Theor Chim Acta (1994) 88: 117–129

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Chimica Acta

Determination of the correlation effects in molecules using the complete error potential

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Received August 4, 1989/Accepted July 7, 1993

Summary. The complete error potential is used for the study of the correlation of molecules. The correlation can be seen as a relaxation of the electrons and a relaxation of the nuclei. From the Fermi sea, the electronic relaxation gives rise to a partial excitation of each orbital which collectively generates a linear, a surface or a volume pressure; the resulting forces acting on the nuclei are defined in a general theory of the intramolecular forces. H_3, H_3^+, the diatoms and the hydrid of the first nine elements are taken as examples.

Key words: Correlation effects in molecules – Complete error potential – Relaxation – Intramolecular forces

1 Introduction

Correlation is a quantum-chemical problem sufficiently important to justify many approaches. Correlation and decorrelation operators [1, 2] display the relations between two states: the non-relativistic model and the independent electron model. In this paper, the first model is assumed to be extremely close to the physical molecule. The second model (as well as correlation and decorrelation processes) is not observable but physically imaginable. The relaxation of the electrons and of the nuclei arises from the correlation and changes the second into the first.

The modification of the values of the physical data arises from these relaxations. The electronic wave is perturbed and *intramolecular forces* act on the nuclei (Sect. 2). The *complete error potential* [3] must be added to the exact Hamiltonian operator so that the approximate wave function is the exact solution of the Schrödinger equation.

The uncorrelated model is regarded as a strained state. The electronic relaxation and *correlation forces* (the forces acting on the nuclei) are obtained by applying the opposite of the complete error potential to the uncorrelated wave function (Sect. 3). After recalling the expression of this potential, we consider the results obtained for the molecular ion H_3^+ and for several diatomic molecules (Sect. 4).

The physical meaning of correlation forces brings out different causes related to the nature of the chemical bond. So, from this work, we can expect: a more understandable molecular model, the forecast of correlation effect, and the characterization of the chemical bond according to correlation effects.

2 Intramolecular forces

A structure is understandable only when one can describe the forces which allow it to exist and to remain. Although molecular mechanics is the usual method of structural chemistry, quantum-chemical studies of the intramolecular forces are rarely performed [4–6].

We have contributed to an approach to the intraatomic forces [7], to the electrostatic intramolecular forces [8, 9] and, since 1983, to the correlation forces [10–14].

2.1 *Definition of the intramolecular forces*

The molecular energy, E, is related to the nuclear configuration (y). This energy can be presented, versus a set of independent variables, by an hypersurface. For a given direction, u, the force F_j acting on the nucleus j, has a component equal to

$$F_j^{(u)} = \frac{\partial E}{\partial R_j^{(u)}}.$$

$R_j^{(u)}$ is the displacement of the nucleus j in the direction u. At the molecular equilibrium,

$$\boldsymbol{F}_j = 0 \quad \text{for all } j.$$

The energy will be usually written as the sum of several contributions:

$$E(y) = \sum_i E_i(y). \tag{1}$$

Consequently, the force $\boldsymbol{F}_j$ can be written:

$$\boldsymbol{F}_j = \sum_i \boldsymbol{F}_{j,i} \quad \text{with} \quad F_{j,i}^{(u)} = \frac{\partial E_i}{\partial R_j^{(u)}}. \tag{2}$$

The molecular equilibrium can be represented in as many ways as there exists different energy partitions. Some of them are well known: the classification of the forces working on the lengths of the bonds (stretching), on the valence angles (bending), on the twisting angles, the interactions between unbonded atoms in molecular mechanics and the sharing between SCF model, correlation and relativity in quantum chemistry; these two partitions can be simultaneous.

2.2 *The complete error potential*

The energy partitions can often be described as successive approximations [15–17]; so we have considered them in terms of error and correction. The complete error potential [3] being restricted to the Schrödinger mechanics, a partition of the exact energy, E_{ex}, should be first taken into consideration:

$$E_{\mathrm{ex}} = E_{\mathrm{nr}} + E_{\mathrm{rel}}$$

E_{nr} is the non-relativistic energy. The subscript nr (non-relativistic) is always omitted below. Using Eq. (2) and E_{rel}, we obtain the intramolecular forces arising from the relativistic effects.

