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Relative information in excited-state orbital-free density functional theory

Ágnes Nagy

Department of Theoretical Physics, University of Debrecen, Debrecen, Hungary

Correspondence
Ágnes Nagy, Department of Theoretical Physics, University of Debrecen,
H-4002 Debrecen, Hungary.
Email: anagy@phys.unideb.hu

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Abstract

Euler equations of the orbital-free excited-state density functional theory of Coulomb systems are derived for specific relative information. Derivation via variational extremization of the relative Fisher information is also presented. Relationships between the Fisher and Shannon information, the local wave vector, and the relative information are displayed.

KEYWORDS

excited-state density functional theory, relative Fisher information, relative Shannon information

1 | INTRODUCTION

Information theory has increasing importance in several fields of science. Among others, chemistry, physics, biology, mathematics, engineering, and materials science benefit much from concepts of information theory. Information-theoretic concepts have proven to be especially useful in density functional theory (DFT).[1] The fundamental paper of Sears et al.[2] presenting a relationship between the quantum mechanical kinetic energy functional and the Fisher information[3] was the beginning. Since then, several papers[4–16] have studied this field. The Shannon information[17] has also been used in the DFT for a long time.[18–29]

DFT is particularly suitable for information-theoretic concepts as the density, the fundamental quantity of DFT, is in fact a probability distribution function. The key information-theoretic quantities, such as Shannon and Fisher information, are functionals of the density. According to the basic theorem of the DFT, the density determines the external potential, and hence the Hamiltonian, consequently of any property of the system. As it turned out, not only the density but some other quantities have this remarkable property. It has been shown[30] that the local Shannon information also determines every property of a finite Coulomb system both in the ground and excited states. Namely, the local Shannon information really contains all "information" about the system; it can also be considered a descriptor of a Coulomb system. We can also ask how these descriptors can be obtained and if there are equations that we can solve to calculate them directly. It has been shown[31] that Euler equations can be conveniently derived for the specific Shannon and Fisher information in the ground-state orbital-free DFT.

In orbital-free DFT, the Euler equation should be solved instead of the Kohn-Sham equations. There is only one Euler equation, while there are several Kohn-Sham equations for a system with many electrons. Therefore, orbital-free DFT can be used to study large systems if adequate approximation for the kinetic energy functional is available. It was found that information theoretical concepts are useful to approximate kinetic energy functionals. It is worth mentioning that there exists an orbital-free scheme in which the knowledge of the kinetic energy functional is not needed.[32,33]

The information-theoretic view has been mainly used in the ground-state DFT, although excited-state investigations would be also very important. Therefore, here, we concentrate on information concepts for excited states.

There are several ways to treat excited states in DFT (see, eg, References [34–42]). Now, consider the time-independent DFT for a single excited state of a Coulomb system.[43–45] Coulomb systems are very common as they include atoms, molecules, or solids. Coulomb density is distinctive because it determines not only its Hamiltonian but the degree of excitation as well. The existence of a universal excited-state variational functional for the sum of the kinetic and electron-electron repulsion energies has been proven. Both the Euler equation and the Kohn-Sham equations have been derived. These equations strongly resemble those of the ground-state theory.

In this paper, the Euler equation of the non-interacting system,

$$\left.\frac{\delta T_s^{\mathrm{Coul}}[n]}{\delta n}\right|_{n=n_k} + w([n_k];\mathbf{r}) = \mu_k \tag{1}$$

is utilized, where T_s^{Coul}, w, and μ are the noninteracting kinetic energy functional, the Kohn-Sham potential, and the chemical potential, respectively. n_k is the density of the kth excited state. The existence of excited-state Euler equations for specific Shannon information is proven. Furthermore, the Euler equation for the relative specific Shannon information is derived. Moreover, derivation of the Euler equation is also presented via variational extremization of the relative Fisher information.

The paper is organized as follows: Section 2 presents the definition of the Fisher and Shannon information, the local wave vector, and the relative information. In Section 3, the Euler equation for the relative specific Shannon information is derived. Section 4 presents the derivation of the Euler equation for the relative specific Shannon information via variational extremization of the relative Fisher information. The last section is devoted to discussion.

