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FUZZY SET THEORY AND QUANTUM CHEMISTRY

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RESUM

Es discuteixen breument algunes consideracions sobre l'aplicació de la Teoria dels Conjunts difusos a la Química quàntica. Es demostra aquí que molts conceptes químics associats a la teoria són adequats per ésser connectats amb l'estructura dels Conjunts difusos.

També s'explica com algunes descripcions teòriques dels observables quàntics es potencien tractant-les amb les eines associades als esmentats Conjunts difusos. La funció densitat es pren com a exemple de l'ús de distribucions de possibilitat al mateix temps que les distribucions de probabilitat quàntiques.

RESUMEN

Se discuten brevemente algunas consideraciones sobre la aplicación de la teoría de los Conjuntos difusos a la Química cuántica. Se demuestra aquí que algunos conceptos químicos asociados a la teoría son adecuados para conectarse con la estructura de los Conjuntos difusos. También se explica de qué modo algunas descripciones teóricas de los observables cuánticos pueden potenciarse mediante la teoría de los Conjuntos difusos. La función densidad se toma como ejemplo del empleo de distribuciones de posibilidad al mismo tiempo que las distribuciones de probabilidad cuánticas.

ABSTRACT

Some considerations on the application of Fuzzy Set Theory in Quantum Chemistry are briefly discussed. It is shown that chemical concepts are well suited to be connected with fuzzy set structure.

It is also explained how some theoretical descriptions of quantum chemical observables can be successfully enhanced throughout Fuzzy Set Theory.

The density function is taken to provide examples of the use of possibility distributions at the same time as the classical probability ones in Quantum Chemistry.

Key words: Quantum Chemistry, Fuzzy Set Theory, Density Function, Possibility Distributions.

INTRODUCTION

Chemistry has its own set of terms and concepts. Among these, those whose origin can be found in the realm of Quantum Chemistry constitute an important tool to help understanding molecular structure, making available to the whole chemical community a picture of the molecular building blocks and their transformations.

Many times, however, the abstract picture Quantum Chemistry gives of the molecules has not the satisfactory generalizable and simple conceptual meaning as to be sufficiently pruned in order to become a chemical everyday word or concept.

It is evident that any effort directed towards the connection between theoretical thinking and chemical pictures should be worthwhile, albeit obviously difficult.

In many aspects of the links between mathematical results coming from Quantum Theory and simplified pictures associated to experimental reasoning, the major difficulty lies in the fuzziness of the concepts which chemists work with.

Take, as an example, the fundamental idea of the chemical bond. Everyone knows that the line or lines which connect atoms in chemical formulae can have a theoretical support which needs, at this moment, a whole encyclopaedia in order to contain all the information gathered on the nature of such a simple picture.

There are sophisticated theoretical tools whose results are not prone to be put in such a way, say, as to be learnt in a freshman's course, consequently lacking a fundamental desideratum, which must be recognized to belong to Quantum Chemistry: The theoretical results usefulness to understand chemical phenomena and thus solve chemical problems better.

In this sense, not only Quantum Chemistry must be reflected in its own results, but it also has an urgent need to relink the actual brilliant findings and outstanding computational development with the overgrown experimental pool. This paper can be viewed as a modest goal to this rather ambitious statement.

FUZZY SETS

Some twenty years ago, Zadeh (1) developed an interesting mathematical idea: The *Fuzzy Set Theory*, which has found widespread use, as can be deduced from a recent review (2).

In fact, a *fuzzy set* is nothing but a simple structure associated to a conventional set. Let us define a set $X = \{x\}$, attached to a function, the *membership* or *characteristic function*, whose arguments are the elements of set X and their values lie on the [0,1] interval. That is:

$$1) \quad \forall\, x \in X \rightarrow \emptyset(x) \in [0,1]$$

Around this definition, the usual operations of set theory can be discovered again in terms of the membership function notion. For example, if A and B are fuzzy sets with membership functions $\emptyset_A$ and $\emptyset_B$ respectively, then the set

2) $C = A \cup B$

is a fuzzy set, whose membership function is defined by means of:

3) $\emptyset_C(x) = \max\{\emptyset_A(x), \emptyset_B(x)\}\ ;\ \forall\ x \in X.$

Or, one can say that A is a subset of B if and only if $\emptyset_A \leqslant \emptyset_B$, that is:

4) $A \subset B \leftrightarrow \emptyset_A \leqslant \emptyset_B,$

and so on.

At a first glance, fuzzy set definition looks somewhat like a probability distribution, but it is not. The membership function can be considered as a *possibility distribution*, quite independently of Probability Theory.

FUZZY SETS AND QUANTUM CHEMISTRY

Zadeh's Fuzzy Set Theory may be connected with some theoretical concepts, which in turn can be attached to simple chemical practice.

