

Shannon Entropies of Atomic Basins and Electron Correlation Effects

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Recibido el 27 de septiembre de 2007; aceptado el 19 de diciembre de 2007

Abstract. Electron correlation effects on atomic basin populations of AIM theory and the resulting de/localization of the basin charge and momentum densities, as measured by local Shannon entropies and basin kinetic energies, are discussed for a series of ten-, fourteen- and eighteen-electron molecules. These results are related to the nature of the chemical environment. Correlation effects on global Shannon entropies and kinetic energies are also examined.

Key words: Shannon entropy, charge density, momentum density, electron correlation, AIM basin.

Resumen. Los efectos de la correlación electrónica sobre las poblaciones de las cuencas atómicas de la teoría AIM, y la des/localización resultante de la densidad de carga en las cuencas, medidas por entropías de Shannon locales y las energías cinéticas de las cuencas, están discutidos para series de moléculas con diez, catorce y dieciocho electrones. Los resultados están relacionados con la naturaleza del ambiente químico. Se estudian también los efectos de la correlación sobre las entropías y energías cinéticas globales.

Palabras clave: Entropía de Shannon, densidad de carga, densidad de momento, correlación electrónica, cuenca AIM.

Introduction

There has been considerable interest over the past years in the application of Shannon's information theory [1] to study problems in quantum chemistry. Most of the recent work in the continuous variable formulation has been devoted to atomic systems with much less emphasis placed on the molecular problem.

Central to information theory is the information entropy, a measure of the level of de/localization of a distribution. The entropy of the electronic charge distribution $\rho(\mathbf{r})$ is defined in terms of this continuous distribution as

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

The electronic charge density is an important theoretical quantity. Apart from forming the basis of density functional theory, it is experimentally accessible from x-ray crystallography and is a useful tool in interpreting the often too complicated multidimensional wavefunction.

A larger value of S_ρ indicates a more delocalized charge density and vice versa. Localization measures are important in quantum chemistry since they are directly related to phenomena such as chemical binding. Furthermore, due to the *ionic*, i.e., localized character of the Hartree-Fock (HF) density, the delocalization of the density can be employed to measure the level of correlation in the (post HF) wavefunctions. This can be readily seen in the analogous Jaynes' entropy (discrete Shannon entropy of the natural orbital occupation numbers, corresponding to the coarse grained distribution) where the HF values are limited to 1 or 2 for occupied (spin)orbitals and 0 for virtual orbitals. Highly correlated wavefunctions include more mixing of virtual orbitals resulting in a more delocalized

distribution of occupation numbers [2]. In this light, we can regard S_ρ as an analytical tool, useful for the analysis of the localization (delocalization) properties of electronic charge densities.

Along with the Schrödinger representation, there is also an equivalent momentum or \mathbf{p} -space representation to formulate quantum mechanical problems (see, for example [3]), although far less work has been devoted to this branch as compared to work in the position representation. The corresponding Shannon momentum space entropy is similarly defined as

$$S_\pi = -\int \pi(\mathbf{p}) \ln \pi(\mathbf{p}) d\mathbf{p}, \quad (2)$$

where $\pi(\mathbf{p})$ is the electronic momentum density. Similarly, S_π is largest for systems where electrons are of *undeterminable* speed and smaller for systems with a high proportion of relaxed (i.e., low \mathbf{p}) electrons.

Delocalization can be equated with an increase in uncertainty which immediately reminds one of the uncertainty principle when \mathbf{r} and \mathbf{p} are considered. The conviction exists in the literature that a proper understanding of the chemical bond is only possible by looking at delocalization effects which stem from consideration of the uncertainty principle [4]. Indeed, there is an uncertainty inequality in terms of the information entropies [5] where the entropy sum S_t shows a lower bound

$$S_t = S_\rho^u + S_\pi^u \geq 3(1 + \ln \pi) = 6.4342. \quad (3)$$

The superscript, u , denotes a unit-normalized density which is also called a shape factor in the literature [6]. The relationship between S , for a system of N electrons, and S^u is simply

$$S^u = S/N + \ln N. \quad (4)$$

The entropy sum has been shown to be a measure of basis set quality and sensitive to the effects of electron correlation in atoms and in diatomic molecules [7]. See Ref. [8] for a review of information entropy applications in quantum chemistry and a detailed list of references.

