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RELATIONS BETWEEN THE DENSITY MATRIX AND THERMODYNAMIC POTENTIAL

by

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ABSTRACT

We propose to study the stability of a polyatomic molecular system in terms of the thermodynamic potential G. This enables us to establish a relation between the bond index and the susceptibility tensor $\partial^2 G/\partial\mu_i\,\partial\mu_j$.

Key-words: Potential thermodynamic; Bond index; Hardness; Density matrix; Linear response theory; Susceptibility.

1 INTRODUCTION

The chemical potential (μ) and the eletronegativity (χ) concept for a microscopic system (atom or molecule) are related by the derivative of the energy of the fundamental state with respect to the number of electrons[1]:

$$\chi = - \mu = - \frac{\partial E[N]}{\partial N} \quad . \tag{1}$$

When we take a atom i, in a molecular system, this definition assumes the particular form:

$$\chi = - \mu = \frac{\partial E[q_i]}{\partial q_i} \quad . \tag{2}$$

where q_i is the electric charge of an atom in the molecule[2].

The hardness of atoms in a molecule, another important concept in quantum chemistry, formulated by Parr and Pearson[3], can be identified as the diagonal of the stiffness matrix[4]:

$$\eta_{ij} = \frac{\partial^2 E[q_k]}{\partial q_i \partial q_j} = - \frac{\partial \mu_j}{\partial q_i} = \frac{\partial \chi_j}{\partial q_i} \quad . \tag{3}$$

The off-diagonal term η_{ij} is zero in two cases: a) as a consequence of the molecular partition in fragments which do not interact and b) if the interaction energy is only long range Coulombic. The first case is a necessary and sufficient condition for validity of the Sanderson principle, as it was observed before by

Ferreira[6] and others[1,2].

Nevertheless, considering the relation between electronic charge, the chemical potential and the thermodynamic potential[6], we should consider:

$$-\frac{\partial \mu_i}{\partial q_i} = \frac{\partial \chi_i}{\partial q_i} \neq 0 \quad , \tag{4}$$

because the off-diagonal elements of the matrix $\partial^2 G/\partial \mu_i \partial \mu_j$ are different from zero.

As it was shown by Giambiagi and Giambiagi[7] I_{ij} expresses the correlation of atomic charge fluctuations in a molecule due to electronic sharing:

$$\tfrac{1}{2} I_{ij} = \langle \hat{q}_i \rangle \langle \hat{q}_j \rangle - \langle \hat{q}_i \hat{q}_j \rangle \quad . \tag{5}$$

The diagonal term I_{ii} is the self-charge in the molecule and the off-diagonal term I_{ij} is the bond index between atoms i and j.

We intend to build the stiffness matrix from the thermodynamic potential G by the inverse matrix $(I)_{ij}$. This study allows us to establish criteria of stability in the chemical bond, from Le Chatelier principle.

2 LINEAR RESPONSE THEORY

The softness (s_i), of an atom in a molecule, is the first derivative of the electronic charge with respect to the chemical potential[8],

$$s_i = - \partial \langle \hat{q}_i \rangle / \partial \mu_i |_{\mu_i = \mu} = \frac{1}{2} \beta I_{ii} \qquad (6)$$

where $\langle \hat{q}_i \rangle$ is defined by

$$q_i = \langle \hat{q}_i \rangle = \sum_{a \in i} \langle \phi_a^+ \phi^{-a} \rangle = \sum_{a \in i} \Pi_a{}^a \qquad (7)$$

where ϕ_a^+ and ϕ^{-a} are annihilation and creation operators associated to orbital a. $\Pi_a{}^b$ are elements of the first-order density matrix.

We propose to study the stability of a polyatomic molecular system, in terms of the *thermodynamic potential* G :

$$G = -\beta^{-1} \mathrm{LnTr} \exp[-\beta(H(\rho) - \sum_{i,j}^{n} \mu_i \hat{q}_i)] \qquad (8)$$

from where we have

$$- \langle \hat{q}_i \rangle = \frac{\partial G}{\partial \mu_i} \quad , \qquad (9)$$

$$\frac{1}{2} \beta I_{ij} = - \frac{\partial \langle \hat{q}_i \rangle}{\partial \mu_j} = \frac{\partial^2 G}{\partial \mu_j \partial \mu_i} \qquad (10)$$

and $\beta = 1/kT$.

When $I_{ii} = 0$ we have $I_{ij} = 0$, but if $I_{ij} \neq 0$ does not imply that I_{ii} is equal to zero; in this case there is only a modification of the electronic cloud due the Coulomb interaction. When there is overlap or sharing we have $I_{ij} \neq 0$ and $I_{ii} \neq 0$.

