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Shannon Entropy in Atoms: A Test for the Assessment of Density Functionals in Kohn-Sham Theory

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Abstract: Electron density is used to compute Shannon entropy. The deviation from the Hartree–Fock (HF) of this quantity has been observed to be related to correlation energy. Thus, Shannon entropy is here proposed as a valid quantity to assess the quality of an energy density functional developed within Kohn–Sham theory. To this purpose, results from eight different functionals, representative of Jacob's ladder, are compared with accurate results obtained from diffusion quantum Monte Carlo (DMC) computations. For three series of atomic ions, our results show that the revTPSS and the PBE0 functionals are the best, whereas those based on local density approximation give the largest discrepancy from DMC Shannon entropy.

Keywords: Shannon entropy; density functional theory; Quantum Monte Carlo; electronic structure of atoms

1. Introduction

In a recent work [1], we proposed an alternative and more practical way to relate an entropy measure to the correlation energy of atomic systems.

Correlation energy has been related to the entropy of entanglement [2] by Collins [3], and this conjecture has been assessed on a series of light atomic ions by Esquivel et al. [4]. Relations with the correlation strength have been also established by Ziesche [5], while many other works have been focused on the link between the nonidempotency of the one-particle density matrix and complexity measures (see, for example, Nagy and Romera [6] and other references therein). In a slightly different context, Romera and Dehesa [7] have introduced a rather sophisticated measure of the electron correlation based on the combination of Shannon and Fischer information. Instead, in the framework of density functional theory (DFT), more recently, Grimme and Hansen [8] have proposed a method of particular interest to recover information about static correlation from the entanglement entropy.

In our approach, we used densities, tested on atomic model systems, obtained from diffusion Monte Carlo (DMC) and Hartree–Fock (HF) calculations, and we observed that the difference between the two sets of entropy (correlation Shannon entropy) shows a significant positive deviation in approaching the conditions at which Coulomb correlation is stronger, namely at critical nuclear binding condition. This study seems to confirm the original idea of Amovilli and March [9] that there might be a relation between such difference and the entanglement entropy. Thus, we reached the conclusion that the correlation Shannon entropy should also be related to the correlation energy [1]. An interesting discussion about the connection of Shannon entropy and many electron correlation has been given recently by Delle Site [10] (see also Ghiringhelli et al. [11]). Trickey et al. [12] criticized this view because of the problems connected to the logarithmic density dependence of Shannon entropy. In their work, they suggest a renormalization of the Shannon term in order to limit this kind of problem. However, this could not be the case of correlation Shannon entropy, that is a difference and is not an absolute quantity.

In this paper, we propose Shannon entropy as a possible indicator to assess the quality of an energy density functional. Typically, such functionals are written in terms of a set of parameters that are calibrated on some large training set made of a variety of molecular properties. Although the fit of the training set is sufficiently good, one cannot be certain that such a functional works properly in all cases. In this regard, Wasserman et al. [13] analyzed errors on both energy and density in order to review the role of self-consistency in DFT, giving simple pedagogical examples. The variational validity of density functionals has been investigated in a previous work by one of us [14]. In that paper, the authors classified some largely used functionals into heuristic and possibly variationally valid on the basis of a comparison with accurate ab initio calculations.

We remark that Shannon entropy depends explicitly on electron density and can be compared directly with the corresponding accurate DMC value. Thus, the purpose of this work is to compare electron density from various functionals with the one obtained from a DMC calculation through the computation of Shannon entropy.

