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ORIGINAL PAPER

Information-theoretic approach to kinetic-energy functionals: the nearly uniform electron gas

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Abstract We strengthen the connection between information theory and quantum mechanical systems using a recently developed dequantization procedure which results in a decomposition of the kinetic energy as the sum of a classical term and a purely quantum term. For the nearly uniform electron gas, we thereby approximate the non-interacting kinetic energy as the sum of the Thomas-Fermi term, which is exact for the uniform electron gas, and the Weizsäcker term, which is proportional to the Fisher information. Electron correlation is included via a nonlocal analytical expression which is a functional of the (N-1)-conditional probability density. This expression is evaluated via a statistically rigorous Monte-Carlo procedure to obtain the correlation energy as a functional of the electron density. We show that this functional is well aproximated by a term which is proportional to the Shannon entropy. Thus the kinetic energy is expressed as the standard Thomas-Fermi term plus terms which are proportional to two of the cornerstones of information theory: the Fisher information, which is a measure of localization, and the Shannon entropy, which is a measure of delocalization.

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1 Introduction

The great potential of quantum information science [1] has led to an increasing interest in the connection between quantum mechanics and information theory. Two of the cornerstones of information theory are the Fisher information, [2,3] which is a measure of localization, and the Shannon entropy, [4] which is a measure of delocalization. The Fisher information and the Shannon entropy are complementary quantities and, for atomic systems, they have been used in conjunction to analyze electron correlation and other electronic properties for which electron localization and electron delocalization are simultaneously important. [5,6] Recently, we suggested [7] that the Fisher information and a term analogous to the Shannon entropy could be used in conjunction for the construction of kinetic-energy functionals in density functional theory. [8] In this paper we strengthen the connection between quantum mechanics and information theory via an information-theoretic construction of the kinetic-energy functional for the nearly uniform electron gas.

Our starting point for the construction of the kinetic-energy functional is the uniform (noninteracting) electron gas. For this system the kinetic-energy functional is given exactly by the Thomas-Fermi term, [9,10]

$$T_{TF} = \frac{3\hbar^2}{10m}(3\pi^2)^{2/3}\int \rho^{5/3} d^3\boldsymbol{r}. \tag{1}$$

For the nearly uniform electron gas, no exact kinetic-energy functional is known. For this system, we obtain an approximate but accurate expression for the kinetic-energy functional as the sum of three terms: the standard Thomas-Fermi term, a term proportional to the Fisher information, and a term proportional to the Shannon entropy.

The Fisher information is

$$\mathscr{I}_{\mathrm{F}} = \int \frac{|\nabla p(\boldsymbol{r})|^2}{p(\boldsymbol{r})} d^3\boldsymbol{r} \tag{2}$$

where $p(\boldsymbol{r}) = p(\boldsymbol{r}_1) = \int |\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)|^2 \, d^3\boldsymbol{r}_2 \ldots d^3\boldsymbol{r}_N$ is the one-electron probability density. The electron density, $\rho(\boldsymbol{r})$, is related to the one-electron probability density by $\rho(\boldsymbol{r}) = Np(\boldsymbol{r})$. Thus $\mathscr{I}_{\mathrm{F}}$ is a functional of the electron density and the greater the *localization* of $\rho(\boldsymbol{r})$, the greater the value of the Fisher information. An alternative starting point for the construction of kinetic-energy functionals is the hydrogen atom. For this system the kinetic-energy functional is given exactly by the Weizsäcker term [11]

$$T_W = \frac{\hbar^2}{8m}\int \frac{|\nabla \rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})} d^3\boldsymbol{r}. \tag{3}$$

Comparison of Eqs. 2 and 3 shows that the Weizsäcker term is identical in information content to the Fisher information (with $T_W = \frac{N\hbar^2}{8m}\mathscr{I}_{\mathrm{F}}$).

The Shannon entropy is

$$\mathscr{E}_{\mathrm{S}} = -\int \rho(\boldsymbol{r}) ln(\rho(\boldsymbol{r})) d^3\boldsymbol{r}. \tag{4}$$

Thus $\mathscr{E}_{\mathrm{S}}$ is a functional of the electron density and the greater the *delocalization* of $\rho(\boldsymbol{r})$, the greater the value of the Shannon entropy.

2 Kinetic energy decomposition

We have developed a dequantization procedure, first based on the Witten deformation [12] and subsequently based on a variational principle, [13] which results in a decomposition of the kinetic energy as the sum of a classical term and a purely quantum term. The N-electron kinetic energy, T_N, can be expressed as

$$T_N = T_{C,N} + T_{W,N}. \tag{5}$$

Here the N-electron classical kinetic energy is $T_{C,N} = \frac{1}{2m}\int p_N |\nabla S_N|^2 d^{3N}\boldsymbol{r}$ where p_N is the N-electron probability density. The N-electron purely quantum kinetic energy is the N-electron Weizsäcker term, $T_{W,N} = \frac{\hbar^2}{8m}\mathscr{I}_{\mathrm{F},N}$, where $\mathscr{I}_{\mathrm{F},N} = \int \frac{(\nabla p_N)^2}{p_N} d^{3N}\boldsymbol{r}$ is the N-electron Fisher information.

