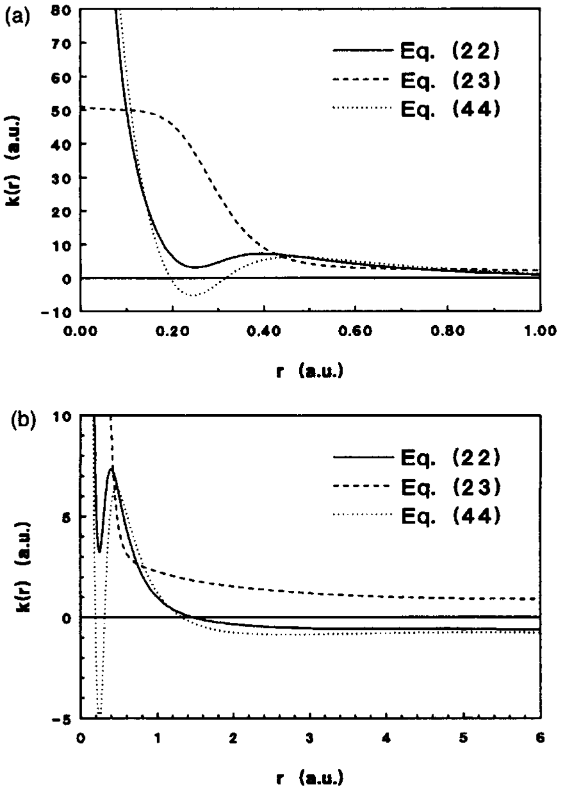

Fig. 1. (a) Short-range and (b) long-range behavior of the single-electron local kinetic energy for Ne atom. The single-electron local kinetic energy is defined through the formulas of the kinetic energy density in Eqs. (22), (23) and (44).

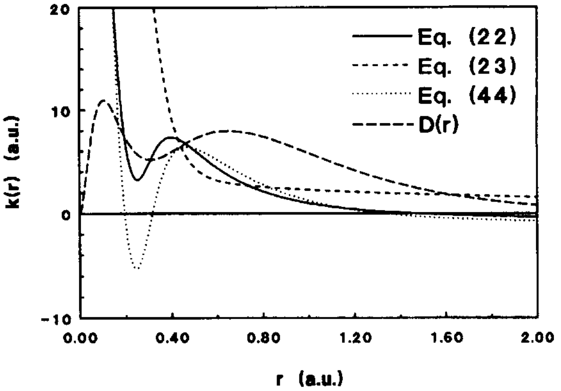

Fig. 2. The short-range behavior of the single-electron local kinetic energy and the radial distribution function for Ne atom.

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.

Acknowledgements

This research was supported by a grant from the National Science Foundation (USA) and was carried out at the University of North Carolina at Chapel Hill. ZZY would like to thank the support of his institution for his visit to the University of North Carolina at Chapel Hill, and the National Natural Science Foundation of China, and the support and hospitality of Prof. Robert G. Parr. The encouragements and the constructive comments from Prof. Parr are gratefully appreciated.

References

[1] P. Hohenberg and W. Kohn, Phys. Rev. 136 (1964) B864.
[2] W. Kohn and L.J. Sham, Phys. Rev. 140 (1965) A1133.
[3] R.G. Parr and W. Yang, Density-functional theory of atoms and molecules (Oxford Univ. Press, New York, 1989).
[4] R.M. Dreizler and E.K.U. Gross, Density functional theory: an approach to the quantum many-Body problem (Springer, Berlin, 1990).
[5] L.H. Thomas, Proc. Camb. Phil. Soc. 23 (1927) 542.
[6] E. Fermi, Z. Phys. 48 (1928) 73.
[7] C.F. von Weizsäcker, Z. Phys. 96 (1935) 431.
[8] P.K. Acharya, L.J. Bartolotti, S.B. Sears and R.G. Parr, Proc. Natl. Acad. Sci. USA 77 (1980) 6978.
[9] J.L. Gázquew and J. Robles, J. Chem. Phys. 76 (1982) 1467.
[10] A.E. DePristo and J.D. Kress, Phys. Rev. A 35 (1986) 438.
[11] H. Lee, C. Lee and R.G. Parr, Phys. Rev. A 44 (1991) 768.
[12] N.H. March and R. Santamaria, Int. J. Quantum Chem. 39 (1991) 585.
[13] D.J. Lacks and R.G. Gordon, J. Chem. Phys. 100 (1994) 4446.
[14] S.K. Ghosh, M. Berkowitz and R.G. Parr, Proc. Natl. Acad. Sci. USA 81 (1984) 8028.
[15] W. Yang, Phys. Rev. A 34 (1986) 4575.
[16] W. Yang, R.G. Parr and C. Lee, Phys. Rev. A 34 (1986) 4586.
[17] A. Holas and N.H. March, J. Mol. Struct. (Theochem) 357 (1995) 193.
[18] O. Goscinski and P. Lindner, J. Math. Phys. 11 (1970) 1313.
[19] B.C. Carlson and J.M. Keller, Phys. Rev. 121 (1961) 659.
[20] J. Katriel and E.R. Davidson, Proc. Natl. Acad. Sci. USA 77 (1980) 4403, and references therein.
[21] L. Pauling and E.B. Wilson, Jr., Introduction to quantum mechanics with applications to chemistry (McGraw-Hill, New York, 1935).
[22] E.C. Kemble, The fundamental principles of quantum mechanics with elementary applications (McGraw-Hill, New York, 1937).
[23] I.N. Levine, Quantum chemistry, 4th Ed. (Prentice Hall, Englewood Cliffs, NJ, 1991).
[24] J.P. Perdew, R.G. Parr, M. Levy and J.L. Balduz, Jr., Phys. Rev. Lett. 49 (1982) 1691.
[25] M. Levy, J.P. Perdew and V. Sahni, Phys. Rev. A 30 (1984) 2745.
[26] T. Koopmans, Physica 1 (1934) 104.
[27] N.C. Handy, M.T. Marron and H.J. Silverstone, Phys. Rev. 180 (1969) 45.
[28] P.-O. Löwdin, Phys. Rev. 97 (1955) 1474.
[29] M.M. Morrell, R.G. Parr and M. Levy, J. Chem. Phys. 62 (1975) 549.
[30] E.R. Davidson, Reduced density matrices in quantum chemistry (Academic Press, New York, 1976).
[31] O.W. Day, D.W. Smith and C. Garrod, Int. J. Quantum Chem. Symp. 8 (1974) 501.
[32] D.W. Smith and O.W. Day, J. Chem. Phys. 62 (1975) 113.
[33] O.W. Day, Jr., Int. J. Quantum Chem. 57 (1996) 391, and references therein.
[34] E. Clementi, and E. Roetti, At. Data Nucl. Data Tables 14 (1974) 117.
[35] Á. Nagy, R.G. Parr and S. Liu, Phys. Rev. A 53 (1996) 3117.