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von Neumann Entropies Analysis in Hilbert Space for the Dissociation Processes of Homonuclear and Heteronuclear Diatomic Molecules

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Abstract. Quantum Information Theory is a new field with potential implications for the conceptual foundations of Quantum Mechanics through density matrices. In particular, information entropies in Hilbert space representation are highly advantageous in contrast with the ones in phase space representation since they can be easily calculated for large systems. In this work, novel von Neumann conditional, mutual, and joint entropies are employed to analyze the dissociation process of small molecules, Cl_2 and HCl, by using the spectral decomposition of the first reduced density matrix in natural atomic orbital-based representation which allows us to assure rotational invariance, *N*- and *v*-representability in the Atoms-in-Molecules (AIM) scheme. Quantum information entropies permit to analyze the dissociation process through quantum mechanics concepts such as electron correlation and entanglement, showing interesting critical points which are not present in the energy profile, such as charge depletion and accumulation, along with bond breaking regions.

Key words: Quantum Information Theory, entanglement, diatomic molecules, *Ab initio* calculations

Resumen. La Teoría de Información Cuántica es un nueva área de investigación con implicaciones potenciales para el desarrollo conceptual de los fundamentos de la Mecánica Cuántica mediante las matrices de densidad. En particular, las entropías de información en la representación del espacio de Hilbert ofrecen amplias ventajas en comparación con las que se definen en la representación del espacio real debido a que pueden ser fácilmente aplicadas en grandes sistemas. En este estudio, se emplean nuevas entropías de von Neumann de tipo condicional, mutuas y conjuntas para analizar el proceso de disociación de moléculas pequeñas, Cl_2 y HCl, usando la descomposición espectral de la matriz densidad reducida de primer orden en una representación natural atómica que permite asegurar su invariancia rotacional, y su *N*- y *v*-representabilidad en un esquema AIM. Las entropías informacionales cuánticas permiten analizar el proceso de disociación mediante conceptos mecánico-cuánticos tales como correlación electrónica y entrelazado, mostrando puntos críticos de interés que no se encuentran en el perfil energético, tales como remoción y acumulación de carga, así como puntos de formación y ruptura de enlace.

Palabras clave: Teoría de información cuántica, entrelazado, moléculas diatómicas, cálculos *ab initio*.

Introduction

The most interesting technological implications of quantum mechanics are based on the notion of entanglement, which is the essential ingredient for both quantum cryptography, quantum computing, and quantum teleportation [1]. While quantum cryptography makes use of photons for transmitting messages, most feasible studies of quantum computers rely on quantum dots (clusters) or molecules and therefore already enter the realm of theoretical chemistry, and though the first experiments regarding quantum teleportation have been performed using photons [2-6], teleportation with the massive particles chemists deal with is, of course, of much higher interest, up to now it remains an open question whether entanglement can be realized with molecules or not [7]. Therefore, it is evident that the new quantum techniques enter the sphere of interest of chemistry, and in consequence theoretical chemistry has to concern itself with entanglement as well. Generally speaking, if two particles are in an entangled state, then even if the particles are physically separated by a great distance, they behave in some respect as a single entity rather than as two separate entities. Entanglement shows up in cases where a former unit dissociates into simpler sub-systems. Corresponding processes are known quite well in chemistry. The real-space partitioning of a molecule into subsystems is still a challenging problem in theoretical chemistry [8-20], because during this process a certain entanglement of the subsystems emerges, and it is very difficult to get rid of it without destroying elementary correlations between the subsystems. So, apart from its evident importance for the foundations of physics, entanglement plays a role in chemistry too. Although information entropies have been used for a variety of studies in quantum chemistry [21-27], applications of entanglement measures in chemical systems are very scarce. Recently, Jaynes and Shannon entropies in a two-electron entangled artificial atom have been studied in the context of correlation energy [28] and the von Neumann entropy was recently used as an alternative measure of the electron correlation to measure the entanglement for He atom and H_2 molecule [29, 30]. Very recently, marginal and non-marginal information measures in Hilbert space have been proposed [31], and applied to small chemical systems, showing than entanglement can be realized in molecules [32].

It is of great interest in Chemistry to understand molecular systems as combination of atoms and molecular fragments. Thus, the concept of AIM has been the focus of great deal of attention [8-20]. Chemical processes involve small changes between atoms and molecular subsystems and it is crucial to understand the interactions (correlation and entanglement) involved in such chemical changes. The main goal of the present study is to show that marginal entropies of bipartite composite systems in Hilbert space [31] are able to reveal all critical points expected in the density profile of the dissociation processes of small chemical systems, most of them not present in the energy profile, such as accumulation and depletion of charge and bond breaking. This is achieved by use of novel measures of conditional, mutual, joint information von Neumann entropies computed by means of the spectral decomposition of the first reduced density matrix in the natural atomic orbital-based representation, assuring rotational invariance, and N and v-representability in the AIM scheme [33]. The Laplacian (LAP) and the Molecular Electrostatic Potential (MEP) are also calculated in order to reveal the structure of the densities.

Preliminaries

In this section we present important concepts of QIT along with the natural atomic probabilities employed for the calculation of the entropies. Besides, definitions of the marginal von Neumann entropies used in this work are presented,

Entanglement and von Neumann Entropies

The uncertainty in a collection of possible observables A_i with corresponding probability distribution $p_i(A)$ is given by its Shannon entropy H(A) [34]

$$H(A) = -\sum_i p_i(A) \ln p_i(A). \tag{1}$$

This measure is suitable for systems described by classical physics, and is useful to measure uncertainty of observables but it is not suitable for measuring uncertainty of the general state of a quantum system. It is the von Neumann entropy which is appropriate to measure uncertainty of quantum systems since it depends on the density matrix (see below).

Suppose that we have two sets of discrete events A_i and B_j with the corresponding probability distributions, $p_i(A)$ and $p_j(B)$. The *relative entropy* between these two distributions is defined as

$$H(A\|B) = -\sum_i p_i(A) \ln \frac{p_i(A)}{p_i(B)}. \tag{2}$$

This function, also known as Kullback-Liebler entropy [35, 36] is a measure of the ‘‘distance’’ between $p_i(A)$ and $p_j(B)$, even though, strictly speaking, it is not a mathematical metric since it fails to be symmetric:

$$H(A\|B) \neq H(B\|A). \tag{3}$$

Another important concept derived from relative entropy concerns the gathering of information. When one system learns something about another, their states become correlated. How correlated they are, or how much information they have about each other, can be quantified by the mutual information. The *Shannon mutual information* between two random variables A and B, having a joint probability distribution $p_{ij}(A,B)$ and marginal probability distributions

$$p_i(A) = \sum_j p_{ij}(A,B) \text{ and } p_j(B) = \sum_i p_{ji}(B,A), \tag{4}$$

is defined as

$$\begin{aligned} H(A:B) &= H(A) + H(B) - H(A,B) \\ &= \sum_{ij} p_{ij}(A,B) \ln \frac{p_{ij}(A,B)}{p_i(A) p_j(B)}. \end{aligned} \tag{5}$$

Where $H(A,B)$ is the joint entropy defined as

$$H(A,B) = -\sum_{ij} p_{ij}(A,B) \ln p_{ij}(A,B), \tag{6}$$

which measures the uncertainty about the whole system AB.

