Local Kinetic Energy and Local Temperature in the Density-Functional Theory of Electronic Structure

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ABSTRACT: Various thermodynamic elements of the density functional theory of electronic structure are reviewed and clarified. Detailed argumentation is given for the particular "del dot del" definition of the local kinetic energy density and local temperature. The temperature measures the "nighness" of an electron pair, thus playing a key role in quantitative (exchange and kinetic energy functionals) and qualitative (electron localization functions) tools based on the electron pair density. Two different derivations are given of the Gaussian model for the phase-space distribution function, from which one obtains an approximation to the entropy of the charge distribution. The full thermodynamic description is briefly discussed.   © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 90: 309–326, 2002

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1. Preface

Both the tone and the substance of the density-functional theory (DFT) [1] remind one of classical thermodynamics. For an electronic ground (equilibrium) state, the electron density determines the state of the system, there exists a total energy that is a functional of the state of the system, and there is a minimum energy principle that deter-

mines the state of the system [2]. There is a finite ambient temperature version of the theory that in most respects can be handled as a thermodynamics [3]. There is an increasing entropy principle. Furthermore, from place to place within an inhomogeneous system, there is a varying electronic kinetic energy density, from which one may infer the existence of a varying "local temperature."

Much already is in the literature about these things. The present work reviews and continues the discussion. We treat a range of aspects in some detail, emphasizing first of all, the question of what is the most appropriate definition of the local temperature. Our review is selective, featuring works from our laboratories since about 1980.

2. Local Kinetic Energy Density

ESSENTIAL AMBIGUITY OF THE LOCAL KINETIC ENERGY DENSITY

For an electron moving in one dimension in a state $\psi(x)$, the total kinetic energy is

$$T[\psi] = -\frac{1}{2} \int_{-\infty}^{\infty} \psi(x) \frac{d^2\psi(x)}{dx^2} \, dx. \tag{1}$$

Equivalently, we have that

$$T[\psi] = -\frac{1}{2} \left[\psi(x) \frac{d\psi(x)}{dx} \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{d\psi(x)}{dx} \frac{d\psi(x)}{dx} \, dx \right]$$
$$= \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\psi(x)}{dx} \frac{d\psi(x)}{dx} \, dx, \tag{2}$$

where the first term is zero from the boundary conditions imposed on solutions to the Schrödinger equation. Equations (1) and (2) give the same numerical value for $T[\psi]$ and hence the same functional derivative

$$\frac{\delta T[\psi]}{\delta \psi} = -\frac{d^2\psi(x)}{dx^2}. \tag{3}$$

But suppose we write

$$T[\psi] = \int t(x) \, dx, \tag{4}$$

where $t(x)$ is the kinetic energy density, defined to be the contribution to kinetic energy from the interval $[x, x+dx]$. What is $t(x)$? From Eq. (1),

$$t(x) = -\frac{1}{2} \psi(x) \frac{d^2\psi(x)}{dx^2} \tag{5}$$

while from Eq. (2)

$$t(x) = \frac{1}{2} \left(\frac{d\psi(x)}{dx} \right)^2. \tag{6}$$

There consequently exists an inherent ambiguity in the definition of the kinetic energy density, and we are left to decide which formula is most reasonable. We now proceed to show that Eq. (6) gives the most acceptable definition for the local kinetic energy.

QUASIPROBABILITY DISTRIBUTIONS

In classical mechanics the state of a system is fully specified by the phase-space distribution function, $F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$, which represents the probability of observing particles at the positions $r_1, r_2, \ldots,$ with respective momenta $p_1, p_2, \ldots$. For real quantum mechanical systems, however, we may consider the state of the system to be fully

specified by the probability of observing particles at positions $r_1, r_2, \ldots,$

$$\rho_N(r_1, r_2, \ldots, r_N) \equiv \sum_{\text{spin}} |\Psi(r_1, s_1; r_2, s_2; \ldots; r_N, s_N)|^2, \tag{7}$$

or, equivalently, the probability of observing particles with momenta $p_1, p_2, \ldots,$

$$\rho_N(p_1, p_2, \ldots, p_N) \equiv \sum_{\text{spin}} |\Psi(p_1, s_1; p_2, s_2; \ldots; p_N, s_N)|^2. \tag{8}$$

[By a real quantum mechanical system, we mean a stationary state of a real-valued Hamiltonian operator. The wave functions for such systems may be described by real functions (and multiplied, if one desires, by arbitrary phase factors, $e^{i\phi}$).]

However, it is useful to define a quantum mechanical analog of the phase-space distribution function. Clearly, unless

$$\int F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N) \, dr_1 \, dr_2, \ldots, dr_N$$
$$= \rho_N(p_1, p_2, \ldots, p_N) \tag{9}$$

and

$$\int F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N) \, dp_1 \, dp_2, \ldots, dp_N$$
$$= \rho_N(r_1, r_2, \ldots, r_N), \tag{10}$$

then $F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$ does not describe the same state as the N density, ρ_N. Moreover, in moving from a description based on the $3N$-dimensional wave function to one based upon a $6N$-dimensional quasiprobability distribution function, one has introduced an ambiguity into the problem. That is, there are many different functions, $F(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$, consistent with the constraints of Eqs. (9) and (10) [4−6]; such functions are called quasiprobability distributions [5−8]. The set of all quasiprobability distributions is given by the formula [5]:

$$F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$$
$$\equiv \left(\frac{1}{2\pi}\right)^{6N} \sum_{\text{spin}} \int\int\int \left\{ f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N) \right.$$
$$\times \prod_{i=1}^N e^{-i(\tau_i \cdot p_i)} e^{-i(\theta_i \cdot (r_i - u_i))} \Psi^* \left(\left\{ r_i - \frac{\tau_i}{2} \right\}_{i=1}^N, s_i \right)$$
$$\times \left. \Psi \left(\left\{ r_i + \frac{\tau_i}{2} \right\}_{i=1}^N, s_i \right) \right\} \prod_{i=1}^N d\theta_i \, d\tau_i \, du_i, \tag{11}$$

where $f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N)$ is any function satisfying

$$f(\{\theta_i\}_{i=1}^N; \{0\}_{i=1}^N) = f(\{0_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N) = 1. \quad (12)$$

A common quasiprobability distribution is the Wigner function, given by

$$f_{\text{Wigner}}(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N) \equiv 1. \quad (13)$$

A defect of this choice is that the resulting quasiprobability distribution is sometimes negative [4, 9]; this is not consistent with the interpretation of $F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$ as a probability distribution function.

Given that nonnegative quasiprobability distribution functions exist [10], they ought to be preferred. However, obtaining positive distribution functions requires that $f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N)$ be a functional of Ψ [11]. That is, there is no single choice for $f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N)$ that yields nonnegative quasiprobability distributions for all ρ_N; this follows from the observation that whenever the same choice of $f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N)$ is taken for every Ψ, the resulting quasiprobability distribution function is bilinear and, as shown by Wigner, bilinear quasiprobability distribution functions are not universally nonnegative [4, 9]. This result also follows from Cohen and Zaparovanny's construction [10] of the set of all nonnegative quasiprobability distribution functions because their construction of nonnegative $F(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$ makes essential use of $\rho_N = |\Psi|^2$ [10].

LOCAL PROPERTIES

In quantum mechanics, it is often important to examine the contribution of a particular electron configuration (in either position or momentum space) to a particular property, Q. Because the total contribution to Q from all possible locations of the electrons must equal the total value of Q, we have

$$\int q(r) \, dr = Q \equiv \langle \Psi | \hat{Q} | \Psi \rangle, \quad (14)$$

where the "property density," $q(r)$, is defined as the contribution of electrons at r to the property Q:

$$q(r) \equiv \sum_{i_k = i_{k-1}+1}^N \sum_{i_{k-1} = i_{k-2}+1}^N \cdots \sum_{i_2 = i_1+1}^N \sum_{i_1 = 1}^N \langle \Psi | \delta(r_{i_1} - r) \times \hat{q}(r_{i_1}, r_{i_2}, \ldots, r_{i_k}) | \Psi \rangle, \quad (15)$$

and

$$\hat{Q} \equiv \sum_{i_k = i_{k-1}+1}^N \sum_{i_{k-1} = i_{k-2}+1}^N \cdots \sum_{i_2 = i_1+1}^N \sum_{i_1 = 1}^N \hat{q}(r_{i_1}, r_{i_2}, \ldots, r_{i_k}) \quad (16)$$

is a k-electron operator. Note that there is an ambiguity in the definition of the property density because Eq. (14) is also satisfied by

$$\tilde{q}(r) \equiv q(r) + g(r), \quad (17)$$

where

$$\int g(r) \, dr = 0. \quad (18)$$

In general, $g(r)$ may be a functional of Ψ.

Not unrelated to this situation is the fact that the correspondence principle linking classical mechanical operators to their quantum mechanical operators is ambiguous. Any observable property, Q, of a classical system can be uniquely expressed as a function of the positions and momenta of the particles composing the system:

$$Q \equiv Q(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N). \quad (19)$$

However, because the quantum mechanical position and momentum operators do not commute, the quantum mechanical operator for the property Q cannot be obtained by simply replacing the positions and momenta in the classical expression with their quantum mechanical analogs

$$\begin{aligned} r_i &\to \hat{r}_i \to r_i, \\ p_i &\to \hat{p}_i \to i\hbar\nabla_i. \end{aligned} \quad (20)$$

Instead, the quantum mechanical operator is given by

$$\begin{aligned} Q(\{\hat{r}_i\}_{i=1}^N; &\{\hat{p}_i\}_{i=1}^N) \\ \equiv \left(\frac{1}{2\pi}\right)^{6N} &\int\int\int\int \left\{ Q(\{R_i\}_{i=1}^N; \{P_i\}_{i=1}^N) \right. \\ &\times \prod_{i=1}^N e^{-i(\tau_i \cdot P_i)} e^{-i(\theta_i \cdot R_i)} f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N) \\ &\left. \times \prod_{i=1}^N e^{i(\tau_i \cdot p_i)} e^{i(\theta_i \cdot r_i)} \right\} \prod_{i=1}^N dR_i \, dP_i \, d\theta_i \, d\tau_i. \quad (21) \end{aligned}$$

From this formula it is clear that different quasiprobability distribution functions yield different correspondence rules for deriving quantum mechanical operators. Because there are many different quasiprobability distributions [Eq. (11)] there are also many different ways to choose the quantum mechanical operator corresponding to a given observable property. While all of these operators must,

by necessity, yield the same expectation value for the property,

$$Q \equiv \langle \Psi | \hat{Q} | \Psi \rangle = \langle \Psi | \hat{\tilde{Q}} | \Psi \rangle, \qquad (22)$$

the local property distributions defined by Eq. (15) will generally differ:

$$q(r) \neq \tilde{q}(r). \qquad (23)$$

This, however, allows us to define a property density by restricting ourselves to phase-space distributions with desirable properties (e.g., nonnegativity [10], maximum entropy [12, 13]). We should plan to pick the most physically relevant choice(s) for a property density, $q(r)$ [14–16].