The language of the chemist resides in the concept of molecules being comprised of atoms. The theoretical foundations of such concepts has been provided by Bader in his theory of Atoms in Molecules (AIM) [9], where the molecular charge density is partitioned into basins corresponding to the atoms of the system. Each of these subsystems is bounded by a zero-flux surface $T(\mathbf{r})$ which satisfies

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n} = 0 \quad \forall \mathbf{r} \in T(\mathbf{r}) \quad (5)$$

where \mathbf{n} is a unit vector normal to the $T(\mathbf{r})$ surface. The entropy of the subsystem Ω_i can be defined as

$$S_{\Omega_i} = - \int_{\Omega_i} \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r} \quad (6)$$

where the integration is over the subsystem or basin, Ω_i . Furthermore, the sum of subsystem entropies gives the global entropy

$$S_{\rho} = \sum_i S_{\Omega_i} \quad (7)$$

or in terms of the unit-normalized subsystem entropies, $S_{\Omega_i}^u$,

$$S_{\rho}^u = \frac{1}{N} \left[\sum_i N_{\Omega_i} S_{\Omega_i}^u - \sum_i N_{\Omega_i} \ln N_{\Omega_i} \right] + \ln N, \quad (8)$$

where N_{Ω_i} is the number of electrons in the basin,

$$N_{\Omega_i} = \int_{\Omega_i} \rho(\mathbf{r}) d\mathbf{r} \quad (9)$$

with $\sum_i N_{\Omega_i} = N$.

Shannon entropies over basins, or local Shannon entropies, can be used to study the structure or localization of the electronic charge density over an atomic basin. They have been used to study basins of diatomic molecules [10]. A simple model was developed therein whereby electron transfer into the basin results in an increase of the electronic repulsions and hence an increase in the entropy. On the other hand, electronic transfer out of the basin results in a decrease of the entropy as the density in the basin is localized due to increased electron-nuclear attraction. The effects of solvation on the atomic basins and functional groups have also been discussed [11]. It was shown that the response of the electrons to solvation is such as to minimize the electron transfer to or from the functional group or basin.

The purpose of this paper is to analyze the effects of electron correlation on molecular electronic densities, globally, and in atomic basins and functional groups. How does electron correlation affect the localization properties of the electronic

charge and momentum densities in systems larger than diatomic species? The effects of electron correlation on atomic basins have been examined [12]. The novelty here is that we propose to study the changes caused by electron correlation on the basins from the Shannon entropy perspective. Do correlation effects localize or delocalize the density over the basin? How do these effects manifest themselves in momentum space? Are there any relationships between correlation effects as measured by entropies in a molecular environment?

Results and Discussion

The wavefunctions of H₂O, HF, NH₃ (ten electron series), CO, HCN (fourteen electron series) and CH₃ OH, CH₃F, C₂H₆, HCl, HOOH (eighteen electron series) and HNO were calculated at the RHF (restricted Hartree-Fock) and CISD (configuration interaction singles and doubles) levels utilizing the 6-31++G(p,d) basis sets using the GAUSSIAN 98 package [13]. These molecules were selected to reflect different charge transfer environments. The geometry parameters were taken mainly from Herzberg [14] and Pople [15]. Global Shannon entropies were calculated from Eqs. (1) and (2) by three-dimensional integration of the charge and momentum densities. The local quantities were calculated using a modified version of the PROAIM [16] program. Integrations were set to have an accuracy of at least $10^{-5} e a_0^{-3}$. Atomic units are used throughout.

We present in Table 1 the values for the global entropies in position and in momentum space along with the kinetic energy (KE). We point out some general observations to orient the reader before moving to the discussion of correlation effects. First, $S_{\pi} > S_{\rho}$ in all the studied molecules at both the HF and CISD levels. This reflects the fact that the momentum density is less structured as compared to the position space density. In general, the symmetry point group of the momentum space density results from introducing the inversion operator i to the corresponding symmetry point group in the position space one. The resulting $\pi(\mathbf{p})$ is of a higher symmetry which should yield a larger entropy.