The mutual information $H(A:B)$ can be written in terms of the Shannon relative entropy. In this sense it represents a distance between the distribution $p(A,B)$ and the product of the marginals $p(A) \times p(B)$ As such, it is intuitively clear that this is a good measure of correlations, since it shows how far a joint distribution is from the product one in which all the correlations have been removed, or alternatively, how distinguishable a correlated state is from a completely uncorrelated one. So we have

$$H(A:B) = H\left[p(AB) \| p(A) \times p(B)\right]. \tag{7}$$

Suppose that we wish to know the probability of observing b_j if a_i has been observed. This is called a conditional probability and is given by

$$p_{ij}(A|B) = \frac{p_{ij}(A,B)}{p_j(B)} \text{ and } p_{ji}(B|A) = \frac{p_{ji}(B,A)}{p_i(A)}. \tag{8}$$

Hence the conditional entropy is,

$$\begin{aligned} H(A|B) &= -\sum_{ij} p_{ij}(A,B) \ln \frac{p_{ij}(A,B)}{p_j(B)} \\ &= -\sum_{ij} p_{ij}(A,B) \ln p_{ij}(A|B) . \end{aligned} \tag{9}$$

This quantity, being positive, tells us how uncertain we are about the value of B once we have learned about the value of A. Now the Shannon mutual information can be rewritten as

$$H(A:B) = H(A) - H(A|B). \tag{10}$$

And the joint entropy as

$$H(A,B) = H(B) + H(A|B). \tag{11}$$

Hence, the Shannon mutual information, measures the quantity of information conveyed about the random variable $A(p(B))$ through measurements of the random variable $B(p(A))$. Note also that, unlike the Shannon relative entropy, the Shannon mutual information is symmetric. Besides, according to the properties of the logarithmic functions (Jensen inequality) it can be established that entropy is a concave function, $-\Sigma p_i x_i \ln \Sigma p_i x_i \geq -\Sigma p_i x_i \ln x_i$ meaning that mixing probability distributions increases entropy, whereas the relative entropy is a convex function, $\Sigma x_i \ln(\Sigma x_i/\Sigma a_i) \leq \Sigma x_i \ln(x_i/a_i)$ i.e., mixing decreases the distance between states (less distinguishable).

The difference between classical and quantum entropies can be seen in the fact that quantum states are described by a density matrix ρ (and not just probability vectors). The density matrix is a positive semidefinite Hermitian matrix, whose trace is unity. An important class of density matrices is the idempotent one, i.e., $\rho = \rho^2$. The states these matrices represent are called pure states. When there is no uncertainty in the knowledge of the system its state is then pure. Another important concept is that of a composite quantum system, which is one that consists of a number of quantum subsystems. When those subsystems are entangled it is impossible to ascribe a definite state vector to any one of them, unless we deal with a bipartite composite system. The most often cited entangled system is the Einstein-Podolsky-Rosen state (EPR) [37,38], which describes a pair of two photons. The composite system is described by $\Psi(1,2) = \frac{(|\uparrow(1)\rangle[|\downarrow(2)\rangle] - [|\uparrow(2)\rangle][|\downarrow(1)\rangle])}{\sqrt{2}}$ which represents the spin directions along the z axis that can either be up or down. We can immediately see that neither of the photons possesses a definite state vector, then if a measurement is made on one photon, let say in the up state, then the other photon will be in the down state. This "assignment" cannot be applied to a general composite system unless its general state is written in a diagonal decomposable form, which not only is mathematically convenient, but also gives a deeper insight into correlations between the two subsystems. According to quantum mechanics the state vector of a composite system, consisting of subsystems A and B, is represented by a vector belonging to the tensor product of the two Hilbert spaces $H_A \otimes H_B$. The general state of this system can be written as a linear superposition of products of individual states:

$$\Psi^{AB} = \sum_m \sum_n c_{mn} \xi_m(A) \psi_n(B). \tag{12}$$

Where $\{\xi_m(A);\ m = 1 \text{ to } M\}$ and $\{\Psi_n(B);\ n = 1 \text{ to } N\}$ are the basis of the subsystems A and B, respectively. This state can always be decomposed in the Schmidt diagonal form:

$$\Psi^{AB} = \sum_l \lambda_l \chi_l(A) \varphi_l(B), \tag{13}$$

where $\chi_l(A)$ and $\varphi_l(B)$ are orthonormal bases for A and B, respectively. Note that in this form the correlations between the two subsystems are completely revealed. If A is found in the state $\chi_p(A)$, for example, then the state of B is in the $\varphi_p(B)$ state. This is clearly a multistate generalization of the EPR-state mentioned earlier.

In order to understand the correlation between two subsystems in a joint pure state we point out that the reduced density matrices of both subsystems, written in the Schmidt decomposed state above, are diagonal and have the same positive spectrum. In particular, the overall density matrix is given by

$$\rho = \sum_{nm} \lambda_n \lambda_m^* \ |\chi_n(A)\rangle\langle\chi_m(A)| \otimes |\phi_n(B)\rangle\langle\phi_m(B)|, \tag{14}$$

whereas the reduced ones are

$$\begin{aligned} \rho_A &= \sum_n \langle\phi_n(B)|\rho|\phi_n(B)\rangle \\ &= \sum_m |\lambda_m|^2 |\chi_m(A)\rangle\langle\chi_m(A)|, \end{aligned} \tag{15}$$

and in analogous way

$$\rho_B = \sum_n |\lambda_n|^2 |\phi_n(B)\rangle\langle\phi_n(B)|. \tag{16}$$

It is important to note that a N-dimensional subsystem can then be entangled with no more than N orthogonal states of another one. Schmidt decomposition is, in general, not practical for more than two entangled subsystems since for say n entangled systems is uncertain to know at the same time a general state such that by observing the state of one of the subsystems we could instantaneously know the state of the other n-1. Clearly, involvement of n-subsystems complicates the analysis and produces an even greater mixture and uncertainty. The same reasoning applies to mixed states of two or more subsystems (i.e., states whose density operator is not idempotent), for which we cannot have the Schmidt decomposition in general.