LOCAL KINETIC ENERGY

Of particular concern in the present work is the local kinetic energy density,

$$t(r) \equiv \sum_{i=1}^{N} \langle \Psi | \delta(r_i - r) \hat{t}(r_i) | \Psi \rangle. \qquad (24)$$

The ambiguity in the operator, $\hat{t}(r)$, is hidden when the local kinetic energy is written in terms of the quasiprobability distribution [8, 15]:

$$t(r) \equiv \int\int \sum_{j=1}^{N} \delta(r_j - r)$$
$$\times \int\int \sum_{i=1}^{N} \frac{p_i^2}{2} F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$$
$$\times dp_1, \ldots, dp_N \, dr_1, \ldots, dr_N$$
$$= N \int\int \sum_{i=1}^{N} \frac{p_i^2}{2} F(r, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$$
$$\times dp_1, \ldots, dp_N \, dr_2, dr_3, \ldots, dr_N. \quad (25)$$

It is clear from this formula that the ambiguity inherent in description of a system with a quasiprobability distribution induces an ambiguity with regard to the local kinetic energy density.

As the kinetic energy of an electron is manifestly nonnegative, it is evident that the local kinetic energy density, $t(r)$, should be nonnegative. Examining Eq. (25) reveals the happy circumstance that since $p_i \cdot p_i$ is nonnegative, we will have:

Theorem 1. *The nonnegativity of the quasiprobability distribution is sufficient (but not necessary) for the nonnegativity of the local kinetic energy density [14]. Conversely, the nonnegativity of $t(r)$ is necessary (but not sufficient) for the nonnegativity of $F(r, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$ [14].*

It is reassuring that nonnegative quasiprobability distribution functions guarantee nonnegative local kinetic energy.

One particularly important class of local kinetic energy functionals conforms to the simplifying assumption:

$$f(\{\theta_i\}_{i=1}^{N}; \{\tau_i\}_{i=1}^{N}) = f(\{\theta_i \cdot \tau_i\}_{i=1}^{N}), \qquad (26)$$

which yields

$$t(r) \equiv \left\langle \sum_{i=1}^{N} \left[\delta(r_i - r) \frac{(\nabla_i \Psi^* \cdot \nabla_i \Psi)}{2} \right] \right\rangle + \alpha \cdot \nabla^2 \rho(r)$$
$$= N \cdot \langle \nabla_r \Psi^*(r, r_2, \ldots, r_N) \cdot \nabla_r \Psi(r, r_2, \ldots, r_N)$$
$$/2 \rangle_{r_2, r_3, \ldots, r_N} + \alpha \cdot \nabla^2 \rho(r) \qquad (27)$$

where

$$\rho(r) \equiv \left\langle \Psi \left| \sum_{i=1}^{N} \delta(r_i - r) \right| \Psi \right\rangle$$
$$= N \cdot \langle \Psi^*(r, r_2, \ldots, r_N) \Psi(r, r_2, \ldots, r_N) \rangle_{r_2, r_3, \ldots, r_N} \qquad (28)$$

is the electron density and α is a real-valued constant determined by the specific choice of $f(\{\theta_i \cdot \tau_i\}_{i=1}^{N})$ [15]. In Eq. (27) we have neglected a term that depends on the divergence of the quantum mechanical current density; this term vanishes whenever Ψ is real or the wave function for a stationary state [15].

This form for the local kinetic energy provided rationale for Bader's atoms-in-molecules partitioning [17, 18] and also played a key role (with $\alpha = -\frac{1}{8}$) in the Ghosh–Berkowitz–Parr local thermodynamic ansatz for electronic density functional theory [19]. However, we now demonstrate that the most reasonable value for the constant α in Eq. (27) is zero. Consequently, Eq. (27) provides no justification for imparting physical significance to the Laplacian of the electron density.

Theorem 2. *Only $\alpha = 0$ in Eq. (27) corresponds to a positive local kinetic energy for all systems. Theorem 1 then implies that unless $\alpha = 0$ in Eq. (27), the local kinetic energy is inconsistent with the requirement that the quasiprobability distribution always be positive.*

Proof. Take the one-electron system with electron density

$$\rho(r) = \nu(\beta, \gamma, \varepsilon, n)\{e^{-\beta r^{2n}} + \varepsilon e^{-\gamma r^2}\}, \qquad (29)$$

where ν is a normalization constant, $n > 1$ is an integer, and β and γ are positive real numbers. Applying the chain rule to $\rho(r) = |\Psi(r)|^2$ and substituting into Eq. (27), we obtain

$$t(r) = \frac{\nabla\rho(r) \cdot \nabla\rho(r)}{8\rho(r)} + \alpha\nabla^2\rho(r)$$

$$= \frac{\left(\frac{\partial\rho(r)}{\partial r}\right)^2}{8\rho(r)} + \alpha \cdot \left[\frac{2}{r}\frac{\partial}{\partial r}\rho(r) + \frac{\partial^2}{\partial r^2}\rho(r)\right]. \quad (30)$$

Substituting Eq. (29) and evaluating at $r = 0$, we find

$$t(r = 0) = \alpha \cdot (-6\varepsilon\gamma) \cdot \nu(\beta, \gamma, \varepsilon, n). \quad (31)$$

Hence, unless $\alpha = 0$, there is a system (the system with the density of Eq. (29) and sign$[\varepsilon] = $ sign$[\alpha]$) with a negative value of the local kinetic energy. From Theorem 1, we conclude that only $\alpha = 0$ is consistent with the requirement of a nonnegative quasiprobability distribution function. ∎

Consequently, the preferred definition of the local kinetic energy is given by

$$t(r) \equiv \left\langle \sum_{i=1}^{N}\left[\delta(r_i - r)\frac{\nabla_i\Psi^* \cdot \nabla_i\Psi}{2}\right]\right\rangle$$

$$= N \cdot \langle\nabla_r\Psi^*(r, r_2, \ldots, r_N)$$

$$\cdot \nabla_r\Psi(r, r_2, \ldots, r_N)/2\rangle_{r_2, r_3, \ldots, r_N}. \quad (32)$$

This definition gives a local kinetic energy density that is manifestly positive, which indicates that the Eq. (32) might be associated with a nonnegative quasiprobability distribution. There is a family of quasiprobability distributions associated with the local kinetic energy of Eq. (32), namely, the distributions obtained by substituting

$$f\left(\{\theta_i\}_{i=1}^{N}; \{\tau_i\}_{i=1}^{N}\right) = \prod_{i=1}^{N} e^{\theta_i \cdot \tau_i/g} \quad (33)$$

into Eq. (11) [15], although these quasiprobability distribution functions generally assume negative values [observe that Eq. (33) does not depend explicitly upon a system's wave function]. However, this does rule out the possibility that for every system, there exists $f(\{\theta_i\}_{i=1}^{N}; \{\tau_i\}_{i=1}^{N})$ such that the $F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$ determined through Eq. (11) is nonnegative and, moreover, the kinetic energy density is given by Eq. (32).

This is to say, for any given property density, $q(r)$, there are typically many different choices for $f(\{\theta_i\}_{i=1}^{N}; \{\tau_i\}_{i=1}^{N})$, corresponding to many different $F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$, all of which coincide for the particular property density, $q(r)$

(though they typically differ for other property densities). Specific to the present case, there are certainly many different quasiprobability distributions, $F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$, consistent with our preferred definition of the local kinetic energy, Eq. (32). These distributions typically differ from one another for other property densities, $q(r)$, but coincide when the property of interest is the kinetic energy. *We postulate that for every system, there exists at least one nonnegative quasiprobability distribution with local kinetic energy given by Eq. (32). Establishing the validity of this postulate is a matter for future research.*

CHOOSING THE BEST QUASIPROBABILITY DISTRIBUTIONS

Given that there are many possible quasiprobability distribution functions, the question of how to choose the most appropriate quasiprobability distribution function warrants consideration. On general statistical grounds, the answer is that we should maximize the entropy of the quasiprobability distribution function [12, 13]

$$-\int\int\int\int\int\int F(\{r_i\}_{i=1}^{N}; \{p_i\}_{i=1}^{N}) \ln\left(F(\{r_i\}_{i=1}^{N}; \{p_i\}_{i=1}^{N})\right)$$

$$\times dr_1, \ldots, dr_N dp_1, \ldots, dp_N \quad (34)$$

subject to such constraints as we may wish to impose, e.g.,

$$F(\{r_i\}_{i=1}^{N}; \{p_i\}_{i=1}^{N}) \geq 0 \quad (35)$$

and/or Eq. (32). Equivalently, we may maximize [20]

$$\lim_{a \to 0}\left(\frac{1}{a}\left(1 - \int\int\int\int\int\int \left(F(\{r_i\}_{i=1}^{N}; \{p_i\}_{i=1}^{N})\right)^{a+1}\right.\right.$$

$$\left.\left. \times dr_1, \ldots, dr_N dp_1, \ldots, dp_N\right)\right). \quad (36)$$

The problem with representations (34) and (36) is that the integrands are generally complex valued (in fact, the integrands are multiply-complex valued since both the even-order roots of a system and the logarithm have branch points); this complicates the process of maximizing the entropy unless all the distributions being searched over satisfy Eq. (35). (According to Cohen and Zaparovanny [10], it is possible to restrict the search to nonnegative distributions [12, 13]; however, this construction becomes increasingly complicated as the number of particles increases.) It would be good to have a formulation of the maximum entropy principle that, while

applicable to distributions that violate Eq. (35), reduces to the normal maximum entropy principle for positive distributions. Better still would be a generalized maximum entropy principle that ensured that the maximum entropy distribution always satisfies Eq. (35), thereby removing the troublesome nonnegativity constraint from the theory altogether.

