Research paper

Thermodynamical transcription of density functional theory with minimum Fisher information

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ABSTRACT

Ghosh, Berkowitz and Parr designed a thermodynamical transcription of the ground-state density functional theory 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. Here we derive the expression of the phase-space Fisher information in the GBP theory taking the inverse temperature as the Fisher parameter. It is proved that this Fisher information takes its minimum for the case of constant temperature. This result is consistent with the recently proven theorem that the phase-space Shannon information entropy attains its maximum at constant temperature.

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1. Introduction

The role of Fisher information [1] in quantum mechanics and density functional theory was first emphasized by Sears, Parr and Dinur [2] more than twenty years ago. They studied the relationship between the quantum mechanical kinetic energy and the Fisher information.

Later, using the principle of extreme physical information the Schrödinger equation [3–5], the Euler equation [6] and the Kohn-Sham equations [7] were derived. Fisher information has been applied among others in studying atoms and molecules [8–21].

The ground-state density functional theory was reformalized as 'thermodynamics' by Ghosh, Berkowitz and Parr [22]. The phase-space distribution function maximizing the phase-space Shannon information entropy was derived. They obtained a local Maxwell-Boltzmann distribution function and introduced the concept of the local temperature. The theory has several applications and extensions [23–43]. Among others, the local thermodynamic formalism was extended to ensembles of excited states [48] and ensemble local temperature was defined.

The Ghosh-Berkowitz-Parr theory is not unique, because one can apply several expressions for the kinetic energy density. Therefore, the local temperature is not unique either. The ambiguity of the local kinetic energy and temperature was addressed by several authors [44–47]. In [46] the N-particle quasiprobability distribution maximising the Shannon limit of the Tsallis entropy was proposed, though it was not worked through. It has recently been proved [49] that it is possible selecting the kinetic energy density

so that the local temperature be a constant for the whole system under consideration. In this case the kinetic energy density is proportional to the electron density and the temperature is proportional to the kinetic energy. Furthermore, the kinetic energy density corresponding to the constant temperature, maximizes the Shannon information entropy. A similar result has been obtained for the ensemble extension of the theory [50].

Here we derive the expression of the Fisher information in the Ghosh-Berkowitz-Parr theory taking the inverse temperature for the Fisher parameter. Then we prove that this Fisher information takes its minimum for the case of constant temperature. That is, we arrive at the remarkable result that at constant temperature the phase-space Shannon information entropy takes its maximum and the phase-space Fisher information has its minimum. These simple and interesting theorems give a deeper insight into the Ghosh-Berkowitz-Parr theory.

The following section provides the summary the Ghosh-Berkowitz-Parr theory. Section 3. presents the new theory with the Fisher information. The last section is devoted to examples and discussion.

2. Thermodynamical transcription of density functional theory

In this section the "thermodynamical" transcription [22] is summarized. In the density functional theory we study a system of N electrons moving in a local external potential $v(\mathbf{r})$. According to the Hohenberg-Kohn theorems [51] the ground-state electron density $n(\mathbf{r})$ determines $v(\mathbf{r})$ up to a trivial additive constant and the ground-state total energy takes its minimum at the true density. Moreover, there exists a non-interacting, Kohn-Sham system,

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where the electrons move independently in a common, local Kohn-Sham potential.

Introduce a phase-space distribution function $f(\mathbf{r}, \mathbf{p})$ with the properties:

$$\int d\mathbf{p} f(\mathbf{r}, \mathbf{p}) = n(\mathbf{r}), \tag{1}$$

$$\int d\mathbf{r} n(\mathbf{r}) = N \tag{2}$$

and

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

m is the electron mass. The non-interacting kinetic energy density $t_s(\mathbf{r})$ integrates to the non-interacting kinetic energy E_{kin}:

$$E_{kin} = \int d\mathbf{r} t_s(\mathbf{r}). \tag{4}$$

The marginal conditions (1)–(3) are satisfied by a number of distribution functions. Note that in the GBP theory it is not required that the phase-space distribution function integrates to the momentum density [52,53].

