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# Information-theoretical quantities in the thermodynamical transcription of the density functional theory

Á. Nagy

*Department of Theoretical Physics, University of Debrecen, H–4002 Debrecen, Hungary,*
*e-mail: anagy@phys.unideb.hu*

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The Ghosh-Berkowitz-Parr idea of density functional theory as local thermodynamics is revisited. It is emphasized that the kinetic energy density and consequently the local temperature are not unique. It is highlighted that the extremal principle for the Shannon entropy and the Fisher information leads to constant temperature. Relations for the phase-space Fisher information, fidelity and relative Rényi entropy are summarized.

*Keywords:* Density functional theory; local thermodynamics; phase-space Shannon entropy; phase-space Fisher information.

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## 1. Introduction

Information theoretical concepts have become very beneficial in several fields in science. They have turned out to be extremely fruitful in density functional theory (DFT). Here a fascinating approach of Ghosh, Berkowitz and Parr [1] is revisited. These authors showed that DFT can be considered a local thermodynamics and introduced a local temperature that varies from point to point. The theory, however, is not unique because the kinetic energy density is not uniquely defined. It has been shown [2, 3] that the phase-space Shannon information entropy [4] takes its maximum and the Fisher information [5] attains its minimum for the case of constant temperature. It has been pointed out [6] that for Coulomb systems there is a simple relation between the total energy and phase-space Fisher information. It has been revealed that the phase-space fidelity between excited states is proportional to the position-space fidelity, with a factor of proportionality depending on the total energies. The phase-space relative entropy has also been studied and found equal to the position-space relative entropy plus a term depending only on the total energies. The relationship between phase-space fidelity susceptibility and Fisher information has also been derived. Investigating the relative Rényi entropy [7] in the special case of constant inverse temperature, the phase-space relative Rényi entropy is a sum of the position-space relative Rényi entropy and a term arising from the momentum space [8]. This quantity can be considered a measure of similarity. It includes more information than the position-space measures, since it also incorporates momentum-space knowledge. In this brief article these results are summarized.

## 2. Ghosh-Berkowitz-Parr theory

Ghosh, Berkowitz and Parr (GBP) [1] formulated density functional theory (DFT) as a ‘thermodynamics’. Their main idea was to find a phase-space distribution function $f(\mathbf{r},\mathbf{p})$ that maximizes the phase-space information entropy

$$S = -k \int d\mathbf{r} d\mathbf{p} f (\ln f - 1), \tag{1}$$

keeping the density

$$\int d\mathbf{p} f(\mathbf{r},\mathbf{p}) = \varrho(\mathbf{r}), \tag{2}$$

and the kinetic energy density

$$\int d\mathbf{p} \frac{p^2}{2} f(\mathbf{r},\mathbf{p}) = t(\mathbf{r}), \tag{3}$$

fixed. Taking into account the conditions (2) and (3) with $\mathbf{r}$-dependent Lagrange multipliers $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$, the variation leads to a Maxwell-Boltzmann-like distribution function

$$f(\mathbf{r},\mathbf{p}) = e^{-\alpha(\mathbf{r})} e^{-\beta(\mathbf{r}) p^2/2}, \tag{4}$$

where $k$ is the Boltzmann constant. Eqs. (3) and (4) result familiar ideal gas expression

$$t(\mathbf{r}) = \frac{3}{2} \frac{\varrho(\mathbf{r})}{\beta(\mathbf{r})}. \tag{5}$$

So $\beta(\mathbf{r})$ is called local inverse temperature. Eq. (4) can be reshaped as

$$f(\mathbf{r},\mathbf{p}) = \left[\frac{2\pi}{\beta(\mathbf{r})}\right]^{-3/2} \varrho(\mathbf{r}) e^{-\beta(\mathbf{r}) p^2/2}. \tag{6}$$

Substituting Eq. (6) into Eq. (1) we arrive at the well-known Sackur-Tetrode expression

$$S = -k \int \varrho(\mathbf{r}) \ln \varrho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} k \int \varrho(\mathbf{r}) \left[3 \ln (2\pi/\beta) + 5\right] d\mathbf{r}. \tag{7}$$

It is worth emphasizing that the kinetic energy density $t(\mathbf{r})$ is not unique. Adding a term that integrates to zero to a given form of $t(\mathbf{r})$ provides the same kinetic energy $E^{\text{kin}}$ as $t(\mathbf{r})$. It has recently been shown [2, 3] that it is possible to select the kinetic energy density that maximizes the phase-space Shannon entropy and minimizes the phase-space Fisher information.