Connection between probability distributions, as defined in Quantum Theory in terms of the density function, according to the first postulate, and possibility distributions of chemical interest is the task which will be sketched here.

One can think of the density function as a formal chemical system observable representation containing all the information on the system one can have. Thus, entangled with the probability interpretation of Quantum Mechanics, density functions must have information on the possibility distributions of the attached molecular system too.

At this stage, the problem can be stated as follows:

> Given a quantum mechanical probability distribution, it is feasible to construct a possibility distribution?

The problem of obtaining a probability distribution from a fuzzy set structure has already been discussed in other contexts (3), and although it is also interesting it will not be dealt with here.

An almost trivial way to answer the question above starts from the heuristic statement that if a possibility distribution exists as a derivation of a probability one, it will not be unique. To see this, let us consider a molecular density function $\varrho(r)$, one can build a new function up, such as:

5) $\pi(V) = \int_V \varrho(r)\, dr,$

integrating over a finite volume V in the position space, where the system is defined. Equation 5, according to the usual Quantum Theory concepts, can be interpreted as the probability of finding the system inside the volume V. But it can also be taken as the degree or strength of localization of the system in V. In fact, if V is taken to be spherical in shape and centered at some point given *a priori*, then π (V) is simply a function of the radius of the sphere defining V, thus $\pi (V) = \pi (R)$.

A sequence of radii: $\{R_i\} \in [0, +\infty]$, will give necessarily a set of function values: $\pi(R_i) \in [0,1]$, and if adequately chosen, will fulfill the inequality:

$$6)\quad \sum_i \pi (R_i) > 1.$$

Thus, π (R) as defined has not the structure of a probability distribution, but nicely outlines the definition of a fuzzy set membership function.

SOME EXAMPLES

As a first application example, let us take a paradigmatic function used in LCAO Theory, a Slater type orbital, which can be written:

$$7)\quad \chi \{n,1,m\} (r, \theta, \varphi) = N (n,\alpha)\, r^{n\;1} \exp (-\alpha r)\, Y\{1,m\} (\theta, \varphi),$$

where N (n, α) is a normalization factor and Y {1,m} a normalized spherical harmonic function. The density function defined as $\varrho = |\chi|^2$ can be easily integrated over a sphere of radius R, yielding:

$$8)\quad \pi(R) = \int_0^R \int_\Omega \varrho (r, \theta, \varphi)\, r^2\, dr\, d\Omega$$
$$= 1 - \exp (-2\alpha R) \sum_{p=0}^{2n} (2\alpha R)^p / p!$$

Taking constant values of the parameters n and α, but allowing the parameter R to vary over a discrete set of values, one can obtain a set of numbers $\{\pi(R_i)\}$, which although being in the interval [0,1] do not correspond to any probability distribution.

The same results may be obtained choosing in equation 5 two volume sets centered at different points A and B. Two fuzzy sets will be generated with membership function π_A and π_B. It is straightforward to see how Zadeh's framework can be applied to such sets. Other volume shapes can be chosen: an ellipsoid, for instance, then π (a, b, c), with {a, b, c} being the ellipsoid's principal axes, will behave in the same manner. A more general way to define π(V) can be related to Daudel's loge theory (4) or to the density function analysis of Bader et al. (5).

ENTROPY AND LOCALIZATION

The possibility distribution, defined in equation 5, and the example in the integral 8, are typical functions of cumulative probability. As such they will behave in a general manner very much like an hyperbolic tangent function.

A possible transformation may be described, such as to confer to every function, obtained through a procedure similar to equation 5, a more convenient shape.

Entropy, within the ideas of *Information Theory*, can be used for this purpose. In fact, this can be achieved defining the entropy function through natural logarithms as: $S(x) = -x\log(x)$ with $x \in [0,1]$, and using the convention $S(0)=0$ in order to prevent the singularity at the origin.

Then $S(x)$ has value on the interval $[0,1]$. If scaled by the number e, it has a maximum at $x= 1/e$ and is a convex function, which can be used as membership function in a fuzzy set definition based on the integral $\pi(R)$.

Taking definition 5, then perhaps, a better membership function defined as an entropy:

9) $S(\pi(R)) = - e\, \pi(R) \log (\pi(R))$

can be used. This seems very convenient, because the interpretation of the membership function in the case of the $\pi(R)$ functions has some difficulties coming from its shape.

Returning again to the Slater function 8, one can see that as $\pi(R)$ increases the values of $S(\pi(R))$ increase from zero until a maximum is reached, and then decreases to nullity as R goes to infinite. Then the entropy S measures the degree of localization and acquires a maximal value when $\pi(R)$ assumes the value 1/e.