We recently [14] showed that the N-electron Weizsäcker term, $T_{W,N}$, can be decomposed as T_W (a one-electron term) and a purely quantum kinetic correlation term, T_W^{corr}, which is given by

$$T_W^{corr} = \frac{\hbar^2}{8m}\int \rho(\boldsymbol{r}) \mathscr{I}_{\mathrm{F}_{\mathrm{one}}^{f}}(\boldsymbol{r}) d^3\boldsymbol{r} \tag{6}$$

where

$$\mathscr{I}_{\mathrm{F}_{\mathrm{one}}^{f}}(\boldsymbol{r}) = \mathscr{I}_{\mathrm{F}_{\mathrm{one}}^{f}}(\boldsymbol{r}_1) = \int \frac{\left[\nabla_{\boldsymbol{r}_1} f(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N|\boldsymbol{r}_1)\right]^2}{f(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N|\boldsymbol{r}_1)} d^3\boldsymbol{r}_2 \ldots d^3\boldsymbol{r}_N \tag{7}$$

and $f(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N|\boldsymbol{r}_1)$ is the probability density associated with a set of values for $\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ given a fixed value for $\boldsymbol{r}_1$. Thus, as discussed in more detail by Delle Site, [15] the purely quantum correlation term is a functional of the (N-1)-conditional probability density.

Then, assuming that the N-electron classical kinetic energy can be decomposed as T_C (a one-electron term) and a classical kinetic correlation term, T_C^{corr}, we can write

$$T_N = T_s + T_C^{corr} + T_Q^{corr} \tag{8}$$

where the noninteracting (or single-electron) kinetic energy is $T_s = T_C + T_W$.

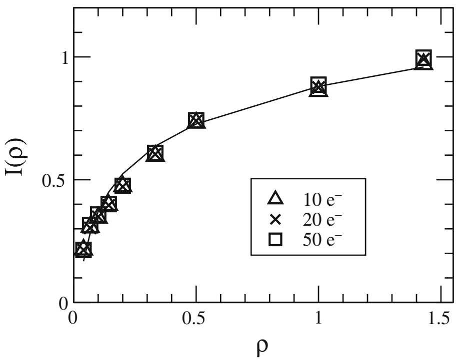

Fig. 1 Calculated values of $\mathscr{I}_{\mathrm{F}_{\mathrm{one}}}^{f}(\boldsymbol{r})$ as a functional of the electron density, $I(\rho)$. The solid line, which is our fit to the points, has the functional form $A + B\ln(\rho)$

3 Results and discussion

For the uniform (noninteracting) electron gas, T_W is zero, and we have argued [14] that T_C is identical to T_{TF}. In this paper we consider the nearly uniform electron gas for which the nonuniformity is due solely to electron correlation. It seems reasonable to assume that the electron-electron interactions cause microscopic “wrinkles” in the electron density which average to zero over macroscopic regions (on an atomic scale). We therefore expect that T_C is close to T_{TF} and that T_C^{corr} is insignificant but that both T_W and T_W^{corr} are significant. We therefore approximate the noninteracting kinetic energy as $T_{TF} + T_W$ and we approximate the correlation energy as T_W^{corr}.

Both T_{TF} and T_W are functionals of the electron density but T_W^{corr} is not (*cf.* Eq. 6). However, it was recently shown by Ghiringhelli and Delle Site [16] that $\mathscr{I}_{\mathrm{F}_{\mathrm{one}}}^{f}(\boldsymbol{r})$ can be evaluated via a statistically rigorous Monte-Carlo procedure to obtain T_W^{corr} as a functional of the electron density, $I(\rho)$. The Ghiringhelli-Delle Site study [16] showed results for large N values (50, 100 and 250 electrons) corresponding to metals. In the present paper, we show results for smaller N values (10, 20 and 50 electrons) corresponding to first and second-row atoms in Fig. 1 and it is clear that $I(\rho)$ has essentially no dependence on the number of electrons. It may be seen from Fig. 1 that the Monte-Carlo procedure suggests a logarithmic dependence of $I(\rho)$ which results in a Shannon entropy expression for T_W^{corr}. Thus the solid line, which is our fit to the points, has the functional form $A + B\ln(\rho)$ with $A = 0.880 \pm 0.021$ and $B = 0.221 \pm 0.011$ and these values for smaller N are in agreement with those for large N [16].

The kinetic-energy functional for the nearly uniform electron gas is thereby expressed as the sum of the standard Thomas-Fermi term and terms which are proportional to two of the cornerstones of information theory: the Fisher information, which is a measure of localization, and the Shannon entropy, which is a measure of delocalization.

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References

1. V. Vedral, *Introduction to Quantum Information Science* (Oxford University Press, Oxford, 2006)
2. R.A. Fisher, Proc. Camb. Philos. Soc. **22**, 700–725 (1925)
3. A. Nagy, J. Chem. Phys. **119**, 9401–9405 (2003)
4. C.E. Shannon, Bell Syst. Tech. J. **27**, 379–423, 623–656 (1948)
5. E. Romera, J.S. Dehesa, J. Chem. Phys. **120**, 8906–8912 (2004)
6. K.D. Sen, J. Antolín, J.C. Angulo, Phys. Rev. A **76**, 032502 (2007) (7 pages)
7. I.P. Hamilton, R.A. Mosna, J. Comput. Appl. Math. (in press)
8. R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989)
9. L.H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542–548 (1927)
10. E. Fermi, Rend. Accad. Lincei **6**, 602–607 (1927)
11. C.F. Weizsäcker, Z. Phys. **96**, 431–458 (1935)
12. R.A. Mosna, I.P. Hamilton, L. Delle Site, J. Phys. A **38**, 3869–3878 (2005)
13. R.A. Mosna, I.P. Hamilton, L. Delle Site, J. Phys. A **39**, L229–L235 (2006)
14. I.P. Hamilton, R.A. Mosna, L. Delle Site, Theor. Chem. Acct. **118**, 407–415 (2007)
15. L. Delle Site, J. Phys. A **40**, 2787–2792 (2007)
16. L.M. Ghiringhelli, L. Delle Site, Phys. Rev. B **77**, 073104 (2008) (4 pages)