Secondly, S_{ρ} is able to correctly determine the localization or structure in the charge density due to the charge transfer environment in the different isoelectronic series. The charge transfer is defined as the amount of electrons moving in or out of the atomic or functional group basin. These basins were selected for analysis based on their being the common factor in the studied molecules. As we shall see below, a comparative analysis of the H or CH₃ basins allows us the opportunity to study the recovery of correlation effects in a systematic manner. One would expect a more localized distribution in position space as the extent of the charge transfer is increased which should give a smaller entropy. One expects that the charge transfer in the ten electron series should behave as NH₃ < H₂O < HF yielding the opposite trend for S_{ρ} which is indeed the case. Note also that S_{π} has the same trend as the expected charge transfer. These trends also hold for other isoelectronic series.

Table 1. Shannon entropies at the HF level, the CISD level and the differences. The first, second, third and fourth rows are S_ρ^u , S_π^u , S_t , and the kinetic energy, respectively.

C ₂ H ₆			CH ₃ F			CH ₃ OH		
4.3841	4.3827	-0.0014	3.6264	3.6369	0.0105	3.9009	3.9076	0.0067
4.6354	4.6580	0.0226	5.4771	5.4822	0.0051	5.1744	5.1854	0.0110
9.0195	9.0407	0.0212	9.1035	9.1192	0.0157	9.0752	9.0931	0.0179
79.143	79.437	0.2940	138.69	138.82	0.1300	114.70	114.95	0.2500
CO			H ₂ O			HCl		
3.2422	3.2462	0.0040	3.0798	3.0974	0.0176	2.4408	2.4413	0.0005
5.6534	5.6661	0.0127	5.4274	5.4339	0.0065	6.8638	6.8737	0.0099
8.8955	8.9123	0.0168	8.5072	8.5313	0.0241	9.3046	9.3150	0.0104
112.36	112.59	0.2300	75.746	75.867	0.1210	459.82	459.90	0.0800
HCN			HF			HNO		
3.5646	3.5563	-0.0083	2.5788	2.6046	0.0258	3.3694	3.3766	0.0072
5.3165	5.3424	0.0259	5.9339	5.9294	-0.0045	5.6281	5.6411	0.0130
8.8811	8.8987	0.0176	8.5126	8.5341	0.0215	8.9975	9.0177	0.0202
92.544	92.875	0.3310	99.700	99.691	-0.0090	129.28	129.54	0.2600
HOOH			NH ₃					
3.4374	3.4523	0.0149	3.5506	3.5578	0.0072			
5.6401	5.6472	0.0071	4.9316	4.9504	0.0188			
9.0774	9.0995	0.0221	8.4822	8.5081	0.0259			
150.26	150.49	0.2300	56.012	56.201	0.1890			

The global entropy S_ρ increases with correlation in all cases with the only exceptions being the C₂H₆ and HCN molecules. The interpretation of the general trend is that the electrons are able to avoid each other as correlation is included and the density spreads out or becomes more delocalized, resulting in a larger entropy.

In the HCN molecule, we observed that in going from the HF to CISD level, the nitrogen atom lost electronic charge to the carbon and the hydrogen atoms. Table 2 indeed shows that the local entropy is smaller for nitrogen and larger for the carbon and hydrogen atoms on going from HF to CISD (data in Table 2 will be discussed below). However, the magnitude of the N-normalized entropy of the nitrogen atom (8.004, at the HF level for example) is much larger than those of the carbon (2.625) and hydrogen (2.406) atoms. Thus the magnitude of the local entropy of the N atom, and the localization effect over the basin introduced by correlation, dominates the global entropy which is the sum of the local entropies [See Eq. (7)].

We also calculated S_ρ at the QCISD/6-31++G(p,d) level using the same geometry to eliminate the possibility of insufficient recovery of correlation, and have confirmed the behavior. That is, S_ρ decreases with correlation for the HCN molecule.

A similar argument to the previous one can also be applied to explain the behaviour in the ethane molecule. Table 2 shows that correlation effects move electrons from the hydrogen

atoms to the carbon atoms and the resulting entropies are smaller for the hydrogen atoms and larger for the carbon atoms. The entropy of the six hydrogen atoms has a larger magnitude than that of the two carbon atoms and thus S_ρ is smaller when correlation is included.

