

Energy bounds for isoelectronic molecular sets and the implicated order

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By representing molecules as vectors whose components are their nuclear charges, a theorem that allows to order Born–Oppenheimer energies of sets of isoprotonic-isoelectronic molecules is stated. Upper and lower bounds for these sets are derived, along with other general energy inequalities involving homonuclear systems and molecules with common molecular fragments. These inequalities imply that the sets of molecules under consideration are endowed with the structure of a partially ordered set (POSET). Some properties related to this structure are discussed.

KEY WORDS: POSET, energy bounds, molecular classification, nuclear charge space, chemical structure

1. Introduction

Most of quantum chemical studies use the Born–Oppenheimer approximation and focus on searching minima and other critical points at the potential energy hypersurface $E(\mathbf{R})$ to characterize molecular geometry and compute molecular properties from the corresponding electronic wave functions. Usually, Hamiltonian operators are assumed to be dependent only on the spatial variables associated with each particle belonging to the system. However, some authors have made efforts to consider nuclear charges as another variable [1–7]. In this context, a more general potential energy function $-E(\mathbf{Z}, \mathbf{R})$ appears, as well as its constant geometry profile $E(\mathbf{Z})$. Analysis of the behavior of this last function have lead to some inequalities that establish interesting energy relations among different sets of isoelectronic molecules [4,6,7]. Recently, some applications of these relations have been reported [8,9].

Those inequalities have two unsettled issues: first, they contain a problematic second-order term on nuclear charge variables, which prevents from setting

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general energy relations between pairs of molecules. Although under certain particular conditions this term can be removed [6,7], a general condition to deal with it has not been reported. Second, they are strongly restricted by nuclear geometry, so they are only valid as long as all related molecules share the same nuclear configuration.

In this paper, we aim at these two issues. We define a sufficient condition to ensure that second-order term being positive definite, so that it can be removed to obtain an inequality that is linear in the nuclear charge variable. Then, starting from the set of molecules defined by such condition, we derived a new inequality that relates molecular energies corresponding to minimum energy configurations. We also illustrate some potentialities of this inequality with some examples. Finally, we introduce a mathematical structure underlying the set of isoprotonic-isoelectronic molecules and their energies.

2. Basic definitions concerning \mathbf{Z} as a variable

2.1. Nuclear charge semispace \mathbb{Z}^N

We shall introduce, following the ideas proposed by Mezey [4,6,10], a vector \mathbf{Z} whose components Z_i are the charges of the nuclei of a molecular system. For our model, each Z_i may take any positive real value, in particular zero components, i.e., dummy nuclei with zero charges are allowed. We shall define the operations vector sum, vector–scalar product and vector–vector inner product in the common way: Given

$$\mathbf{Z}^k = (Z_1^k, \dots, Z_N^k), \quad \mathbf{Z}^m = (Z_1^m, \dots, Z_N^m), \quad \alpha \in \mathbb{R}^+,$$

then

$$\begin{aligned} \mathbf{Z}^m + \mathbf{Z}^k &= (Z_1^m + Z_1^k, \dots, Z_N^m + Z_N^k), \\ \alpha \mathbf{Z}^k &= (\alpha Z_1^k, \dots, \alpha Z_N^k), \\ \mathbf{Z}^k \mathbf{Z}^m &= \sum_i Z_i^k Z_i^m. \end{aligned} \tag{1}$$

On previous works [4–7,10,11] an structure of Euclidean space has been assumed to this set of charge vectors with the operations defined above. This is not rigorous since, although \mathbf{Z} vectors were allowed to be “added” and “multiplied by an scalar” according to the usual definitions, actually only positive scalars had been used. Even though it seems to satisfy all the axioms of a linear space, the existence of the inverse element has not been shown. Besides, in those papers the inner product between vectors is allowed but is not necessarily associated with an Euclidean metric. To avoid confusion, we will associate to \mathbf{Z} vector set an structure of *vector semispace* with inner product, instead of an Euclidean Space

structure. A vector semispace defined over the positive real field \mathbb{R}^+ , is a vector space with the vector sum provided by an structure of Abelian semigroup noted additively [12].