2 | RELATIVE INFORMATION

The Shannon information[17] is defined as

$$S_f = -\int f(\mathbf{r}) \ln f(\mathbf{r}) d\mathbf{r}, \tag{2}$$

where the probability density function $f(\mathbf{r})$ satisfies

$$\int f(\mathbf{r}) d\mathbf{r} = 1. \tag{3}$$

For a system with electron density n, the Shannon information is often written as

$$S = -\int n(\mathbf{r}) \ln n(\mathbf{r}) d\mathbf{r}, \tag{4}$$

where the density is normalized to the number of electrons N. Therefore, $S = NS_f - N \ln N$. S can be expressed with the local Shannon information $n(\mathbf{r})s(\mathbf{r})$

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

where $s(\mathbf{r}) = -\ln n(\mathbf{r})$ is the specific Shannon information (Shannon information per particle).[31]

Shannon information is related to the local wave number introduced by Nagy and March[46] as the ratio of the density gradient to the electron density

$$\mathbf{q}(\mathbf{r}) = -\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})}. \tag{6}$$

Therefore,[9,10,31]

$$\mathbf{q}(\mathbf{r}) = \nabla s(\mathbf{r}). \tag{7}$$

The local wave number was found to be favorable to describe the atomic shell structure.[46,47]

If we have another (reference) probability density function $f^{\mathrm{ref}}(\mathbf{r})$, we can determine the relative or Kullback-Leibler information (also called cross-entropy)[48]

$$G_f = \int f(\mathbf{r}) \ln \frac{f(\mathbf{r})}{f_{\mathrm{ref}}(\mathbf{r})} d\mathbf{r} \tag{8}$$

as information obtained by using $f(\mathbf{r})$ instead of $f_{\mathrm{ref}}(\mathbf{r})$. G is a measure of the deviation of $f(\mathbf{r})$ from the reference density $f_{\mathrm{ref}}(\mathbf{r})$. $G_f \geq 0$ with equality if and only if $f = f_{\mathrm{ref}}$ almost everywhere. The relative information obtained from the density takes the form

$$G = \int n(\mathbf{r}) \ln \frac{n(\mathbf{r})}{n_{\mathrm{ref}}(\mathbf{r})} d\mathbf{r} = N G_f . \tag{9}$$

The relative local wave vector was defined as[49]

$$\tilde{\mathbf{q}}(\mathbf{r}) = \mathbf{q}(\mathbf{r}) - \mathbf{q}_{\mathrm{ref}}(\mathbf{r}), \tag{10}$$

where

$$\mathbf{q}_{\mathrm{ref}}(\mathbf{r}) = -\frac{\nabla n_{\mathrm{ref}}(\mathbf{r})}{n_{\mathrm{ref}}(\mathbf{r})}. \tag{11}$$

Utilizing Equation (7), we are led to

$$\tilde{\mathbf{q}}(\mathbf{r}) = \nabla[s(\mathbf{r}) - s_{\mathrm{ref}}(\mathbf{r})] = -\nabla \ln\left(\frac{n(\mathbf{r})}{n_{\mathrm{ref}}(\mathbf{r})}\right). \tag{12}$$

Fisher information[3] is defined as

$$I_f = \int \frac{|\nabla f(\mathbf{r})|^2}{f(\mathbf{r})} d\mathbf{r} \tag{13}$$

or if it is expressed with the density

$$I = \int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} d\mathbf{r}. \tag{14}$$

I is related to the Weizsäcker kinetic energy[50]

$$T_{\mathrm{w}} = \frac{1}{8} \int \frac{|\nabla n|^2}{n} d\mathbf{r}. \tag{15}$$

T_{w} is proportional to the Fisher information:

$$T_{\mathrm{w}} = \frac{1}{8} I = \frac{N}{8} I_f . \tag{16}$$

I can be expressed with the local Fisher information $n(\mathbf{r})i(\mathbf{r})$ as

$$I = \int n(\mathbf{r}) i(\mathbf{r}) d\mathbf{r}, \tag{17}$$

where $i(\mathbf{r}) = (|\nabla n(\mathbf{r})| / n(\mathbf{r}))^2$ is the specific Fisher information (Fisher information per particle).[31] The local wave number establishes a link between the Shannon and Fisher information. Namely, $\mathbf{q}$ is the gradient of the specific Shannon information, while the square of $\mathbf{q}$ gives the specific Fisher information: $i = |\nabla s|^2 = q^2$.

