Fisher and Shannon Information in Orbital-Free Density Functional Theory

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(Dated: September 15, 2014)

Abstract

The Euler equation of the orbital-free density functional theory is formulated with the specific Shannon and Fisher information. One of the new forms contains only the specific Shannon information. In spherically symmetric systems the Euler equation can be formalized with the specific Fisher information only. Both the Fisher information and the length of the local wave vector are descriptors of the spherically symmetric Coulomb systems.

I. INTRODUCTION

Information theoretical concepts play more and more important role in physics and chemistry. They have turned to be useful in density functional theory, too. It started with the fundamental paper of Sears, Parr and Dinur [1]. In this paper a relationship between the quantum mechanical kinetic energy functional and the Fisher information [2] was established. The kinetic energy functional is of primary importance in orbital-free density functional theory. This approach has a great advantage over the Kohn-Sham scheme: only a single equation, the Euler equation, has to be considered independently from the number of electrons. In the Kohn-Sham method, on the other hand, many Kohn-Sham equations have to be solved for a large system with a lot of electrons. As the orbital-free scheme means a huge simplification in the calculations, very large systems can be treated with it. This is the reason of the long-standing interest in orbital-free dft. There is, however, a serious problem here rooted in the lack of knowledge of the kinetic energy functional. Finding a good approximation for the kinetic energy functional is of paramount importance. Among the several approaches within the orbital-free method we will concentrate here only on the information theoretical ones.

Since the fundamental paper of Sears, Parr and Dinur [1] the relationship between the Fisher information and the kinetic energy has been discussed in several papers [3–15]. On the other hand, another important information concept, the Shannon [16] information has been used in several fields of phyics. It has proved to be a very useful tool in analyzing atoms and molecules [1, 17–31].

In this paper the Euler equation of the orbital-free density functional theory is presented with the Shannon [16] and Fisher [2] information. The paper is organized as follows: After presenting the definition and some properties of the Fisher and Shannon information we summarize the relationship between the local wave-vector, the Shannon and Fisher information [9]. Then the reader is shortly reminded to the derivation of the Euler equation from the principle of extreme physical information. Finally, the Euler equation is reformulated with the Shannon and Fisher information.

II.   FISHER AND SHANNON INFORMATION

Consider a system specified by a parameter θ. The probability density function $p(x|\theta)$ satisfies

$$\int p(x|\theta)dx = 1. \tag{1}$$

Fisher information [2] defined as

$$I(\theta) = \int p(x|\theta) \left[\frac{\partial ln p(x|\theta)}{\partial \theta} \right]^2 dx = \int \frac{[p'(x|\theta)]^2}{p(x|\theta)} dx \tag{2}$$

gives the ability to estimate a parameter . The special case of translation invariance

$$p(x|\theta) = p(x + \theta) = p(\gamma) \tag{3}$$

leads to

$$\frac{\partial p(x|\theta)}{\partial \theta} = \frac{\partial p(x + \theta)}{\partial (x + \theta)} = \frac{\partial p(\gamma)}{\partial \gamma} . \tag{4}$$

Then the Fisher information (Eq. (2)) has the form

$$I(\theta) = \int \frac{1}{p(x + \theta)} \left[\frac{\partial p(x + \theta)}{\partial (x + \theta)} \right]^2 dx. \tag{5}$$

As the expression does not depend on θ, we may set it zero:

$$I(\theta = 0) = \int \frac{[p'(x)]^2}{p(x)} dx . \tag{6}$$

The Fisher information is a local measure, describes the 'narrowness' of a distribution. According to the Cramer-Rao inequality [32]

$$Var x \geq I^{-1}. \tag{7}$$

For the special case of a normal distribution the Fisher information is equal to the inverse variance. The consequence of the relation (7) is that a narrower distribution corresponds to a larger Fisher information.

Considering a distribution function with a vector variable the expression (6) has the form

$$I(\theta = 0) = \int \frac{[\nabla p(\mathbf{r})]^2}{p(\mathbf{r})} d\mathbf{r} . \tag{8}$$

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This expression is closely related to the full Weizsäcker kinetic energy [33]

$$T_w = \frac{1}{8} \int \frac{|\nabla n|^2}{n} d\mathbf{r}, \tag{9}$$

that is, the Weizsäcker kinetic energy [33] is proportional to the Fisher information:

$$T_w = \frac{N}{8} I , \tag{10}$$

where the number of electrons N arising from the fact that the electron density n is normalized to N, while the probability density function is normalized to 1.

Fisher information has proved to be very useful in studying several systems [4, 5, 34–37]. Even phase-space Fisher information [38] has been introduced.