## 3. Extreme of phase-space Shannon entropy and Fisher Information

Consider first the phase-space Shannon entropy (7). The variation

$$S - \zeta \left( \int t(\mathbf{r}) d\mathbf{r} - E^{\text{kin}} \right), \tag{8}$$

gives the kinetic energy density

$$t = \frac{3}{2} \frac{k\varrho}{\zeta}. \tag{9}$$

Comparing Eqs. (5) and (9) we can observe that $\beta = \zeta$, that is, the inverse temperature $\beta$ is constant as the Lagrange multiplier $\zeta$ in Eq. (8) is constant

$$\beta = \frac{3}{2} \frac{N}{E^{\text{kin}}}. \tag{10}$$

Turn now to the phase-space Fisher information

$$I_g(\beta) = \int \frac{\left[ \frac{\partial g(\mathbf{r},\mathbf{p}|\beta)}{\partial \beta} \right]^2}{g(\mathbf{r},\mathbf{p}|\beta)} d\mathbf{r} d\mathbf{p}, \tag{11}$$

where the phase-space distribution function

$$g(\mathbf{r},\mathbf{p}|\beta) = \frac{1}{N} f(\mathbf{r},\mathbf{p}) = \frac{1}{N} \left[ \frac{\beta(\mathbf{r})}{2\pi} \right]^{3/2} \varrho(\mathbf{r}) e^{-\beta(\mathbf{r})p^2/2}, \tag{12}$$

normalized to 1 is applied. The integration for $\mathbf{p}$ leads to

$$I_g(\beta) = \frac{3}{2N} \int \frac{\varrho(\mathbf{r})}{(\beta(\mathbf{r}))^2} d\mathbf{r}. \tag{13}$$

Minimizing $I_g$ with keeping $E^{kin}$ fixed

$$I_g + \xi \left( E^{\text{kin}} - \frac{3}{2} \int \frac{\varrho(\mathbf{r})}{\beta(\mathbf{r})} d\mathbf{r} \right), \tag{14}$$

we obtain again that the inverse temperature is constant $\beta = 2/(N\xi)$ and the kinetic energy density is proportional to the electron density. The relationship between the Fisher information and the kinetic energy is

$$I_g = \frac{2}{3} \left( \frac{E^{\text{kin}}}{N} \right)^2. \tag{15}$$

In the original GBP theory the non-interacting Kohn-Sham approach was utilized. Observe that the derivation above can be done in the true, interacting system, too. As the interacting and the non-interacting kinetic energies are different, the thermodynamic quantities will also be different in these systems. The advantage of selecting the true, interacting system is that in Coulomb systems and in equilibrium nuclear geometry, the virial theorem

$$E = -E^{\text{kin}}, \tag{16}$$

can be utilized. $E$ and $E^{\text{kin}}$ are the true (interacting) total and kinetic energies. Then Eq. (15) gives

$$I_g = \frac{2}{3} \left( \frac{E}{N} \right)^2, \tag{17}$$

and obviously, $E$ can be expressed with $I_g$.

Though the GBP theory was originally formalized for the ground state, it can also be applied for excited states. Utilizing the extention of DFT to individual excited states in Coulomb systems [9–11] the relationship between the Fisher information and the true (interacting) total energy is [6]

$$I_g^i = \frac{2}{3} \left( \frac{E_i}{N} \right)^2. \tag{18}$$

Then the $i$th excitation energy can be written as

$$E_i - E_0 = N \sqrt{\frac{3}{2}} \left( \sqrt{I_g^0} - \sqrt{I_g^i} \right), \tag{19}$$

where $E_0$, $I_g^0$ and $E_i$, $I_g^i$ are total energy and Fisher information of the ground and the $i$th excited states.