Reference [3] gives the non-relativistic definition and theory of the complete error potential. The equations numbered (*i*) in [3] will be numbered (3-*i*) in this paper. For the *n*th state of a molecule, the complete error potential is written as

$$P_n = P_n^{nu}(y) + p_n^{\mathrm{el}},$$

with

$$P_n^{nu}(y) = E_n(y) - \langle E_n(y) \rangle \qquad (3\text{-}13)$$

$$P_n^{\mathrm{el}} = \langle E_n(y) \rangle - E_n(y) + \langle \Delta E_n^{\mathrm{err}}(y) \rangle - \Delta E_n^{\mathrm{err}}(y) + V_n(x, y) - \langle V_n(x, y) \rangle. \qquad (3\text{-}19)$$

The bracket $\langle V_n(x, y) \rangle$ has a zero value, x and y are the electronic and nuclear coordinates, $V_n(x, y)$ is the potential added to the exact Hamiltonian $\hat{H}(x, y)$, which takes into account the approximations

$$\hat{H}^{\mathrm{app}}(x, y) = \hat{H}(x, y) + V_n(x, y) = \hat{T}(y) + \hat{H}_{\mathrm{e}}(x, y) + V_n(x, y).$$

$\hat{T}(y)$ is the nuclear kinetic operator and $\hat{H}_{\mathrm{e}}(x, y)$ is the electronic Hamiltonian. $\Delta E_n^{\mathrm{err}}(y)$ is defined by the relation

$$\Delta E_n^{\mathrm{err}}(y) = E_n^{\mathrm{app}}(y) - E_n(y) \qquad (4)$$

and is equal to the difference between the eigenvalues of approximate Hamiltonian operator $\hat{H}^{\mathrm{app}}(x, y)$ and the eigenvalues of the exact Hamiltonian operator $\hat{H}(x, y)$.

Finally, we obtain

$$P_n = \langle \Delta E_n^{\mathrm{err}}(y) \rangle - \Delta E_n^{\mathrm{err}}(y) + V_n(x, y) \qquad (3\text{-}20)$$

or

$$P_n = I_n(y) + V_n(x, y). \qquad (3\text{-}21)$$

2.3 The intramolecular corrective forces

The term $I_n(y)$ can be considered as a potential in the space of the nuclear configurations. Following Eq. (6-22), we deduce the expression of the intramolecular forces arising from the error

$$F_j^{(u),\mathrm{err}} = -\frac{\partial I_n(y)}{\partial R_j^{(u)}} = \frac{\partial \Delta E^{\mathrm{err}}(y)}{\partial R_j^{(u)}} \qquad (3\text{-}22)$$

The correction being the opposite of the error, the corrective forces which are to be applied to the approximate model are

$$F_j^{(u),\mathrm{corr}} = \frac{\partial I_n(y)}{\partial R_j^{(u)}} = -\frac{\partial \Delta E^{\mathrm{corr}}(y)}{\partial R_j^{(u)}}. \qquad (5)$$

Equation (4) gives the same result as the a priori partition of Eq. (1). Owing to this method, the energy partition and the associated electronic correction potential can be deduced simultaneously. It will be noticed that the term E should be written E^{corr} in [11–14] and E^{err} in [3]. In this paper, the superior index "corr" or "err" are used only if confusion may occur. The position of the p nuclei is defined by a set of $3p - q$ independent parameters, q parameters determining the location of the molecule ($q \leqslant 6$). Thus, the interest of the internal coordinates, worked out by the molecular mechanics, is easily understandable. The internuclear distances are overabundant ($p(p-1)/2$) as soon as $p > 4$. Moreover, the chemists prefer to use angular coordinates, stretching and bending potential rather than the internuclear potentials alone. Under the action of the potential, of the correctives forces $(-\Delta E^{\mathrm{err}}(y) + C)$, the molecular configuration moves from the configuration associated to the approximate wave function $\phi^{\mathrm{app}}(x, y)$ to the eigenfunction of the exact Hamiltonian. These forces will have a physical sense only if the error has a physical sense. Neglecting the correlation will be corrected for by studying the correlation forces as exemplified in the following chapters.