One formulation of the maximum entropy principle that is equivalent to Eqs. (34) and (36) for nonnegative distributions but, unlike Eqs. (34) and (36), is well defined also for distributions violating the nonnegativity constraint, is

$$
\lim_{\substack{(2k+1)/(2n+1)\to\infty}} \left(\frac{2k+1}{2n+1} \left(1 \right. \right.
$$
$$
\left. \left. - \iiiint\!\!\!\iint \left(F(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N) \right)^{2(n+k+1)/(2k+1)} \right. \right.
$$
$$
\left. \left. \times \, dr_1, \dots, dr_N \, dp_1, \dots, dp_N \right) \right), \qquad (37)
$$

where k and n are positive integers. The generalized entropy function (37) enables us to pose several interesting questions regarding the link between nonnegative distribution functions, the maximum entropy distribution function, and the local kinetic energy given by Eq. (32).

Question. *Take $F(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$ to be a functional of $f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N)$ via Eq. (11). Maximize Eq. (37) with respect to $f(\{\theta_i\}_{i=1}^N; \{\tau_i\}_{i=1}^N)$. Is the resulting quasiprobability distribution function, $F^{(S)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$, nonnegative? Is the local kinetic energy associated with $F^{(S)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$ given by Eq. (32)?*

Note. *If $F^{(S)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$ is nonnegative, then, owing to the equivalence of Eqs. (36) and (37) for nonnegative distributions, it follows that $F^{(S)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$ is the nonnegative distribution function with greatest entropy.*

Question. *Let $F^{(P)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$ be the nonnegative quasiprobability distribution function with greatest entropy. Can the local kinetic energy for this function be expressed as a closed-form expression in terms of the molecular wave function, Ψ? If so, is the expression equal to Eq. (32)?*

Note. *The local kinetic energy from the "maximum entropy" quasiprobability distribution function would be preferred over that derived from other positive distribution functions. However, if the maximum entropy ansatz does not yield a simple expression for the local kinetic energy, the local kinetic energy of Eq. (32) remains preferred*

by virtue of its inherent nonnegativity and simplicity. Ideally, of course, Eq. (32) would be derived from the maximum entropy principle.

Question. *Among quasiprobability distribution functions with local kinetic energy given by Eq. (32), let the one that maximizes Eq. (37) etc. be denoted $F^{(T)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$. Is $F^{(T)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)$ nonnegative?*

Note. *Ideally, we would have that*

$$
F^{(S)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N) = F^{(P)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N)
$$
$$
= F^{(T)}(\{r_i\}_{i=1}^N; \{p_i\}_{i=1}^N) \qquad (38)
$$

and hence

$$
t^{(S)}(r) = t^{(P)}(r) = t^{(T)}(r) = t^{[\text{Eq. (32)}]}(r). \qquad (39)
$$

If the local kinetic energies associated with these various ways of constructing an "optimal" quasiprobability distribution are not all equivalent, the preferred definition of the local kinetic energy would be that associated with the positive quasiprobability distribution with largest entropy, $t^{(P)}(r)$.

OTHER FORMS FOR THE LOCAL KINETIC ENERGY DENSITY

We briefly mention several other forms for the local kinetic energy density. Ghosh, Berkowitz, and Parr proposed [19]

$$
t_{\text{GBP}}(r) = \left\langle \Psi \left| \sum_{i=1}^N \delta(r_i - r) \left(-\frac{\nabla_i^2}{2} \right) \right| \Psi \right\rangle + \frac{1}{8} \nabla^2 \rho(r)
$$
$$
= -N \cdot \left\langle \Psi^*(r, r_2, \dots, r_N) \cdot \nabla_r^2 \Psi(r, r_2, \dots, r_N) \right.
$$
$$
\left. /2 \right\rangle_{r_2, r_3, \dots, r_N} + \frac{\nabla^2 \rho(r)}{8}
$$
$$
= t(r) - \frac{\nabla^2 \rho(r)}{8}, \qquad (40)
$$

and Berkowitz subsequently justified this form with a maximum entropy argument using an approximate phase-space distribution [cf. Eq. (69)] [21]. Yet another alternative is the "local energy form" [22]

$$
t_{\text{YLW}}(r) = \left\langle \Psi \left| \sum_{i=1}^N \delta(r_i - r) \left(-\frac{\nabla_i^2}{2} \right) \right| \Psi \right\rangle
$$
$$
= t(r) - \frac{\nabla^2 \rho(r)}{4}, \qquad (41)
$$

that Yang, Liu, and Wang proposed based on the local energy resolution of the Schrödinger equation. It follows from our Theorem 2, however, that both

of these alternative definitions for the local kinetic energy fail to give a positive kinetic energy density for general systems. Indeed, both definitions give negative kinetic energy densities near the bond midpoints of certain homonuclear diatomic molecules. Thus $t_{GBP}(r)$ and $t_{YLW}(r)$ sometimes fail to correspond to a nonnegative quasiprobability distribution function.

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3. Local Temperature

DEFINITION OF LOCAL TEMPERATURE

Based on these considerations, we conclude that local kinetic energy density of an electronic system should be given by the "del dot del" formula [23] of Eq. (6) or its three-dimensional generalization for N-electrons, Eq. (32). That is,

$$T[\Psi] \equiv \int t[\Psi; r] \, dr, \qquad (42)$$

where

$$t[\Psi; r] \equiv \left\langle \sum_{i=1}^{N} \left[\delta(r_i - r) \frac{(\nabla_i \Psi^* \cdot \nabla_i \Psi)}{2} \right] \right\rangle = t(r), \quad (43)$$

as suggested in Eq. (32). Correspondingly, in density functional theory (DFT) we have that the electronic kinetic energy is a functional of the electron density, $\rho(r)$, and thus

$$T[\rho] \equiv \int t[\rho; r] \, dr \qquad (44)$$

where the local kinetic energy density is given by

$$t[\rho; r] \equiv t[\Psi[\rho]; r] = t(r). \qquad (45)$$

In DFT, two different choices of $\Psi[\rho]$ are of primary interest. First, there is the exact wave function $\Psi_{Levy}[\rho]$, as defined through the constrained search procedure [24, 25] with the true kinetic energy $T[\rho]$. Alternatively, we may consider the Kohn–Sham [26] single determinant, $\Phi_{KS}[\rho]$, with the kinetic energy

$$T_s[\rho] \equiv \langle \Phi[\rho] | \hat{T} | \Phi[\rho] \rangle. \qquad (46)$$

The difference between $T[\rho]$ and $T_s[\rho]$ is quite small, being on the order of the correlation energy [27]. The Kohn–Sham determinant, $\Phi_{KS}[\rho]$, describes a system of noninteracting fermions that we may reasonably regard as the electronic equivalent of an inhomogeneous ideal gas. For this "ideal gas" reference,

$$T_s[\rho] \equiv \int t_{KS}[\rho; r] \, dr, \qquad (47)$$

where

$$t_{KS}[\rho; r] \equiv t[\Phi_{KS}[\rho]; r] = \sum_{i=1}^{N} \frac{\nabla(\phi_i^{KS}(r))^* \cdot \nabla \phi_i^{KS}(r)}{2}$$
$$= \sum_{i=1}^{N} \frac{\nabla \rho_i^{KS}(r) \cdot \nabla \rho_i^{KS}(r)}{8 \rho_i^{KS}(r)}, \qquad (48)$$

where $\{\phi_i^{KS}(r)\}_{i=1}^{N}$ and $\{\rho_i^{KS}(r)\}_{i=1}^{N}$ are the Kohn–Sham spin-orbitals and orbital densities, respectively. We may then define a local temperature $\theta(r)$ and inverse temperature $\beta(r)$ by analogy to the ideal gas:

$$t_{KS}[\rho; r] \equiv \frac{3}{2} \rho(r) k \theta[\rho; r] = \frac{3}{2} \frac{\rho(r)}{\beta[\rho; r]}. \qquad (49)$$

That is,

$$k\theta[\rho; r] \equiv \frac{2 t_{KS}[\rho; r]}{3\rho(r)} = \frac{\sum_{i=1}^{N} \nabla \phi_i^{KS}(r) \cdot \nabla \phi_i^{KS}(r)}{3\rho(r)}$$
$$= \frac{1}{\beta(r)}. \qquad (50)$$

The calculation of the local temperature from the Kohn–Sham orbitals (assumed real) is elementary, and since the Kohn–Sham orbitals are readily computed from the electron density [27, 28], the calculation of $\theta(r)$ and $\beta(r)$ from $\rho(r)$ is straightforward. The constant k is arbitrary; we include it to emphasize the analogy with the classical theory.

What about the real system as opposed to the corresponding noninteracting reference system? The analogy with classical thermodynamics tells us what we should do here: Take exactly the same temperature, Eq. (50), at each point. For since the classical and Kohn–Sham systems have exactly the same $\rho(r)$ and the same chemical potential μ, they can be imagined to be in equilibrium with each other—thus their temperature profiles must be precisely the same. One may profitably approach additional properties of the real system in ways modeled after various treatments of classical real gasses [29–32]. One sees from Eq. (50) that cusp, long-range, and other conditions obeyed by the Kohn–Sham orbitals transfer straightforwardly to corresponding conditions on $\theta(r)$ and $\beta(r)$. Note that

$$\theta(r) \geq 0 \qquad (51)$$

with $\theta(r) = 0$ the natural zero of the temperature scale. The local temperature is usually positive, with a notable exception being on the bonding axis of a one-electron diatomic molecule (where the local temperature is zero). Eq. (51) may be considered to be the DFT analogue of the zeroth law of thermodynamics.

An elementary example from chemistry is the hydrogen-like atom of nuclear charge Z, for which

$$\rho_Z(\mathbf{r}) \equiv \left(\frac{Z^3}{\pi}\right) e^{-2Zr}. \tag{52}$$

From this we find

$$k\theta(\mathbf{r}) = \frac{1}{\beta(\mathbf{r})} = \frac{Z^3}{3}. \tag{53}$$

The local temperature is constant for one-electron atoms.

Also, since the energy of the hydrogen-like system, $-Z^2/2$, is equal to the negative of the ionization potential (IP), we have

$$\frac{3}{2}k\theta(\mathbf{r}) = \text{IP}, \tag{54}$$

a relation that is true in the limit of large $\mathbf{r}$ for more general atomic or molecular systems.

