

Local temperature in an electronic system

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It is argued that the most appropriate definition of the local temperature $T(\mathbf{r})$ for the ground state of an electronic system is provided by the formula $\frac{3}{2}\rho(\mathbf{r})kT(\mathbf{r}) = \frac{1}{8}\sum_i [(\nabla\rho_i \cdot \nabla\rho_i)/\rho_i]$, where $\rho(\mathbf{r})$ is the total electron density and the ρ_i are Kohn-Sham orbital densities. $T(\mathbf{r})$ is everywhere non-negative. For atoms, $T(\mathbf{r})$ is nearly stepwise constant. $T(\mathbf{r})$ behaves very much like the Politzer average local ionization energy index. Accordingly, $T(\mathbf{r})$ measures reactivity toward attack by an electron-attracting reagent. Exchange energies and Compton profiles are calculated for several atoms using this definition of the local temperature.

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I. INTRODUCTION

In Ref. [1] the local temperature in an electronic system was introduced, and subsequently it has been found to be useful in several connections [2–6]. Here we (a) argue for a particular definition for the temperature (for which there are options), (b) verify by calculations that the local temperature is nearly piecewise constant in an atom (in agreement with early findings of Ghosh and Balbás [7]), (c) determine the local temperature at the boundary of an atom or molecule and show that it measures chemical reactivity in the same sense as does the Politzer average local ionization energy index [8], and (d) compute exchange energies and Compton profiles for several atoms using this local temperature definition.

II. DEFINITION OF LOCAL TEMPERATURE

The local temperature $kT(\mathbf{r})$ is naturally defined as two-thirds of the Kohn-Sham kinetic energy per electron at each point in space,

$$E_{\text{kin}} = \int t(\mathbf{r}) d\mathbf{r} = \frac{3}{2} \int \rho(\mathbf{r}) kT(\mathbf{r}) d\mathbf{r}, \quad (1)$$

where $\rho(\mathbf{r})$ is the electron density. Ambiguity arises in the definition of $T(\mathbf{r})$ because of ambiguity in $t(\mathbf{r})$. If the functions $u_i(\mathbf{r})$ are the one-electron Kohn-Sham orbitals, one can take

$$t(\mathbf{r}) = -\frac{1}{2} \sum_i u_i^* \nabla^2 u_i = \frac{1}{8} \sum_i \frac{|\nabla\rho_i|^2}{\rho_i} - \frac{1}{4} \nabla^2 \rho \quad (2)$$

or

$$t(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla u_i(\mathbf{r})|^2 = \frac{1}{8} \sum_i \frac{|\nabla\rho_i|^2}{\rho_i}, \quad (3)$$

where $\rho_i = |\nabla u_i|^2$ and $\rho = \sum \rho_i$. Or, one can take any average at all of these formulas, as, for example, the form favored in the original Ghosh-Berkowitz-Parr theory [1]:

$$t(\mathbf{r}) = \frac{1}{8} \sum_i \frac{|\nabla\rho_i|^2}{\rho_i} - \frac{1}{8} \nabla^2 \rho. \quad (4)$$

Any amount of $\nabla^2 \rho$ (indeed ∇^2 of an arbitrary well-behaved function) can be added to $t(\mathbf{r})$ without affecting the value of E_{kin} .

Equation (4) makes the local temperature zero at the boundary of an atom or molecule and ordinarily positive elsewhere. However, an exception is the midpoint of H_2^+ for large internuclear distances [9]. Inclusion of the $\nabla^2 \rho$ term also leads to difficulties in the calculation of directional Compton profiles [2]. Similar unfavorable consequences were reported in a recent calculation of the potential energy curve for H_2 [10].