According to equations (8-10) we can write relations between the variations of electronic charge and chemical potential as a linear response,

$$\delta q_i = \sum_j \frac{\partial \langle \hat{q}_i \rangle}{\partial \mu_j} \delta \mu_j = \sum_j \frac{\partial^2 G}{\partial \mu_i \partial \mu_j} \delta \mu_j' = \sum_j I_{ij} \delta \mu_j' \ , \qquad (11)$$

whose inverse is given by

$$\delta \mu_i' = \sum_j \frac{\partial \mu_i}{\partial q_j} \delta q_j = \sum_j \frac{\partial^2 E}{\partial q_i \partial q_j} \delta q_j = \sum_j I^{ij} \delta q_j \qquad (12)$$

where $\delta \mu_i' = -(2/\beta \delta \mu_i)$ and the matrix $(I)^{ij}$ is the susceptibility, wich is expresses by

$$I^{ij} = \frac{(-1)^{i+j} \Delta_{ij}}{\det(I_{ij})} \ , \qquad (13)$$

Δ_{ij} bying the minor of I_{ij} in matrix $(I)_{ij}$.

3 STABILITY CONDITIONS

We can find other relations between self-charge and bond index, from the stability criterion of the system.

In equilibrium we have $dG = 0$ and $d^2G > 0$

$$\sum_{ij} \frac{\partial^2 G}{\partial \mu_i \partial \mu_j} \delta \mu_i \delta \mu_j = \sum_{ij} I_{ij} \delta \mu_i \delta \mu_j > 0 \ , \qquad (14)$$

This imposes the condition that all minors of the susceptibility

matrix must be positive.

In the most usual form, we take into account that the variation of charge in atom i can be partitioned in the following way;

$$\delta q_i = \sum_k^n \delta q_{ik} \tag{15}$$

where $\delta q_{ik} = -\delta q_{ki}$ is the charge transfer from atom i to atom k. For any i-k pair of atoms we have

$$I_{ii}\, I_{kk} - I_{ik}^2 > 0 \quad , \tag{16}$$

The positivity of all minors and the Schwartz's inequality for random operators in Hilbert's space[9,10] garantees that the determinant (eq.(16)) is positive.

Therefore, from eqs.(11-16) we obtain

$$I^{ii} + I^{kk} - 2I^{ik} > 0 \tag{17}$$

or in term of the inverse matrix,

$$I_{ii} + I_{kk} + 2I_{ik} > 0 \tag{18}$$

which is a consequence of the Le Chatelier principle. We conclude that the charge involved in the bond should always be smaller than half of the sum of self-charges of i and k.

4 ATOMIC HARDNESS IN A POLYATOMIC MOLECULE

Due to the importance of the concepts of hardness η_i and softness s_i, different approaches have been proposed in order to describe them. As it was discussed in the previous sections, in our formulation the concept of hardness comes from the introduction of a thermodynamic potential to describe chemical bonds. One of the main consequences consist in clarifying the contribution of the bond index, not usually considered.

From the definition of hardness $\eta_i = \partial^2 E/\partial^2 q_i$ we can write $\eta_i = (2/\beta) I^{ii}$ or, in terms of the inverse element,

$$\eta_{ii} = \eta_i = \frac{\eta_i^\circ}{(1 - f_i)} \tag{19}$$

$$f_i = \frac{1}{I_{ii}\Delta_{ii}} \sum_k (-1)^{i+k+1} I_{ik}\Delta_{ik} \tag{20}$$

which for a diatomic system given us,

$$\eta_A = \frac{\eta_A^\circ}{(1 - f)} \tag{21}$$

where

$$f = \frac{I_{AB}^2}{I_{AA}I_{BB}} \tag{22}$$

which expresses the correlation between charge fluctuation. It is easy to see that $0 < f_i < 1$.

When there is only long range Coulombic interaction ($I_{ij}=0$, i.e. $f_i = 0$) the hardness will be $\eta_i^\circ = 2/\beta I_{ii}$, as usual.

5 CHARGE TRANSFER BETWEEN TWO ATOMS IN A MOLECULE

In this section we study the charge transfer (δq_{ij}), the variation of the chemical potential ($\delta\mu_{ij}$) between two atoms and their chemical bond stability.

Taking the linear system (12) and the charge partition proposed in (15), we can express the variation of chemical potential as a function of the charge transfer from all pairs of atoms,

$$\delta\mu_i' = \sum_{jk} I^{ij}\delta q_{jk} \tag{23}$$

or

$$\delta\mu_i' = \sum_{j} (I^{ii}\delta q_{ij} + I^{ij}\delta q_{ji}) + \sum_{jk} (I^{ij}\delta q_{jk} + I^{ik}\delta q_{kj}) \tag{24}$$

The first sum involve variables belonging to only two atoms, whereas the second sum contains variables belonging to three different atoms.