To take into account the nuclear configuration from this perspective, each component of any nuclear charge vector is associated with a three-dimensional vector which defines the position of the corresponding nucleus.

$$\begin{array}{ccccccc} (Z_1, Z_2, \dots, Z_N) & & & & & & \\ \downarrow & \downarrow & \dots & \downarrow & & & \\ \mathbf{R}_1 & \mathbf{R}_2 & \dots & \mathbf{R}_N. & & & \end{array} \quad (2)$$

We will start with a constant geometry approach so that the i th component of any nuclear charge vector will be associated with a unique spatial vector \mathbf{R}_i . In this context, working with a fixed geometry means that we are constrained to the $E(\mathbf{Z})$ manifold defined by nuclear charges.

2.2. The polyhedron

Previous works have focused in certain convex subsets of \mathbb{Z}^N that allow to take advantage of the concavity properties of the potential energy function. This sets have been defined in different ways: Mezey used convex hulls and simplexes [4,6], while Daza and Villaveces considered geometrical simplexes and simplicial complexes [7,11]. In this work we will consider polyhedra in \mathbb{Z}^N , since they include the previous ideas within a simpler mathematical frame.

Definition 1. Given a set $\mathbb{S} \subset \mathbb{Z}^N$, $\mathbb{S} = \{\mathbf{Z}^1, \dots, \mathbf{Z}^p\}$, we define the polyhedron generated by \mathbb{S} as:

$$\mathbb{P}(\mathbb{S}) = \left\{ \mathbf{Z} : \mathbf{Z} = \sum_k^p \alpha_k \mathbf{Z}^k, \mathbf{Z}^k \in \mathbb{S}, \sum_k^p \alpha_k = 1, \alpha_k \geq 0 \right\}. \quad (3)$$

The vectors $\mathbf{Z}^k \in \mathbb{S}$ are the polyhedron vertices and p is the dimension of the polyhedron. In the following we will be involved in the search of relations between elements of this type of sets.

2.3. A first energy relation between isoelectronic molecules

Daza [7] showed that Born–Oppenheimer operator – whose expected value generates the potential energy function – of any element in a polyhedron in \mathbb{Z}^N

can be expressed in terms of its vertices as:

$$\hat{\mathcal{H}}_e(\mathbf{Z}) + \hat{\mathcal{V}}_{NN}(\mathbf{Z}) = \sum_k^p \alpha_k \left(\hat{\mathcal{H}}_e(\mathbf{Z}^k) + \hat{\mathcal{V}}_{NN}(\mathbf{Z}^k) \right) + \sum_{l>k}^p \sum_k^{p-1} \sum_{j>i}^m \sum_i^{m-1} \alpha_k \alpha_l \frac{(\mathbf{Z}_i^k - \mathbf{Z}_i^l)(\mathbf{Z}_j^l - \mathbf{Z}_j^k)}{R_{ij}}, \quad (4)$$

which may be abbreviated as:

$$\hat{\mathcal{H}}_e(\mathbf{Z}) + \hat{\mathcal{V}}_{NN}(\mathbf{Z}) = \sum_k^p \alpha_k \left(\hat{\mathcal{H}}_e(\mathbf{Z}^k) + \hat{\mathcal{V}}_{NN}(\mathbf{Z}^k) \right) + \frac{1}{2} \sum_k^p \sum_l^p \alpha_k \alpha_l (\mathbf{Z}^k - \mathbf{Z}^l) \mathbf{R}^{-1} (\mathbf{Z}^l - \mathbf{Z}^k)^T, \quad (5)$$

where

$$\mathbf{R}^{-1} \begin{pmatrix} 0 & R_{12}^{-1} & \dots & R_{1N}^{-1} \\ R_{12}^{-1} & 0 & \dots & R_{2N}^{-1} \\ \vdots & \vdots & \vdots & \vdots \\ R_{1N}^{-1} & R_{2N}^{-1} & \dots & 0 \end{pmatrix}. \quad (6)$$