2. Calculations and Discussion of Results

Let us begin with an overview of the calculations. We computed the electron density for three series of atomic ions in the ground state, namely He-like, N-like, and Ne-like ions. In order to have a fairly general view of the results, we have chosen at least a representative functional for any rung of the so-called Jacob's ladder [15]. A standard Kohn–Sham (KS) DFT calculation was performed on each system by using the GAMESS-US package [16]. A universal basis set of even tempered (16s,16p,3d,2f) Gaussian atomic orbitals was used, with $0.007 \leq \alpha_{sp} \leq 458.752$, $0.7 \leq \alpha_d \leq 2.8$ and $1 \leq \alpha_f \leq 2$. For N-like ions, we used an unrestricted approach. For N- and Ne-like series, we considered only valence electrons and we used Burkatzki, Filippi, and Dolg (BFD) pseudopotentials [17]. Quantum Monte Carlo (QMC) computations were performed by means of the program CHAMP [18]. In this case, the atomic wavefunction is optimized at the variational Monte Carlo (VMC) level in the form of a one-determinant Slater–Jastrow wavefunction [19,20] and subsequently used at the DMC level. In DMC, we used a time step of 0.025 a.u. and the method of Casula [21] to go beyond the locality approximation. At DMC level, the electron density was recovered from the fractional number of electrons contained in a sphere of arbitrary radius centered on the nucleus. This quantity can be easily obtained from the configurations generated from fixed node DMC mixed distribution during the simulation thanks to the spherical symmetry of the test cases studied in this work. Electron densities are finally utilized to compute the Shannon entropy according to the definition

$$S = - \int d\mathbf{r} \rho(r) \ln \rho(r) \tag{1}$$

as performed in our recent work [1].

Tables 1–3 record our resulting entropies. In these tables, we show also total energy and kinetic energy for comparison between the various approaches. For KS-DFT, the kinetic energy is the single particle kinetic energy that deviates significantly from correlated kinetic energy computed at the QMC level. In all three series of data, the most interesting cases are those of the anions H^-, C^-, and F^-, being closer to the limit of weak binding. We remind the reader that the critical nuclear charges are, respectively, 0.911028 [22], 5.85 [23], and 8.74 [23] for the three series of atomic ions. In all cases, the DMC value of entropy is larger than the HF one due to the effect of electronic Coulomb correlation on this property. The highest difference occurs for the three anions considered in this work. In this regard, a good energy density functional should be in agreement with the DMC corresponding value. In order to verify if this is a valid criterion to assess the quality of a given functional, we have tested eight functionals representative of the Jacob's ladder.

Table 1. Total energy, kinetic energy, and Shannon entropy for some atomic systems of the He-like series calculated at different level of computation. Data are in atomic units (a.u.).

| Method	Total Energy	Kinetic Energy	Entropy	Total Energy	Kinetic Energy	Entropy	Total Energy	Kinetic Energy	Entropy
	H^-			He			Li^+		
RHF	−0.48793	0.48793	9.8889	−2.86163	2.86148	4.0100	−7.23599	7.23474	1.1203
SVWN	−0.51425	0.48054	10.8040	−2.83479	2.76771	4.2066	−7.14240	7.05513	1.2467
PW91	−0.53052	0.50957	10.6541	−2.89995	2.86266	4.1155	−7.26720	7.22341	1.1834
PBE0	−0.52450	0.50023	10.2064	−2.89513	2.85773	4.0816	−7.26205	7.21907	1.1659
B3LYP	−0.53065	0.51090	10.2912	−2.90806	2.86808	4.0927	−7.27821	7.22723	1.1733
revTPSS	−0.53325	0.50611	10.3734	−2.91200	2.87003	4.0424	−7.28824	7.24107	1.1396
CAMB3LYP	−0.53100	0.50802	10.0120	−2.90138	2.85372	4.1173	−7.26518	7.21801	1.1816
ωB97X	−0.52898	0.50860	9.9390	−2.90437	2.87235	4.0709	−7.28655	7.27475	1.1302
B2PLYP	−0.52488	0.50280	10.0224	−2.90463	2.86924	4.0547	−7.26813	7.23682	1.1480
VMC	−0.52755(4)	0.5248(6)	10.3775	−2.90359(7)	2.912(4)	4.0106	−7.27991(4)	7.292(6)	1.1204
DMC	−0.52779(2)	0.5237(9)	10.3119	−2.90386(7)	2.908(3)	4.0256	−7.27997(4)	7.298(6)	1.1143

Table 2. Total energy, kinetic energy and Shannon entropy for some atomic systems of the N-like series calculated at different level of computation. Data are in a.u.