RELATION BETWEEN LOCAL TEMPERATURE AND POLITZER AVERAGE LOCAL IONIZATION POTENTIAL

Given that the local temperature is proportional to the ionization potential for hydrogen-like systems, should the local temperature be related to a local measure of the ionization potential. Such a local measure of the ionization potential was introduced by Politzer in the context of Hartree–Fock theory [33–37]:

$$I(\mathbf{r}) \equiv \frac{\sum_{i=1}^{N} -\varepsilon_i \cdot \rho_i(\mathbf{r})}{\sum_{i=1}^{N} \rho_i(\mathbf{r})} = \frac{\sum_{i=1}^{N} -\varepsilon_i \cdot \rho_i(\mathbf{r})}{\rho(\mathbf{r})}, \tag{55}$$

where $\rho_i(\mathbf{r})$ are the occupied orbital densities and ε_i are the occupied orbital energies. Clearly the quantity $I(\mathbf{r})$ is equally interesting (and approximately the same [33]) when the Kohn–Sham orbital densities and energies are employed in Eq. (55). (The primary difference is one of interpretation: The identification of $I(\mathbf{r})$ as a local ionization potential for the Hartree–Fock case relies upon the use of Koopmans' theorem to identify $-\varepsilon_i$ as an approximate ionization potential [38]. Playing a similar role in the Kohn–Sham theory is Janak's theorem [39].)

To derive a relationship between the local ionization potential and the local temperature,

$$k\theta(\mathbf{r}) = \frac{\sum_{i=1}^{N} \nabla\phi_i^{\text{KS}}(\mathbf{r}) \cdot \nabla\phi_i^{\text{KS}}(\mathbf{r})}{3\rho(\mathbf{r})}. \tag{56}$$

We start with the Kohn–Sham equations

$$\left\{-\frac{\nabla^2}{2} + v_{\text{KS}}[\rho;\mathbf{r}]\right\}\phi_i^{\text{KS}}(\mathbf{r}) = \varepsilon_i^{\text{KS}}\phi_i^{\text{KS}}(\mathbf{r}). \tag{57}$$

Multiplying both sides of Eq. (57) by $\phi_i^{\text{KS}}(\mathbf{r})$, summing over i, and dividing by $\rho(\mathbf{r})$ we obtain

$$\frac{\sum_{i=1}^{N} \phi_i^{\text{KS}}(\mathbf{r})\left(-\frac{\nabla^2}{2}\right)\phi_i^{\text{KS}}(\mathbf{r})}{\rho(\mathbf{r})} + v_{\text{KS}}[\rho;\mathbf{r}] = -I(\mathbf{r}). \tag{58}$$

Next, using the identity

$$\sum_{i=1}^{N} \phi_i^{\text{KS}}(\mathbf{r})\left(-\frac{\nabla^2}{2}\right)\phi_i^{\text{KS}}(\mathbf{r})$$

$$= \sum_{i=1}^{N} \frac{\nabla\phi_i^{\text{KS}}(\mathbf{r}) \cdot \nabla\phi_i^{\text{KS}}(\mathbf{r})}{2} - \sum_{i=1}^{N} \frac{\nabla^2}{4}\left|\phi_i^{\text{KS}}(\mathbf{r})\right|^2$$

$$= t(\mathbf{r}) - \frac{1}{4}\nabla^2\rho(\mathbf{r}), \tag{59}$$

we find that

$$\frac{3}{2}k\theta(\mathbf{r}) + v_{\text{KS}}[\rho;\mathbf{r}] - \frac{\nabla^2\rho(\mathbf{r})}{4} = -I(\mathbf{r}). \tag{60}$$

Politzer reasons that $I(\mathbf{r})$ measures the energy required to remove an electron from the neighborhood of the point $\mathbf{r}$ so that $I(\mathbf{r})$ is a reactivity index for electrophilic attack. It has been shown that the isosurfaces of $\theta(\mathbf{r})$ and $I(\mathbf{r})$ are parallel in a number of cases, though $\theta(\mathbf{r})$ appears to be more sensitive than $I(\mathbf{r})$ in bonding regions [40]. Thus lower temperature is associated with greater ease of removing electrons. An additional consequence of Eq. (60) concerns the temperature at the boundary of an atom, for which we get:

$$\lim_{r\to\infty}\left\{\frac{3}{2}k\theta(\mathbf{r})\right\} + \lim_{r\to\infty}\{v_{\text{KS}}[\rho;\mathbf{r}]\} - \frac{1}{4}\lim_{r\to\infty}\left\{\frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})}\right\}$$

$$= \lim_{r\to\infty}\{I(\mathbf{r})\}$$

$$\lim_{r\to\infty}\left\{\frac{3}{2}k\theta(\mathbf{r})\right\} + 0 - \tfrac{1}{4}\{8 \cdot \text{IP}\} = \varepsilon_{\text{HOMO}}^{\text{KS}}$$

$$\lim_{r\to\infty}\left\{\frac{3}{2}k\theta(\mathbf{r})\right\} = \text{IP}, \tag{61}$$

using the well-known fact that the highest-occupied Kohn–Sham molecular orbital energy, $\varepsilon_{\text{HOMO}}^{\text{KS}}$, is exactly the negative of the ionization potential [41, 42].

4. Approximate Quasidistribution Functions

ENTROPY

"Temperature" in DFT would just be a defined mathematical term unless it functions together with an entropy, with the entropy having the properties expected of a "thermodynamic" entropy. In this

section, we define and expound the nature of the entropy concept in ground-state DFT.

We already have introduced the entropy above, but, even for a noninteracting system, constructing an N-particle positive quasiprobability distribution function, $F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$, is very cumbersome. Following Ghosh, Berkowitz, and Parr [19], we proceed by defining a two-coordinate phase-space density:

$$f(r; p) \equiv \iiint \left\{ \sum_{i=1}^{N} \delta(r_i - r)\delta(p_i - p) \right\}$$
$$\times F(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N)$$
$$\times dr_1\, dr_2, \ldots, dr_N\, dp_1\, dp_2, \ldots, dp_N. \quad (62)$$

From the constraint of Eq. (10), we have that

$$\int f(r; p)\, dp = \rho(r). \quad (63)$$

In order to obtain explicit density functionals, we relax the constraint that

$$\int f(r; p)\, dr = \rho(p), \quad (64)$$

requiring only that the Kohn–Sham local kinetic energy (and hence the local temperature) be reproduced:

$$\int \frac{p^2}{2} f(r; p)\, dp = t_{KS}(r) = \sum_{i=1}^{N} \frac{\nabla \phi_i^{KS}(r) \cdot \nabla \phi_i^{KS}(r)}{2}. \quad (65)$$

Note that an $f(r; p)$ that satisfies constraints (63) and (65), but not Eq. (64), is not an entirely proper quasiprobability distribution function.

As discussed above, one selects $f(r; p)$ using information theory, thereby selecting the least biased distribution that satisfies constraints (63) and (65). Unlike the situation above, however, where maximizing the entropy expression (34) is too difficult to be done explicitly, maximizing the entropy

$$S[f] = -k \iint f(r; p) \ln f(r; p)\, dr\, dp \quad (66)$$

subject to constraints (63) and (65) is straightforward. Specifically, forcing the constraints with the local Lagrange multipliers $\alpha(r) - 1$ and $\beta(r)$, we have

$$0 = \delta \left\{ S[f] - \int (\alpha(r) - 1) \left\{ \int f(r; p)\, dp - \rho(r) \right\} dr \right.$$
$$\left. - \int \beta(r) \left\{ \int p^2 f(r; p)\, dp - t_{KS}(r) \right\} dr \right\} \bigg/ \delta f(r; p) \quad (67)$$

and thus

$$f(r; p) = e^{-\alpha(r)} e^{-\beta(r) p^2}. \quad (68)$$

Substitution of form (68) into the constraint equations (63) and (64) gives

$$f(r; p) = \left(\frac{\beta(r)}{2\pi} \right)^{3/2} \rho(r) e^{-\beta(r) p^2/2}, \quad (69)$$

where $\beta(r)$ is defined as in Eq. (50). Equation (69) is simply a local Maxwell–Boltzmann distribution law for the electrons. We note that

$$f(r; p) \geq 0. \quad (70)$$

Thus we may interpret $f(r; p)$ as an approximate probability distribution function for the average position and momentum of electrons in the system.

The maximizing entropy is found to be

$$S \equiv -k \int \rho(r) \left\{ \ln \rho(r) - \frac{3}{2}(1 + \ln(2\pi) - \ln \beta(r)) \right\} dr, \quad (71)$$

from which we may define the entropy density,

$$s(r) \equiv -k \int f(r; p) \ln f(r; p)\, dp$$
$$= -k\rho(r) \ln \rho(r)$$
$$+ \frac{3}{2}\rho(r)(1 + \ln(2\pi) - \ln \beta(r)). \quad (72)$$

As is to be expected for a local Boltzmann distribution, the local entropy satisfies an equation resembling the classical Sackur–Tetrode equation [19]. One may argue that one should define the local entropy through reference to the uniform electron gas, thereby obtaining [19]

$$s(r) - s_{ug}(r) \equiv \frac{3}{2} k\rho(r) \ln \left[\frac{\beta_{ug}(r)}{\beta(r)} \right]$$
$$= \frac{3}{2} k\rho(r) \ln \left[\frac{\theta(r)}{\theta_{ug}(r)} \right], \quad (73)$$

where the local temperature of the uniform electron gas is given by [43]

$$\theta_{ug}(r) = \frac{(3\pi^2)^{2/3} \rho^{2/3}(r)}{5}. \quad (74)$$

The choice of Eq. (32) to define the local kinetic energy may be supported by computing the value of the approximate entropy functional, Eq. (71), for different definitions for the local kinetic energy. Comparison among the "positive" [Eq. (32)], Ghosh–Berkowitz–Parr [Eq. (40)], and Yang–Liu–Wang [Eq. (41)] alternatives reveals that S is largest for the "positive" form (32) [43], supporting our hope that more precise maximum entropy arguments like those given above would yield similar conclusions.

DENSITY AND LOCAL TEMPERATURE BIFUNCTIONALS

There are two excellent tests for the $\mathfrak{f}(r;p)$ of Eq. (69). Integration of it over r will give an approximate momentum density, $\rho(p)$, and from it an approximate Compton profile. Results are very good (but not exact), as may be seen by treating the hydrogen atom exactly [44]. In fact, the results obtained are fairly insensitive to which definition of the local kinetic energy one uses [44, 45]. (The reader will observe that the only effect of using the Ghosh–Berkowitz–Parr [Eq. (40)] or the Yang–Liu–Wang [Eq. (41)] definitions of the local kinetic energy density in Eq. (65) is the definition of $\beta(r) \equiv 1/k\theta(r)$.)