When two subsystems become entangled, the composite state can be expressed as a superposition of the products of the corresponding Schmidt basis vectors. From Eq. (13) it follows that the ith vector of either subsystem has a probability of $|\lambda|^2$ associated with it. We are, therefore, uncertain about the state of each subsystem, the uncertainty being larger if the probabilities are evenly distributed. Since the uncertainty in the probability distribution is naturally described by the Shannon entropy, this classical measure can also be applied in quantum theory. In an entangled system this entropy is related to a single observable. The general state of a quantum system, is described by its density matrix ρ. Let the observables a_i and b_j, pertaining to the subsystems A and B, respectively, have a discrete and non degenerate spectrum, with probabilities $p(a_i)$ and $p(b_j)$. For simplicity let us define them as $p_i(A)$ and $p_j(B)$ In addition, let the joint probability be $p_{ij}(A,B)$. Then

$$\begin{aligned} H(A) &= -\sum_i p_i(A) \ln p_i(A) \\ &= -\sum_{ij} p_{ij}(A,B) \ln \sum_j \ p_{ij}(A,B), \end{aligned} \tag{17}$$

and similarly for H(B).

An indication of correlation is that the sum of the uncertainties in the individual subsystems is greater than the uncertainty in the total state. Hence, the Shannon mutual information is a good indicator of how much the two given observables are correlated. However, this quantity, as it is inherently classical, describes the correlations between single observables only. The quantity that is related to the correlations in the overall state as a whole is the von Neumann mutual information which depends on the density matrix. The von Neumann entropy [39], may be considered as the proper quantum analog of the Shannon entropy [40] for a system described by a density matrix ρ, and is defined as

$$S(\rho) = -Tr(\rho \ln \rho). \tag{18}$$

The Shannon entropy is equal to the von Neumann entropy only when it describes the uncertainties in the values of the observables that commute with the density matrix, i.e., if ρ is a mixed state composed of orthogonal quantum states, otherwise

$$S(\rho) \leq H(A), \tag{19}$$

where *A* is any observable of a system described by ρ. This means that there is more uncertainty in a single observable than in the whole of the state [41].

Let ρ_A and ρ_B be the reduced density matrices of subsystems *A* and *B*, respectively, and let ρ be the matrix of a composite system, then the entropies of two subsystems are somewhat analogous to its classical counterpart, but instead of referring to observables it is related to the two states which are bounded by the following Araki-Lieb [42] inequality

$$S(\rho_A) + S(\rho_B) \geq S(\rho) \geq \left|S(\rho_A) - S(\rho_B)\right|. \tag{20}$$

Physically, the left-hand side implies that we have more information (less uncertainty) in an entangled state than if the two states are treated separately, hence by treating the subsystems separately the correlations (entanglement) are being neglected. Also, equality in the left-hand side holds when both systems are independent for $\rho_{A,}$ i.e., if the composite system is in a pure state, then $S(\rho) = 0$, and from the right-hand side it follows that $S(\rho_A) = S(\rho_B)$ (Schmidt decomposition Eq. (13)).

As in the classical case, two important relations can be established [40], namely, the entropies of independent systems add up

$$S(\rho_A \otimes \rho_B) = S(\rho_A) + S(\rho_B). \tag{21}$$

Further, concavity reflects the fact that mixing states increases uncertainty, i.e.,

$$S\left(\sum \lambda_i \rho_i\right) \geq \sum \lambda_i S(\rho_i). \tag{22}$$

According to the definition of the Shannon mutual information which relates only two observables, a quantum analog can be defined which measures the correlation between whole subsystems. The *von Neumann mutual information* between two subsystems ρ_A and ρ_B of a joint state ρ_{AB} is defined a

$$S(\rho_A : \rho_B) = S(\rho_A) + S(\rho_B) - S(\rho_{AB}). \tag{23}$$

As in the case of the Shannon mutual information this quantity can be interpreted as a distance between two quantum states, the correlated joint state (ρ_{AB}) and the uncorrelated one $\rho_A \otimes \rho_B$, which may be represented through a relative entropy

$$S(\rho_A : \rho_B) = S(\rho_{AB} \| \rho_A \otimes \rho_B). \tag{24}$$

Hence, the relative quantum entropy is an important quantity to classify and quantify quantum correlations [40, 41]. This measure (Eq. 24) possess important properties. It is invariant to unitary transformations (the distance between states can not be affected under a change in the basis)

$$S(\rho \| \sigma) = S\left(U \rho U^{+} \middle\| U \sigma U^{+}\right). \tag{25}$$

Partial tracing over a part of the system produces a loss of information and hence the subsystems are more difficult to distinguish

$$S(Tr\rho \| Tr\sigma) \leq S(\rho \| \sigma). \tag{26}$$

Therefore, the relative entropy decreases under any combination of these two operations which means that quantum distinguishability never increases.

In order to determine the properties of any good measure of entanglement we have to establish that a bipartite state is "disentangled" if it is in a separable form

$$\rho_{AB} = \sum_i \lambda_i \rho_i^A \otimes \rho_i^B. \tag{27}$$

These are the most general states that can be created by local operations and classical communication, Eqs (25) and (26), which contain no quantum correlations as entanglement can only be created through global operations [40, 41]. Then in order to quantify entanglement is necessary to establish the following: (i) For a disentangled state (separable), the measure of entanglement should be zero, $E(\rho) = 0$, (ii) under any local unitary transformations there is only a change of basis, which is completely reversible for the given entangled state, and then a change of basis should not change the amount of entanglement, i.e.,

$$E(\sigma) = E(U_A \otimes U_B \sigma U_A^{+} \otimes U_B^{+}). \tag{28}$$

Finally, local operations, classical communication and tracing of an ensemble σ which is transformed into subsystems σ_i with probabilities p_i, can not increase the expected entanglement. i.e.,

$$E(\sigma) \geq \sum_i p_i E(\sigma_i) \,. \tag{29}$$

In summary we can conclude that in order to quantify quantum correlations between entangled subsystems, a good measure of quantum correlation has to be non-increasing under local operations (acting separately on A and B), and hence the only way the subsystems become entangled and gain information about each other is by interacting. We will return to the latter below.