Method	Total Energy	Kinetic Energy	Entropy	Total Energy	Kinetic Energy	Entropy	Total Energy	Kinetic Energy	Entropy
	C^-			N			O^+		
UHF	−5.35111	3.59151	16.5669	−9.67304	6.80209	11.2305	−15.27536	10.78233	7.5464
USVWN	−5.44029	3.52699	17.7825	−9.72520	6.75214	11.5299	−15.29526	10.73464	7.7365
UPW91	−5.48765	3.58086	17.6413	−9.79981	6.83133	11.4282	−15.39928	10.84028	7.6524
UPBE0	−5.47450	3.58184	17.1388	−9.79225	6.81302	11.3493	−15.39264	10.81020	7.6112
UB3LYP	−5.46483	3.59524	17.3775	−9.78493	6.83758	11.3852	−15.38900	10.83889	7.6330
UrevTPSS	−5.49420	3.61922	16.8359	−9.81463	6.82378	11.3659	−15.41653	10.82372	7.6172
UCAMB3LYP	−5.46771	3.62211	17.0112	−9.78632	6.83303	11.4052	−15.38512	10.82775	7.6555
UωB97X	−5.46535	3.66699	16.8368	−9.78760	6.86984	11.3268	−15.39130	10.87310	7.5819
UB2PLYP	−5.43696	3.61515	16.6868	−9.74356	6.79620	11.3129	−15.38589	10.81562	7.5928
VMC	−5.46486(4)	3.6547(5)	16.8599	−9.78662(5)	6.8672(9)	11.2796	−15.39153(8)	10.855(2)	7.5655
DMC	−5.47112(2)	3.6689(3)	16.8686	−9.79314(2)	6.9054(5)	11.2699	−15.39865(2)	10.9094(6)	7.5608

Table 3. Total energy, kinetic energy, and Shannon entropy for some atomic systems of the Ne-like series calculated at different level of computation. Data are in a.u.

Method	Total Energy	Kinetic Energy	Entropy	Total Energy	Kinetic Energy	Entropy
		F^-			Ne	
RHF	−23.98621	18.82316	10.994	−34.70905	27.73954	5.272
SVWN	−24.21194	19.00417	12.025	−34.87089	27.72792	5.722
PW91	−24.35071	18.97835	11.934	−35.05853	27.97595	5.601
PBE0	−24.30801	18.93859	11.530	−35.02224	27.90528	5.481
B3LYP	−24.32192	18.96881	11.655	−35.03774	27.94395	5.545
revTPSS	−24.34359	18.95492	11.753	−35.05088	27.93728	5.553
CAMB3LYP	−24.32105	18.97777	11.607	−35.03248	27.93379	5.571
ωB97X	−24.32782	19.00417	11.532	−35.04599	27.98958	5.475
B2PLYP	−24.20896	18.92158	11.326	−34.93208	27.87075	5.422
VMC	−24.3011(1)	19.075(3)	11.4523	−35.01487(8)	27.998(3)	5.441
DMC	−24.31239(3)	19.201(1)	11.4481	−35.02504(3)	28.166(1)	5.440

In Figure 1, we show the deviation from the DMC reference of Shannon entropy computed for the three anions and with different approaches. The HF and the functional based on local density approximation (SVWN) show the highest discrepancy from the DMC results. All the other functionals considered in this work fall in between these two sets of results. While the deviation for HF is negative because of Coulomb correlation, an approximate functional could lead to both positive or negative deviations. For the three anions, the best functionals appear to be the revTPSS and the PBE0, the first one belonging to the meta-GGA category and the second to the hybrid-GGA one. Moreover, it is interesting to note that the quantity plotted in Figure 1 is strictly connected to the Kullback–Leibler divergence [24] of the various calculated densities with respect to the DMC one.
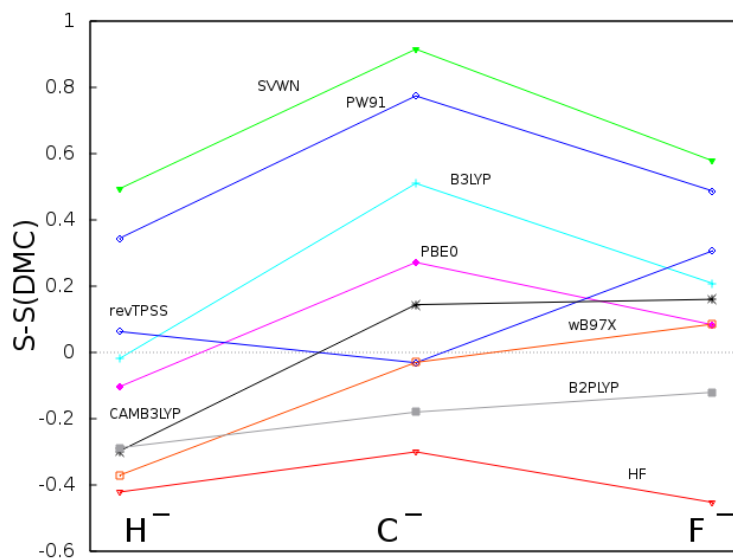
Figure 1. Deviation from DMC of Shannon entropy computed for the three anions, H^-, C^-, and F^-, using eight functionals representative of the Jacob's ladder and HF.