In analogy to the diatomic case, we define the variation of chemical potential betwen pairs of atoms,

$$\delta\mu_{ij}' = I^{ii}\delta q_{ij} + I^{ij}\delta q_{ji} \tag{25}$$

and for three differents elements i, j and k by

$$\delta\mu_{ijk}' = I^{ij}\delta q_{jk} + I^{ik}\delta q_{kj} \ . \tag{26}$$

Now using eqs.(25,26) we can express the chemical potential of each atom in a polyatomic molecule by

$$\delta\mu_i' = \sum_j^n \delta\mu_{ij}' + \sum_{jk}^n \delta\mu_{ijk}' \quad , \tag{27}$$

since $\delta\mu_{ij}' = \mu_{ij}^\circ - \mu_{ij}$ and $\mu_{ij} = \mu_{ji}$ (in equilibrium).

The charge transfer in the formation of the pair $i-j$ can be studied solving the linear system, eq.(27).

Using the constraint $\delta q_{ij} = -\delta q_{ji}$ we obtain a general expression for the charge variation given by

$$\delta q_{ij} = \frac{(\mu_{ji}^\circ - \mu_{ij}^\circ)}{I^{ii} + I^{jj} - 2I^{ij}}$$

$$= \frac{(\mu_{ji}^\circ - \mu_{ij}^\circ)\det(I_{ij})}{\Delta_{ii} + \Delta_{jj} - (-1)^{i+j}2\Delta_{ij}} \quad . \tag{28}$$

For the diatomic case the constraint is $\delta q_A = -\delta q_B = \delta q$, which give us the following relation to the charge variation δq

$$\delta q = \frac{(\mu_B^\circ - \mu_A^\circ)(I_{AA}I_{BB} - I_{AB}^2)}{I_{AA} + I_{BB} + 2I_{AB}} \tag{29}$$

where $\delta\mu_i' = \mu_i^\circ - \mu$.

We remark that the positive sign of δq depends only on the difference between μ_A° and μ_B°. Therefore the atom A receives charge from atom B if $\mu_B^\circ > \mu_A^\circ$. The charge transfer in the chemical bond is zero if the chemical potentials of atoms A and B are the same.

Another important relationship emerges from the analysis of the behavior of the charge and chemical potential to atom i, as a function of the variation of the same parameters in the atom j. To get this result we choose the set of independent variables belonging to the atom j,

$$\frac{\partial q_{ij}}{\partial q_{ji}} = \frac{I_{ii}}{I_{ij}} \quad , \quad \frac{\partial q_{ij}}{\partial \mu'_{ji}} = \frac{I_{ij}^2 - I_{ii} I_{jj}}{I_{ij}} \qquad (30)$$

and

$$\frac{\partial \mu'_{ij}}{\partial q_{ji}} = \frac{1}{I_{ij}} \quad , \quad \frac{\partial \mu'_{ij}}{\partial \mu'_{ji}} = - \frac{I_{jj}}{I_{ij}} \qquad (31)$$

6 DISCUSSIONS

When we make explicit the correlation of the charge fluctuations we can see that f_i diminishes the charge transfer and therefore increases the hardness of atoms and molecules. If the correlation is weak, i.e., $f_i << 1$, we obtain the definition of hardness in the linear pertubation theory[2] $\eta_i \simeq \eta_i^{\circ}(1+f_i)$. If there are only electrostatic interations, f_i is equal to zero because $I^{ij} = 0$. Therefore I^{ij} expresses the efect of electronic sharing which is very important in the covalent bonds.[11,12]

The thermodynamic caracter of molecular system has been discussed by many authors.[13-15] The introduction of function G allows us to establish relations between the self-charge and bond indices, which are obtained from the density matrix.

We can also see that our approach will allow us to study the stability of chemical bonds in a 2n-dimensional Riemannian manifold, where n is the number of atoms in a molecule.

It is possible to establish relations between $G(\mu_j)$ and a potential $U(\mu_i, q_j)$. We identify the Catastrophe theory with the theory of chemical bonds using equilibrium statistical thermodynamic.[16] In our approach we reveal the thermodynamic aspect of the density matrix by introducing the function G. We obtain relations between bond indices, self-charge, hardness and softness, which are

observables of the microscopic system. Thus our approach is in the spirit of Nalewajski[14] and Tisza.[17]

The basic variable in our approch is the susceptibility tensor $\partial^2 G/\partial\mu_i\,\partial\mu_j$ which express the linear response of atomic charge with the variation of chemical potential.

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