The relative Fisher information corresponding Equation (13) is

$$J_f = \int f(\mathbf{r}) \left| \nabla \left(\ln \frac{f(\mathbf{r})}{f_{\mathrm{ref}}(\mathbf{r})} \right) \right|^2 d\mathbf{r} \tag{18}$$

or with the density

$$J = \int n(\mathbf{r}) \left| \nabla \left(\ln \frac{n(\mathbf{r})}{n_{\mathrm{ref}}(\mathbf{r})} \right) \right|^2 d\mathbf{r}. \tag{19}$$

This quantity has already found several interesting applications.[51–56] J can also be rewritten as

$$J = \int n(\mathbf{r}) \left| \frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} - \frac{\nabla n_{\mathrm{ref}}(\mathbf{r})}{n_{\mathrm{ref}}(\mathbf{r})} \right|^2 d\mathbf{r}. \tag{20}$$

3 | EULER EQUATION FOR THE RELATIVE SPECIFIC SHANNON INFORMATION

The noninteracting kinetic energy $T_{\mathrm{s}}^{\mathrm{Coul}}[n]$ can be divided into two terms:

$$T_{\mathrm{s}}^{\mathrm{Coul}}[n] = T_{\mathrm{w}}[n] + T_{\mathrm{p}}^{\mathrm{Coul}}[n] \ , \tag{21}$$

where T_{w} is the Weizsäcker kinetic energy. Analogous to the standard DFT,[57–60] we can call the term $T_{\mathrm{p}}^{\mathrm{Coul}}$ Pauli energy. The functional derivatives are

$$\frac{\delta T_{\mathrm{w}}}{\delta n} = \frac{1}{8} \left| \frac{\nabla n}{n} \right|^2 - \frac{1}{4} \frac{\nabla^2 n}{n} \tag{22}$$

and

$$v_{\mathrm{p}}([n];\mathbf{r}) = \frac{\delta T_{\mathrm{p}}^{\mathrm{Coul}}[n]}{\delta n}, \tag{23}$$

where v_{p} is the Pauli potential. Therefore, the Euler Equation (1) of the kth excited state can be rewritten as

$$\left. \frac{\delta T_{\mathrm{w}}[n]}{\delta n} \right|_{n=n_k} + v_{\mathrm{p}}([n_k];\mathbf{r}) + w([n_k];\mathbf{r}) = \mu_k. \tag{24}$$

$\frac{\delta T_{\mathrm{w}}}{\delta n}$ can be expressed with the specific Shannon information and the local wave vector as

$$\frac{\delta T_{\mathrm{w}}}{\delta n} = \frac{1}{4} \nabla^2 s(\mathbf{r}) - \frac{1}{8} |\nabla s(\mathbf{r})|^2 = \frac{1}{4} \nabla q(\mathbf{r}) - \frac{1}{8} [q(\mathbf{r})]^2. \tag{25}$$

Then, the Euler Equation (1) of the kth excited state takes the form

$$\frac{1}{4} \nabla^2 s_k(\mathbf{r}) - \frac{1}{8} |\nabla s_k(\mathbf{r})|^2 + v_{\mathrm{p}}([n_k];\mathbf{r}) + w([n_k];\mathbf{r}) = \mu_k. \tag{26}$$

Formally, this equation is the same derived earlier[31] for the ground state:

$$\frac{1}{4} \nabla^2 s_0(\mathbf{r}) - \frac{1}{8} |\nabla s_0(\mathbf{r})|^2 + v_{\mathrm{p}}([n_0];\mathbf{r}) + w([n_0];\mathbf{r}) = \mu_0, \tag{27}$$

where the subscript 0 refers to the ground state. It is the consequence of the fact that the Euler Equation (1) also has the same form for the ground and the excited states. The excited-state theory of Coulomb systems[43–45] was constructed to ensure proper orthogonality conditions for the excited states.