In Coulomb systems the asymptotic decay of the excited state density $\varrho_i$ is governed by the vertical ionization potential $E_0^{N-1} - E$

$$\lim_{r \to \infty} \frac{\partial \ln \bar{\varrho}(r)}{\partial r} = -\sqrt{8(E_0^{N-1} - E)}, \tag{20}$$

where $E_0^{N-1}$ is the ground-state energy of the $N-1$ electron system. In case of Coulomb external potential the excited state density determines all properties of the system including the phase-space distribution function and the phase-space Fisher information.

## 4. Phase-space Rényi and relative Rényi entropies, fidelity and fidelity susceptibility

The Rényi entropy of order $q$ is a one-parameter extension of the Shannon entropy:

$$R_f^{(q)} = \frac{1}{1-q} \ln \int [f(\mathbf{r})]^q d\mathbf{r}, \quad \text{for} \quad 0 < q < \infty \quad \text{and} \quad q \neq 1, \tag{21}$$

for a density function $f(\mathbf{r})$. The limit $q \to 1$ gives the Shannon entropy:

$$S_f = -\int f(\mathbf{r}) \ln f(\mathbf{r}) d\mathbf{r}. \tag{22}$$

The relative Rényi entropy of order $q$ defined as

$$R^q_{f,f_{\text{ref}}} = \frac{1}{q-1}\ln\int\frac{f^q(\mathbf{r})}{f^{q-1}_{\text{ref}}(\mathbf{r})}d\mathbf{r}, \tag{23}$$

provides the deviation of $f(\mathbf{r})$ from a reference density $f_{\text{ref}}(\mathbf{r})$. The limit $q \to 1$ leads to the relative or Kullback-Leibler entropy or cross-entropy [12]

$$I_{KL}(f, f_{\text{ref}}) = \int f(\mathbf{r})\ln\frac{f(\mathbf{r})}{f_{\text{ref}}(\mathbf{r})}d\mathbf{r}. \tag{24}$$

In DFT the quantity

$$F(f,g) = \int f^{1/2}g^{1/2}d\mathbf{r}, \tag{25}$$

provides fidelity [13, 14]. It measures the 'difference' between the densities $f(\mathbf{r})$ and $g(\mathbf{r})$.

Consider now a distribution function having a parameter $\theta$ and take $f(\theta)$ and $f(\theta+\delta\theta)$. Then expanding $f(\theta+\delta\theta)$ around $f(\theta)$ and substituting it into Eq. (25), we arrive at

$$F(\theta,\theta+\delta\theta) = 1 - \frac{1}{2}(\delta\theta)^2\chi + ..., \tag{26}$$

where

$$\chi = \frac{1}{4}\int\frac{1}{f}\left(\frac{\partial f}{\partial\theta}\right)^2, \tag{27}$$

is the fidelity susceptibility [13, 14]. Comparing the definitions of $\chi$ and the Fisher information, we can notice that they are proportional: $\chi = (1/4)I$.

We can easily determine the relative Rényi entropy with $f(\theta)$ and $f(\theta+\delta\theta)$ as

$$R^q_{f(\theta),f(\theta+\delta\theta)} \approx 2q\chi(\delta\theta)^2. \tag{28}$$

The Kullback-Leibler entropy can be obtained with the limit $q \to 1$

$$I^{KL}_{f(\theta),f(\theta+\delta\theta)} \approx 2\chi(\delta\theta)^2. \tag{29}$$

Observe that for small $\delta\theta$ the relative Rényi entropy is proportional to the Kullback-Leibler entropy

$$R^q_{f(\theta),f(\theta+\delta\theta)} \approx qI^{KL}_{f(\theta),f(\theta+\delta\theta)}. \tag{30}$$

## 5. Phase-space relative Rényi entropy

Applying the phase-space distribution function (12) the relative Rényi entropy takes the form

$$R^q_{f,f_{\text{ref}}} = \frac{1}{q-1}\ln\int B(\mathbf{r})Q(\mathbf{r},\mathbf{p})d\mathbf{r}d\mathbf{p}, \tag{31}$$

where

$$B(\mathbf{r}) = \left(\frac{\beta(\mathbf{r})}{2\pi}\right)^{3q/2}\left(\frac{\beta_{\text{ref}}(\mathbf{r})}{2\pi}\right)^{3(1-q)/2}, \tag{32}$$

and

$$Q(\mathbf{r},\mathbf{p}) = \sigma^q(\mathbf{r})\sigma^{1-q}_{\text{ref}}(\mathbf{r})e^{-[q\beta(\mathbf{r})+(1-q)\beta_{\text{ref}}(\mathbf{r})]p^2/2}. \tag{33}$$