Natural Atomic Probabilities In Information Theory

We have recently shown [33] that there is an information-theoretic justification for performing Löwdin symmetric transformations [43] on the atomic Hilbert space, to produce orthonormal atomic orbitals of maximal occupancy for the given wavefunction, which are derived in turn from atomic angular symmetry subblocks of the density matrix, localized on a particular atom and transforming to the angular symmetry of the atoms. This alternative information derivation [33] was achieved by minimizing the entropy deficiency between the joint density ρ^{AB} (a reduced first density matrix of a composite fermionic system of the subsystems A and B) with respect to the atomic independent subsystems ρ^A and ρ^B , such that

$$\delta\left\{S\left(\rho^{AB} : \rho^{A} \otimes \rho^{B}\right) - \lambda(Tr(\rho^{AB}) - 1)\right\} = 0 \,, \tag{30}$$

according to the constraint

$$Tr(\rho^{AB}) = 1. \tag{31}$$

The advantages of these kind of atoms-in-molecules (AIM) approaches [44, 45] are that the resulting natural atomic orbitals are *N*- and *v*-representables [33], positively bounded, and rotationally invariant [46, 47]. An analogous information-theoretic approach was derived [48] in relation with the Hirshfeld stockholder partitioning of the molecular electron density in Cartesian space [14]

Hilbert Space Partitioning in Molecular Fragments

According to the preliminaries above we have recently proposed new measures of correlation and entanglement through marginal (H-type) and non-marginal (R-type) von Neumann entropies [31,32]. In this section we will briefly summarize the arguments which support the use of H-type entropies as good measures of entanglement, before proceeding to analyze their capabilities for chemical use. As we have mentioned above, any good measure of entanglement should not increase the quantum correlations by local transforming the subunits of the whole system through classical communication. Besides, it was mentioned that entanglement can only be created by global operations between subsystems by provoking their interaction. Taking this into account, we have proposed [31] that a molecule might be considered as a system formed by atomic subsystems, which could be studied through atomic or molecular fragments by means of natural atomic probabilities [33]. These probabilities are obtained by diagonalizing the atomic blocks (one center local transformation) of the molecular density matrix which transforms as angular symmetry representations of the isolated atoms, the resulting orthonormal orbitals are thus naturally optimal for the atom in the molecular binding environment. Then, the whole set of diagonalized atomic orbitals is symmetrically orthogonalized as to remove the interatomic overlap, while preserving the atom-like character of the orbitals as nearly as possible [46]. Thus, the natural atomic probabilities are obtained by local unitary transformations and partial tracing of the molecular density matrix which should decrease the entanglement (Eqs. 26 and 29) by losing information between subsystems. The resulting density matrix is atomic-block diagonal and its spectral decomposition reduces to the atomic angular symmetry instead of the irreducible representation of the symmetry point group of the molecule, hence it can not be reduced to a convex sum of independent subsystems, and therefore its entanglement is not zero. It has been discussed that marginal density matrices with trace-class operators may have their own diagonal representations in terms of orthonormal and complete states in their respective subspaces which do not have marginal (subsystem) probabilities of the composite probability and as a result, the conditional entropies may be negative [49, 50]. This in fact was used to define a new class of entropies which reveal interesting features of quantum entropies [31, 32]. In this study we have restricted ourselves to the study of a class of entropies (H-type) which possess marginal probabilities of molecular fragments through global operations (joint probability) which permit to reveal their interaction. Thus, we may define atomic density operators through natural atomic probabilities in Cartesian space

$$\rho^{A} = \sum_{ilm} p_{ilm}(A) \left|\chi_{ilm}(A)\right|^{2} . \tag{32}$$

And then we may define molecular fragments in an analogous way

$$\rho^{M} = \sum_{A=1}^{M} \rho(A). \tag{33}$$

In Hilbert space we may define a measure of quantum correlations between molecular fragments for a bipartite system through natural atomic probabilities and their joint probability. As we mentioned before, in the study of a bipartite system decomposed through a Schmidt orthogonalization, there are no more than *N* states that might be entangled (Eqs. 15 and 16). In the natural atomic decomposition scheme we employ there are *m* states pertaining to molecular fragment *A*, i.e., $\{p_i(A);\ i = 1 \text{ to } m\}$ with *n* states corresponding to molecular fragment B: $\{ p_j(B);\ j = 1 \text{ to } n\}$, thus, we may define the joint entropy through global operations by correlating $m \times n$ states as

$$p_{ij}(A,B) = \left(\frac{p_i(A) + p_j(B)}{m+n} \right). \tag{34}$$

Providing that the following constraints are met:

$$\sum_i \sum_j P_{ij}(A,B) = \sum_i P_i(A) = \sum_j P_j(B) = \sum_i P_{ij}(A/B) = 1. \tag{35}$$

And the marginal probabilities are written as

$$P_{ij}(A \mid B) = \frac{P_{ij}(A,B)}{\sum_i P_{ij}(A,B)}. \tag{36}$$

We are now in position of using definitions of section 2.1, related to the von Neumann entropies, taking into account that in our natural atomic scheme of probabilities, equality in Eq. (19) holds, and instead of referring to observables we deal with subsystems (molecular fragments), that is why von Neumann entropies are adequate for our study, though we keep the H-terminology to emphasize the orthogonal and commuting properties of the subspaces we are dealing with. It is easy to show that all relations concerning to H(A), H(B), H(A,B), H(A:B) and H(A/B) are fulfilled with the definitions above (Eqs 34-36), along with some useful inequalities [31] which follow immediately from Eqs. (5)-(9),

$$\begin{aligned} &H(A) \ge 0 \\ &H(A \mid B) \ge 0 \\ &H(A \mid B) \le H(A) \\ &H(A,B) \le H(A) + H(B) \\ &H(A:B) \ge 0 \\ &H(A:B) \equiv H(B:A) \\ &H(A,B) \equiv H(B,A) \\ &H(A,B) \ge H(A:B) \end{aligned} \tag{37}$$

Results and discussion

In the present study we analyze novel von Neumann marginal entropies of bipartite composite systems in Hilbert space to assess their utility for revealing the expected critical points in the density profile of the dissociation processes of small chemical systems such as HCl and Cl_2. The electronic structure calculations performed in this study were carried out with the Gaussian 03 suite of programs [51] and the natural atomic probabilities were obtained by use of the NBO 5.G program [52]. Regions of charge accumulation and depletion were analyzed by means of the isosurface of the Laplacian of the density (LAP) [53]. The bond breaking along with electrophilic and nucleophilic regions were studied through the molecular electrostatic potential (MEP) [53].

The Cl_2 molecule was calculated at the UB3LYP/6-31G level of theory by requesting that the HOMO and LUMO be mixed so as to destroy spin and spatial symmetries [51] and allow an homolytic kind of bond breaking. In order to achieve the dissociation we scan the molecule from 0.4 to 6.4 Å in order to cover twice the van der Waals radii of the atoms. Our results are depicted in Figures 1 to 13, from where several interesting observations can be mentioned. The energy profile is shown in Figure 1 from which an equilibrium energy of -920.316472 a.u. at the internuclear equilibrium distance of 2.16 Å is obtained.

The correlation energy is depicted in Figure 2, which was obtained by measuring the difference between the DFT and the UHF values, with a maximum at 1.3 Å.