The Shannon information [16] is defined as

$$S = - \int p(\mathbf{r}) \ln p(\mathbf{r}) d\mathbf{r}. \tag{11}$$

For a system with electron density n, the Shannon information can be written as

$$S = - \int n(\mathbf{r}) \ln n(\mathbf{r}) d\mathbf{r} = \int n(\mathbf{r}) s(\mathbf{r}) d\mathbf{r}, \tag{12}$$

where $n(\mathbf{r})s(\mathbf{r})$ is the local Shannon information and $s(\mathbf{r})$ is the specific Shannon information (Shannon information per particle). The Fisher information can also be written as

$$I = \int n(\mathbf{r}) i(\mathbf{r}) d\mathbf{r}, \tag{13}$$

where $n(\mathbf{r})i(\mathbf{r})$ is the local Fisher information and $i(\mathbf{r})$ is the specific Fisher information (Fisher information per particle).

Recently, a simple relationship between the Shannon and Fisher information has been explored [8, 9, 39] via the local wave-number introduced by Nagy and March [40] as the ratio of the density gradient to the electron density

$$\mathbf{q}(\mathbf{r}) = -\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})}, \tag{14}$$

The local wave-number [40] is useful in characterizing the shell structure of atoms [40, 41]. One can immediatelly see that

$$\mathbf{q}(\mathbf{r}) = \nabla s(\mathbf{r}), \tag{15}$$

$$i = \left(\frac{\nabla n}{n}\right)^2 = q^2 \tag{16}$$

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and

$$i = |\nabla s|^2. \tag{17}$$

That is, the local wave-vector $\mathbf{q}$ is the gradient of the Shannon information per particle, the square of the local wave-vector is the Fisher information per particle and the square of the gradient of the Shannon information per particle is the Fisher information per particle.

III. THE EULER EQUATION AND THE PRINCIPLE OF EXTREME PHYSICAL INFORMATION

The Euler equation of the density functional theory [42]

$$\frac{\delta E}{\delta n} = \mu \;, \tag{18}$$

where $E[n]$ is the total energy functional, can be written also in the non-interacting system as

$$\frac{\delta T_s}{\delta n} + v_{\mathrm{KS}} = \mu \;, \tag{19}$$

where T_s, v_{KS} and μ are the non-interacting kinetic energy, the Kohn-Sham potential and a Lagrange multiplier arising from the condition that the number of electrons is fixed, respectively. The non-interacting kinetic energy can be partitioned into two terms:

$$T_s = T_w + T_p \;, \tag{20}$$

where T_w is the full Weizsäcker kinetic energy (9) and the term T_p is called Pauli energy [43–46] arising from the Pauli principle. The functional derivatives are

$$\frac{\delta T_w}{\delta n} = \frac{1}{8} \left| \frac{\nabla n}{n} \right|^2 - \frac{1}{4} \frac{\nabla^2 n}{n} = n^{-1/2} \left(-\frac{1}{2} \nabla^2 \right) n^{1/2} \tag{21}$$

and

$$v_p = \frac{\delta T_p}{\delta n} \;, \tag{22}$$

where v_p is the Pauli potential. Therefore the Euler equation (18) can be rewritten as

$$\frac{\delta T_w}{\delta n} + v_p + v_{\mathrm{KS}} = \mu \;. \tag{23}$$

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It can also be written as a Schrödinger-like equation for the square root of the density

$$\left[-\frac{1}{2}\nabla^2 + v_p + v_{\text{KS}}\right] n^{1/2} = \mu n^{1/2}. \tag{24}$$

The Euler equation can be derived from the principle of extreme physical information [47], two. Here the derivation for the time independent case is summarized. The principle of extreme physical information [32] states that the 'physical information' K of the system is extremum

$$K = I - J = extrem., \tag{25}$$

where I is the fixed form of 'intrinsic' information defined above (Eqs. (6) and (8)). J is the bound Fisher information that is responsible for all constraints that are imposed by the physical phenomenon under measurement. Now, we minimize the Fisher information (6) with the following conditions: (a) The wave function is antisymmetric. As it was shown in [47, 48] this requirement can be taken into account by a local potential $w_p(\mathbf{r})$. (b) The density is kept fixed, that is, the density of the non-interacting system should be be equal to that of the interacting one. This requirement is taken into account by a local potential $w_{\text{KS}}\mathbf{r})$. (c) The electron density is normalized to N. This constraint is included by a Lagrange multiplicator ν.

The minimization

$$\frac{\delta}{\delta n}\left[\int \frac{|\nabla n|^2}{n}d\mathbf{r} + \int n w_p d\mathbf{r} + \int n w_{\text{KS}} d\mathbf{r} - \nu \int n d\mathbf{r}\right] = 0 \tag{26}$$

gives the Euler equation

$$\left|\frac{\nabla n}{n}\right|^2 - 2\frac{\nabla^2 n}{n} + w_p + w_{\text{KS}} = \nu \tag{27}$$

or

$$8\frac{\delta T_w}{\delta n} + w_p + w_{\text{KS}} = \nu . \tag{28}$$

Comparing Eq. (28) with the Euler equation (23) we see that

$$w_p(\mathbf{r}) = 8v_p(\mathbf{r}) , \tag{29}$$

$$w_{\text{KS}}(\mathbf{r}) = 8v_{\text{KS}}(\mathbf{r}) \tag{30}$$

and

$$\nu = 8\mu . \tag{31}$$

In the following section Eq. (27) will be utilized to formalize the Euler equation with Fisher and Shannon information.