As a second test, one may Fourier transform $\mathfrak{f}(r;p)$, thereby obtaining an approximation to the first-order density matrix [46]

$$
\gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right) \equiv \sum_{i=1}^{N} \phi_i^{KS}\left(r + \frac{s}{2}\right)\phi_i^{KS}\left(r - \frac{s}{2}\right)
$$
$$
\approx \int \mathfrak{f}(r;p)e^{ip\cdot s}\,dp
$$
$$
\approx \rho(r)e^{-s^2/2\beta(r)}. \qquad (75)
$$

Both the kinetic energy,

$$
T[\gamma] = \int -\frac{1}{2}\left[\nabla_s^2 \gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right]_{s=0} dr, \qquad (76)
$$

and particle number,

$$
N[\gamma] = \frac{1}{2}\iint \left|\gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right|^2 ds\,dr \qquad (77)
$$

can be written as functionals of the first-order density matrix [46, 47]. Similarly, for a system in which all the Kohn–Sham orbitals are doubly occupied, the exchange energy is given by

$$
E_x[\gamma] = -\frac{1}{4}\iint \frac{\left|\gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right|^2}{s} ds\,dr. \qquad (78)
$$

Substitution of the approximate expression (75) into Eqs. (76)–(78) gives expressions for energy components as bifunctionals of $\rho(r)$ and $\beta(r)$ [46, 47]:

$$
T[\rho, \beta] \equiv \frac{3}{2}\int \frac{\rho(r)}{\beta(r)}\,dr \qquad (79)
$$

$$
N[\rho, \beta] = \frac{\pi^{3/2}}{2}\int \rho^2(r)\beta^{3/2}(r)\,dr \qquad (80)
$$

$$
E_x[\rho, \beta] = -\frac{\pi}{2}\int \rho^2(r)\beta(r)\,dr. \qquad (81)
$$

Similarly, the celebrated Colle–Salvetti approximate formula for the correlation energy [48] may be expressed as a bifunctional [49]:

$$
E_c^{CS}[\rho, \beta] = -a\int \left[\rho(r) + b\rho^{-2/3}(r)\right.
$$
$$
\times \left(\frac{3\rho(r)}{2\beta(r)} - \frac{\nabla\rho(r)\cdot\nabla\rho(r)}{4\rho(r)} + \frac{\nabla^2\rho(r)}{8}\right)
$$
$$
\left.\times e^{-c\rho^{-1/3}(r)}\middle/ 1 + d\rho^{-1/3}(r)\right]dr. \qquad (82)
$$

These functionals for the number of particles and the exchange energy have been tested by inserting the Hartree–Fock densities and both the preferred definition of $\beta(r)$ [from Eq. (65)] [45],

$$
\beta(r) \equiv \frac{3\rho(r)}{\sum_{i=1}^{N} \nabla\phi_i^{KS}(r)\cdot\nabla\phi_i^{KS}(r)}, \qquad (83)
$$

and the Ghosh–Berkowitz–Parr form of $\beta(r)$ [from Eq. (40)] [46]

$$
\beta_{GBP}(r) \equiv \frac{3\rho(r)}{\sum_{i=1}^{N} \nabla\phi_i^{KS}(r)\cdot\nabla\phi_i^{KS}(r) - \frac{\nabla^2\rho(r)}{4}}. \qquad (84)
$$

These are early examples of the use of local temperature (or local kinetic energies) in approximate functionals.

The results obtained using $\beta_{GBP}(r)$ are somewhat better than those obtained using the preferred definition of $\beta(r)$. This can be rationalized by considering the spherically averaged Taylor series expansion of $|\gamma(r + s/2; r - s/2)|^2$ about $s = 0$. One obtains exactly [21, 47]

$$
\int \left|\gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right|^2 d\Omega_s
$$
$$
= \rho^2(r)\Gamma(r,s) = \rho^2(r)\left[1 - \frac{s^2}{\beta_{GBP}(r)} + \cdots\right], \qquad (85)
$$

which agrees with the Taylor series expansion of [cf. Eq. (75)]

$$
\left(\rho(r)e^{-s^2/2\beta(r)}\right) = \rho^2(r)\left[1 - \frac{s^2}{\beta(r)} + \cdots\right]
$$
$$
\approx \rho^2(r)\Gamma(r,s) \qquad (86)
$$

through second order if we choose the Ghosh–Berkowitz–Parr form for the inverse temperature. Thus we may derive Eqs. (80) and (81) by using a Gaussian approximation to $\Gamma(r,s)$; this amounts to an approximation resummation of the Taylor series in the interelectronic distance, s [21, 47].

From this perspective it is interesting to consider an alternative resummation, this one motivated by

the electron gas [47]:

$$\int \left| \gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right) \right|^2 d\Omega_s = \rho^2(r)\Gamma(r,s)$$

$$\approx \rho^2(r)\left[\frac{3\sin\left(s\sqrt{\frac{5}{\beta(r)}}\right) - s\sqrt{\frac{5}{\beta(r)}}\cos\left(s\sqrt{\frac{5}{\beta(r)}}\right)}{\left(s\sqrt{\frac{5}{\beta(r)}}\right)^3}\right]^2, \quad (87)$$

which, following Lee and Parr, we call the "trigonometric resummation." Substituting this result into Eqs. (80) and (81), one obtains the approximate functionals

$$N^T[\rho;\beta] = \frac{3\pi^3}{5^{3/2}}\int \rho^2(r)\beta^{3/2}(r)\,dr, \qquad (88)$$

$$E_x^T[\rho;\beta] = \frac{-9\pi}{20}\int \rho^2(r)\beta(r)\,dr. \qquad (89)$$

The Hohenberg–Kohn theorem indicates that $\beta(r)$ is a functional of the electron density. Make the simplifying assumption that $\beta(r)$ is a *function* of $\rho(r)$ (local density approximation). Then dimensional analysis shows that

$$\beta(r) = C\rho^{-2/3}(r). \qquad (90)$$

If one determines the constant by forcing the normalization conditions, Eqs. (80) and (88) on the density to be exact, one obtains values of G for the "Gaussian" and T for the "trigonometric" resummations of Eq. (85), respectively,

$$C_G = \frac{2^{2/3}}{\pi} \qquad (91)$$

and

$$C_T = \frac{\sqrt[3]{5}}{(3\pi^2)^{2/3}}. \qquad (92)$$

Substitution into the formulas for the kinetic and exchange energies gives [17]

$$T^G[\rho] = \frac{3\pi}{2^{5/3}}\int \rho^{5/3}(r)\,dr$$

$$\approx 2.9686\int \rho^{5/3}(r)\,dr, \qquad (93)$$

$$E_x^G[\rho] = -2^{-1/3}\int \rho^{4/3}(r)\,dr$$

$$\approx -0.7937\int \rho^{4/3}(r)\,dr, \qquad (94)$$

$$T^T[\rho] = \frac{3(3\pi^2)^{2/3}}{10}\int \rho^{5/3}(r)\,dr$$

$$\approx 2.8712\int \rho^{5/3}(r)\,dr, \qquad (95)$$

$$E_x^T[\rho] = \frac{-3^{4/3}}{4\pi^{1/3}}\int \rho^{4/3}(r)\,dr$$

$$\approx -0.7386\int \rho^{4/3}(r)\,dr. \qquad (96)$$

These last formulas are no more nor less than the Thomas–Fermi [50, 51] and Dirac [52] functionals for the kinetic energy and the exchange energy, respectively. The only assumptions used in this derivation of the Thomas–Fermi–Dirac energy functionals are the resummation approximation of Eq. (87), and the assumption that the local temperature at a point only depends on the density at that point (local density approximation). It is remarkable, indeed, that the only place the Pauli exclusion principle enters the derivation is through the normalization condition on the first-order density matrix, Eq. (77). As is to be expected from the derivations, Eqs. (93) and (94) are usually better than Eqs. (95) and (96) for atoms (as judged by values computed using Hartree–Fock densities). Both formulas are less accurate than Eq. (79) (exact!) and Eqs. (81) and (89) [47, 53].

LOCAL TEMPERATURE IN APPROXIMATE DENSITY FUNCTIONALS

Using, e.g., the Zhao–Morrison–Parr (ZMP) method [27, 28] for any reasonable density $\rho(r)$, the corresponding Kohn–Sham orbitals and hence the inverse temperature, $\beta(r)$, can be computed using Eq. (83). As shown in the last section, it is permissible, indeed desirable, to include $\beta(r)$ explicitly in approximate density functionals. Nobody can quarrel with formulas such as

$$T[\rho, \beta] \equiv \frac{3}{2}\int \frac{\rho(r)}{\beta(r)}\,dr$$

or

$$E_x[\rho;\beta] = -\frac{\pi}{2}\int \rho^2(r)\beta(r)\,dr$$

if one demonstrates that they are useful. There is a certain physical appeal to $\beta(r)$, which calls for some sort of thermodynamic description, perhaps built from the phase-space distribution function, $\mathfrak{f}(r;p)$.

Inclusion of $\beta(r)$ or $\theta(r)$ is, of course, equivalent to inclusion of the local kinetic energy density. Many contemporary works are doing these things [45, 54–61]. Note that since $\theta(r)$ is a sum of grad-grad terms, one may think of $\theta(r)$ as a "second-order orbital gradient" term, $\theta^2(r)$ as a "fourth-order orbital gradient" term, and so on; $\theta(r)$ brings information into play about the momentum distribution.

For atoms and molecules, there is no strong justification for scaling the temperature by the corresponding uniform electron gas temperature. Using Eqs. (56) and (74), one has

$$\frac{\theta(r)}{\theta_{\text{ug}}(r)} = \frac{5}{3^{5/3}\pi^{4/3}} \frac{\sum_{i=1}^{N} \nabla\phi_i^{\text{KS}}(r) \cdot \nabla\phi_i^{\text{KS}}(r)}{\rho^{5/3}(r)}$$

$$\approx 0.1741 \frac{\sum_{i=1}^{N} \nabla\phi_i^{\text{KS}}(r) \cdot \nabla\phi_i^{\text{KS}}(r)}{\rho^{5/3}(r)}. \quad (97)$$

This expression is awkward and it introduces artificialities in dealing with cusp conditions and long-range behavior. It seems better to just deal with $\rho(r)$ and $\beta(r)$ or $\rho(r)$ and $\theta(r)$. This is not to say, however, that comparing $\beta(r)$ values in different circumstances is not of interest. To the contrary, a smaller $\beta(r)$ or larger $\theta(r)$ for one situation relative to another, implies a greater concentration of charge, as we shall describe later.

5. Further Developments

TOWARD A FULL THERMODYNAMIC SYSTEM

The successes of preceding treatment suggest that one might seek a "full" thermodynamic treatment of electrons. That is, one may seek thermodynamic state functionals, intensive local functions and their extensive conjugates, etc., thereby obtaining equations describing the electrons in atoms and molecules that resemble the equations of classical thermodynamics [29, 63].