Euler Equations (26) and (27) can be rewritten with the local wave vectors as

$$\frac{1}{4}\nabla \mathbf{q}_k(\mathbf{r}) - \frac{1}{8}[q_k(\mathbf{r})]^2 + v_{\mathrm{p}}([n_k];\mathbf{r}) + w([n_k];\mathbf{r}) = \mu_k \tag{28}$$

and

$$\frac{1}{4}\nabla \mathbf{q}_0(\mathbf{r}) - \frac{1}{8}[q_0(\mathbf{r})]^2 + v_{\mathrm{p}}([n_0];\mathbf{r}) + w([n_0];\mathbf{r}) = \mu_0. \tag{29}$$

The relative specific Shannon information is now defined as

$$\tilde{s}_k(\mathbf{r}) = s_k(\mathbf{r}) - s_0(\mathbf{r}) = -\ln\left(\frac{n_k(\mathbf{r})}{n_0(\mathbf{r})}\right). \tag{30}$$

It is related to the relative local wave vector

$$\tilde{\mathbf{q}}_k(\mathbf{r}) = \mathbf{q}_k(\mathbf{r}) - \mathbf{q}_0(\mathbf{r}) = \nabla \tilde{s}_k(\mathbf{r}), \tag{31}$$

where the ground state is selected for the reference state. The difference of the Euler Equation (24) for the *k*th excited state and the ground state gives

$$\left.\frac{\delta T_{\mathrm{w}}[n]}{\delta n}\right|_{n=n_k} - \left.\frac{\delta T_{\mathrm{w}}[n]}{\delta n}\right|_{n=n_0} + v_{\mathrm{p}}([n_k];\mathbf{r}) - v_{\mathrm{p}}([n_0];\mathbf{r}) + w([n_k];\mathbf{r}) - w([n_0];\mathbf{r}) = \mu_k - \mu_0. \tag{32}$$

Combining Equations (26) to (32), we are led to the Euler equation for the relative specific Shannon information

$$\frac{1}{4}\nabla^2 \tilde{s}_k(\mathbf{r}) - \frac{1}{8}|\nabla \tilde{s}_k(\mathbf{r})|^2 - \frac{1}{4}\nabla s_0(\mathbf{r})\nabla \tilde{s}_k(\mathbf{r}) + \tilde{v}_{\mathrm{p}}([n_k,n_0];\mathbf{r}) + \tilde{w}([n_k,n_0];\mathbf{r}) = \tilde{\mu}_k. \tag{33}$$

The Euler equation can be reformulated for the relative local wave vector:

$$\frac{1}{4}\nabla \tilde{\mathbf{q}}_k(\mathbf{r}) - \frac{1}{8}[\tilde{q}_k(\mathbf{r})]^2 - \frac{1}{4}\mathbf{q}_0(\mathbf{r})\tilde{\mathbf{q}}_k(\mathbf{r}) + \tilde{v}_{\mathrm{p}}([n_k,n_0];\mathbf{r}) + \tilde{w}([n_k,n_0];\mathbf{r}) = \tilde{\mu}_k, \tag{34}$$

where

$$\tilde{w}([n_k,n_0];\mathbf{r}) = w([n_k];\mathbf{r}) - w([n_0];\mathbf{r}), \tag{35}$$

$$\tilde{v}_{\mathrm{p}}([n_k,n_0];\mathbf{r}) = v_{\mathrm{p}}([n_k];\mathbf{r}) - v_{\mathrm{p}}([n_0];\mathbf{r}) \tag{36}$$

and

$$\tilde{\mu}_k = \mu_k - \mu_0. \tag{37}$$

We can define the relative specific Fisher information as

$$j_k(\mathbf{r}) = \left|\nabla\left(\ln\frac{n_k(\mathbf{r})}{n_o(\mathbf{r})}\right)\right|^2. \tag{38}$$

j_k can be expressed with the relative local wave vector or with the relative specific Shannon information

$$j_k(\mathbf{r}) = |\tilde{\mathbf{q}}_k(\mathbf{r})|^2 = |\nabla \tilde{s}_k(\mathbf{r})|^2. \tag{39}$$

Equation (39) creates a link between the relative specific Shannon and Fisher information: $\tilde{\mathbf{q}}_k$ is the gradient of the relative specific Shannon information, while the square of $\tilde{\mathbf{q}}_k$ provides the relative specific Fisher information.