Calculating the expectation value of the operator decomposed in such a way (5), for $\psi_{\mathbf{Z}}(\mathbf{r})$, yields:

$$E(\mathbf{Z}) = \sum_k^p \alpha_k \langle \psi_{\mathbf{Z}}(\mathbf{r}) | \hat{\mathcal{H}}_e(\mathbf{Z}^k) | \psi_{\mathbf{Z}}(\mathbf{r}) \rangle + \frac{1}{2} \sum_k^p \sum_l^p \alpha_k \alpha_l (\mathbf{Z}^k - \mathbf{Z}^l) \mathbf{R}^{-1} (\mathbf{Z}^l - \mathbf{Z}^k)^T. \quad (7)$$

Now we will substitute the function $\psi_{\mathbf{Z}}(\mathbf{r})$ by the eigen-functions $\psi_{\mathbf{Z}^k}(\mathbf{r})$ of the Hamiltonian of each vertex. Taking into account the variational theorem, we find the inequality:

$$E(\mathbf{Z}) \geq \sum_k^p \alpha_k E(\mathbf{Z}^k) + \underbrace{\frac{1}{2} \sum_k^p \sum_l^p \alpha_k \alpha_l (\mathbf{Z}^k - \mathbf{Z}^l) \mathbf{R}^{-1} (\mathbf{Z}^l - \mathbf{Z}^k)^T}_{\mathcal{Q}}. \quad (8)$$

This inequality brings on a relation between the energies of \mathbf{Z} and the \mathbf{Z}^k molecules. However, the second-order term \mathcal{Q} poses problems to compare molecular energies [6,7]. While it can be granted that \mathcal{Q} is positive definite, it can be removed without altering the inequality. Notwithstanding there is no nuclear geometry, independently of nuclear charges [6], such that $\mathcal{Q} \geq 0$.

Although, there are some sets of nuclear charge vectors that exhibit this property independently of the geometry, until now only few particular cases have been found [6,7,11].

On the other hand, it has been required that all molecules implied in the inequality are in the same nuclear configuration, so this result would be useful only when the equilibrium geometries of \mathbf{Z} and the \mathbf{Z}^k are close enough. Despite of its limitations, Stankevich has been able to use this results to explain the stability of $B - N$ substituted carbon nanotubes [8]. In the following sections, we will introduce some further developments which increase the scope of former works.

3. Subsets of \mathbb{Z}^N with $\mathcal{Q} \geq 0$

Inasmuch as \mathcal{Q} depends on vertices generating the polyhedron, the problem of defining a subset of \mathbb{Z}^N such that $\mathcal{Q} \geq 0$ can be solved choosing an appropriate set of vertices. In the following we will define a set with this property.

Definition 2. Be \mathbb{T} the set of permutations \mathcal{P} that can be decomposed in transpositions (i, j) without common terms. We define subsets $\mathbb{S}_a \subset \mathbb{Z}^N$ as those that satisfy:

$$\text{If } \mathbf{Z}^k \in \mathbb{S}_a \wedge \mathbf{Z}^l \in \mathbb{S}_a \Rightarrow \exists \mathcal{P} \in \mathbb{T} : \mathbf{Z}^k = \mathcal{P}\mathbf{Z}^l. \quad (9)$$

We will now show that any of these sets, i.e. those with elements fulfilling (9), makes \mathcal{Q} positive definite and let us establish a stronger energy relation between an element of the polyhedron $\mathbb{P}(\mathbb{S}_a)$ and its vertices.