The fundamental idea behind this "full thermodynamic description" of electrons in atoms and molecules is to regard each point in space, r, as a system with volume dr, pressure $\pi(r)$, number of electrons $\rho(r)$, chemical potential $u(r)$, temperature $\theta(r)$, entropy $\mathfrak{s}(r)$, and energy $e(r)$. In the ground state, of course, $u(r)$, $\theta(r)$, $\mathfrak{s}(r)$, $\pi(r)$, and $e(r)$ are functionals of the electron density. Away from the molecular ground state, however, we may decouple the other functions from $\rho(r)$, thereby defining a more general local energy functional, $e[p, \mathfrak{s}; r]$, which we take here to be a functional of the "extensive" variables of the system: the electron density and entropy density. We define the generalized total energy as the sum of the subsystems' generalized local energy:

$$\mathfrak{E}[\rho, \mathfrak{s}] \equiv \int e[p, \mathfrak{s}; r] \, dr. \quad (98)$$

The total entropy,

$$\mathcal{S}[\mathfrak{s}] \equiv \int \mathfrak{s}(r) \, dr \quad (99)$$

and number of electrons

$$N[\rho] \equiv \int \rho(r) \, dr \quad (100)$$

are defined similarly.

To obtain local thermodynamic equations, we minimize $\mathfrak{E}[\rho, \mathfrak{s}]$ subject to constraints on the electron density and entropy density:

$$\rho(r) = \rho_0(r), \quad (101)$$
$$\mathfrak{s}(r) = \mathfrak{s}_0(r). \quad (102)$$

By analogy to classical thermodynamics, the local temperature and local chemical potential enter as Lagrange multipliers forcing the local entropy, $\mathfrak{s}(r)$, and local particle number, $\rho(r)$, to be correct:

$$\delta\left\{\mathfrak{E}[\rho, \mathfrak{s}] - \int \theta(r)\big(\mathfrak{s}(r) - \mathfrak{s}_0(r)\big) \, dr - \int u(r)\big(\rho(r) \right.$$
$$\left. - \rho_0(r)\big) \, dr\right\} = 0. \quad (103)$$

Thus

$$\left(\frac{\delta\mathfrak{E}[\rho, \mathfrak{s}]}{\delta\mathfrak{s}(r)}\right)_{\substack{\rho(r)=\rho_0(r) \\ \mathfrak{s}(r)=\mathfrak{s}_0(r)}} = \theta(r), \quad (104)$$

$$\left(\frac{\delta\mathfrak{E}[\rho, \mathfrak{s}]}{\delta\rho(r)}\right)_{\substack{\mathfrak{s}(r)=\mathfrak{s}_0(r) \\ \rho(r)=\rho_0(r)}} = u(r). \quad (105)$$

It also would be convenient to assume that the local analog of

$$E = TS - PV + \mu N \quad (106)$$

is given by

$$e[\rho, \mathfrak{s}; r] \equiv \theta(r)\mathfrak{s}(r) - \pi(r) + u(r)\rho(r), \quad (107)$$

from which one may proceed, via the functional Legendre transform, to obtain the whole gamut of "classical looking" local thermodynamic formulas [29, 63].

While this may be formally correct, the practical utility of such arguments is limited unless one can define the quantities entering into Eq. (107) in a consistent way. This is nontrivial. Consider the case where our system is in its ground state, so that $\mathfrak{s}(r)$ is a functional of $\rho(r)$. One then has the definitions

$$e(r) = t(r) + \rho(r)v^{\text{eff}}(r), \quad (108)$$

$$\theta(r) = \frac{2t(r)}{3k\rho(r)}, \quad (109)$$

$$\mathfrak{s}(r) = - \int \mathfrak{f}(r, p) \ln \mathfrak{f}(r, p) \, dp, \quad (110)$$

$$t(\boldsymbol{r}) = \int \frac{p^2}{2} \mathfrak{f}(\boldsymbol{r}, \boldsymbol{p}) \, d\boldsymbol{p}, \tag{111}$$

$$v^{\text{eff}}(\boldsymbol{r}) = v(\boldsymbol{r}) + \frac{1}{2} \left\langle \Psi[\rho] \left| \sum_{i=2}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}|} \right| \Psi[\rho] \right\rangle_{2,3,\ldots,N} . \tag{112}$$

(The phase-space distribution function, $\mathfrak{f}(\boldsymbol{r}, \boldsymbol{p})$, and the Levy constrained-search wave function, $\Psi[\rho]$, are, of course, functionals of the electron density. To make the subsequent argument less abstract, one may wish to consider the Kohn–Sham system $[v^{\text{eff}}(\boldsymbol{r}) = v^{\text{KS}}(\boldsymbol{r})]$ and/or use the approximate expression, Eq. (68), for $\mathfrak{f}(\boldsymbol{r}, \boldsymbol{p})$.) It is not clear that $\mathfrak{E}[\rho, \mathfrak{s}]$ can be chosen in such a way that Eqs. (104) and (108)–(111) are consistent with one another. In addition, take the usual definitions for the local chemical potential [64],

$$u(\boldsymbol{r}) = v^{\text{KS}}(\boldsymbol{r}) - \mu \tag{113}$$

$[\mu = (\partial \mathfrak{E}[\rho, \mathfrak{s}[\rho]] / \partial N)_{v(\boldsymbol{r})}$ is the electronic chemical potential [65]], and the local pressure [66],

$$\pi(\boldsymbol{r}) = -\tfrac{1}{3} \text{Tr} \left[\overset{\leftrightarrow}{\sigma} \right] \tag{114}$$

($\overset{\leftrightarrow}{\sigma}$ is the stress tensor). It seems unlikely that Eqs. (104), (105), and (107) can still be valid. This is at the heart of the local thermodynamic dilemma. One may choose to define the key local functions [Eqs. (108)–(114)] so that the definitions of these functions resemble their classical counterparts. Alternatively, one may opt to relate various local functions to one another with equations that resemble the thermodynamic relations between analogous variables [Eqs. (104)–(107)] in classical thermodynamics. *In general, however, one may not do both.* Taking the view that the state functions, variational principles, etc. are more important to the thermodynamic description that the specific definitions of the variables, we will have the validity of Eqs. (104)–(107) at the expense of potentially losing the physically appealing connections between the local kinetic energy and the temperature [Eq. (109)], the local pressure and the stress tensor [Eq. (114)], and the local chemical potential and the external potential [Eq. (113)]. Within this local thermodynamics, the local temperature enters as a Lagrange multiplier associated with the entropy density [Eq. (103)] and not as an "average kinetic energy" of the electrons [Eq. (109)]. Therefore, Eq. (109) will be valid only if, somewhat fortuitously, it is identical to Eq. (104).

Some flexibility is inherent in local thermodynamic description because we have added a local descriptor, $\mathfrak{s}(\boldsymbol{r})$, that is not necessary to describe electronic ground states. Thus a practical procedure for deriving a local thermodynamic description of atoms and molecules is to take the key relations between the local variables of state, Eqs. (104)–(107), and then exploit the flexibility in the description to satisfy Eqs. (108)–(114) as nearly as possible. Reference [63] uses this procedure to explore local thermodynamic descriptions within the local density approximation: Starting with Eqs. (104)–(107), $\mathfrak{s}(\boldsymbol{r})$ is chosen so that conceptually appealing definitions for the local thermodynamic functions are obtained.

A few of the other subtleties that characterize the "full" local thermodynamic description of electrons in atoms and molecules are as follows:

1. How can one obtain a "thermodynamic" description when, as in most atoms and molecules, the number of electrons is small? The answer is that the statistical nature of "local thermodynamics" results not from the "average over many ensembles" as in classical thermodynamics, but from the inherent probabilistic nature of quantum mechanics [as encapsulated, for instance, in the quasiprobability distribution function for electrons Eq. (11)].

2. The identification of variables as "extensive" and "intensive," so readily done in classical thermodynamics, is nontrivial in the quantum density functional theory analog. [For instance, even within the classical-looking model given above, it is not immediately obvious that the local temperature, Eq. (50), is the "intensive" function and the local entropy, Eq. (72), is the "extensive" function.]

3. The lack of extensive and intensive variables is related to the fact that the quantities arising in the local thermodynamic description are rarely homogeneous. For instance,

$$E(2S, 2N, 2V) = 2E(S, N, V) \tag{115}$$

in local thermodynamics but, in general,

$$\mathfrak{E}\big[2\rho(\boldsymbol{r}), 2\mathfrak{s}(\boldsymbol{r})\big] \neq 2\mathfrak{E}\big[\rho(\boldsymbol{r}), \mathfrak{s}(\boldsymbol{r})\big]. \tag{116}$$

Consider how useful Eq. (116) would be: One could use a 1-electron reference system to compute all the properties of an N-electron system! Given this appeal, one might attempt to use the ambiguities inherent in the additional variable, $\mathfrak{s}(\boldsymbol{r})$, to recover the homogeneities of classical thermodynamics; but the

resulting theory seems to be very complicated and inconsistent with the standard definitions for the local thermodynamic variables [Eqs. (108)–(114)].

4. In a local thermodynamic description, electrons are confined by the external potential (which is the "local" part of the "local chemical potential"). That is, the external potential is the natural analog of the "volume" in a local thermodynamics. Is it certain, then, that the local pressure (which would be the conjugate function to the point-by-point resolution of the volume [66] should be included in Eq. (107)?

LOCAL TEMPERATURE AS A NIGHNESS INDEX

The importance of the local temperature, $\theta(r) \equiv 1/k\beta(r)$, by now should be clear. It measures the kinetic energy of electrons in just the way temperature measures kinetic energy for a classical perfect gas—Eq. (50). However, it also measures the probability of observing two electrons close together. To see this, consider a system where each orbital is doubly occupied. Then the probability of observing one electron at the point $r + s/2$ and another electron at the point $r - s/2$ is given by

$$\rho_2\left(r + \frac{s}{2}; r - \frac{s}{2}\right) \equiv \rho\left(r + \frac{s}{2}\right)\rho\left(r - \frac{s}{2}\right)$$
$$- \frac{\left|\gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right|^2}{2}. \quad (117)$$

The quantity $\frac{1}{2}|\gamma(r + s/2; r - s/2)|^2$ represents the interdependence of electrons; that is, $\frac{1}{2}|\gamma(r+s/2; r - s/2)|^2$ is the correction to the "totally independent electron approximation"

$$\rho_2\left(r + \frac{s}{2}; r - \frac{s}{2}\right) \equiv \rho\left(r + \frac{s}{2}\right)\rho\left(r - \frac{s}{2}\right). \quad (118)$$

Indeed, $\frac{1}{2}|\gamma(r + s/2; r - s/2)|^2$ is simply

$$\frac{1}{2}\left|\gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right|^2 \equiv -\rho\left(r + \frac{s}{2}\right)\rho\left(r - \frac{s}{2}\right)$$
$$\times h_x\left(r + \frac{s}{2}; r - \frac{s}{2}\right), \quad (119)$$

where $h_x(r + s/2; r - s/2)$ is the Fermi hole correlation function. [The use of a Slater determinant wave function, implicit in Eq. (117), indicates that the Coulomb hole is everywhere zero in this model.]