Here, the shape function [15] $\sigma(\mathbf{r}) = \varrho(\mathbf{r})/N$ is used instead of the density. Observe that the condition

$$q\beta(\mathbf{r}) + (1-q)\beta_{\text{ref}}(\mathbf{r}) > 0, \tag{34}$$

should be satisfied for the existence of the integral in Eq. (31). Inequality (34) can be considered as a constraint for selecting the kinetic energy density. Alternatively, in the case of constant temperatures it is a constraint for selecting the value of the Rényi parameter $q$. The integration leads to

$$R^q_{f,f_{\text{ref}}} = \frac{1}{q-1} \times \ln\int\left(\frac{\beta^q\beta^{1-q}_{\text{ref}}}{q\beta+(1-q)\beta_{\text{ref}}}\right)^{3/2}\sigma^q\sigma^{1-q}_{\text{ref}}. \tag{35}$$

In the constant temperature case Eq. (35) gives

$$R^q_{f,f_{\text{ref}}} = R^q_{\beta,\beta_{\text{ref}}} + R^q_{\sigma,\sigma_{\text{ref}}}, \tag{36}$$

where

$$R^q_{\beta,\beta_{\text{ref}}} = \frac{3}{2(q-1)}\ln\left[\left(\frac{\beta^q\beta^{1-q}_{\text{ref}}}{q\beta+(1-q)\beta_{\text{ref}}]}\right)\right], \tag{37}$$

and

$$R^q_{\sigma,\sigma_{\text{ref}}} = \frac{1}{q-1}\ln\left[\int\sigma^q\sigma^{1-q}_{\text{ref}}d\mathbf{r}\right]. \tag{38}$$

The momentum-space term $R^q_{\beta,\beta_{\text{ref}}}$ contains only $\beta$, $\beta_{\text{ref}}$ and $q$. The second term $R^q_{\sigma,\sigma_{\text{ref}}}$ is the position-space relative Rényi entropy.

## 6. Discussion

The phase-space relative Rényi entropy can be considered a novel measure of similarity [8]. We can look at it as an extension of earlier quantum similarity measures to the phase space. One of the most frequently used similarity indicators is the Carbó index [16]

$$R_{AB} = \frac{\int d\mathbf{r}\varrho_A(\mathbf{r})\varrho_B(\mathbf{r})}{\sqrt{\int d\mathbf{r}\varrho^2_A(\mathbf{r})\int d\mathbf{r}\varrho^2_B(\mathbf{r})}}, \tag{39}$$

showing resemblance of densities $\varrho_A(\mathbf{r})$ and $\varrho_B(\mathbf{r})$. A generalization of this marker is the generalized quantum similarity index (QSI) [17]

$$QSI^\gamma = \frac{\int d\mathbf{r}(\varrho_A(\mathbf{r})\varrho_B(\mathbf{r}))^{\gamma/2}}{\sqrt{\int d\mathbf{r}\varrho_A(\mathbf{r})^\gamma\int d\mathbf{r}\varrho_B(\mathbf{r})^\gamma}}, \tag{40}$$

where $\gamma$ is a real number. Observe that $\gamma = 1$ provides the fidelity and $\gamma = 2$ gives the Carbó index. The phase-space relative Rényi entropy can also be regarded as a similarity index

[8]. $R^q_{f,f_{\text{ref}}}$ measures the difference of the phase-space distribution function $f$ from the reference function $f_{\text{ref}}$. In addition to the position-space term (38), it contains a momentum-space term (37). So, this index is more general than the previous ones as it incorporates momentum-space information, too. It can be used for systems having the same density. For example, we can compare the true interacting and the non-interacting Kohn-Sham systems. See details in [8].

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