3 Applications of the error theory to the correlation

When the independent electron model is well defined for a molecular state, the "correlation decrease" is defined for a given molecular geometry (y) and electronic state, by

$$\Delta E^{\mathrm{corr}}(y) = -\Delta E^{\mathrm{err}}(y) = E^{nr}(y) - E^{\mathrm{SCF}}(y). \tag{6}$$

For the molecular geometry (y), the energies $E^{nr}(y)$ and $E^{\mathrm{SCF}}(y)$ are respectively equal to the energies calculated in the non-relativistic and self-consistent field approximations.

This correlation decrease is considered as the standard definition of "correlation energy". Correlation forces are defined by derivation as stated in Eq. (4).

3.1 Intramolecular correlation forces

If E^{corr} is expressed in terms of the internal coordinates Q_k ($k = 1, \ldots, 3p - q$), a new set of forces U_k ($k = 1, \ldots, 3p - q$) can be derived. Near the equilibrium position, the elementary work is equal to

$$dT = \sum_{k=1}^{3p-q} U_k \, dQ_k, \tag{7}$$

with

$$U_k = \frac{\partial \Delta E^{\mathrm{corr}}}{\partial Q_k}.$$

For a diatomic molecule, the internal coordinate is the internuclear distance R, we obtain

$$F = \frac{d\Delta E^{\mathrm{corr}}}{dR}. \tag{8}$$

$F > 0$ is a contraction force and $F < 0$ is an expansion force. The strength of the correlation force can be calculated from the "deformation energy arising from the

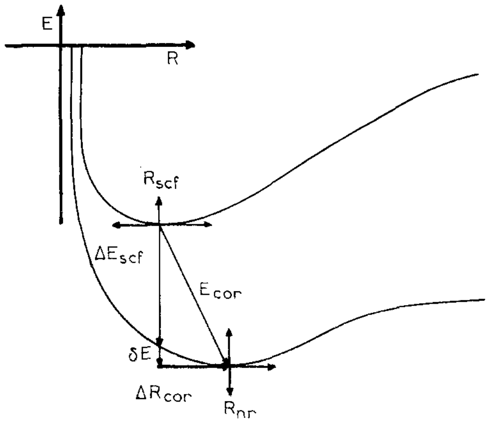

Fig. 1. Work of the correlation forces; R internuclear distances axis; E energies axis; R_{SCF} self-consistent field equilibrium distance; R_{nr} non-relativistic equilibrium distance; ΔR_{cor} correlation deformation; E_{cor} correlation energy; ΔE_{SCF} correlation decrease; δE: work of the correlation forces

Table 1

Molecules	R_{SCF}	R_{nr}	E_{cor}	δE	E_0	F_{eq}	$\delta E/E_0$ (%)
NH...	1.7	1.9614	– 0.2317	– 0.0162	– 0.0457	– 0.06	35
N_2...	1.996	2.098	– 0.535	– 0.0178	– 0.165	– 0.15	11
F_2...	2.491	2.637	– 0.7297	– 0.0064	– 0.059	– 0.074	10.8
BeO...	2.4	2.5	– 0.14	– 0.002	– 0.028	– 0.016	7
C_2...	2.3	2.35	– 0.5115	– 0.00001	– 0.1755	– 0.0045	5.7
H_2...	1.3875	1.4009	– 0.041	– 0.00005	– 0.001	– 0.005	5
B_2...	3.1	3.003	– 0.3231	– 0.0015	– 0.0431	+ 0.024	3.5
FH...	1.693	1.737	– 0.3776	– 0.0013	– 0.041	– 0.029	3
O_2...	2.28	2.30	– 0.6470	– 0.0017	– 0.087	– 0.084	2
OH...	1.8	1.834	– 0.31	– 0.001	– 0.05	– 0.04	2
Li_2...	5.2	5.1	– 0.1248	– 0.0002	– 0.0308	+ 0.002	0.7
CH...	2.086	2.124	– 0.1967	– 0.0017	– 0.0287	– 0.008	0.6
He_2^{++}...	1.26	1.32	– 0.043	– 0.0005	– 0.001	– 0.008	0.5
BeH...	2.538	2.54	– 0.1051	– 0.000004	– 0.011	– 0.002	0.04
BH...	2.336	2.34	– 0.1522	– 0.0000018	– 0.0122	– 0.0052	0.02
LiH...	3.015	3	– 0.0826	– 0.0000002	– 0.0406	+ 0.0015	0.0005

