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Chemistry

Transcription of ground-state density-functional theory into a local thermodynamics

(local temperature/entropy/electronic structure)

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ABSTRACT The concepts of local temperature, local entropy, and local free energy density are introduced within the framework of the ground-state density-functional theory of many-electron systems, and a complete local thermodynamic picture is then developed. A view emerges of the electron cloud, as analogous to a classical inhomogeneous fluid moving under gradients of temperature, pressure, and an effective potential, described by a locally Maxwellian distribution.

Density functional theory (1, 2) provides a way to characterize a nonhomogeneous many-electron system in terms of the electron density and through its connection with quantum hydrodynamics (3) permits one to view an electron cloud as a fluid in three-dimensional space. From this picture, one can obtain much physical insight through the study of local behavior rather than global quantities such as the total internal energy. However, although the total energy is determined uniquely by the electron density, the nonlocal nature of the energy functional prevents the density at a particular point from providing a complete characterization of the electron fluid at that point. To obtain a local description of a quantum system, it therefore is necessary to introduce certain other local ($\vec{r}$-dependent) quantities. In the present work, we define, within the ground-state density-functional framework, several local quantities of thermodynamic-like character. We thereby provide a macroscopic thermodynamic language for describing the behavior of the microscopic electron fluid. In view of the nonuniformity of the electron cloud and the nonhomogeneity of microscopic energy functionals, one-to-one correspondence with macroscopic thermodynamics is, however, not expected.

Completing this thermodynamic description is motivated by various successes of such macroscopic concepts in providing a better understanding of microscopic chemical phenomena. Thus we have the chemical potential (4) (as equivalent with the electronegativity concept of chemistry), the hardness of a species (5), and frontier reactivity indices (6, 7). We also have the formulation of density-functional analogs of the Gibbs–Duhem equation (4) and Maxwell's relations (8) of classical thermodynamics.

In what follows, we introduce the concept of a local temperature corresponding to the electronic motion and also an entropy associated with the electron distribution. We then maximize this entropy to obtain a unique distribution function in phase space. Finally, we recover some thermodynamic equations and identify Gibbs free energy. This provides us with a consistent local thermodynamic description of the microscopic system.

Theory

We consider a system of N electrons moving under the influence of an external potential $v(\vec{r})$. Following Kohn and Sham (9), the ground-state energy $E[\rho]$, a unique functional of the density $\rho(\vec{r})$, can be written as a sum of kinetic (noninteracting) energy (T_s) and potential energy (E_{pot}) contributions,

$$E[\rho] = T_s[\rho] + E_{pot}[\rho]. \quad [1]$$

The corresponding energy densities, although not unique, are defined so as to lead to the global quantities on integration:

$$\varepsilon(\vec{r}, \rho) = t_s(\vec{r}, \rho) + \varepsilon_{pot}(\vec{r}, \rho), \quad [2]$$

where $E[\rho] = \int \varepsilon(\vec{r}, \rho) d\vec{r}$. This picture of the system has N noninteracting quantum particles moving in an effective potential $v_{ks}(\vec{r}, \rho)$ given by $v_{ks} = \delta E_{pot}[\rho]/\delta\rho$. It entails no approximations whatsoever.

We consider the various density functionals to be results of ensemble averages over the dynamical variables. Hence, to each element of the continuous probability fluid we associate a distribution function $f(\vec{r}, \vec{p})$ in phase space that satisfies the following properties:

$$\rho(\vec{r}) = \int d\vec{p} f(\vec{r}, \vec{p}); \int d\vec{r} \rho(\vec{r}) = N; \quad [3]$$

$$t_s(\vec{r}, \rho) = \int d\vec{p} \frac{p^2}{2} f(\vec{r}, \vec{p}); \quad [4]$$

$$\varepsilon(\vec{r}, \rho) = \int d\vec{p} f(\vec{r}, \vec{p}) \left[\frac{p^2}{2} + v_{pot}(\vec{r}, \rho)\right]. \quad [5]$$

Density functional theory permits one to express $v_{pot}(\vec{r}, \rho)$ solely in terms of $\rho(\vec{r})$ [and $v(\vec{r})$]. The function $f(\vec{r}, \vec{p})$ should also give the current density, $\vec{j}(\vec{r}) = \int d\vec{p}\, \vec{p}\, f(\vec{r}, \vec{p})$. This vanishes for the ground state, but would be of interest for the treatment of excited states and time-dependent phenomena.