Equation (2) is clearly unacceptable because it would require the temperature to be negative at the boundaries of atoms and molecules. Equation (4) received theoretical support from a derivation of it by Berkowitz [11], who calculated the kinetic energy density from the expression

$$-\frac{1}{2} [\nabla_{r'}^2 \gamma(r, r')]_{r=r'} = -\frac{1}{2} \left[\nabla_s^2 \gamma \left(r + \frac{s}{2}, r - \frac{s}{2} \right) \right]_{s=0} \quad (5)$$

and obtained Eq. (4). However, if one instead uses the more symmetrical expression

$$\frac{1}{2} [\nabla_r \nabla_{r'} \gamma(r, r')]_{r=r'} = \frac{1}{2} \left[\left(\frac{1}{4} \nabla_r^2 - \nabla_s^2 \right) \gamma \left(r + \frac{s}{2}, r - \frac{s}{2} \right) \right]_{s=0} \quad (6)$$

one finds Eq. (3).

A recent study concerning information entropy favors Eq. (3) over Eq. (4) [6]. Most importantly, Eq. (3) makes the temperature everywhere positive:

TABLE I. The Hartree-Fock (HF) and the exchange-only density-functional (DF) one-electron energies of the Be, Ne, Ar, and Kr atoms in Ry.

		1s	2s	2p	3s	3p	3d	4s	4p
Be	HF	-9.465	-0.619						
	DF	-8.251	-0.619						
Ne	HF	-65.545	-3.864	-1.701					
	DF	-61.639	-3.436	-1.701					
Ar	HF	-237.221	-24.644	-19.143	-2.555	-1.182			
	DF	-228.911	-22.313	-17.474	-2.199	-1.182			
Kr	HF	-1040.331	-139.806	-126.020	-21.699	-16.663	-7.650	-2.306	-1.048
	DF	-1022.120	-133.210	-120.468	-19.329	-14.777	-6.633	-1.987	-1.048

$$\frac{3}{2}\rho(\mathbf{r})kT(\mathbf{r}) = \frac{1}{8}\sum_i \frac{\nabla\rho_i\nabla\rho_i}{\rho_i}. \quad (7)$$

We take this formula as defining $T(\mathbf{r})$.

Close to an atomic nucleus, ρ is mainly ρ_{1s} and satisfies the cusp condition $\nabla\rho/\rho = -2Z$. Equation (7) thus gives

$$\frac{3}{2}kT(\mathbf{r}) \approx \frac{1}{2}Z^2 \quad (\text{near an atomic nucleus}). \quad (8)$$

Far from all nuclei, ρ is mainly the highest occupied orbital density ρ_H and $\rho_H \sim \exp(-2\sqrt{2}I r)$, where I is the ionization energy. Equation (7) now gives

$$\frac{3}{2}kT(\mathbf{r}) \approx I \quad (\text{far from all nuclei}). \quad (9)$$

For hydrogenlike atoms, Eq. (8) is valid for all r . For other atoms, one expects a more or less monotonic decrease of

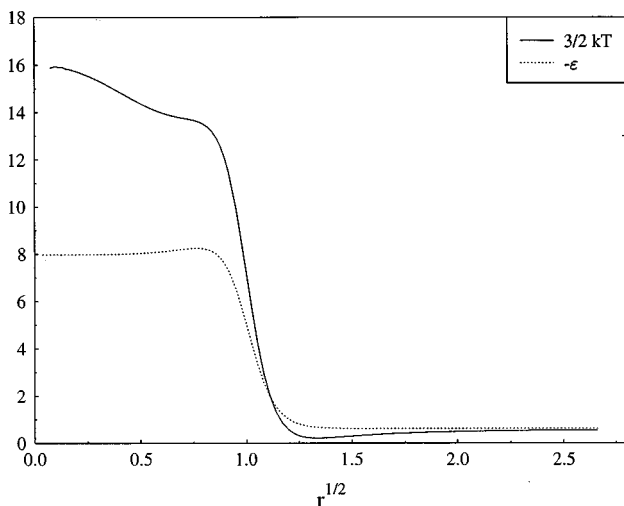


FIG. 1. $\frac{3}{2}kT(r)$ and $\bar{\varepsilon}(r)$ for the Be atom.