The global entropy S_π is also seen to increase with correlation with the exception being HF. In general, correlation effects move electrons from the bonding regions to those closer to the nuclei. Electrons therefore possess higher kinetic energy. As a result the momentum density includes larger \mathbf{p} which results in a wider distribution of the momentum density i.e. larger entropic values. This behavior can also be seen from the kinetic energy (second moment of the momentum density) values presented in Table 1. The kinetic energy increases with correlation for all molecules except HF. Thus the response of S_π to correlation is the same (increases) as that of the kinetic energy.

We have systematically probed the problem of the KE in the HF molecule. We have used the following methods; HF, CISD, MP2 and QCISD employing the STO-3G, 6-31G, 6-31G(d,p), 6-31++G(d,p), cc-pvdz, aug-cc-pvdz basis sets. The geometries were optimized at the HF level for each basis set. These results are directly relevant to the recovery of KE correlation in the HF molecule with respect to different post-HF methods and basis sets, however a detailed analysis does

Table 2. Shannon entropies over atomic basins, Bader atomic populations, kinetic energies (per electron) over atomic basins, at the HF level, the CISD level and the differences.

	$S_{\Omega_i}^u$		N_{Ω_i}		KE/N_{Ω_i}				
C ₂ H ₆									
C	2.4480	2.4752	0.0272	5.7836	5.8513	0.0677	6.5020	6.4510	-0.0510
H	3.0022	2.9960	-0.0062	1.0721	1.0496	-0.0225	0.6100	0.6260	0.0160
CH ₃ F									
C	2.1723	2.2131	0.0408	5.1935	5.2838	0.0903	7.1655	7.0745	-0.0910
F	2.4356	2.4427	0.0071	9.7473	9.6993	-0.0480	10.215	10.259	0.0440
H	2.9518	2.9502	-0.0016	1.0194	1.0057	-0.0137	0.6241	0.6399	0.0158
CH ₃ OH									
C	2.1793	2.2323	0.0530	5.2163	5.3308	0.1145	7.1407	7.0207	-0.1200
H1	2.9474	2.9420	-0.0054	1.0268	1.0093	-0.0175	0.6234	0.6401	0.0167
H2	2.9863	2.9819	-0.0044	1.0615	1.0422	-0.0193	0.6192	0.6349	0.0157
H3	2.0440	2.1278	0.0838	0.3889	0.4219	0.0330	0.8858	0.8855	-0.0003
O	2.7718	2.7585	-0.0133	9.2454	9.1540	-0.0914	8.1291	8.2131	0.0840
CO									
C	2.1901	2.1909	0.0008	4.6102	4.6120	0.0018	7.9689	7.9662	-0.0027
O	2.8135	2.8130	-0.0005	9.3893	9.3874	-0.0019	8.0537	8.0551	0.0014
H ₂ O									
H	2.0205	2.1165	0.0960	0.3781	0.4146	0.0365	0.8905	0.8889	-0.0016
O	2.6794	2.8117	0.1323	9.2438	9.1708	-0.0730	8.1214	8.1923	0.0709
HCl									
Cl	2.2439	2.2400	-0.0039	17.239	17.213	-0.0260	26.644	26.687	0.0430
H	2.7599	2.7867	0.0268	0.7607	0.7945	0.0338	0.6627	0.6824	0.0197
HCN									
C	2.1131	2.1850	0.0719	4.7750	4.9148	0.1398	7.7450	7.5680	-0.1770
H	2.7035	2.7374	0.0339	0.7954	0.8194	0.0240	0.6592	0.6694	0.0102
N	3.0813	3.0224	-0.0589	8.4302	8.2660	-0.1642	6.5288	6.6695	0.1407
HF									
F	2.4882	2.4998	0.0116	9.7627	9.7245	-0.0382	10.187	10.222	0.0350
H	1.5762	1.7264	0.1502	0.2372	0.2755	0.0383	1.0413	1.0318	-0.0095
HNO									
H	1.7944	1.8966	0.1022	0.3374	0.3718	0.0344	0.9410	0.9309	-0.0101
N	2.6943	2.7042	0.0099	7.3298	7.3401	0.0103	7.4169	7.4241	0.0072
O	2.5319	2.5216	-0.0103	8.3331	8.2878	-0.0453	8.9518	9.0128	0.0610
HOOH									
H	1.9652	2.1033	0.1381	0.3638	0.4187	0.0549	0.9153	0.8763	-0.0390
O	2.6007	2.5938	-0.0069	8.6363	8.5813	-0.0550	8.6608	8.7259	0.0651
NH ₃									
H	2.4889	2.5374	0.0485	0.6230	0.6500	0.0270	0.7463	0.7554	0.0091
N	2.9494	2.9256	-0.0238	8.1308	8.0498	-0.0810	6.7173	6.7987	0.0814