IV. EULER EQUATION, FISHER AND SHANNON INFORMATION

The Euler equation (27) can be rewritten applying Eqs. (14) - (16). We can immediatelly obtain

$$\nabla \mathbf{q} = -\nabla^2(\ln n) = \nabla^2 s = \left|\frac{\nabla n}{n}\right|^2 - \frac{\nabla^2 n}{n} = q^2 - \frac{\nabla^2 n}{n}. \tag{32}$$

Therefore the first two terms in Eq. (27) can be rewritten as

$$\left|\frac{\nabla n}{n}\right|^2 - 2\frac{\nabla^2 n}{n} = -q^2 + 2\nabla^2 s = -i + 2\nabla^2 s. \tag{33}$$

Substituting Eq. (33) into Eq. (27) we arrive at the new form of the Euler equation

$$2\nabla^2 s - i + w_p + w_{\text{KS}} = \nu. \tag{34}$$

Utilizing Eq. (17) another form can be gained:

$$2\nabla^2 s - |\nabla s|^2 + w_p + w_{\text{KS}} = \nu. \tag{35}$$

The new forms (34) and (35) of the Euler equation constitute the main results of the paper. Eq. (34) contains both the Shannon and the Fisher information and the effective potential $w_{eff} = w_p + w_{\text{KS}} - \nu$. On the other hand, in Eq. (35) appears only the Shannon information and the effective potential.

V. DESCRIPTORS OF COULOMB SYSTEMS

According to the density functional theory, the ground-state electron density determines every property of the electron system [42]. In case of a Coulomb system, however, not only the electron density has this feature. Other quantities have also been turned out to be descriptors of a Coulomb system. The shape function, or density per particle was the

first quantity, that has been shown [49] to be adequate for describing a Coulomb system. Reactivity indicators [50] as Fukui function, local softness, softness kernel, electrostatic potential, local kinetic energy and local temperature [51] also provide a full description of a Coulomb system. Even broader families [53, 54] of descriptors for Coulomb systems have been presented.

Recently, it has been proved that the local Shannon information $n(\mathbf{r})s(\mathbf{r}) = -n(\mathbf{r}) \ln n(\mathbf{r})$ is also capable of fully determining every property of a Coulomb system [55]. It is trivial that the specific Shannon information $s(\mathbf{r})$ is also adequate for describing a Coulomb system. Using $s(\mathbf{r})$ instead of $n(\mathbf{r})$ in the Euler equation is interesting if the effective potential $w_{eff} = w_p + w_{\mathrm{KS}} - \nu$ can also be expressed with $s(\mathbf{r})$. A series of publications [56–59] proposed that the kinetic energy can be written as a sum of two terms. One of them is propotional to the Fisher information, the other resembles the Shannon information. We mention here that Massen and Panos [60] proposed a relationship between the phase-space Shannon information and the kinetic energy. It is well-known that the LDA correlation energy in the high-density limit contains a term which is proportional to the local Shannon information [59]. Therefore it is very likely that approximations for the effective potential w_{eff} can be constructed with $s(\mathbf{r})$.

The local wave-number $\mathbf{q}$ is also a descriptor for Coulomb systems. It follows from the definition of $\mathbf{q}$ (Eq.(14)):

$$\mathbf{q}(\mathbf{r}) = -\frac{\nabla n}{n} = -\nabla \ln n, \tag{36}$$

as

$$\ln n = -\int_{\mathbf{r_0}}^{\mathbf{r}} \mathbf{q}(\mathbf{r})d\mathbf{r}. \tag{37}$$

The constant in Eq. (37) can be given by the normalization of the density n.

VI. EXAMPLE AND DISCUSSION

As a special case consider now spherically symmetric systems, where the density depends only on the radial distance r. In that case Eq. (33) takes the form

$$\left|\frac{\nabla n}{n}\right|^2 - 2\,\frac{\nabla^2 n}{n} = -q^2 + 2q' + 4\frac{q}{r}. \tag{38}$$

Then the Euler equation (27) can be expressed with the wave vector

$$-q^2 + 4\frac{q}{r} + 2q' + w_p + w_{\text{KS}} = \nu. \tag{39}$$

Using Eq. (16) the Fisher information appears in the Euler equation (39)

$$-i + 4\frac{i^{1/2}}{r} + 2(i^{1/2})' + w_p + w_{\text{KS}} = \nu. \tag{40}$$

That is, there exist an Euler equation for the Fisher information, too, in spherically symmetric Coulomb systems. Moreover, both the Fisher information and the length of the wave vector are also descriptors of the spherically symmetric Coulomb systems.

In summary, the Euler equation of the orbital-free density functional theory is presented with the specific Shannon [16] and Fisher [2] information. One of the new forms contains only the specific Shannon information (and the effective potential, of course). In case of spherically symmetric systems the Euler equation can be formalized with the specific Fisher information only.

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Acknowledgments