The most general form of such a distribution function can be written, following Cohen (10, 11), in terms of the Kohn–Sham orbitals ψ_j. Thus

$$f(\vec{r}, \vec{p}) = A \sum_{j=1}^{N} \int \exp[-i\vec{\theta}\cdot\vec{r} - i\vec{\tau}\cdot\vec{p} + i\vec{\theta}\cdot\vec{u}] g(\vec{\theta}, \vec{\tau}) \psi_j^*\left(\vec{u} - \frac{1}{2}\vec{\tau}\right)\psi_j\left(\vec{u} + \frac{1}{2}\vec{\tau}\right) d\vec{\theta}\, d\vec{\tau}\, d\vec{u}, \quad [6]$$

where A is a constant and $g(\vec{\theta}, \vec{\tau})$ is any function satisfying $g(0, \vec{\tau}) = g(\vec{\theta}, 0) = 1$. The marginal conditions of Eqs. 3–5 thus do not define $f(\vec{r}, \vec{p})$ uniquely; choice of different suitable $g(\vec{\theta}, \vec{\tau})$ generates different positive $f(\vec{r}, \vec{p})$. Here selection of a convenient $f(\vec{r}, \vec{p})$ is achieved through imposing the criterion of maximum entropy.

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We define an entropy density and entropy in terms of $f(\vec{r}, \vec{p})$,

$$s(\vec{r}) = -k\int d\vec{p}f[\ln f - 1]; \; S = \int d\vec{r}s(\vec{r}), \qquad [7]$$

and obtain the most probable distribution by maximizing this functional subject to the constraints of correct density (Eq. **3**) and correct kinetic energy density (Eq. **4**). Thus,

$$f(\vec{r}, \vec{p}) = e^{-\alpha(\vec{r})}e^{-\beta(\vec{r})p^2/2}, \qquad [8]$$

where $\alpha(\vec{r})$ and $\beta(\vec{r})$ are $\vec{r}$-dependent Lagrange multipliers. We now define a local temperature $T(\vec{r})$ in terms of the kinetic energy density, by equating the latter to the ideal gas expression for kinetic energy,

$$t_s(\vec{r}, \rho) = \frac{3}{2}\rho(\vec{r})kT(\vec{r}), \qquad [9]$$

where k is the Boltzmann constant.

On substituting Eq. **8** in Eqs. **3** and **4**, we find

$$\beta(\vec{r}) = \frac{1}{kT(\vec{r})} \qquad [10]$$

and

$$f(\vec{r}, \vec{p}) = \lambda(\vec{r})^3\rho(\vec{r})e^{-p^2/2kT(\vec{r})} \qquad [11]$$

with

$$\rho(\vec{r}) = \lambda(\vec{r})^{-3}e^{-[v_{\text{eff}}(\vec{r},\rho)-\mu]/kT(\vec{r})}, \qquad [12]$$

where we have the chemical potential $\mu = -\alpha(\vec{r})/\beta(\vec{r}) + v_{\text{eff}}(\vec{r}, \rho)$ and $\lambda(\vec{r}) = [2\pi kT(\vec{r})]^{-1/2}$. Eq. **8** thus takes the more familiar form

$$f(\vec{r}, \vec{p}) = e^{\mu/kT}\,e^{-[(p^2/2)+v_{\text{eff}}]/kT}. \qquad [13]$$

Eq. **12** may be written more compactly

$$\rho(\vec{r}) = \rho_0(\vec{r})e^{-v_{\text{eff}}(\vec{r})/kT(\vec{r})}. \qquad [14]$$

The forms of the distribution functions indicate that the fluid system is characterized by a local Maxwell-Boltzmann distribution law.

Substituting Eq. **11** into Eq. **7**, we obtain the entropy density

$$\begin{aligned} s(\vec{r}) &= -k\rho(\ln(\lambda^3\rho) - 1) + \frac{3}{2}k\rho \\ &= -k\rho\ln\rho + \frac{3}{2}k\rho\ln T + \frac{1}{2}k\rho[5 + 3\ln(2\pi k)]. \end{aligned} \qquad [15]$$

Eq. **15** is a Sackur–Tetrode equation and can also be written as

$$s(\vec{r}) = \frac{3}{2}k\rho[c + \ln(t_s/t_0)], \qquad [16]$$

where t_0 is the Thomas–Fermi kinetic energy density and c is a constant.

