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Shannon entropy of 1-normalized electron density

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The calculations of the 1-normalized Shannon entropy of Hartree-Fock electron density, S_η, and its variation with the number of electrons, $[\partial S_\eta/\partial N]_Z$, are reported for He-Xe atoms in the ground states. The N variation is shown as related to the Fukui function of the density functional theory and it becomes identically equal to zero if the electron density in N-electron system is described by the homogeneous electron gas.

During the recent years, the Shannon information entropy of electronic density, $\rho(\mathbf{r})$, defined as

$$S_\rho = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r})\, d\mathbf{r} \qquad ...(1)$$

has been used in the analysis of several chemical and physical phenomena[1-10]. Substituting in Eq.(1), $\rho(\mathbf{r}) / N$, instead of $\rho(\mathbf{r})$ defines the 1-normalised entropy, S_η, which is related to S_ρ according to

$$S_\eta = (S_\rho/N) + \ln N \qquad ...(2)$$

The quantity S_η is usually positive. In this communication we report on an interesting property of the derivative $(\partial S_\eta/\partial N)_z$ for N -electron systems. On differentiating S_η with respect to N, we obtain

$$[\partial S_\eta/\partial N]_Z = -(1/N^2)\, S_\rho - (1/N) \int (\partial\rho/\partial N)_Z \ln\rho(\mathbf{r})\, d\mathbf{r} \qquad ...(3)$$

For a homogeneous electron gas, $[\partial\rho/\partial N]_Z = \rho(r)/N$ which reduces Eq. (3) to $[\partial S_\eta/\partial N]_Z = 0$.

The quantity $[\delta\rho(\mathbf{r})\backslash\delta N]_Z$ in equation (3) defines the Fukui function[11] - the chemical reactivity parameter in the density functional theory[12]. Thus, Eq. (3) provides a connection between an important reactivity parameter and the Shannon entropy of electron density.

We have used a modified Hartree-Fock 86 code[13] and obtained the numerical HF wave functions for He-Xe atoms in the ground state. These wave functions have been used to calculate S_ρ, S_η and $(\partial S_\eta/\partial N)_z$ as given by

Table 1 - The results of 1-normalised Shannon entropy, S_η and its derivative with respect to N for He - Xe using HF densities. All quantities in a.u.

Z	Atom	State	S_η	$\partial S_\eta/\partial N$
2.0	He	^1S	2.698	0.713
3.0	Li	^2S	3.701	1.703
4.0	Be	^1S	3.624	0.990
5.0	B	^2P	3.405	0.776
6.0	C	^3P	3.106	0.515
7.0	N	^4S	2.802	0.485
8.0	O	^3P	2.550	0.415
9.0	F	^2P	2.299	0.298
10.0	Ne	^1S	2.055	0.321
11.0	Na	^2S	2.330	0.722
12.0	Mg	^1S	2.395	0.565
13.0	Al	^2P	2.446	0.529
14.0	Si	^3P	2.419	0.403
15.0	P	^4S	2.359	0.373
16.0	S	^3P	2.299	0.328
17.0	Cl	^2P	2.222	0.260
18.0	Ar	^1S	2.134	0.261
19.0	K	^2S	2.302	0.476
20.0	Ca	^1S	2.363	0.399
21.0	Sc	^2D	2.298	0.290
22.0	Ti	^3F	2.219	0.257
23.0	V	^4F	2.135	0.258
24.0	Cr	^7S	1.956	0.269
25.0	Mn	^6S	1.963	0.199
26.0	Fe	^5D	1.882	0.210
27.0	Co	^4F	1.800	0.210
28.0	Ni	^3F	1.718	0.210
29.0	Cu	^2S	1.563	0.299
30.0	Zn	^1S	1.556	0.267
31.0	Ga	^2P	1.574	0.278

Contd....

Table 1 - The results of 1-normalised Shannon entropy, S_η and its derivative with respect to N for He - Xe using HF densities. All quantities in a.u. (Contd...)

Z	Atom	State	S_η	$\partial S_\eta / \partial N$
32.0	Ge	^1P	1.568	0.230
33.0	As	^4S	1.550	0.222
34.0	Se	^1P	1.534	0.205
35.0	Br	^2P	1.511	0.174
36.0	Kr	^1S	1.481	0.176
37.0	Rb	^2S	1.576	0.286
38.0	Sr	^1S	1.621	0.252
39.0	Y	^2D	1.614	0.206
40.0	Zr	^3F	1.595	0.186
41.0	Nb	^6D	1.525	0.191
42.0	Mo	^7S	1.491	0.179
43.0	Tc	^6S	1.508	0.168
44.0	Ru	^5F	1.431	0.166
45.0	Rh	^4F	1.396	0.160
46.0	Pd	^1S	1.305	0.155
47.0	Ag	^2S	1.324	0.202
48.0	Cd	^1S	1.331	0.185
49.0	In	^2P	1.352	0.192
50.0	Sn	^3P	1.357	0.175
51.0	Sb	^4S	1.355	0.161
52.0	Te	^3P	1.353	0.151
53.0	I	^2P	1.347	0.143
54.0	Xe	^1S	1.336	0.135

Eqs(1)-(3), respectively. In each case, we calculated S_η corresponding to $N \pm 0.1$and estimated the derivative $(\partial S_\eta / \partial N)_z$ as numerical difference. The electron occupation was changed in the outermost orbital for each atom. Our results are presented in Table 1. Interestingly, the isonuclear variation with N of S_η attains a minimum at the halogen atoms. Within the local plasma model[14] Ho *et al.*[15] have shown that S_η can be used directly to estimate the mean excitation energy in the cases of H-Ar atoms. The present calculations can be used to carry out similar calculations in the cases of K-Xe atoms.

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