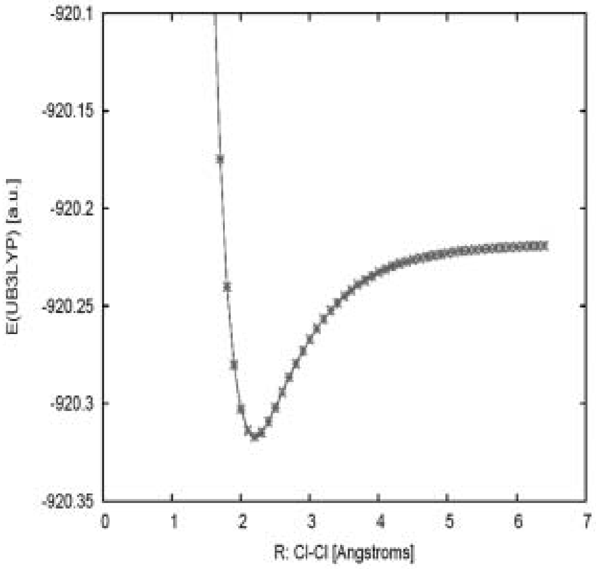

Fig. 1. Energy profile (a.u.) for the dissociation process of the chlorine molecule.

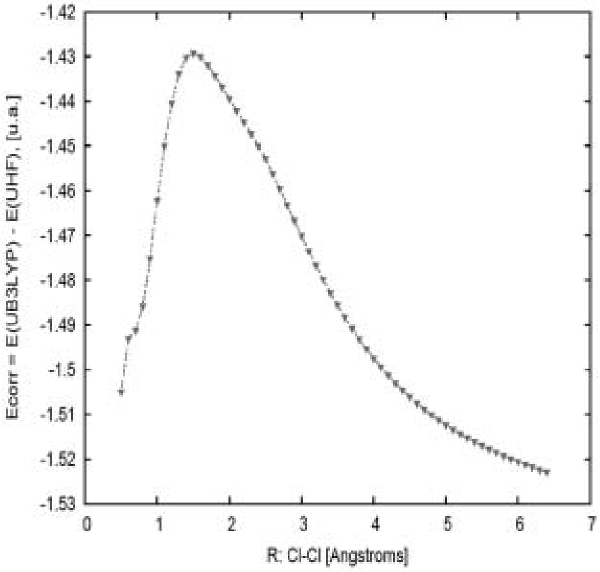

Fig. 2. Energy Correlation energy ($E_{UB3LYP} - E_{UHF}$) (a.u.) for the dissociation process of the chlorine molecule.

In order to analyze the von Neumann entropies we set A=B=*Cl* as the bipartite system and we may note that all inequalities given in Eq. (37) are fulfilled (conservation relations were also checked). Besides, the conditional entropies plotted in Figure 3 (H(A/B) or H(B/A) for this molecule) are very much alike the entropies of the subsystems (H(A) or H(B)), and three critical points are clearly observed. At 0.5 Å the entropic quantities in Figure 3 show a minimum which can be associated to the accumulation of charge in the internuclear region as it can be observed from Figure 4 wherein mapping of the Laplacian to the isosurface of the density at the plane of the molecule is depicted.

At 1.0 Å, the conditional and subsystem entropies show a very pronounced maximum which is associated with the separation of the atoms as it may be observed from the Laplacian of the density at the internuclear plane where a slight charge depletion (in dotted lines) is shown (see Figure 5).

At 2.6 Å, the entropic measures show a minimum where the curvature of the entropies change abruptly, this occurs at the equilibrium distance which may be corroborated by means of the map of the MEP calculated at the isosurface of the density at the internuclear plane. Figure 6 shows two separate regions of negative charge (electrophilic region).

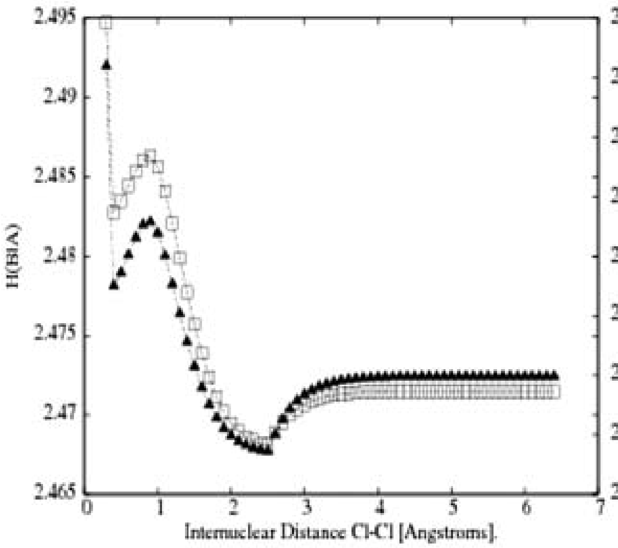

Fig. 3. von Neumann conditional entropy H(B/A) (open boxes) and the entropy for the susbsystem H(B) (solid triangles) for the dissociation of Cl_2.

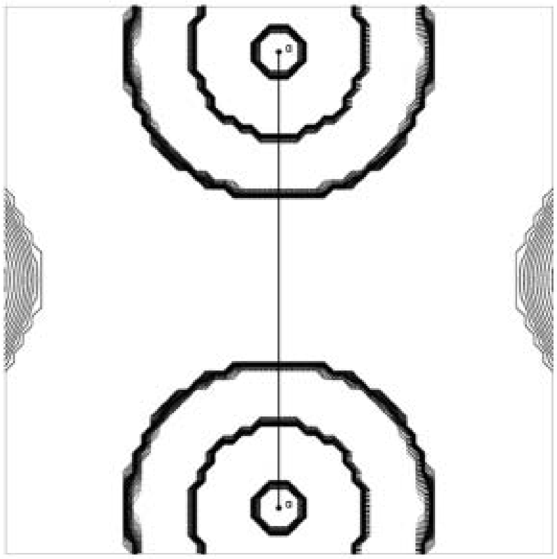

Fig. 4. Isosurface of the Laplacian at an internuclear distance of 0.5 Å for the chlorine molecule (charge accumulation in solid lines and charge depletion in dotted lines).

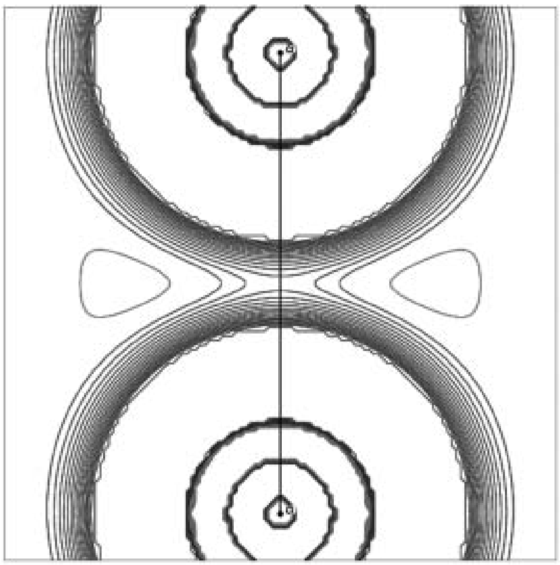

Fig. 5. Isosurface of the Laplacian at an internuclear distance of 1.0 Å for the chlorine molecule (charge accumulation in solid lines and charge depletion in dotted lines).