The spherical average of $\frac{1}{2}|\gamma(r + s/2; r - s/2)|^2$,

$$\gamma^2[r; s] \equiv \frac{1}{8\pi} \int \left|\gamma\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right|^2 d\Omega_s$$
$$\equiv \frac{\rho^2(r)\Gamma^2(r, s)}{2}, \quad (120)$$

then, provides a distribution function for the characteristic "correlation" or "interdependence" length between pairs of electrons with center of mass at r. That is, $\gamma^2(r, s)$ represents the probability that a pair of electrons has center of mass r and characteristic correlation length s. Thus, from Bayes's theorem, the probability distribution function for the correlation length is $\gamma^2(r, s)$ divided by the probability that the center of mass is at r, $P_{COM}(r)$. Combining the approximation,

$$P_{COM}(r) \equiv \rho(r), \quad (121)$$

with the Gaussian approximation to $\Gamma(r, s)$, Eq. (75), gives

$$\frac{\gamma^2(r, s)}{P_{COM}(r)} \equiv \frac{\rho^2(r)\Gamma(r, s)}{2P_{COM}(r)} \approx \frac{\rho^2(r)\Gamma(r, s)}{2\rho(r)} \approx \frac{\rho(r)}{2}e^{-s^2/\beta(r)}$$
$$(122)$$

as a probability distribution function for the characteristic electron correlation length, s. Then the expected value of the correlation length is given by

$$\langle s \rangle \equiv \int_0^\infty s\left(\rho(r)e^{-s^2/\beta(r)}\right)4\pi s^2 \, ds$$
$$= \pi\rho(r)\beta^2(r) = \frac{\pi\rho(r)}{k^2\theta^2(r)}. \quad (123)$$

That the average correlation length should decrease as the temperature increases should be unsurprising, following, as it does, from the identification of $\sqrt{\beta(r)}$ as the spread of the Gaussian distribution in Eq. (122).

We conclude that, for a given density, $\rho(r)$, high local temperature is associated with short correlation lengths and hence strongly correlated electrons. Thus the local temperature represents the average "packedness" or "chumminess" of an electron pair as it varies from point to point in an electronic system. We dub it the "nighness" index. The local temperature measures nighness!

There is an ambiguity in the preceding interpretation because the local temperature is, of course, a functional of the electron density. We may remove the ambiguity by normalizing the distribution of

correlation lengths with respect to s. Forcing the normalization constraint,

$$\int \mathcal{N} \cdot \rho(r)e^{-s^2/\beta(r)}\, dr \equiv 1, \qquad (124)$$

gives the normalized correlation length distribution

$$\mathcal{N} \cdot \rho(r)e^{-s^2/\beta(r)} = \frac{2}{\sqrt{\pi \cdot \beta^3(r)}}e^{-s^2/\beta(r)}. \qquad (125)$$

The expectation value for the correlation length is then given by

$$\langle s \rangle = \sqrt{\frac{\beta(r)}{\pi}} = \sqrt{\frac{1}{k\pi}} \cdot \theta^{-1/2}(r). \qquad (126)$$

Once again, we recognize that expected correlation length between electrons decreases as the temperature increases, confirming the assertion that the characteristic interelectronic separation of electrons with center of mass r is inversely related to the local temperature, $\theta(r)$.

Recall that the neglect of the Coulomb hole is implicit in Eq. (117). In this model, electrons with different spins move independently of one another,

$$\rho_2^{\alpha\beta}\left(r + \frac{s}{2}; r - \frac{s}{2}\right) \equiv \rho^\alpha\left(r + \frac{s}{2}\right)\rho^\beta\left(r - \frac{s}{2}\right), \quad (127)$$

while same-spin electrons are correlated by the Pauli exclusion principle,

$$\rho_2^{\alpha\alpha}\left(r + \frac{s}{2}; r - \frac{s}{2}\right) \equiv \rho^\alpha\left(r + \frac{s}{2}\right)\rho^\alpha\left(r - \frac{s}{2}\right) \\ - \left|\gamma^{\alpha\alpha}\left(r + \frac{s}{2}; r - \frac{s}{2}\right)\right|^2. \quad (128)$$

Here,

$$\gamma^{\alpha\alpha}(r; r') \equiv \sum_{i=1}^{N/2} \phi_{i,\alpha}^{\text{KS}}(r)\phi_{i,\alpha}^{\text{KS}}(r') = \frac{\gamma(r,r')}{2} \qquad (129)$$

denotes the α-spin part of the Kohn–Sham density matrix, which is obtained by summing over only the α-spin Kohn–Sham orbitals and $\rho^\alpha(r) = \gamma^{\alpha\alpha}(r,r)$. It is clear from Eq. (128) that the entire analysis of Eqs. (117)–(126) is easily transferred to spin-resolved pair density, from which it follows that $\theta(r)$ is an indicator of the average "correlation length" between electrons of the same spin with center of mass r. In particular, the local temperature reflects the effects of the Pauli exclusion principle on the electron pairs with center of mass r. This suggests that the local temperature may play a key role in qualitative studies of molecular electronic structure and bonding.

LOCAL TEMPERATURE AS THE SOLE INGREDIENT IN ELECTRON LOCALIZATION FUNCTIONS

For some time, a number of authors have been using analysis similar to that of the previous section to derive prescriptions for identifying regions within an atom or molecule where electron pairs pile up; such indicators are called electron localization functions (ELFs) [67–71]. One may deduce from Eq. (123) that there should be a capable indicator of electron localization based upon the local temperature. Indeed, a recent computational study has explored the link between local thermodynamics and electron localization [72].

Typically, however, it not as interesting to find which electron pairs are most localized (the core orbitals are always the most localized!) as it is to find the regions of a molecule where electrons are "especially" localized (relative to some suitable reference). Based on Eq. (123), we anticipate that

$$\frac{\theta_{\text{ref}}(r)}{\theta(r)} \gtrsim 1 \qquad (130)$$

and

$$\frac{\theta_{\text{ref}}(r)}{\theta(r)} - \frac{\theta(r)}{\theta_{\text{ref}}(r)} = \frac{\theta_{\text{ref}}^2(r) - \theta^2(r)}{\theta_{\text{ref}}(r) \cdot \theta(r)} \gtrsim 0 \qquad (131)$$

are associated with regions where electrons are relatively localized. For the purposes of generating plots, it is useful to map the range of Eq. (130) or (131) onto a finite interval. Using the transformation of Schmider and Becke, Eq. (130) becomes [68]

$$\nu(r) \equiv \frac{\frac{\theta_{\text{ref}}(r)}{\theta(r)}}{1 + \frac{\theta_{\text{ref}}(r)}{\theta(r)}}. \qquad (132)$$

One has $0 \leq \nu(r) \leq 1$ and one may associate $\nu(r) \gtrsim \frac{1}{2}$ with regions of high electron localization. In practice, the present authors find that the more symmetric formula [based on Eq. (131)],

$$\kappa(r) \equiv \tanh\left(\frac{\theta_{\text{ref}}^2(r) - \theta^2(r)}{\theta_{\text{ref}}(r) \cdot \theta(r)}\right), \qquad (133)$$

provides less ambiguous figures than $\nu(r)$.

For the reference temperature one commonly uses the local temperature from the uniform electron gas with density $\rho(r)$, Eq. (74). With this choice of reference, $\nu(r)$ reduces to the electron localization measure of Schmider and Becke [68].

Since atoms and molecules are poorly described by the electron gas functionals, we anticipate that, for exploring the valence electron structure of molecules, it will be better to compare the nighness map

for the molecule with the nighness map of the superposed undistorted atoms

$$\theta_{\text{ref}}(\boldsymbol{r}) = \sum_{\text{atoms}} \theta_\alpha(\boldsymbol{r}). \qquad (134)$$

Such a reference has the added benefit of only differing substantially from the true $\theta(\boldsymbol{r})$ in valence regions of the molecule, thus potentially generating less cluttered plots.

6. Conclusion

SUMMARY

What emerges is that the "electron gas" in a ground-state atom or molecule is surprisingly ideal-gas like and well described by Boltzmann statistics, cf. Eq. (69). The controlling potential is the Kohn–Sham effective potential of the quantum theory, and the local temperature, $\theta(\boldsymbol{r})$, is a local resolution of the Kohn–Sham kinetic energy. For some time, $\beta(\boldsymbol{r})$ has been appearing in suggested forms of density functional energy components; we encourage such continued use. The local kinetic energy should be defined in the classic $\nabla\Psi \cdot \nabla\Psi$ way.

Starting from the exact DFT, the key to reaching the Maxwell–Boltzmann or "Gaussian" model is to concentrate on the Taylor series expansion for the spherical averaged square of the first-order density matrix, Eq. (85), in terms of the interelectron distance s. Approximating it in the Thomas–Fermi–Dirac manner leads to the uniform electron gas formulation. More accurate, however, is a Gaussian resummation with the same first two terms. The Gaussian model of Lee and Parr results; this has been shown to give good results and admits of systematic improvement.

Precisely the same Gaussian model may be derived from information theory: maximize

$$\mathcal{S}[\mathfrak{f}] = -k \int\int \mathfrak{f}(\boldsymbol{r}; \boldsymbol{p}) \ln \mathfrak{f}(\boldsymbol{r}; \boldsymbol{p}) \, d\boldsymbol{r} \, d\boldsymbol{p}$$

to find the least biased phase-space distribution function that gives the correct electron density and the correct local kinetic energy density. For the special case where $\beta(\boldsymbol{r})$ is a function of $\rho(\boldsymbol{r})$, a Sackur–Tetrode equation for $S[\rho]$ is recovered.

The Gaussian model also plays a role in the identification of the local temperature as a "nighness" indicator for an electron pair, measuring the "compactness" of the exchange hole. From this, the standard electron localization functions follow.

SUGGESTIONS FOR FUTURE RESEARCH

This subject of research is quite open-ended, with many aspects yet to be clarified, and many things yet to be done. For example, it should pay to work in the following problem areas:

1. **Local kinetic energy density.** Several questions were raised concerning the appropriateness of Eq. (32) as the definition for the local kinetic energy density. Most important is to establish whether or not there exists a nonnegative quasiprobability distribution function with local kinetic energy given by Eq. (32).