not lie within the scope of this paper. For this reason we have opted for a precise resumen instead of presenting another data table for the 24 calculations. The first observation is that the virial ratio for all calculations remains within one percent of the expected value of two. This balance between the potential and kinetic energies eliminates the possibility that the KE behavior in the HF molecule could be an artifact caused by non equilibrium geometry.

We also observed that better correlation does not always mean a higher value of KE. In particular, in the cases of MP2/STO-3G, MP2/6-31G, CISD/6-31++G(d,p), MP2/6-31++G(d,p), all have a lower value of KE in comparison to the HF value. More curiously, in many instances, a larger correlation energy gain shows a smaller gain in KE, e.g., in the majority of the CISD vs. MP2 calculations. A one-to-one correspondence between the total energy and one-electron properties does not exist in Møller-Plesset theory and this case could be a good example. In the Møller-Plesset theory, the total energy is calculated using the n th order correction while the KE is calculated using a wavefunction that is corrected in an analogous manner. However, the two quantities E and Ψ are not connected via the Schrödinger equation.

With respect to the basis set completeness, we observed that the energy difference between a 6-31++G(d,p) and cc-pvdz calculation is less than 0.01 hartree. However, the difference in KE is between 0.5 to 1. hartree. This implies that the cc-pvdz basis set does a better job in describing the core orbitals which adds direct numerical weight to the KE. In summary, for a high enough correlation method, QCISD in this case, and a large enough basis set, the KE is always larger when compared with the HF value. A larger basis set that describes well the core orbitals also eliminates the said irregularity.

In the case of S_r , correlation always induces a larger value which shows that it is indeed sensitive to correlation

and reinforces the results for the diatomics [7]. An in-depth study of global entropies and different correlated methods (including FCI) has also been presented for the H_2O molecule where the behavior of S_t with electron correlation was also discussed [17]. Note also that the bound in Eq. (3) is obeyed for all molecules. Also interesting is that S_t clusters around a particular value for each isoelectronic series: ten electron series (≈ 8.5), fourteen electron series (≈ 8.9) and eighteen electron series (≈ 9). The value of the sixteen electron molecule (8.99) falls in between those of the fourteen and eighteen member series. This implies the existence of a mono-tonic relationship between S_t and the number of electrons in the electronic distributions of bound systems.

One can ask if the correlation effects, as measured by the magnitude of the differences (Δ) between CISD and HF values, are related with the extent of charge transfer within a particular isoelectronic series. One observes for the ten electron series that Δ for the S_p values obeys the trend $NH_3 < H_2O < HF$ which suggests that charge transfer is larger in systems that include larger correlation effects. Note also that Δ for S_π , S_t and KE all follow the opposite trend, i.e. larger correlation effects correspond to smaller charge transfer effects. One notes that a charge transfer usually results in the atom which donates electrons being more localized and the other which receives electrons being more delocalized. In other words two opposite effects. As one will see shortly, such generalizations cannot be done when considering larger molecular environments.

The results for these trends are suggestive but not conclusive in the eighteen electron series. One would expect in the CH_3 subset that the charge transfer behaves as $C_2H_6 < CH_3OH < CH_3F$ (See Table 4). The Δ for S_p indeed exhibits the expected trend of $C_2H_6 < CH_3OH < CH_3F$. The Δ values for S_π , S_t and KE also follow the expected trend with regard to charge transfer in this subset of the eighteen electron series;

Table 3 Shannon entropies over the OH functional group basin, OH functional group electron populations, kinetic energies (per electron) over the OH basin, at the HF level, the CISD level and the differences.