correlation"

$$\delta E = \int_{R_{\mathrm{SCF}}}^{R_{nr}} F\,dr = E^{nr}(R_{nr}) - E^{nr}(R_{\mathrm{SCF}}) \tag{9}$$

or in a more general way,

$$\delta E = \int_{y_{\mathrm{SCF}}}^{y_{nr}} T\,dy = E^{nr}(y_{nr}) - E^{nr}(y_{\mathrm{SCF}}). \tag{10}$$

Figure 1 is an illustration of Eq. (9). From Eqs. (9) or (10) we obtain the strength of the correlation force, at equilibrium

$$F_{\mathrm{eq}}^{\mathrm{corr}} \simeq \frac{\delta E}{\Delta R} \quad \text{or} \quad U_{k,\mathrm{eq}}^{\mathrm{corr}} \simeq \frac{\delta E}{\Delta Q_k}, \tag{11}$$

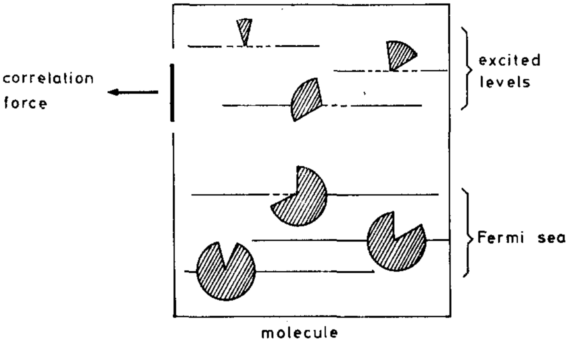

Fig. 2. Intramolecular vaporization

with

$$\Delta R = R_{nr} - R_{\mathrm{SCF}} \quad \text{or} \quad \Delta Q_k = Q_k^{nr} - Q_k^{\mathrm{SCF}}.$$

If the coordinate Q_k is the volume of the molecular polyhedron, U^{corr} is identical to a correlation pressure arising from the relaxation of the electronic cloud.

For a linear or planar molecule, a surface pressure or an expansion force can also be defined.

Numerical data related to the correlation in diatomic molecules are reported in Table I, using energy values given in literature, issued from *ab initio* methods. Molecular dilation often occurs especially for true molecules and for molecular fragments. The values of the deformation energy arising from the correlation are not always negligible parts of correlation energy.

3.2 The correlation of a molecule compared to the liquid-vapour equilibrium

The changes in the molecular geometry and the building up of new orbitals, weakly occupied, by the excitation of the SCF orbitals (as it concerns a partial occupation number) are two inseparable aspects of the correlation. These are illustrated in Fig. 2 where the orbitals are represented by their energy levels and their occupation numbers in the SCF and non-relativistic models [19]. The nearly full levels and the nearly empty levels, respectively, can be compared to a condensed state and a vapour in equilibrium, taking into consideration the well-known model of Eyring [20]. In Eyring's model vapour mirrors the fluid vacancies. In the correlation it can happen that partially occupied excited orbitals mirror the partially empty SCF orbitals.

For these reasons, in previous publications [3, 10–13] and communications, this change in the distribution of the electrons on energy levels was called "intramolecular vaporization". But the analogy is not complete and therefore it will be better to speak about an intramolecular "pseudovaporization". Energy levels and occupation numbers can be calculated, if not many, by Schrödinger mechanics, if many by Dirac's statistics.