$T(\mathbf{r})$ from the value given by Eq. (8) to the value given by Eq. (9).

III. COMPARISON WITH THE POLITZER AVERAGE LOCAL ORBITAL ENERGY INDEX

Equations (7)–(9) may be usefully compared with formulas governing what we may call the Politzer average local orbital energy index [8], $\bar{\varepsilon}(\mathbf{r})$. The definition is

$$\bar{\varepsilon}(\mathbf{r}) = \sum_i \frac{\rho_i \varepsilon_i}{\rho} = -\bar{I}(\mathbf{r}), \quad (10)$$

where the ε_i are Kohn-Sham orbital energies, Politzer employs Hartree-Fock orbitals and orbital energies, which are somewhat different (but not much different) from Kohn-Sham quantities. $\bar{\varepsilon}(\mathbf{r})$ is negative. $|\bar{\varepsilon}(\mathbf{r})|$ is what Politzer terms the average local ionization energy index $\bar{I}(\mathbf{r})$.

Now, again, close to an atomic nucleus, ρ is mainly ρ_{1s} , and Eq. (10) gives

$$\bar{\varepsilon}(\mathbf{r}) \approx \varepsilon_{1s} \quad (\text{near an atomic nucleus}). \quad (11)$$

Far from all nuclei, ρ is primarily ρ_H and $\varepsilon_H = -I$ exactly. Hence Eq. (10) gives

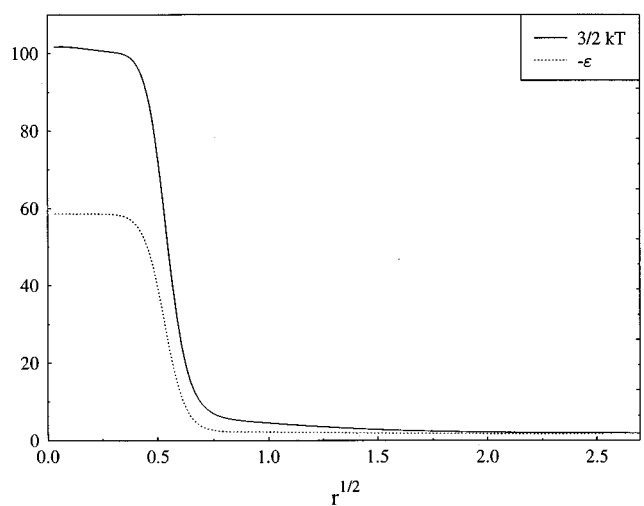
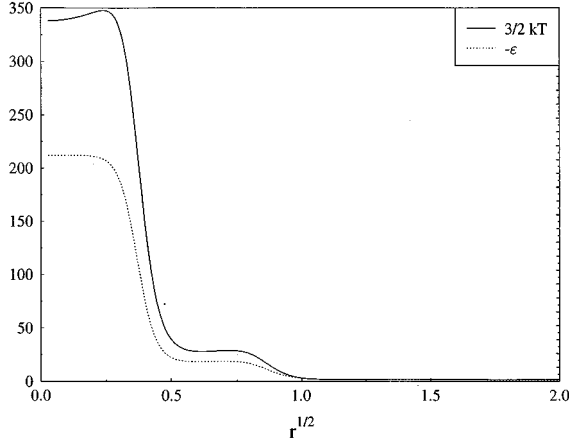
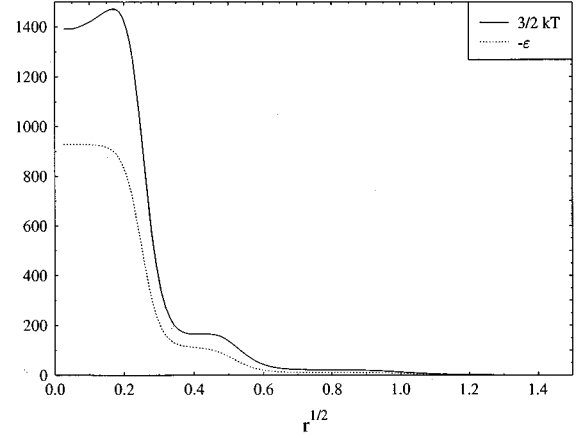


FIG. 2. $\frac{3}{2}kT(r)$ and $\bar{\varepsilon}(r)$ for the Ne atom.