Eq. **12** leads to the chemical potential

$$\mu = kT(\vec{r})\ln(\lambda^3\rho) + v_{\text{eff}}(\vec{r}, \rho), \qquad [17]$$

which can be compared with the corresponding Kohn–Sham expression

$$\mu = v_{\text{ks}}(\vec{r}, \rho) + v_{\text{q}}(\vec{r}, \rho), \qquad [18]$$

where $v_q(\vec{r}, \rho)$ ($\equiv \delta T_s/\delta\rho$) is the density-functional version of the quantum potential introduced by Bohm (12, 13). The term $kT\ln(\lambda^3\rho)$ in Eq. **17** is the intrinsic chemical potential (14) of a system of noninteracting classical particles.

Thus we have two equally valid pictures of an interacting quantum system of interest having chemical potential μ and density ρ: a noninteracting quantum system moving in a potential v_{ks} or a noninteracting classical system moving in the different potential v_{eff} with the local temperature $T(\vec{r})$. The two potentials are related by a quantum correction,

$$v_{\text{eff}} = v_{\text{ks}} + (v_{\text{q}} - kT\ln(\lambda^3\rho)). \qquad [19]$$

We now turn our attention to the local pressure. The concept of a local pressure in a quantum system has been discussed by a number of authors (15–19). The definitions mainly differ in the choice of different energy components for the purpose. We here employ the Kohn–Sham noninteracting kinetic energy functional for defining a local pressure. First we introduce a stress tensor through the relation

$$\nabla\cdot\overleftrightarrow{\sigma} = -\rho\nabla\frac{\delta T_s}{\delta\rho} \qquad [20]$$

and then define pressure by

$$p_s = -\frac{1}{3}\operatorname{tr}\overleftrightarrow{\sigma}. \qquad [21]$$

Employing the following form of the single-particle kinetic energy density (20),

$$t_s = \sum_i \frac{1}{8}\frac{\nabla\rho_i\cdot\nabla\rho_i}{\rho_i} - \frac{1}{8}\nabla^2\rho, \qquad [22]$$

where ρ_i are the Kohn–Sham orbital densities, the expression for pressure becomes

$$p_s = \rho kT. \qquad [23]$$

This pressure can thus be called kinetic pressure and Eq. **23** is analogous to the ideal gas law.

Due to lack of simple homogeneity in them, energy density functionals can be obtained from the corresponding potentials (functional derivatives) only through a functional integration with respect to the density (and not by simple multiplication by it). Characterizing the integration path by a single parameter α—i.e., choosing $\rho_\alpha \equiv \rho(\vec{r}, \alpha) = \alpha\rho(\vec{r})$ and varying α from 0 to 1—one can write (14, 21)

$$\varepsilon_{\text{pot}}(\vec{r}, \rho) = \int_0^1 d\alpha\rho(\vec{r})v_{\text{ks}}(r; \rho_\alpha). \qquad [24]$$

Using Eq. **18**, this simplifies to

$$\varepsilon_{\text{pot}}(\vec{r}, \rho) = \rho(\vec{r})\left[\int_0^1 \mu[\rho_\alpha]d\alpha - v_q\right], \qquad [25]$$

where from Eq. **22**, in terms of orbital energies ε_i,

$$\begin{aligned} v_q &= \frac{1}{\rho}\left[\frac{1}{8}\sum_i \frac{\nabla\rho_i\cdot\nabla\rho_i}{\rho_i} - \frac{1}{4}\nabla^2\rho\right] - \frac{1}{\rho}\left[\sum_i \varepsilon_i\rho_i - \mu\rho\right] \\ &= \frac{3}{2}kT - \frac{1}{8}\frac{\nabla^2\rho}{\rho} - \frac{1}{\rho}\left[\sum_i \varepsilon_i\rho_i - \mu\rho\right]. \end{aligned} \qquad [26]$$

The energy density $\varepsilon(\vec{r})$ can be obtained from Eqs. **2**, **9**, and **25**. With the help of Eqs. **15** and **23**, this leads to

$$\varepsilon(\vec{r}) - T(\vec{r})s(\vec{r}) + p_s(\vec{r}) = \rho(\vec{r}) \int_0^1 \mu[\rho_\alpha]d\alpha + \rho(\vec{r})[kT \ln(\lambda^3\rho) - v_q]. \qquad [27]$$

The whole right-hand side of Eq. **27** is the Gibbs free energy density $g(\vec{r})$.