Utilizing Equation (33), the relative specific Fisher information can be given as

$$j_k(r) = 2\nabla^2 \tilde{s}_k(\mathbf{r}) - 2\nabla s_0(\mathbf{r})\nabla \tilde{s}_k(\mathbf{r}) + 8\tilde{v}_{\mathrm{p}}([n_k,n_0];\mathbf{r}) + 8\tilde{w}([n_k,n_0];\mathbf{r}) - 8\tilde{\mu}_k. \tag{40}$$

j_k can also be expressed with the local wave vector

$$j_k(\mathbf{r}) = 2\nabla \tilde{\mathbf{q}}_k(\mathbf{r}) - 2\mathbf{q}_0(\mathbf{r})\tilde{\mathbf{q}}_k(\mathbf{r}) + 8\tilde{v}_{\mathrm{p}}([n_k,n_0];\mathbf{r}) + 8\tilde{w}([n_k,n_0];\mathbf{r}) - 8\tilde{\mu}_k. \tag{41}$$

4 | DERIVATION OF THE EULER EQUATION FOR THE RELATIVE SPECIFIC SHANNON INFORMATION VIA VARIATIONAL EXTREMIZATION OF THE RELATIVE FISHER INFORMATION

The Euler equation for the relative specific Shannon information can be derived with variational extremization of the relative Fisher information. The derivation is similar to that of the Euler equation of the ground-state DFT with the variation of Fisher information.[4] We minimize the relative Fisher information J (19 or 20) with the density of the given excited state $n = n_k$ and the ground state as the reference state $n_{\mathrm{ref}} = n_0$. The variation is carried out with the following constraints: (a) The wave function is antisymmetric. As was shown in Nagy[4] and Flores and Keller,[61] this requirement can be taken into account by a local potential u_p. (b) The density n_k is fixed to ensure that the density of the noninteracting system is equal to that of the interacting one. A local potential u takes care of this demand. (c) A Lagrange multiplicator ν is applied with the normalization of n_k. The variation

$$\frac{\delta}{\delta n_k}\left[\int n_k(\mathbf{r})\left|\nabla\left(\ln\frac{n_k(\mathbf{r})}{n_0(\mathbf{r})}\right)\right|^2 d\mathbf{r} + \int n_k(\mathbf{r})u_{\mathrm{p}}(\mathbf{r})d\mathbf{r} + \int n_k(\mathbf{r})u(\mathbf{r})dr - \nu\int n_k(\mathbf{r})d\mathbf{r}\right] = 0 \tag{42}$$

leads to the Euler equation

$$8\left(\frac{\delta T_{\mathrm{w},k}}{\delta n_k} - \frac{\delta T_{\mathrm{w},0}}{\delta n_0}\right) + u_{\mathrm{p}}(\mathbf{r}) + u(\mathbf{r}) = \nu. \tag{43}$$

We can immediately see that Equation (43) is the same as the Euler Equation (32) if we write

$$u_{\mathrm{p}}(\mathbf{r}) = 8\tilde{v}_{\mathrm{p}}([n_k,n_0];\mathbf{r}), \tag{44}$$

$$u(\mathbf{r}) = 8\tilde{w}([n_k,n_0];\mathbf{r}) \tag{45}$$

and

$$\nu = 8\tilde{\mu}_k\ . \tag{46}$$

Using the definition of s, $\tilde{s}$, $\mathbf{q}$, and $\tilde{\mathbf{q}}$, we can readily obtain Euler Equations (33) and (34) for relative specific Shannon information and the relative local wave vector.

5 | DISCUSSION

The main results of this paper include the excited-state Euler equations for the specific Shannon information and local wave vector and the relative specific Shannon information and the relative local wave vector. The theory can be applied to degenerate states as well. As was shown in

Ayers et al.[45], utilizing subspace densities instead of the density, the formalism remains the same. Therefore, the form of the excited-state Euler equations derived here is unchanged.

Observe that the Euler equation for s_k (Equation 26) (or $\mathbf{q}_k$ (Equation 28)) contains only the potentials of the given excited state. On the other hand, the Euler equation for $\tilde{s}_k$ (Equation 33) (or $\tilde{\mathbf{q}}_k$ (Equation 34)) incorporates the difference of the excited- and ground-state potentials. Of course, we expect it as the relative information always measures deviation from some reference state.