FIG. 3. $\frac{3}{2}kT(r)$ and $\bar{\varepsilon}(r)$ for the Ar atom.FIG. 4. $\frac{3}{2}kT(r)$ and $\bar{\varepsilon}(r)$ for the Kr atom.

$$\bar{\varepsilon}(\mathbf{r}) \approx \varepsilon_{\text{H}} = -I \quad (\text{far from all nuclei}). \quad (12)$$

For hydrogenlike atoms, Eq. (11) is valid for all r . Furthermore, $\varepsilon_{1s} = -\frac{1}{2}Z^2$ exactly. Accordingly,

$$-\bar{\varepsilon}(\mathbf{r}) = \frac{3}{2}kT(\mathbf{r}) = \frac{1}{2}Z^2 \quad (\text{for hydrogenlike atoms}). \quad (13)$$

Up to a constant multiplier $\bar{\varepsilon}(\mathbf{r})$ and $T(\mathbf{r})$ are one and the same.

For other systems, we infer from Eqs. (8) and (11) that

$$\frac{-\bar{\varepsilon}(\mathbf{r})}{\frac{3}{2}kT(\mathbf{r})} \approx \frac{-\varepsilon_{1s}}{\frac{1}{2}Z^2} \quad (\text{near an atomic nucleus}), \quad (14)$$

and from Eqs. (9) and (12) that

$$-\frac{\bar{\varepsilon}(\mathbf{r})}{\frac{3}{2}kT(\mathbf{r})} \approx 1 \quad (\text{far from all nuclei}). \quad (15)$$

Since of course ε_{1s} is reasonably close to $\frac{1}{2}Z^2$, it appears that $-\bar{\varepsilon}(\mathbf{r})$ and $\frac{3}{2}kT(\mathbf{r})$ are much the same for all r . The calculations reported below confirm this suggestion.

IV. METHOD OF CALCULATION AND RESULTS

As the exact forms of the exchange-correlation energy and potential functionals are not known, one cannot easily get the exact solution of the Kohn-Sham (KS) equations

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r}) \right] u_i(\mathbf{r}) = \varepsilon_i u_i(\mathbf{r}), \quad (16)$$

$$\sum_i (u_i)^2 = \rho. \quad (17)$$

However, when the electron density itself is known, it is possible to obtain an exact solution. The Kohn-Sham poten-

tial, the one-electron orbitals, and the orbital energy can be determined from the density, and several methods are known for solving this inverse problem [12–18]. The procedure used in the present work is as follows. We know that the solution is unique whenever it exists. That means that starting out from any appropriate starting potential we can obtain the true Kohn-Sham potential (within a constant) and one-electron energies and wave functions if the procedure converges.

What we have done here is to take a simple $X\alpha$ potential as a starting potential. The Kohn-Sham equations (16) and (17) are then solved self-consistently and the orbitals $u_i^{(1)}$ and the density $\rho^{(1)}$ of the first iteration are obtained. If the maximum relative difference of this density $\rho^{(1)}$ and the input density ρ is larger than an appropriately chosen small constant the Kohn-Sham potential of the next iteration is constructed. (A useful convergent construction of the potential of the $(i+1)$ th iteration is $V^{(i+1)} = V^{(i)}[\rho/\rho^{(i)}]$.) Then the Kohn-Sham equations are solved again self-consistently. The process is continued until the Kohn-Sham potential leading to the input density is obtained. In the present work the exchange-only scheme is employed and so the Hartree-Fock density is the input. The very accurate Hartree-Fock wave functions of Bunge [18] are used. Inclusion of electron correlation would have very small effects on the computed temperatures.