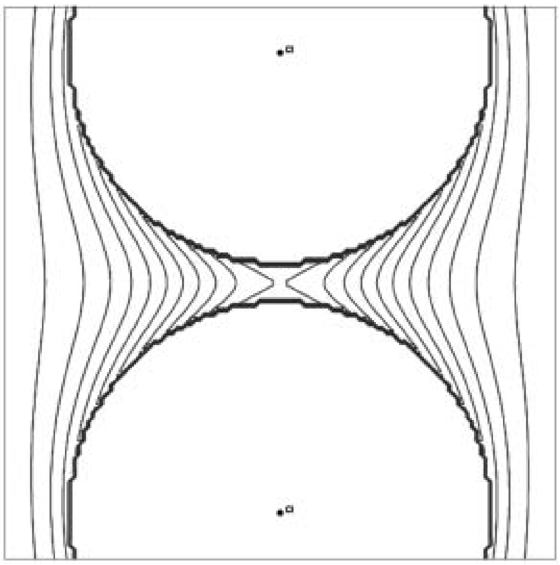

Fig. 6. Isosurface of the MEP at an internuclear distance of 2.6 Å for the chlorine molecule.

At 4.0 Å, a plateau region starts for the entropies, which may be associated with the final dissociation stage of the atoms (See Figure 7 for the MEP).

In Figure 8, the mutual and the joint von Neumann entropies are presented for the dissociation of Cl_2 . As in the case of the conditional and subsystem entropies, we may notice the same critical points we have already discussed, however, the behavior of these entropies shows an interesting inverse relationship, wherein the mutual entropy, which measures the correlation (and entanglement) of the subsystems seem to have a maximum at the equilibrium distance and becomes stabilized as the atoms become dissociated, which is in contrast with the expected classical behavior in which the one expects that the entropy increases as the atoms behave as independent and isolated systems. This is a clear feature of long range correlations which may be due to entanglement.

The HCl molecule was dissociated by scanning the interatomic distance from 0.3 Å through 3.9 Å to cover a region up to twice the van der Waals radii of chlorine by analyzing the interaction between the subsystems A (chloride) and B (hydrogen).The calculated energy at the internuclear equilibrium distance of 1.32 Å was -460.776280 a.u. at the UB3LYP/6-31G level of theory. In Figure 9 we have plotted the energy profile for the dissociation process of HCl. We may note that the correlation energy profile is very similar to the one of the total energy. As in the case of the Cl_2 molecule, all entropies obey the balance relationships and inequalities of Eq. (37).

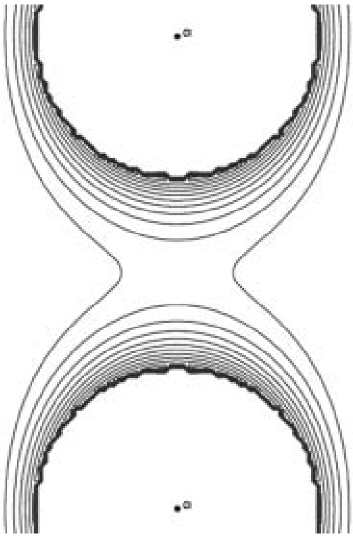

Fig. 7. Isosurface of the MEP at an internuclear distance of 4.0 Å for the chlorine molecule.

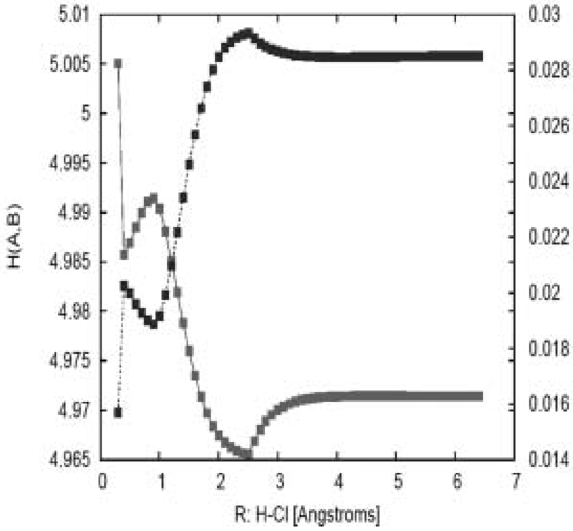

Fig. 8. H(A:B) (solid circles) and joint H(A,B) (open circles) von Neumann entropies for the dissociation process of the Cl_2 molecule.

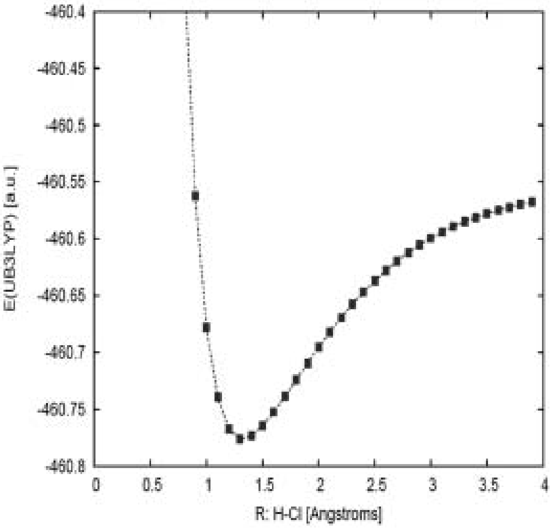

Fig. 9. Energy profile (a.u.) for the dissociation process of the HCl.

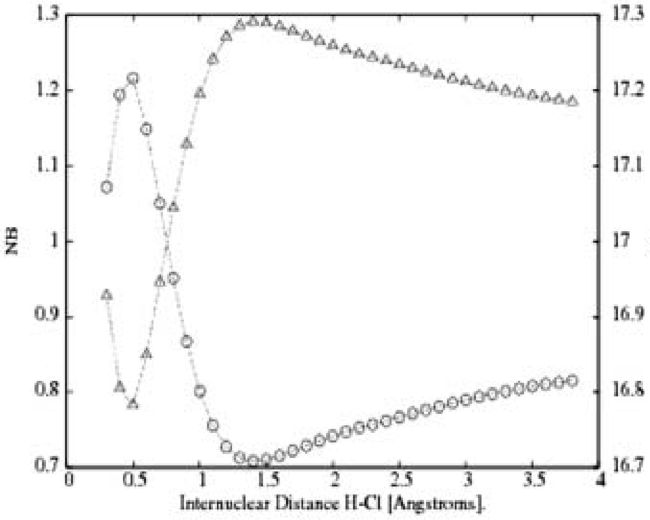

Fig. 10. Charges for the subsystems A=Cl (NA open triangles) and B=H (N_B open circles) along the dissociation path for the hydrogen chloride molecule. RX stands for the internuclear distance.