Take the distribution function that maximizes the Shannon information entropy

$$S = \int d\mathbf{r} s(\mathbf{r}), \tag{5}$$

$$s(\mathbf{r}) = -k \int d\mathbf{p} f(\ln f - 1) \tag{6}$$

subject to the constraints above, that is, the correct density (Eq. (1)) and the correct non-interacting kinetic energy (Eq. (3)) are fixed. k is the Boltzmann constant. The maximizing distribution function is a local Maxwell-Boltzmann type function:

$$f(\mathbf{r}, \mathbf{p}) = e^{-\alpha(\mathbf{r})} e^{-\beta(\mathbf{r})p^2/2m}. \tag{7}$$

$\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are $\mathbf{r}$-dependent Lagrange multipliers. Substituting the distribution function (7) into the constraint (3) we are led to

$$t_s(\mathbf{r}) = \frac{3}{2} \frac{n(\mathbf{r})}{\beta(\mathbf{r})}. \tag{8}$$

Introducing the local temperature $T(\mathbf{r})$ with the definition

$$\beta(\mathbf{r}) = \frac{1}{kT(\mathbf{r})}, \tag{9}$$

the non-interacting kinetic energy density takes the form of the ideal gas expression:

$$t_s(\mathbf{r}) = \frac{3}{2} n(\mathbf{r}) kT(\mathbf{r}) \tag{10}$$

and the distribution function can be rewritten as

$$f(\mathbf{r}, \mathbf{p}) = [2\pi m kT(\mathbf{r})]^{-3/2} n(\mathbf{r}) e^{-p^2/2mkT(\mathbf{r})}. \tag{11}$$

The local temperature is expressed with the kinetic energy density and can vary from point to point. It is important to emphasize that the local temperature is not uniquely defined as the kinetic energy density is not unique. Adding a term that integrates to zero to the kinetic energy density results another kinetic energy density with the same kinetic energy but different local temperature. Usually the gradient form of the kinetic energy density is applied, because it is everywhere positive, though any form resulting the kinetic energy can do.

3. Fisher information

The Fisher information [1] measures the information that we can obtain for the parameter θ of the distribution function $g(x|\theta)$. It is defined as

$$I_g(\theta) = \int \frac{\left[\frac{\partial g(x|\theta)}{\partial \theta}\right]^2}{g(x|\theta)} dx. \tag{12}$$

Consider now the phase-space distribution function normalized to 1:

$$\varrho(\mathbf{r}, \mathbf{p}) = \frac{1}{N} f(\mathbf{r}, \mathbf{p}) = \frac{1}{N} \left[\frac{\beta(\mathbf{r})}{2\pi m}\right]^{3/2} n(\mathbf{r}) e^{-\beta(\mathbf{r})p^2/2m} \tag{13}$$

and take β for the parameter θ of the distribution function. The phase-space Fisher information is now defined as

$$I(\beta) = \int \frac{\left[\frac{\partial \varrho(\mathbf{r}, \mathbf{p}|\beta)}{\partial \beta}\right]^2}{\varrho(\mathbf{r}, \mathbf{p}|\beta)} d\mathbf{r} d\mathbf{p}. \tag{14}$$

Note that it is a generalization of the original definition as β in the GBP theory is a function of $\mathbf{r}$. Substituting Eq. (13) into Eq. (14) and integrating for the momentum, the phase-space Fisher information takes the form

$$I(\beta) = \frac{3}{2N} \int \frac{n(\mathbf{r})}{(\beta(\mathbf{r}))^2} d\mathbf{r}. \tag{15}$$

We can express the phase-space Fisher information with the non-interacting kinetic energy density t_s instead of β:

$$I(t_s) = \frac{2}{3N} \int \frac{(t_s(\mathbf{r}))^2}{n(\mathbf{r})} d\mathbf{r}. \tag{16}$$

Now, we minimize the Fisher information (16) under the condition that the kinetic energy E_{kin} is fixed:

$$\widetilde{I} = \frac{2}{3N} \int \frac{(t_s(\mathbf{r}))^2}{n(\mathbf{r})} d\mathbf{r} + \xi \left(E_{kin} - \int t_s(\mathbf{r}) d\mathbf{r}\right). \tag{17}$$

ξ is the Lagrange multiplier. Note that a given ground-state Kohn–Sham problem is considered, therefore the density $n(\mathbf{r})$ is fixed. The variation leads to

$$\frac{4}{3N} \frac{t_s}{n} - \xi = 0. \tag{18}$$

Using Eqs. (9) and (10) it can be rewritten as

$$\beta = \frac{2}{N\xi}. \tag{19}$$

As the Lagrange multiplier ξ is a constant, the inverse temperature β (and the temperature T) is also constant.

Because of Eq. (4) the value of the temperature is given by

$$\frac{1}{\beta} = kT = \frac{2}{3N} E_{kin}. \tag{20}$$

That is, the kinetic energy density for which the Fisher information is minimum gives constant temperature. Furthermore, the kinetic energy density is proportional to the electron density and the temperature is proportional to the kinetic energy. Previously, we found that the maximum of the phase-space Shannon information entropy was also obtained for constant temperature [49]. It is remarkable that both the minimum phase-space Fisher information and the maximum phase-space Shannon information entropy are attained at constant temperature.