There is an important theorem for Coulomb systems, Kato's theorem.[62,63] It is valid both for ground and excited states.[41,42]

$$\left.\frac{\partial \bar{n}_k(\mathbf{r})}{\partial\,|\mathbf{r}-\mathbf{R}_\beta|}\right|_{\mathbf{r}=\mathbf{R}_\beta} = -2Z_\beta n_k(\mathbf{r}=\mathbf{R}_\beta). \tag{47}$$

$\bar{n}_k$ is the spherical average of the density around the nucleus at $\mathbf{R}_\beta$ with atomic number Z_β. Therefore, the cusp for the specific Shannon information is

$$\left.\frac{\partial \bar{s}_k(\mathbf{r})}{\partial\,|\mathbf{r}-\mathbf{R}_\beta|}\right|_{\mathbf{r}=\mathbf{R}_\beta} = -2Z_\beta. \tag{48}$$

Equation (48) holds for the ground state too. Consequently, we obtain zero for the relative specific Shannon information

$$\left.\frac{\partial \bar{\tilde{s}}_k(\mathbf{r})}{\partial\,|\mathbf{r}-\mathbf{R}_\beta|}\right|_{\mathbf{r}=\mathbf{R}_\beta} = 0. \tag{49}$$

Thus,

$$j_k(\mathbf{r}=\mathbf{R}_\beta) = 0. \tag{50}$$

The asymptotic decay of the electron density n_k.[58,64–66]

$$\lim_{r\to\infty}\frac{\partial \ln \bar{n}_k(r)}{\partial r} = -\sqrt{8I_k} \tag{51}$$

is governed by the vertical ionization potential I_k of the N-electron system

$$I_k = E_0^{N-1} - E_k. \tag{52}$$

E_0^{N-1} is the ground-state energy of the $N-1$ electron system. Therefore,

$$\lim_{r\to\infty}\frac{\partial \bar{s}_k(r)}{\partial r} = \sqrt{8I_k}\,. \tag{53}$$

$k = 0$ gives the asymptotic behavior for s_0. The relative specific Shannon information behaves as follows:

$$\lim_{r\to\infty}\frac{\partial \bar{\tilde{s}}_k(r)}{\partial r} = \sqrt{8I_k}-\sqrt{8I_0}. \tag{54}$$

It gives the decay of the relative specific Fisher information

$$\lim_{r\to\infty} j_k^{1/2} = \sqrt{8I_k}-\sqrt{8I_0}. \tag{55}$$

As an illustration, consider the hydrogen atom. The ground-state density is

$$n_0(r) = \frac{Z^3}{\pi}e^{-2Zr}, \tag{56}$$

where r and Z are the radial distance and the atomic number, respectively. Atomic units are used in the paper. The specific Shannon information takes the form

$$s_0(r) = -\ln(n_0(r)) = 2Zr - \ln\left(Z^3/\pi\right). \tag{57}$$

In the Euler Equation (27), $w_0(r) = -Z/r$ is the Coulomb potential, and the Pauli potential is zero, because we have only one electron. $\mu_0 = -Z^2/2$ is the energy corresponding to the 1*s* state.

The first excited state is degenerate. Therefore, a subspace density[45] is constructed from the average of the densities of the 2*s* and 2*p* states:

$$n_1(r) = \frac{Z^3}{64\pi}\left(Z^2r^2 - 2Zr + 2\right)e^{-Zr}. \tag{58}$$

The specific Shannon information takes the form

$$s_1(r) = -\ln n_1(r) = Zr - \ln\left(Z^3/64\pi\right) - \ln\left(Z^2r^2 - 2Zr + 2\right). \tag{59}$$

It is interesting to observe that the Pauli potential is not zero. Although there is only one electron, the Pauli potential does not disappear because the subspace density is used. It can be easily calculated from the Euler Equation (26)

$$v_{p1}(r) = \frac{Z^2}{2}\frac{Z^2r^2 - 2Zr + 3}{\left(Z^2r^2 - 2Zr + 2\right)^2}. \tag{60}$$

$w_1(r) = -Z/r$ is the Coulomb potential, and $\mu_1 = -Z^2/8$ is the energy corresponding to the 2*s* and 2*p* states. Figure 1 presents the Pauli potential. As expected, the Pauli potential is positive and reaches zero at infinity.