Lemma 1. Given $\mathbb{S}_a = \{\mathbf{Z}^1, \dots, \mathbf{Z}^k, \dots, \mathbf{Z}^p\}$ and $\mathbf{Z} \in \mathbb{P}(\mathbb{S}_a)$, then

$$E(\mathbf{Z}) \geq \sum_{k=1}^p \alpha_k \mathbf{Z}^k. \quad (10)$$

Proof. Recall the general expression for \mathcal{Q} :

$$\mathcal{Q} = \frac{1}{2} \sum_k^p \sum_l^p \alpha_k \alpha_l (\mathbf{Z}^k - \mathbf{Z}^l) \mathbf{R}^{-1} (\mathbf{Z}^l - \mathbf{Z}^k)^T. \quad (11)$$

Since $\alpha_k \geq 0 \forall k$, if all the terms $(\mathbf{Z}^k - \mathbf{Z}^l) \mathbf{R}^{-1} (\mathbf{Z}^l - \mathbf{Z}^k)^T$ are greater or equal than zero, then their sum will be greater, or equal than zero. Consider one of such terms: expanding the inner products yields:

$$(\mathbf{Z}^k - \mathbf{Z}^l) \mathbf{R}^{-1} (\mathbf{Z}^l - \mathbf{Z}^k)^T = \sum_{j \neq i}^m \sum_{i=1}^m \frac{(Z_j^k - Z_j^l)(Z_i^l - Z_i^k)}{R_{ij}}. \quad (12)$$

If the condition stated in the lemma is fulfilled, the only non-zero terms in the sum will be those with indexes i, j corresponding to transposed components of the \mathbf{Z}^k vector. In such cases we will have $Z_j^l = Z_i^k$ and $Z_i^l = Z_j^k$, so:

$$\frac{(Z_j^k - Z_j^l)(Z_i^l - Z_i^k)}{R_{ij}} = \frac{(Z_j^k - Z_i^k)(Z_j^k - Z_i^k)}{R_{ij}} \geq 0. \quad (13)$$

Thus, the only non-zero terms in (11) are positive definite and we conclude:

$$\frac{1}{2} \sum_k^p \sum_l^p \alpha_k \alpha_l (\mathbf{Z}^k - \mathbf{Z}^l) \mathbf{R}^{-1} (\mathbf{Z}^l - \mathbf{Z}^k)^T \geq 0. \quad (14)$$

Then, for $\mathbf{Z} \in \mathbb{P}(\mathbb{S}_a)$ inequality (8) can be reduced to:

$$E_{\mathbf{R}}(\mathbf{Z}) \geq \sum_k^p \alpha_k E_{\mathbf{R}}(\mathbf{Z}^k). \quad (15)$$

□

Lemma 1 let us set a lineal relation between the molecular energy of any element in the polyhedron and those of its vertices.

Because of all elements of the set \mathbb{S}_a differ only by permutations of their components, for any $\mathbf{Z}^k \in \mathbb{S}_a$ we have:

$$\sum_{i=1}^N Z_i^k = m. \quad (16)$$

Thus, for any element in the polyhedron $\mathbb{P}(\mathbb{S}_a)$:

$$\sum_{i=1}^N Z_i = \sum_{i=1}^N \sum_{k=1}^p \alpha_k Z_i^k = \sum_{k=1}^p \alpha_k \sum_{i=1}^N Z_i^k = m. \quad (17)$$

In other words, nuclear charge vectors in the polyhedron so defined correspond to sets of isotropic molecules, i.e. molecules with the same total nuclear charge.

4. An energy relation for molecules in stable configurations

From lemma 1, we will derive a new inequality that relates energies of some pairs of isotropic–isoelectronic molecules, in their minimum energy configurations. For a set of proper vertices \mathbb{S}_a , we can assume, without losing generality, that $E(\mathbf{Z}^1) \leq E(\mathbf{Z}^i) \forall i$; i.e., we can choose the vertex with the lower energy, thus equation (15) is simplified to:

$$E_{\mathbf{R}}(\mathbf{Z}) \geq E_{\mathbf{R}}(\mathbf{Z}^1). \quad (18)$$

The subindex emphasizes that this results holds for any nuclear geometry as long as it is constant, i.e. it is the same for both terms of the inequality. As a particular case it holds for the minimum energy configuration of \mathbf{Z}, \mathbf{R}'