In Table 4, we report the mean absolute relative errors (MARE) computed by considering all the entropy data of this work for each method with respect to the DMC set of results. In this Table, HF and VMC values are also reported in order to fix two reference values, namely, non-correlated and correlated ab initio calculations. Again, revTPSS and PBE0 appear to be the best ones. None of the eight functionals achieve the quality of VMC, whereas SVWN and PW91 lead to worse results than HF.

Table 4. Mean absolute relative error (MARE) on Shannon entropy computed at different levels with respect to DMC.

Method	MARE
RHF	0.0329
SVWN	0.0508
PW91	0.0405
PBE0	0.0111
B3LYP	0.0167
revTPSS	0.0115
CAMB3LYP	0.0171
ωB97X	0.0151
B2PLYP	0.0165
VMC	0.0024

Finally, it is interesting to notice that, looking at the energies of Tables 1–3 and following the classification suggested by Amovilli et al. [14], PBE0 is possibly variationally valid, while revTPSS should be considered as heuristic.

3. Conclusions

In this work, we have presented results of Shannon entropy for a list of selected atomic systems by means of electron density obtained from various functionals in KS theory and from QMC. The purpose of this test study is to verify the sensitivity of Shannon entropy with respect to the variation of density functionals in order to use this property in the design of new approximate energy density functionals. The main results of the present work are displayed in Figure 1 and Table 4. The density functionals considered in this study show clearly a different behavior in the comparison with DMC. None of them reach the accuracy of, for example, VMC, namely a good ab initio case. SVWN and PW91 present an MARE greater than HF and the best functionals of this study are PBE0 and revTPSS. PBE0 energies lie above the DMC energies and can also be classified, following Amovilli et al. [14], as possibly variationally valid, while revTPSS is more heuristic, the energies in this case being lower than those from DMC.

Although the number of illustrative examples considered in this work is limited, this suggests that different functionals give different Shannon entropies and that such differences are not negligible, being a significant fraction of the difference between HF and DMC Shannon entropy. We remark that the correlation Shannon entropy is strongly related to Coulomb correlation [1]. DMC is a good reference for testing Shannon entropy computed at the KS-DFT level. The KS electron density is easily achievable from standard packages of quantum chemistry calculations, while DMC electron density needs more attention if one requires a very accurate density function. For the future, if the electron density cannot be obtained from any convenient method, like, for example, a full CI calculation, it is very important to improve the techniques for the reconstruction of highly accurate electron densities for molecular systems that can be studied at a DMC level. We believe that the approach presented in this note could be a valid tool for the development of new energy density functionals.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

SWVN   Slater, Vosko, Wilk, and Nusair functional [25]

PW91   Perdew and Wang 1991 functional [26]

PBE0   Perdew–Burke–Ernzerhof with 0.25 Hartree–Fock exchange functional [27,28]

B3LYP   Becke, three-parameter, Lee–Yang–Parr hybrid functional [29,30]

revTPSS   revised Tao, Perdew, Staroverov, and Scuseria meta-GGA functional [31,32]

CAMB3LYP   Cambridge B3LYP functional [33]

ωB97X   long-range corrected Becke 97 hybrid functional [34]

B2PLYP   double hybrid BLYP functional [35]

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