H-OH								
2.8192	2.9598	0.1406	9.6219	9.5854	-0.0365	7.8373	7.8764	0.0391
CH ₃ -OH								
2.9115	2.9114	-0.0001	9.6343	9.5759	-0.0584	7.8367	7.8902	0.0535

Table 4. Shannon entropies over the CH₃ functional group basin, CH₃ functional group electron populations, kinetic energies (per electron) over the CH₃ basin, at the HF level, the CISD level and the differences.

CH ₃ -F								
3.5276	3.5357	0.0081	8.2517	8.3009	0.0492	4.7412	4.7357	-0.0055
CH ₃ -OH								
3.5543	3.5636	0.0093	8.3659	8.4245	0.0586	4.6860	4.6762	-0.0098

$C_2H_6 > CH_3OH > CH_3F$. In the remainder of the molecules, HOOH and HCl, the trends for S_ρ and S_π are in agreement with the proposed model if one considers the charge transfer as the removal of electrons from the H basin. The situation is reversed for S_t and the KE. In the fourteen electron systems, Δ of all properties are smaller for CO (larger charge transfer) as compared to HCN where charge transfer is defined as the transfer of electrons out of the C basin.

Are there any trends to the magnitudes of the correlation effects in position space as compared to momentum space within the different isoelectronic series? In the fourteen electron series, Δ is larger in momentum space for both CO and HCN. This trend is supported by NH_3 in the ten electron series, however, Δ in position space is larger for H_2O and HF. This mixture of trends also carry over to the eighteen electron systems.

We now turn our attention to atomic basins. We present in Table 2 the local entropies, atomic populations and kinetic energies over the atomic basins, at the HF and CISD levels, along with their differences. We will use the kinetic energies over atomic basins as a guide to what is occurring in momentum space since there does not exist a definition of an atomic basin in momentum space, within the AIM framework. One notes, however, from Table 1 that S_π and the KE behave similarly.

The results show that correlation can add or remove electrons from the basin depending on the system studied. The effect of the addition of electrons is a delocalization of the charge density (larger entropy) over the basin while removal of electrons over the basin leads to a localization (smaller entropy). This confirms the model proposed for diatomic species [10] but now taking into account correlation effects. Exceptions to this are the O atom in the H_2O molecule and the F atom in the HF and CH_3F molecules. We would speculate that the highly electronegative nature of the O and the F atoms, which is already accentuated by the ionic Hartree-Fock approximation, is responsible for these exceptions. A clearer pattern is expected to emerge once larger basis sets and a better correlation treatment are included.

Interestingly, one also observes that the signs for the Δ 's corresponding to the $S_{\Omega_i}^u$ and KE/N_{Ω_i} are opposite for many of the basins. That is, localization (delocalization) of the charge density over the basin in position space is accompanied by an increase (decrease) of the basin kinetic energy. See, for example, the basins of the CH_3OH molecule. This hints at something akin to an uncertainty type relationship for atomic basins.

In general, correlation increases the electron populations of the H atom basins if it is attached to an electronegative atom such as F, O or Cl while the population is reduced if it is attached to a carbon atom. The exception to this is the HCN molecule which has been discussed above. These increases (decreases) in population are accompanied by delocalization (localization) of the charge density over the H basins, and a decrease of the KE over the basin when H is attached to the electronegative O or F. The C atom basin populations all increase with correlation with an accompanying increase in entropy and decrease in the KE over the basins.

The same type of analysis can be performed for the OH and CH_3 functional groups by considering the molecules given in Tables 4 and 5. We opted not to include HO-OH and H_3C-CH_3 in the analysis due to the cancellation effect caused by the symmetry. The two situations are different since electrons are being added to the OH functional basin while they are being removed over the CH_3 functional basin. In the case of addition for the OH basin, the effect of correlation is to lower the basin population which is however accompanied with delocalization in the case of H_2O . The KE over the basin also increases as a result. For electron removal over the CH_3 basin, correlation increases the basin population accompanied by a delocalization of the basin density and a reduction of the KE of the basin.