The relative specific Shannon information is given by

$$\tilde{s}_1(r) = s_1(r) - s_0(r) = \ln 64 - Zr - \ln\left(Z^2r^2 - 2Zr + 2\right). \tag{61}$$

The derivative of $\tilde{s}_1$ takes the form

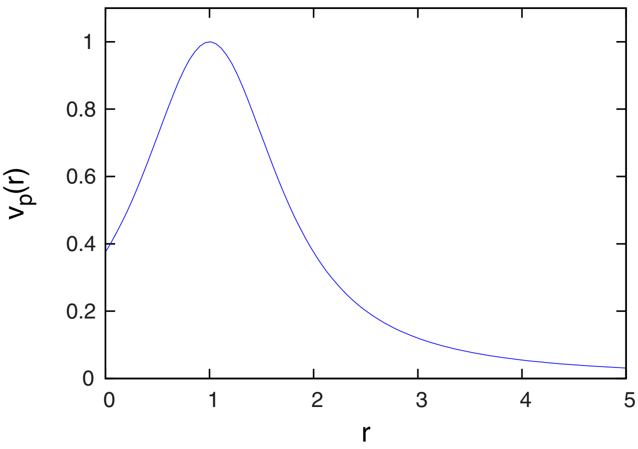
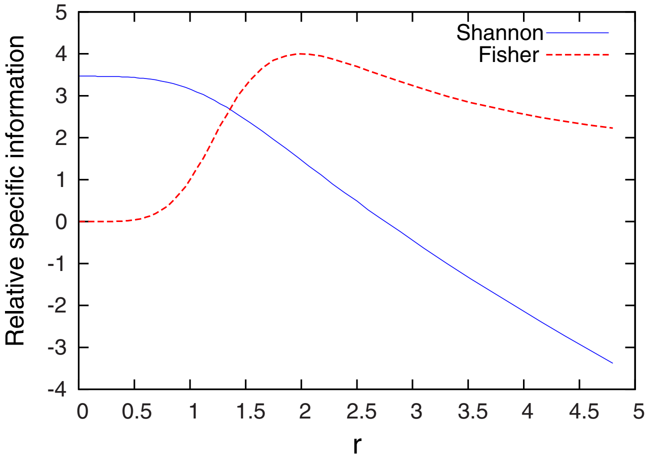


FIGURE 1 Pauli potential for the first excited state of the hydrogen atom as a function of the radial distance r

FIGURE 2 Relative specific Shannon (blue solid line) and Fisher information (red dashed line) for the first excited state of the hydrogen atom as a function of the radial distance *r*



$$\tilde{s}_1'(r) = s_1'(r) - s_0'(r) = -\frac{Z^3 r^2}{Z^2 r^2 - 2Zr + 2}. \tag{62}$$

The relative specific Fisher information can be given as

$$j_1(r) = \left(\tilde{s}_1'(r)\right)^2 = \frac{Z^6 r^4}{\left(Z^2 r^2 - 2Zr + 2\right)^2}. \tag{63}$$

Figure 2 presents the relative specific Shannon and Fisher information. The relative Shannon information measures the deviation of the excited-state density from the ground-state density. For large *r*, it is almost linear ($\tilde{s} \approx -Zr$). On the other hand, the relative specific Fisher information contains the derivative of the densities; therefore, it incorporates a higher-order deviation from the reference state. It is zero at $r = 0$ (Equation 50) and goes to Z^2 at infinity.

Information-theoretic concepts have proven to be very fruitful in the studies of other chemical reactions. Reactivity and selectivity descriptors are mainly used in the ground-state theory, although several of these descriptors can be linked to excitability. Years ago, the present author proposed that the first excitation energy can be used as a reactivity index instead of hardness.[67] Nowadays, excited-state reactivity is a new frontier.[68–70] A recent paper studies chemical selectivity through well-selected excited states.[71] It is believed that involving the concept of relative specific Shannon information may be profitable in analyzing reactivity.

In summary, relative information is investigated within the excited-state theory of Coulomb systems. Euler equations are derived for the specific Shannon information and local wave vector and the relative specific Shannon information and the relative local wave vector. These information theoretical concepts are expected to be useful in studying excited-state reactivity.

ORCID

Ágnes Nagy https://orcid.org/0000-0003-2605-9644

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