This maximum is displaced over R in terms of the parameters n and α, in such a way as localization is found nearest to origin as any of the two conditions hold: *a)* n is decreased and *b)* α is increased, in good accord with the well known properties of one-electron basis functions, Thus *diffuse* Slater orbitals will present entropy maximal at R values far away from $R=0$ and core orbitals near the same point. Two Slater orbitals can be compared numerically in this manner, and from the conventional fuzzy set point of view can be treated as two convex fuzzy sets described by entropy membership functions.

LOCALIZATION AND MOLECULES

Using this mathematical picture, a fuzzy localization procedure on a set of density functions $P=\{ \varrho_i\}$ may be described as follows:

a) A region R in the position space is chosen.

b) To each density function of the set P, a function $\pi_i(R)$ can be computed with equation 5 for any region of the set.

c) An entropy membership function $S(\pi_i(R))$ defines a fuzzy set F_i on the whole set of possible regions.

The order of localization of the density functions set P can be obtained using a fuzzy localization procedure with the additional condition:

d) The density function ϱ_i can be said more localized in the region R than the density function ϱ_j if the following inequality holds: $S(\pi_i(R)) > S(\pi_j(R))$.

The above conditions can be used, in turn, to describe a molecule. If some density function is known and a localization procedure is performed on this function, it is only necessary to use the definitions *a, b* and *c* adding the following ones:

e) There is some finite region M for which $S(\pi(M)) > \mu$ is true, being $\mu \in [0,1]$ a constant cut achieving certain entropy value.

f) The space where the molecule is embedded can be decomposed into a bonding volume defined as:

$$B_\mu = \bigcup_i M_i$$

and the remaining regions N_μ, where:

$$\forall M_k \in N_\mu, \text{ then } S(\pi(M_K)) < \mu.$$

In this context the bonding volume is the fuzzy representation of the molecule and the complementary set $N\mu$ plays the role of the molecular nonbonding regions.

FUZZY DENSITY FUNCTIONS SETS

The previous discussion has been essentially associated to a unique density function. But it is possible to obtain some kind of relationship between desinty pairs, which can be related to the same system: MO pairs, for instance, or two densities attached to different states or molecular structures. In this last choice, an attempt to answer the question, which has a daily importance in chemical research. «How similar is a molecule to another?», was made some time ago (6). Answering this new question has implications, perhaps, in the scene of Structure - Activity relationships (7).

But the interesting fact appears when given two density functions, $\{\varrho_A, \varrho_B\}$, and O being a positive definite operator, one computes the *correlation coefficient:*

$$10) \quad r = < \varrho_A, \mid O \mid \varrho_B > \left(< \varrho_A \mid O \mid \varrho_A > < \varrho_B \mid O \mid \varrho_B > \right)^{-1/2}$$

in order to find some relationship between the density pair $\{\varrho_A, \varrho_B\}$. Then, as by construction the following property holds:

11) $r = \varnothing(\varrho_A, \varrho_B) \in [0,1]$

The measure of the correlation coefficient generates a membership function in the cartesian product of the available densities, which plays the role of a fuzzy set, being easy to show that the property 11 fullfills Zadeh's fuzzy set description. As a consequence, one has no need at all to attach any statistical significance to every correlation coefficient, but the power to create an order within the density function set, which can be related to the ordering structure of molecular properties present into the systems described by the density functions.

FINAL REMARKS

Correlation coefficients and euclidean distances are related measures when computed over a numerable set of objects. On the other hand, the concept of localization is in the same way related to the fuzzy idea of chemical bond, the sharing of electrons between atoms to form molecular structures. Localization and energy minimization are strongly related computational features (10).

When solving Schrödinger's equation in the LCAO-MO Theory framework by means of a direct minimization procedure using elementary Jacobi rotations, as described in reference (8), the rotations must be applied to MO's belonging to different molecular shells, including virtual or empty orbitals. It is well known that orbital mixing within the same shell leaves the energy invariant. This property allows us to perform Jacobi rotations, in order to obtain not only optimal orbitals throughout intershell mixing, but localized ones by means of intrashell mixing: adopting Edminston-Ruedenberg's localization algorithm (9), for instance, which consists of maximization of the sum of Coulomb selfrepulsion of the set of MO's within a given shell.

This procedure can be easily related to maximal variation of coulombic euclidean distances between pairs of MO intrashell density functions. In this sense, localization procedures, which are not unique, on the contrary as energy minimization, may be considered as allowed manipulations of the quantum mechanical tools, due to the fuzzy set structure underlying the definition of localized densities.

COROLLARY

Perhaps, as a conclusion, one can say that it is possible to add, for chemical purposes, a simple corollary to the first postulate:

> Every set of density functions generates a collection of fuzzy sets.

This corolary is nothing more than the statement of the geometrical character supporting Quantum Theory applied to Chemistry. How far this fuzzy connection can go into the increment of chemical lore can only be seen with further understanding and practice.

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