The statistical equilibrium suggests the use of thermodynamic parameters playing the role, at the molecular scale, of "macroscopic variable" like pressure, entropy, etc. in a fluid. These homonymous of macroscopic variables could describe the global effect of the correlation.

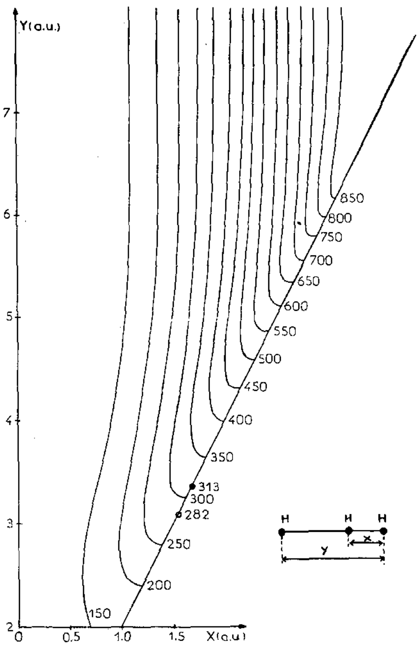

Fig. 3. Isocorrelation lines for the linear H_3^+ configurations; X length of the shorter bond; Y internuclear separation: The correlation energy is expressed in millihartree

4 Study of correlation and correlation force in the molecular ion H_3^+ and some diatomic molecules

The use of the second quantization method allows the direct calculation of the correlation decrease; it has been calculated for the linear and isoscele triangular configurations as explained in [11].

4.1 Linear configuration

The isocorrelation lines are drawn on Fig. 3. The set of the symmetrical configurations is represented by the straight line D1 defined by its equation: $Y = 2X$. Along this line, the derivative is negative, consequently the correlation force is an expansion force and the molecular symmetry is preserved. Near the equilibrium, F has a value equal to -1.1×10^{-2} a.u. (1 a.u. $= 8.2 \times 10^{-8}$ N). For the asymmetrical configurations the gradient vector has always a negative component, the other being almost zero. So above the D1 line, the gradient vector is parallel to the X axis and under the D1 line, it is parallel to the Y axis. This means that under the action of the correlation force an asymmetrical configuration will change to a symmetrical one.

4.2 Isosceles configuration

Figure 4 shows the isocorrelation lines for the isoscele triangular configurations of H_3^+. D and X are respectively the height and the base of the isoscele triangle. The correlation force is easily obtained in three areas:

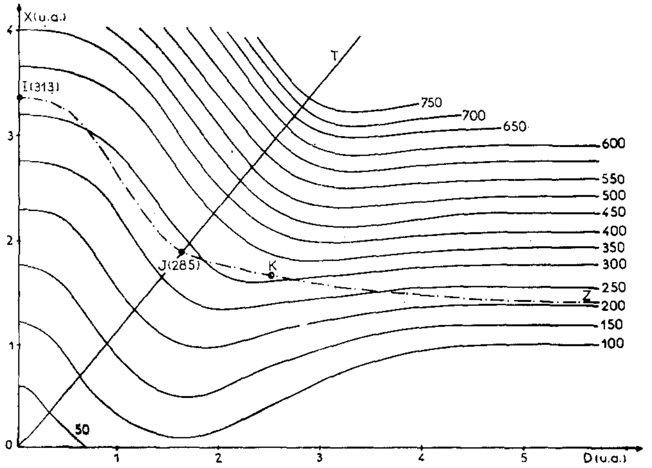

Fig. 4. Isocorrelation lines for the triangular H_3^+ configurations; X base of the isosceles triangle; D height of the isosceles triangle. The correlation energy is expressed in millihartree

The straight line T, defined by its equation ($X = 2D/\sqrt{3}$) represents the set of equilateral triangles. Along this direction, the derivative is negative; consequently the correlation force is an expansive force and the molecular symmetry is preserved. At the equilibrium position, located at the J point ($x \simeq 1.88$ a.u.), the correlation force, $F_{\mathrm{eq}}^{\mathrm{corr}} = -0.9$ a.u. and the surface pressure, $A \simeq -0.5$ a.u. (1 a.u. for the pressure equal to 2.9×10^{13} J/m^2).