$$E_{\mathbf{R}'}(\mathbf{Z}) \geq E_{\mathbf{R}'}(\mathbf{Z}^1). \quad (19)$$

Now, if there exists a minimal energy configuration for \mathbf{Z}^1 , $\min_{\mathbf{R}} E_{\mathbf{R}}(\mathbf{Z}^1) = E_{\mathbf{R}'}(\mathbf{Z}^1)$, then necessarily $E_{\mathbf{R}'}(\mathbf{Z}^1) \geq E_{\mathbf{R}'}(\mathbf{Z}^1)$, so we have:

$$\min_{\mathbf{R}} E_{\mathbf{R}}(\mathbf{Z}) \geq \min_{\mathbf{R}} E_{\mathbf{R}}(\mathbf{Z}^1). \quad (20)$$

The vectors \mathbf{Z}^i differ only by transpositions of their components, thus they correspond to different points of the same potential energy hypersurface profile $E(\mathbf{R})$. Since the last inequality refers to the geometry corresponding to the absolute minimum of that hypersurface, we can replace \mathbf{Z}^1 by any \mathbf{Z}^i and the result still holds. Then, we conclude:

Theorem 1. Given $\mathbf{Z}^i \in \mathbb{S}_a$, and $\mathbf{Z} \in \mathbb{P}(\mathbb{S}_a)$, then

$$\min_{\mathbf{R}} E(\mathbf{Z}) \geq \min_{\mathbf{R}} E(\mathbf{Z}^i), \quad (21)$$

as long as both minima exist.

This theorem establishes a sufficient condition for the existence of an order relation between two isoprotonic molecules in their minimum energy configurations.¹

Given two molecules with nuclear charge vectors \mathbf{Z}^A and \mathbf{Z}^B , we want to know how their energies are related. Therefore, we must determine if: (a) $E(\mathbf{Z}^A) \geq E(\mathbf{Z}^B)$ or (b) $E(\mathbf{Z}^B) \geq E(\mathbf{Z}^A)$. To check (a) we act with the set of permutations \mathbb{T} over \mathbf{Z}^A , to generate the set $\mathbb{S}_A = \{\mathbf{Z}^{A1} \dots \mathbf{Z}^{Ap}\}$. According to theorem 1, if $\mathbf{Z}^B \in \mathbb{P}(\mathbb{S}_A)$ then $E(\mathbf{Z}^B) \geq E(\mathbf{Z}^A)$. This is true if and only if $\mathbf{Z}^B = \sum_i \alpha_i \mathbf{Z}^{Ai}$ (definition 1); that means, if the linear equations system

$$\begin{aligned} \sum_i \alpha_i Z_1^{Ai} &= Z_1^B \\ \sum_i \alpha_i Z_2^{Ai} &= Z_2^B \\ &\vdots \\ \sum_i \alpha_i Z_N^{Ai} &= Z_N^B \end{aligned} \quad (22)$$

¹From here on, we will write $E(\mathbf{Z}) \geq E(\mathbf{Z}^k)$ instead of $\min_{\mathbf{R}} E(\mathbf{Z}) \geq \min_{\mathbf{R}} E(\mathbf{Z}^k)$, and the minimal energy configuration restriction will be implicitly assumed.

is solved by a set of positive reals $\alpha_i \leq 1$. Conversely, to check the second inequality (b), we act with \mathbb{T} over \mathbf{Z}^B , generating the set $\mathbb{S}_B = \{\mathbf{Z}^{B^1} \dots \mathbf{Z}^{B^p}\}$. If the linear equations system

$$\begin{aligned} \sum_i \alpha_i Z_1^{Bi} &= Z_1^A \\ \sum_i \alpha_i Z_2^{Bi} &= Z_2^A \\ &\vdots \\ \sum_i \alpha_i Z_N^{Bi} &= Z_N^A \end{aligned} \tag{23}$$

is solved by a set of real numbers $0 \leq \alpha \leq 1$ then $E(\mathbf{Z}^A) \geq E(\mathbf{Z}^B)$.