In Figure 10 the subsystem charges are displayed in order to show the charge transfer process between subsystems along the dissociation path.

The conditional entropies are depicted in Figure 11, showing the non symmetric nature of this molecule, i.e., H(A/B) ≠ H(B/A), which follow the behavior of the corresponding entropies of the subsystems, H(A) and H(B), respectively (Figures 12 and 13) in agreement with Eq. (37), particularly $H(A|B) \leq H(A)$.

The mutual and joint measures are presented in Figure 14, which behave as in the case of Cl_2 , i.e., they have the opposite behavior with the mutual quantity measuring correlations and decreasing as the internuclear distance grows up to a point wherein it gets stabilized, i.e., the atoms have long range interactions most likely due to entanglement.

Analyses of the maps of the Laplacian and the MEP on the isosurface of the density for the HCl molecule are shown in Figures 15-20. In Figure 15, the Laplacian shows an important region of depletion of charge on the H atom, which is slightly embedded into the chloride atom, which seem to cause a charge deformation on the chloride atom. The latter is clearly shown in all entropic measures at 0.5 Å (Figures 11-14).

Then, at a 0.7 Å (Figure 16) the Laplacian indicates a clear separation between the isosurface of each atom (chloride-acummulation and hydrogen-depletion), which is revealed by all entropic measures as one can see from Figures 11-14.

Next, at a 1.3 Å the Laplacian indicates a complete separation of the isosurfaces and most important, the radial symmetry of the charge which signals the equilibrium geometry along the internuclear axis (see Figure 17). This critical point is also

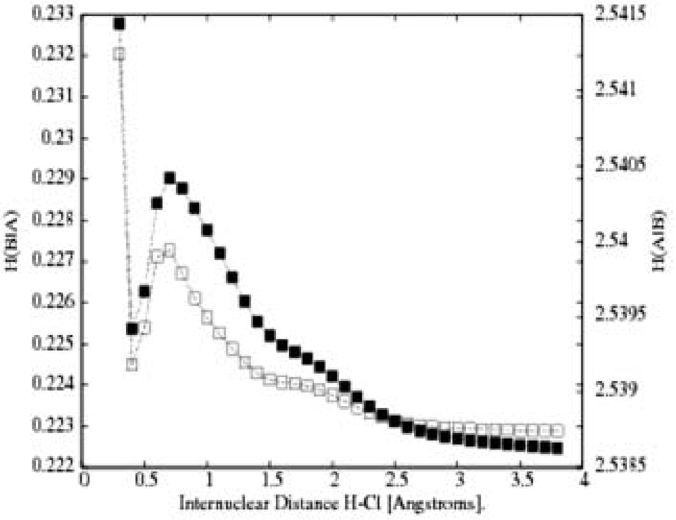

Fig. 11. von Neumann conditional entropies H(A/B) (solid boxes) and H(B/A) (open boxes) for the dissociation path of the hydrogen chloride molecule.

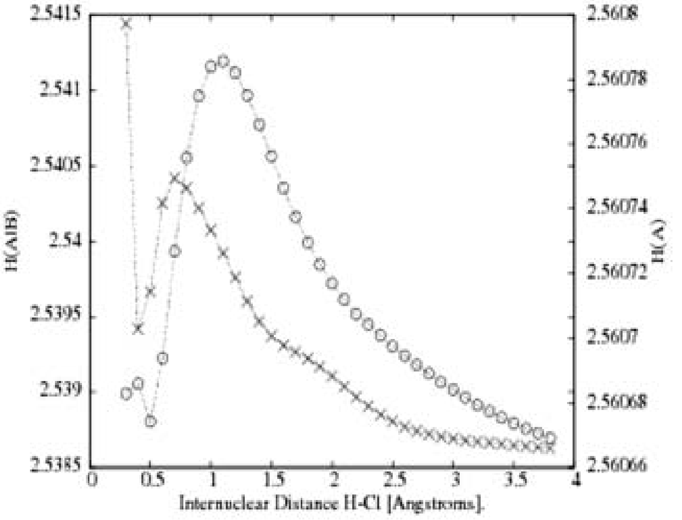

Fig. 12. von Neumann conditional entropies H(A/B) (stars) and H(A) (open circles) for the dissociation path of the hydrogen chloride molecule.

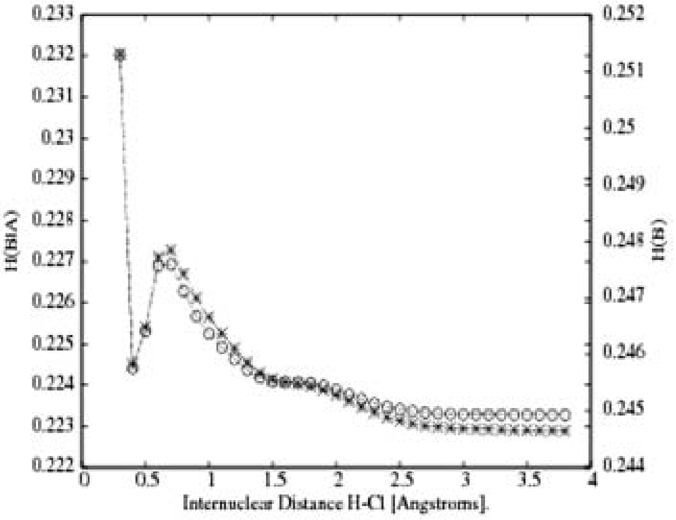

Fig. 13. von Neumann conditional entropies H(B/A) (stars) and H(B) (open circles) for the dissociation path of the hydrogen chloride molecule.