In Table I are presented the exchange-only density-functional and the Hartree-Fock (HF) one-electron energies for the Be, Ne, Ar, and Kr atoms. As has already been pointed out [15,17], with the exception of the highest occupied orbital, the density functional and the HF orbital energies are different, with the HF energies more negative. (Accurate density-functional orbital energies, including correlation, have recently been determined by Zhao, Morrison, and Parr [19].) In Figs. 1–4, $\frac{3}{2}kT(\mathbf{r})$ and $-\bar{\varepsilon}(\mathbf{r})$ are shown for these atoms, as calculated from Eqs. (7) and (10), respectively. Atomic units are used in the figures.

In order to compare our new and our older definitions of the local temperature, we recalculate the exchange energy from [14]

TABLE II. Exchange energies for noble-gas atoms (a.u.).

Atom	Exact	LDA ^a	GP ^b	Present ^c
He	1.03	0.88	0.91	1.09
Ne	12.11	11.03	11.57	12.81
Ar	30.18	27.86	29.24	31.70
Kr	93.9	88.62	94.26	97.31
Xe	179.1	170.6	181.7	185.89

^aLDA indicates the Thomas-Fermi-Dirac results.

^bThe GP calculations are from Ref. [3]. These employed Eq. (4) of the present text to define the local temperature.

^cThe present calculations employ Eq. (3) to define the local temperature.

$$E_x[\rho] = \frac{\pi}{2} \int \rho^2(\mathbf{r}) \beta(\mathbf{r}) \beta(\mathbf{r}) d\mathbf{r}, \quad (18)$$

with $\beta(\mathbf{r}) = 1/kT(\mathbf{r})$, following Ghosh and Parr [3], and also recalculate noble-gas Compton profiles from the formula

$$J(q) = \frac{1}{2} \int_{|q|}^{\infty} \chi(\mathbf{p}) p^{-1} d^3 p = (2\pi)^{-1} \int d^3 r \beta(\mathbf{r})^{1/2} \rho(\mathbf{r}) \times \exp[-\beta(\mathbf{r})q^2/2], \quad (19)$$

following Parr, Rupnik, and Ghosh [2]. Results are shown in Tables II and III. Given that Eqs. (18) and (19) are themselves necessarily approximate, the calculations do not clearly discriminate between the new and old formulas for $T(\mathbf{r})$.

TABLE III. Compton profiles $J(q)$ for noble-gas atoms. PRG denotes the calculations reported in Ref. [2], in which local temperatures were defined using Eq. (4) of the present text. The present calculations use Eq. (3) to define the local temperature. HF labels Hartree-Fock results.