Conclusions

The response of the molecular charge density to electron correlation effects is probed by analysis of the Shannon entropies in position and momentum space, in particular at the atomic and functional group levels. Both of these entropies, along with the kinetic energy, are observed to increase with correlation, with a few exceptions. The entropy sum increases with the inclusion of correlation in all cases and provides further evidence of the sensitivity of this quantity to these effects. This sum is shown to cluster around a particular value for a given isoelectronic series which suggests that it may be used for characterization. The differences between S_ρ values at the CISD and HF levels suggest that correlation effects are larger for systems with larger charge transfer while these differences for S_π , S_t and the KE are larger in systems with smaller charge transfer. These trends are stronger for the ten electron molecules than the eighteen electron ones and indicate a reciprocal trend between position and momentum space. Analysis of electron correlation effects in atomic basins shows that correlation can add or remove electrons from a particular basin. Removal of electrons from basins occurs for electronegative atoms. The C atom basins all increase in population with correlation while the behavior of the H atom basins is dependent on its environment. The removal of electrons from a basin generally results in a localization of the basin charge density which substantiates a previous model. We observe that the de/localization of the basin density due to electron correlation is accompanied by an decrease/increase of the basin kinetic energy. Electron correlation in the CH_3 functional group increases the functional group population which is accompanied by a delocalization of the group charge density and increase of the group kinetic energy. It would be interesting to see if these observed trends hold on studying more complex systems such as those with metal-metal or metal-ligand interactions.

Acknowledgment

The authors thank the Consejo Nacional de Ciencias y Tecnología (CONACyt) and the PROMEP program of the Secretario de Educación Pública in México for support.

References

1. Shannon, C. E. *Bell Syst. Tech. J.* **1948**, 27, 379-423, reprinted in Shannon C. E. Claude Elwood Shannon: collected papers, IEEE Press New York, **1993**.
2. Collins D. M. *Z. Naturforsch.* 1993, 48a, 68-74; Ramírez, J. C.; Hernández-Pérez, J. M.; Sagar, R. P.; Esquivel, R. O.; Hô, M.; Smith Jr., V. H. *Phys. Rev. A.* **1998**, 58, 3507-3515 and references therein.
3. Thakkar, A. J. *Adv. Chem. Phys.* **2003**, 128, 303-352.
4. Kutzelnigg, W. *Angew. Chem. Internat. Edit.* **1973**, 12, 546-562; Backsay, G. B.; Reimers, J. R.; Nordholm, S. J. *Chem. Ed.* **1997**, 74, 1494-1502; Nordholm, S. J. *Chem. Ed.* **1988**, 65, 581-584.
5. Bialynicki-Birula, I.; Mycielski, J. *Commun. Math. Phys.* **1975**, 44, 129-132.
6. De Proft, F.; Ayers, P. W.; Sen, K. D.; Geerlings, P. J. *Chem. Phys.* **2004**, 120, 9969-9973.
7. Hô, M.; Sagar, R. P.; Pérez-Jorda, J. M.; Smith Jr., V. H.; Esquivel, R. O. *Chem. Phys. Lett.* **1994**, 219, 15-20.
8. Gadre, S. R. *Rev. Mod. Quant. Chem.* **2002**, 1, 108-147.
9. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.
10. Hô, M.; Smith Jr. V. H.; Weaver, D. F.; Gatti, C.; Sagar, R. P.; Esquivel, R. O. *J. Chem. Phys.* **1998**, 108, 5469-5475.
11. Hô, M.; Clark, J.; Smith, Jr. V. H.; Weaver, D. F.; Gatti, C.; Sagar, R. P.; Esquivel, R. O. *J. Chem. Phys.* **2000**, 112, 7572-7580.
12. Gatti, C.; MacDougall, P. J.; Bader, R. F.W. *J. Chem. Phys.* **1988**, 88, 3792-3804.
13. Frisch, M.J.; Trucks, G.W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Repogle, E. S.; Gomperts, R.; Andrés, J. L.; Raghavachari, K.; Binkley, J. S.; González, C.; Martín, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 98, Gaussian Inc., Pittsburgh, PA, **1998**.
14. Herzberg, G. *Molecular Spectra and Molecular Structure*, Prentice-Hall, New York, **1996**.
15. Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, **1986**.
16. Obtained from Bader, R. F. W. Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.
17. Hô, M.; Smith Jr., V. H.; Weaver, D. F.; Sagar, R. P.; Esquivel, R. O.; Yamamoto, S. *J. Chem. Phys.* **1998**, 109, 10620-10627.