As in corresponding macroscopic cases (21–23), the local thermodynamics that characterizes nonuniform microscopic electronic systems is thus described in terms of the field quantities $T(\vec{r})$, $p_s(\vec{r})$, $v_{eff}(\vec{r})$ [or $v_q(\vec{r})$], and μ.

As an example, consider the ground state of the hydrogen atom. Eq. **22** becomes

$$t_s(r, \rho) = \frac{1}{8}\frac{\nabla\rho\cdot\nabla\rho}{\rho} - \frac{1}{8}\nabla^2\rho \qquad [28]$$

and one readily finds from Eq. **9**

$$T(r) = Z/3kr. \qquad [29]$$

The local temperature is very high near the nucleus, consistent with the requirement of very high velocity to prevent collapse to the nucleus.

Discussion

Definitions of the local quantities are not always unique. In particular, there is a certain arbitrariness in the choice of the coefficient in the Laplacian term in Eq. **22**. Although this term does not contribute to the total kinetic energy, it is this term that brings interesting quantum effects to the kinetic energy density (24) and hence the local temperature. We strongly prefer the coefficient ⅛, however, which corresponds to the definition (20)

$$t_s = -\frac{1}{2}\nabla_s^2\rho_1\left(\vec{r} + \frac{\vec{s}}{2}; \vec{r} - \frac{\vec{s}}{2}\right)\bigg|_{s\to 0}. \qquad [30]$$

The resulting kinetic energy density, Eq. **22**, corresponds to the ideal gas law, Eq. **23**, satisfies the local virial theorem for the hydrogen atom, and leads to a local temperature that vanishes at large distance for any atom (25). And, very importantly, it appears to give a local temperature that is everywhere positive for every atom, which we have not rigorously proved but which we have verified by numerical tests with Hartree–Fock densities for many atoms.

Reminiscent of the kinetic temperature earlier defined by Born and Green (26) and Mazo and Kirkwood (27) for liquids, the local temperature we have here defined is an internal, microscopic, kinetic, or quantum temperature. It is different from the external temperature, which is zero for the ground state. The finite-temperature density-functional theory proposed by Mermin (28), in contrast, corresponds to nonzero external temperature.

The total global entropy, as determined by summing over the whole system of the entropy density of Eq. **15**, does not have the value zero one usually associates with a quantum-mechanical pure state. Our entropy is not the entropy associated with the energy distribution, however, but the microscopic entropy associated with the density distribution ρ. Eq. **16** shows an interesting connection of the entropy density with the ratio of the kinetic energy density to its Thomas–Fermi value.

While we have obtained the basic formulas for $T(\vec{r})$, $s(\vec{r})$, and $v_{eff}(\vec{r})$ by starting from a distribution function $f(\vec{r}, \vec{p})$, one could omit all considerations of $f(\vec{r}, \vec{p})$ and merely postulate Eqs. **9**, **15**, and **19**.

This description is analogous to that of an inhomogeneous fluid (gas) of noninteracting classical particles moving in an effective potential v_{eff} (not the Kohn–Sham potential). The distribution of particles at any point is locally Maxwellian, characterized by a local temperature. There is no net current density—a result of movement in all directions. However, the thermal (kinetic) energy is a result of this motion. The temperature, pressure, and effective potential gradients maintained by the density distribution itself generate the steady motion.

Our dynamic picture of stability can be compared with the corresponding static picture of Bohm (12, 13), who explains the stability by a balance of the classical electrostatic forces and a force of quantum origin determined by the density distribution. However, both our local temperature and the Bohm potential are manifestations of an imaginary velocity field defined by Hirschfelder *et al.* (29). There is neither external heat bath to maintain the temperature gradient nor external source to provide the quantum potential—in either picture they are maintained by the density distribution itself.

The local thermodynamic description here developed of an electron fluid may provide new insights into various physical and chemical phenomena. One immediate application is to the problem of chemical binding. The study of chemical binding has traditionally proceeded through the consideration of changes in electron density, kinetic energy density, or forces (30) during molecule formation. However, one can hope that the considerations of free energy density (and other local quantities) would lead to better understanding of the phenomena of chemical binding. The redistribution of electron density during molecule formation may be thought of as the merging of two inhomogeneous fluid drops to form a new inhomogeneous fluid drop. A joint attack using density functional and quantum hydrodynamic considerations may be helpful to develop this picture of chemical binding.

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