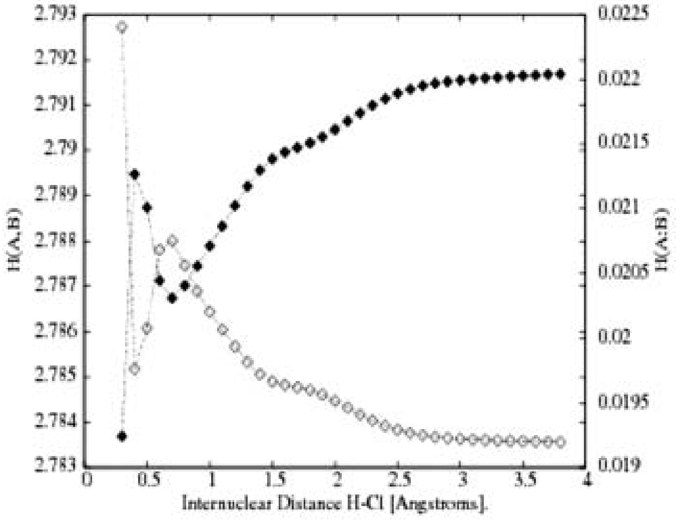

Fig. 14. von Neumann mutual H(A:B) (solid boxes) and joint entropies H(A,B) (open boxes) for the dissociation path of the hydrogen chloride molecule.

revealed in all entropic measures as a change in the curvature of these quantities (Figures 11-14), except for the H(A=Cl) which show a maximum in that point (Fig 13).

At a 1.9 Å the MEP shows the beginning of the dissociation process by a separation of the isosurfaces of the atoms (see Figure 18), which is also shown in the entropies as a new change in the curvature of these measures at this point (Figs 11-14).

Finally, at a 2.5 Å, the MEP indicates the rupture of the bond as the atoms get separated and their isosurfaces barely interact (see Figure 19). This critical point is also revealed by

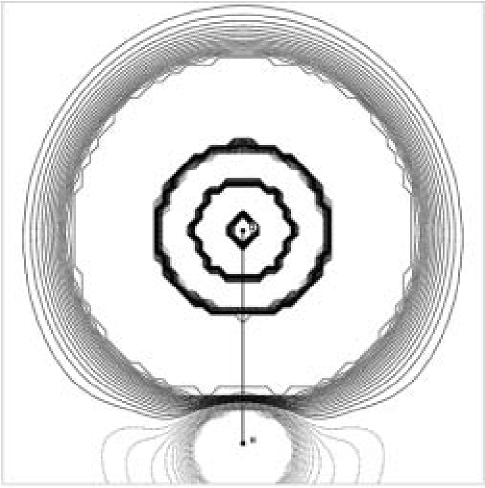

Fig. 15. Map of the Laplacian to the isosurface of the density at the molecular plane at an internuclear distance of 0.5 Å. (charge accumulation in solid lines and charge depletion in dotted lines).

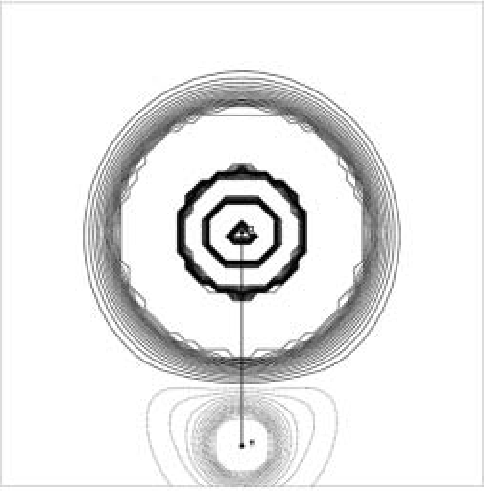

Fig. 16. Map of the Laplacian to the isosurface of the density at the molecular plane at an internuclear distance of 0.7 Å. (charge accumulation in solid lines and charge depletion in dotted lines)

Fig. 17. Map of the Laplacian to the isosurface of the density at the molecular plane at an internuclear distance of 1.3 Å. (charge accumulation in solid lines and charge depletion in dotted lines).

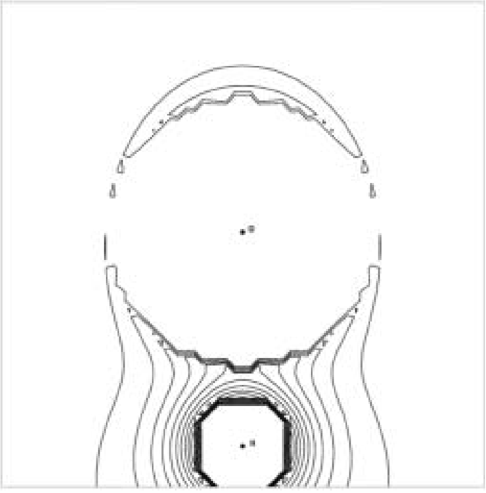

Fig. 18. Map of the MEP to the isosurface of the density at the molecular plane at an internuclear distance of 1.9 Å.

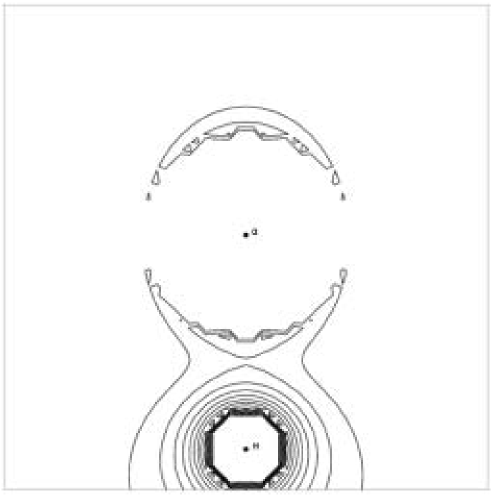

Fig. 19. Map of the MEP to the isosurface of the density at the molecular plane at an internuclear distance of 2.5 Å.

all entropic measures (see Figs 11-14). It is worth mentioning that most of the critical points above discussed are present in the charge transfer profile shown in Figure 10.

Conclusion

In the present study we have employed novel von Neumann marginal entropies of bipartite composite systems in Hilbert space (H-type entropies) to assess their utility for revealing all the critical points in the density profile of the dissociation processes of small chemical systems such as HCl and Cl_2, which are not present in the energy profile. Our study revealed regions of charge accumulation and depletion that were analyzed by means of the isosurface of the Laplacian of the density [54]. The H-type entropies also revealed bond dissociation cleavage along with electrophilic and nucleophilic regions which were studied through the Molecular Electrostatic Potential. It is worth mentioning that we also performed a basis set analysis to assess the reliability of our observations by using different basis sets such as the 6-311G, 6-311+G*, 6-311+G**, 6-31G, 6-31+G*, 6-31+G**, and 6-31G* ones, and the structure of the H-entropies remain the same as discussed throughout the study. Furthermore, calculations of the counterpoise correction [55] for the HCl molecule were also performed to assess the so called basis set superposition error (BBSE) [56], again the structure of the H-type entropies do not change.

Aside of the potential use of von Neumann entropies as Hilbert space descriptors of chemical reactivity and processes, their utility as measures of entanglement has been recently claimed [31].

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