The set of the linear, symmetrical configurations, studied in Sect. 4.1, is represented by the X axis. The shape of the isocorrelation lines, near the X axis, implies the instability of the linear configuration.

When $D > 4$ a.u., the gradient vector is almost parallel to the X axis and the X component has a negative value. The correlation force is an expansive one, the value of the X component increases and the D component value remains constant. The geometry of H_3^+ draws near the equilateral configuration. Since the isocorrelation lines are quasi equidistant, the X component is stationary and its value is equal to -0.02 a.u.

4.3 Checking the intramolecular pseudovaporization

Figures 5 and 6 illustrate the results related to the alteration of the geometry due to the correlation force. In brief, the *symmetrization principle* and the *expansion principle* applied to the most symmetrical configuration are confirmed in the case of H_3^+. These two principles are deduced from the internal molecular pseudovaporization and lead to the equilibrium of the components and to the expansion of the set.

4.4 Correlation force in two subsets of diatomic molecules

Figure 7 shows the variations of the correlation force at equilibrium for a set of homonuclear diatomic molecules and for the associated hydrides versus the atomic

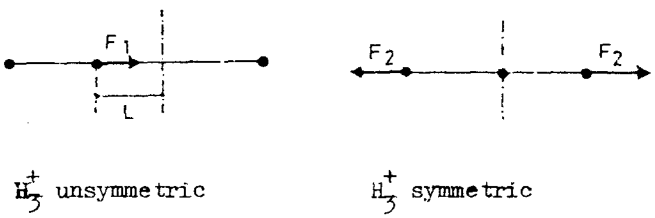

Fig. 5. Correlation forces for the linear H_3^+ configurations. F_1 symmetrization force; F_2 expansion force. $L = Y/2 - X$ (see caption of Fig. 3)

number of the element. The two lines are similar but the value of F, for an hydride, lies between the value related to H_2 and the value related to the homonuclear diatomic molecule. Most of these forces are expansion forces; N_2 provides the highest value among the expansion force (0.15 a.u.) when the highest value for the contraction force is obtained for B_2 (0.03 a.u.). (Twenty years ago, Smeyers ([21] had observed on an experimental basis that the contraction forces are less frequent and weaker than the dilatation one as in this sample). We suggest [12] that the dilatation appears in true molecules or in the molecular fragments, when the contraction forces appear in aggregates or in Van der Waals molecules. So, in the hightly bonded molecules, the correlation pressure due to the intramolecular pseudovaporization, would be a restraining effect for the bonding orbital formation.

4.5 Partitioning correlation force

Should the correlation force be a criterion for distinguishing between the chemical bonding and the nonbonding (or supermolecular bond).?

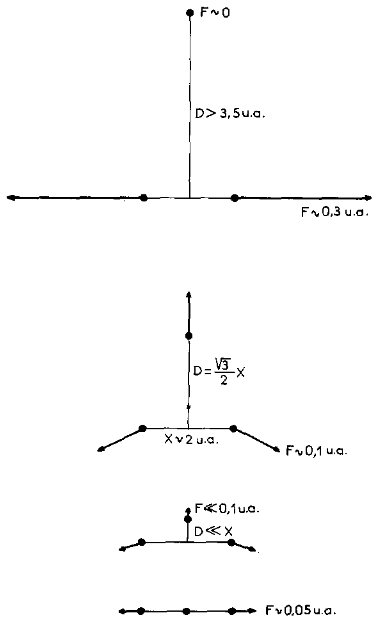

Fig. 6. Correlation forces for the triangular H_3^+ configurations

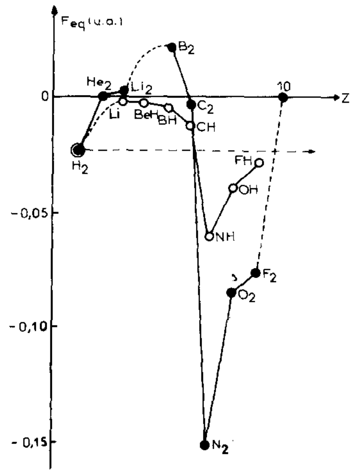

Fig. 7. Correlation forces at equilibrium (F_{eq}) for the homonuclear diatomic molecules and the associated hydride versus the Z atomic number (1 a.u. = 8.2×10^{-8} N).