q	He			Ne			Ar			Kr			Xe		
	PRG	Present	HF	PRG	Present	HF	PRG	Present	HF	PRG	Present	HF	PRG	Present	HF
0.0	1.02	0.823	1.07	2.98	2.50	2.73	5.49	4.78	5.06	7.93	6.79	7.19	10.82	9.34	9.74
0.1	1.01	0.819	1.06	2.96	2.49	2.72	5.44	4.75	5.04	7.85	6.75	7.15	10.69	9.28	9.69
0.2	0.976	0.806	1.02	2.91	2.47	2.70	5.27	4.66	4.96	7.62	6.64	7.05	10.35	9.12	9.52
0.3	0.924	0.784	0.956	2.83	2.43	2.65	5.02	4.52	4.82	7.27	6.46	6.86	9.84	8.86	9.22
0.4	0.858	0.755	0.878	2.72	2.38	2.59	4.70	4.33	4.62	6.84	6.23	6.57	9.21	8.52	8.77
0.5	0.781	0.719	0.791	2.59	2.31	2.51	4.34	4.10	4.35	6.36	6.95	6.20	8.54	8.12	8.21
0.6	0.700	0.678	0.700	2.45	2.24	2.41	3.96	3.84	4.04	5.87	5.64	5.77	7.89	7.69	7.59
0.8	0.540	0.583	0.527	2.14	2.06	2.17	3.22	3.28	3.33	4.97	4.98	4.85	6.73	6.79	6.38
1.0	0.399	0.481	0.382	1.82	1.86	1.89	2.59	2.72	2.66	4.24	4.33	4.04	5.83	5.96	5.45
1.2	0.288	0.380	0.271	1.53	1.64	1.61	2.10	2.22	2.11	3.68	3.77	3.44	5.16	5.26	4.84
1.4	0.205	0.289	0.191	1.27	1.42	1.35	1.74	1.81	1.70	3.26	3.32	3.03	4.65	4.71	4.44
1.6	0.145	0.210	0.134	1.06	1.22	1.12	1.47	1.49	1.42	2.95	2.97	2.76	4.23	4.27	4.16
1.8	0.103	0.147	0.095	0.876	1.03	0.927	1.27	1.27	1.22	2.69	2.70	2.58	3.88	3.92	3.91
2.0	0.073	0.099	0.068	0.730	0.855	0.771	1.12	1.11	1.08	2.49	2.50	2.44	3.57	3.63	3.68
3.0	0.015	0.008	0.015	0.331	0.347	0.346	0.712	0.740	0.736	1.74	1.81	1.86	2.42	2.48	2.50
4.0	0.004	0.000	0.004	0.187	0.187	0.194	0.486	0.536	0.520	1.22	1.30	1.33	1.72	1.74	1.71
5.0	0.001	0.000	0.001	0.123	0.131	0.124	0.333	0.376	0.359	0.873	0.924	0.933	1.30	1.31	1.30
10.0	0.000	0.000	0.000	0.024	0.031	0.022	0.073	0.078	0.075	0.246	0.260	0.260	0.47	0.498	0.510

V. DISCUSSION

The first conclusion is that the local temperature has a near piecewise constancy similar to the piecewise constancy of the Hartree-Fock local kinetic energy per particle earlier reported by Ghosh and Balbás [7]. This behavior closely follows the piecewise exponential nature of the density [20]. Different shells of atoms can be described as having different, more or less constant, temperatures. In the hydrogen atom there is a single constant temperature given by Eq. (13). Atoms with higher atomic numbers possess characteristic values of the temperature for the K, L, M, \dots shells.

The second conclusion is that the local temperature and the Politzer local average orbital energy index behave similarly. They are proportional at long distances from all nuclei. Where the local temperature is high, the average local ionization energy is high (average local orbital energy is very negative). Politzer and co-workers already have argued that small $\bar{I}(\mathbf{r})$ values characterize molecular sites most reactive to electrophilic reagents [8]. Low local temperature serves the same purpose. It is easier for a site to donate electrons the less bound its highest-energy electron are—the lower the local temperature is at its boundaries. This conforms with the fact that electronegativity is lowered if the ionization potential is lowered. In density-functional language, the local chemical potential is increased if the local ionization potential is decreased.

In our work, the idea of a local temperature first came up in a use of entropy of information in the construction of an approximate density-functional theory [1], and that provided interesting numerical predictions [2,3]. Direct use of a more simple entropy appears to be of value [6]. If either a temperature or an entropy is useful, the other must be as well.

In the present work, we have pinned down what appears

to be the best local temperature definition. The result we have found, that temperature is approximately piecewise constant in an atom, is unexpected, as is the result that whenever atomic nuclei are present the temperature does not fall off to zero at infinity. But note that there is a classical analog to the stepwise constant temperature, in a system separated into parts by adiabatic semipermeable walls (for which the equilibrium condition can be $\mu/T = \text{const}$).

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