2. **Non-ideal-gas correction.** The Boltzmann gas working so well, one hopes that the corrections for nonideality could be generated in ways similar to those employed in the statistical mechanics of macroscopic real gasses. DFT work in this direction has already begun [29, 30].

3. **DFT reactivity principles in thermodynamic language.** One should try to restate known (or new) DFT reactivity principles (e.g., the maximum global hardness principle [73–76] or the site reactivity preference principle [77–79]) in purely thermodynamic language [72].

4. **The quantity $\nabla^2\rho(\boldsymbol{r})$.** This quantity appears to be hard to understand in simple physical terms, especially "thermodynamic" terms, and one needs to understand it better. See, however, the discussion of Bader [17]. Also note the importance of $\nabla^2\rho(\boldsymbol{r})$ as an ingredient in the analysis of chemical reactivity by Tachibana [80–82].

5. **Prototype purely classical problem.** How do the exact mechanics, thermodynamics, and statistical mechanics for some simple model system behave. Even a two-dimensional problem would be instructive, for example, a plateful of particles held on the plate by harmonic attraction to the center, with a temperature gradient imposed.

6. **Bifunctional ρ, β theory.** Can we construct a method in which the original Hohenberg–Kohn theory, which is a method for determining $\rho(\boldsymbol{r})$ and $E[\rho]$ by solving one Euler equation, is replaced by a method for determining $\rho(\boldsymbol{r})$ and $\beta(\boldsymbol{r})$ and $E[\rho, \beta]$ by solving two equations (with workable boundary conditions). It would be permissible to include in the method the ZMP method for determining

$\beta(r)$ from $\rho(r)$, but the Kohn–Sham method would not appear otherwise.

7. **A full thermodinamic description.** One should continue to try to cast a bifunctional theory so that it resembles thermodynamics, in which $\rho(r)$ and $\beta(r)$ are the "state variables" and some "free energy" is the state function [29, 62, 63]. That such theories exist follows from the fact we are adding to the density functional theory a superfluous variable, $\beta(r)$. But how does one construct a theory of this type that is internally consistent, has equations which resemble the classical theory insofar as possible, and recovers the appropriate thermodynamic limits (of which the most important are the large particle number ($N \rightarrow \infty$) and the classical ($\hbar \rightarrow \infty$) limits)?

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References

1. Parr, R. G.; Yang, W. Density-Functional Theory of Atoms and Molecules; Oxford University Press: New York, 1989.
2. Hohenberg, P.; Kohn, W. Phys Rev 1964, 136, B864–B871.
3. Mermin, N. D. Phys Rev 1965, 137, A1441–A1443.
4. Wigner, E. Phys Rev 1932, 40, 749.
5. Cohen, L. J Math Phys 1966, 7, 781.
6. Cohen, L. Time-Frequency Analysis; Prentice Hall Upper Saddle River: NJ, 1995.
7. Dahl, J. P. Theor Chim Acta 1992, 81, 329.
8. Springborg, M.; Dahl, J. P. In Local Density Approximations in Quantum Chem. and Solid State Phys.; Dahl, J. P.; Avery, J., Eds.; Plenum: 1984; pp. 381–412.
9. Wigner, E. P. In Perspectives in Quantum Theory; Yourgrau, W.; van der Merwe, A., Eds.; MIT: Cambridge, 1971; pp. 25–36.
10. Cohen, L.; Zaparovanny, Y. I. J Math Phys 1980, 21, 794.
11. Groblicki, R. J Math Phys 1983, 24, 841.
12. Loughlin, P. J.; Atlas, L. E.; Pitton, J. W. IEEE Trans Signal Process 1994, 42, 2697.
13. Pitton, J. W. Multidimen Syst Signal Process 1998, 9, 439.
14. Cohen, L. J Chem Phys 1984, 80, 4277.
15. Cohen, L. J Chem Phys 1979, 70, 788.
16. Cohen, L.; Lee, C. Found Phys 1987, 17, 561.
17. Bader, R. F. W. Atoms in Molecules: A Quantum Theory; Clarendon: Oxford, 1990.
18. Bader, R. F. W.; Preston, H. J. T. Int J Quantum Chem 1969, 3, 327.
19. Ghosh, S. K.; Berkowitz, M.; Parr, R. G. Proc Natl Acad Sci USA 1984, 81, 8028.
20. Stuart, A.; Ord, J. K. Kendall's Advanced Theory of Statistics, Vol. 1, Distribution Theory; Halsted: New York, 1994.
21. Berkowitz, M. Chem Phys Lett 1986, 129, 486.
22. Yang, Z. Z.; Liu, S. B.; Wang, Y. A. Chem Phys Lett 1996, 258, 30.
23. Nagy, A.; Liu, S. B.; Parr, R. G. Phys Rev A 1999, 59, 3349.
24. Levy, M.; Perdew, J. P. NATO ASI Ser Ser B 1985, 123, 11.
25. Levy, M. Proc Natl Acad Sci USA 1979, 76, 6062.
26. Kohn, W.; Sham, L. J. Phys Rev 1965, 140, A1133–A1138.
27. Zhao, Q.; Parr, R. G. J Chem Phys 1993, 98, 543.
28. Zhao, Q.; Morrison, R. C.; Parr, R. G. Phys Rev A 1994, 50, 2138.
29. Nagy, A.; Parr, R. G. THEOCHEM 2000, 501, 101.
30. Robles, J. J Chem Phys 1986, 85, 7245.
31. Ghosh, S. K.; Berkowitz, M. J Chem Phys 1985, 83, 2976.
32. Nagy, A.; Parr, R. G. Phys Rev A 1990, 42, 201.
33. Politzer, P.; Abu-Awwad, F.; Murray, J. S. Int J Quantum Chem 1998, 69, 607.
34. Brinck, T.; Murray, J. S.; Politzer, P. Int J Quantum Chem 1993, 48, 73.
35. Politzer, P.; Murray, J. S.; Grice, M. E.; Brinck, T.; Ranganathan, S. J Chem Phys 1991, 95, 6699.
36. Murray, J. S.; Seminario, J. M.; Politzer, P.; Sjoberg, P. Int J Qantum Chem 1990, 645.
37. Sjoberg, P.; Murray, J. S.; Brinck, T.; Politzer, P. Canadian J Chem Rev Canadienne Chimie 1990, 68, 1440.
38. Koopmans, T. Physica 1934, 1, 104.
39. Janak, J. F. Phys Rev B 1978, 18, 7165.
40. Gal, T.; Nagy, A. Mol Phys 1997, 91, 873.
41. Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, Jr., J. L. Phys Rev Lett 1982, 49, 1691.
42. Almbladh, C. O.; von Barth, U. Phys Rev B 1985, 31, 3231.
43. Nagy, A.; Parr, R. G. Int J Quantum Chem 1996, 58, 323.
44. Parr, R. G.; Rupnik, K.; Ghosh, S. K. Phys Rev Lett 1986, 56, 1555.

45. Maximoff, S. N.; Scuseria, G. E. J Chem Phys 2001, 114, 10591.
46. Ghosh, S. K.; Parr, R. G. Phys Rev A 1986, 34, 785.
47. Lee, C.; Parr, R. G. Phys Rev A 1987, 35, 2377.
48. Colle, R.; Salvetti, O. Theor Chim Acta 1975, 37, 329.
49. Lee, C.; Yang, W.; Parr, R. G. Phys Rev B 1988, 37, 785.
50. Thomas, L. H. Prod Camb Phil Soc 1927, 23, 542.
51. Fermi, E. Z Phys 1928, 48, 73.
52. Dirac, P. A. M. Proc Cambridge Phil Soc 1930, 26, 376.
53. Nagy, A.; Parr, R. G.; Liu, S. B. Phys Rev A 1996, 53, 3117.
54. Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. Phys Rev Lett 1999, 82, 5179.
55. Becke, A. D. Int J Quantum Chem 1994, 625.
56. Becke, A. D. J Comput Chem 1999, 20, 63.
57. Schmider, H. L.; Becke, A. D. J Chem Phys 1998, 109, 8188.
58. Van Voorhis, T.; Scuseria, G. E. J Chem Phys 1998, 109, 400.
59. Van Voorhis, T.; Scuseria, G. E. Mol Phys 1997, 92, 601.
60. Koehl, R. M.; Odom, G. K.; Scuseria, G. E. Mol Phys 1996, 87, 835.
61. Becke, A. D. Int J Quantum Chem 1983, 23, 1915.
62. Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. Phys Rev Lett 1999, 82, 2544.
63. Nagy, A.; Parr, R. G. Proc Ind Acad Sci 1994, 106, 217.
64. Berkowitz, M.; Parr, R. G. J Chem Phys 1988, 88, 2554.
65. Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. J Chem Phys 1978, 68, 3801.
66. Bartolotti, L. J.; Parr, R. G. J Chem Phys 1980, 72, 1593.
67. Chattaraj, P. K.; Chamorro, E.; Fuentealba, P. Chem Phys Lett 1999, 314, 114.
68. Schmider, H. L.; Becke, A. D. THEOCHEM 2000, 527, 51.
69. Becke, A. D.; Savin, A.; Stoll, H. Theor Chim Acta 1995, 91, 147.
70. Savin, A.; Nesper, R.; Wengert, S.; Fassler, T. F. Angew Chem Int Ed Engl 1997, 36, 1809.
71. Becke, A. D.; Edgecombe, K. E. J Chem Phys 1990, 92, 5397.
72. Chattaraj, P. K.; Chamorro, E.; Fuentealba, P. Chem Phys Lett 1999, 314, 114.
73. Ayers, P. W.; Parr, R. G. J Am Chem Soc 2000, 122, 2010.
74. Pearson, R. G. J Chem Educ 1999, 76, 267.
75. Pearson, R. G. Acc Chem Res 1993, 26, 250.
76. Pearson, R. G. J Chem Educ 1987, 64, 561.
77. Yang, W.; Parr, R. G. Proc Natl Acad Sci USA 1985, 82, 6723.
78. Parr, R. G.; Yang, W. J Am Chem Soc 1984, 106, 4049.
79. Ayers, P. W.; Levy, M. Theor Chem Acc 2000, 103, 353.
80. Tachibana, A. J Chem Phys 2000, 115, 3497.
81. Tachibana, A. Theor Chem Acc 1999, 102, 188.
82. Tachibana, A. In Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of Prof. Robert G. Parr; Sem, K. D., Ed.; World Scientific, Singapore, in press.