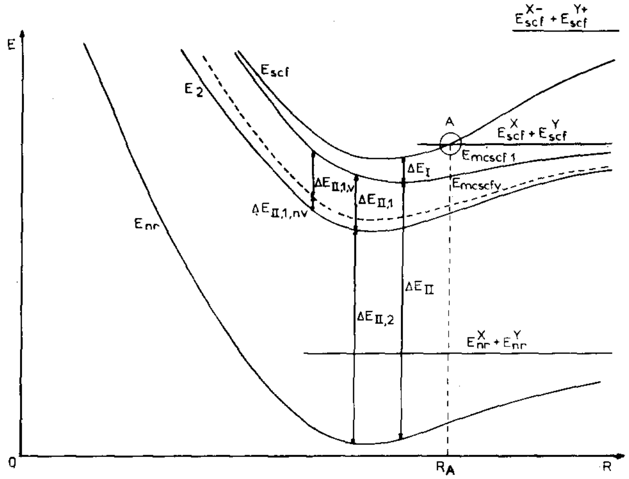

Fig. 8. Energies of several diatomic molecule models. R internuclear distances; E energies; E_{SCF} uncorrelated molecular energy; E^X_{SCF}, E^Y_{SCF} uncorrelated energy of the X, Y atom; A upper limit of the validity for the SCF model; E_{MCSCF1} energy of the simplest multiconfigurational model; E_{MCSCFV} optimized energy of the valence configuration; E_2 lower energy without atomic correlation; E_{nr} non-relativistic energy; E^X_{nr}, E^Y_{nr} non-relativistic energy of the X, Y atom; ΔE_I energy decrease due to the fundamental expansion; ΔE_{II} energy decrease due to the fundamental attraction; $\Delta E_{II,1}$ interaction energy decrease between uncorrelated atoms; $\Delta E_{II,2}$ energy decrease due to the atomic correlation; $\Delta E_{II,1,v}$ decrease of the internal correlation energy between uncorrelated atoms; $\Delta E_{II,1,nv}$ decrease of the external correlation energy between uncorrelated atoms

The discussion seems to be easier if the distinct causes [22–30] contributing to the correlation force are studied separately, as explained in [14]. This analysis leads to a partition of the correlation energy which is summarized in Fig. 8 (the Δi are negative). The molecule is by convenience supposed to be diatomic.

Resulting from this energy partition, correlation force is partitioned following the set of the ΔE_i. The two above reported principles derive only of the $\Delta E_I = E_{MCSCF} - E_{SCF}$ by minimization term.

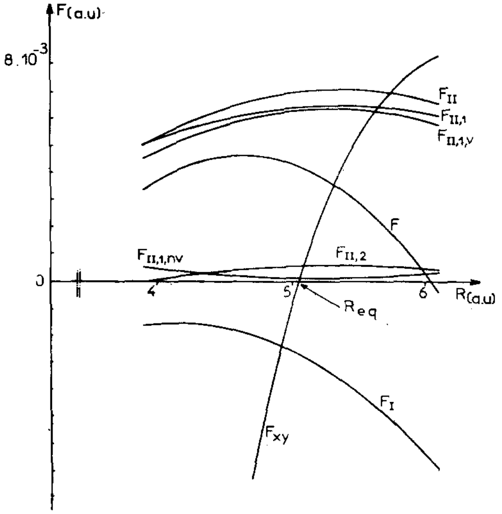

Fig. 9. Correlation forces in Li_2. F_{XY} interatomic force; R_{eq} internuclear equilibrium distance; F_I fundamental repulsion force; F_{II} fundamental attraction force; $F = F_I + F_2$: F is the correlation force; $F_{II,1}$ attraction force between uncorrelated atoms; $F_{II,2}$ atomic correlation force; $F_{II,1,v}$ internal attraction force between uncorrelated atoms; $F_{II,1,nv}$ external force between uncorrelated atoms

For a diatomic molecule, a force

$$F_i = \frac{\partial \Delta_i}{\partial R}$$

derives from each term. Figure 9 gives the different forces F_i, named and discussed in Ref. [5] and here, calculated from the literature [31, 32] for the diatom Li_2.

The intermolecular force F_{XY} versus the internuclear separation R determines the equilibrium, close to $R = 5$ a.u. The limit of stability of the SCF model (defined on Fig. 8) is $R_A = 6.37$ a.u. In the considered interval

$$(3.9 \text{ a.u.} < R < 6.1 \text{ a.u.})$$

the different contributions are contraction forces (positive sign) except the so called "fundamental repulsive force" F_I (corresponding to the antibonding orbitals). One observes that F_I is not the leading part in total correlation force F, in agreement with that Li_2 is not a true chemical molecule.

The $F_{II} = F - F_I$ "attractive interatomic force" is equivalent to F_{XY} for $R > 15$ a.u. In F_{II} the so called "intraatomic correlation force" F_{II2} is negligible with respect to "interatomic correlation force" F_{II1}. In F_{II1} the part of nonvalence orbitals F_{II1nv} is negligible with respect to the part of valence orbitals. F_{II1v}. Finally the so called external correlation, identical to F_{II1nv} has a restricted part in the total correlation F.

5 Conclusion

The use of the complete error potential allows the study of intramolecular forces. At equilibrium, the intramolecular forces are defined from a partition of the energy; these forces have a physical meaning only if the energy partition has a physical meaning. So, the correlation looks like a process which is defined first and foremost mathematically but it is also physically imaginable. The correlation process breaks a molecular state (defined by the SCF model) arising from a strain described by the complete error potential. The electronic and nuclear terms of this potential include the relaxation of the nuclear configuration.

The electronic relaxation may be associated with an intramolecular change which creates holes in the SCF orbitals and consequently creates some weakly occupied orbitals.

The nuclear relaxation results from the work of the correlation forces. A correlation pressure may be calculated; according to the molecular geometry this pressure can be a linear, surface, or volume pressure. For the tightly bonded molecules, the pressure defines the dilatation and symmetrization forces; so these forces act with a moderating effect. The values of the energy and forces depend strongly on the nature of the molecule. At equilibrium, the order of magnitude is usually less than 15×10^{-2} a.u. for the dilation force and less than 3×10^{-2} for the contraction force.

Finally, it appears that the correlation in the isosteric series follows the periodic table of the elements in agreement with the correlation pressure of the electronic cloud.

The result of the correlation process may be expressed in terms of energy as usual or in terms of forces; although both description are not equivalent. *A zero force may correspond to a large energy.* For instance for two nonbonded atoms it is a vanishing correlation force but the correlation energy is the sum of the correlation energy of the two atoms.

The correlation could offer a good criterion to classify the chemical bond: the attractive correlation force characterizes the clusters, the repulsive characterizes the real molecule, and the zerovalue the Van der Waals molecule.

One useful aspect of this approach is a derivation of possible empirical rules that could qualitatively provide an estimate of correlation effects in various systems.

On the other hand, we suggest the use of quantities similar to the thermodynamical ones but to the scale of molecular structure. Their mutual relations should be compared with those of the fluids.

Acknowledgements. The authors are indebted to Professor Koski, Drs Kaufman and Haribaran for their hospitality and help concerning the work of the models H_3, H_3^+. The french authors are indepted for discussions on the correlation effects with Professors J. Cizek and J. Paldus, on the correlation partition with Professor A. J. C. Varandas, and for many useful suggestions to Professor Y. G. Smeyers.

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