In other words, the existence of solutions bounded between zero and one, for any of these two linear equations systems, establishes a sufficient condition for the existence of an order relation between the energies of molecules in their equilibrium geometries. Now, we will show some examples that illustrate the capabilities of this result.

4.1. Higher bounds for sets of isoprotonic molecules

In previous works has been suggested that homonuclear systems may constitute higher bounds for energies of isoprotonic molecules; although this has been proved only for diatomic and triatomic molecules in one particular – and not always chemically meaningful – nuclear geometry [7,11]. The theorem 1 allows us to extend this result to polyatomic molecules in minimum energy configurations.

Corollary 1. The energy of any set of n-atomic isoprotonic-isoelectronic molecules in their minimum energy configurations is bounded from above by the energy of the corresponding homonuclear system.

Proof. Let \mathbf{Z}^1 be an arbitrary nuclear charge vector:

$$\mathbf{Z}^1 = (Z_1, \dots, Z_m), \tag{24}$$

where $\sum_{i=1}^m Z_i^1 = NyZ_i \neq 0 \forall i$. We want to prove that its energy is less or equal than the energy of the homonuclear system, $(\frac{N}{m}, \dots, \frac{N}{m})$. To prove this we will use mathematical induction. First, we permute the first two components of \mathbf{Z}^1 , generating the vector:

$$\mathbf{Z}^2 = (Z_2, Z_1, Z_3, \dots, Z_m).$$

According to theorem 1, for $\mathbf{Z}^a = \frac{1}{2}\mathbf{Z}^1 + \frac{1}{2}\mathbf{Z}^2$ we have the inequality:

$$E(\mathbf{Z}^a) \geq E(\mathbf{Z}^1),$$

$$E\left(\frac{Z_1 + Z_2}{2}, \frac{Z_1 + Z_2}{2}, Z_3, \dots, Z_m\right) \geq E(Z_1, Z_2, \dots, Z_m), \quad (25)$$

This inequality defines a higher bound for the original vector. Now we permute the third component of \mathbf{Z}^a with its first and second components, to obtain a new set of vectors

$$\begin{aligned} \mathbf{Z}^a &= \left(\frac{Z_1 + Z_2}{2}, \frac{Z_1 + Z_2}{2}, Z_3, \dots, Z_m\right), \\ \mathbf{Z}^b &= \left(Z_3, \frac{Z_1 + Z_2}{2}, \frac{Z_1 + Z_2}{2}, Z_4, \dots, Z_m\right), \\ \mathbf{Z}^c &= \left(\frac{Z_1 + Z_2}{2}, Z_3, \frac{Z_1 + Z_2}{2}, Z_4, \dots, Z_m\right). \end{aligned} \quad (26)$$

With these vectors acting as vertices, we construct a new vector: $\mathbf{Z}^y = \frac{1}{3}\mathbf{Z}^a + \frac{1}{3}\mathbf{Z}^b + \frac{1}{3}\mathbf{Z}^c$. From theorem 1 we obtain $E(\mathbf{Z}^y) \geq E(\mathbf{Z}^a)$ and taking into account inequality (25) we get:

$$E(\mathbf{Z}^y) \geq E(\mathbf{Z}^1),$$

$$\begin{aligned} E\left(\frac{Z_1 + Z_2 + Z_3}{3}, \frac{Z_1 + Z_2 + Z_3}{3}, \frac{Z_1 + Z_2 + Z_3}{3}, Z_4, \dots, Z_m\right) \\ \geq E(Z_1, Z_2, \dots, Z_m). \end{aligned} \quad (27)$$

We can repeat this procedure with the vector \mathbf{Z}^y ; successive steps will converge into the homonuclear system. Let us suppose that we have proved:

$$E\left(\sum_{i=1}^n \frac{Z_i}{n}, \dots, \sum_{i=1}^n \frac{Z_i}{n}, Z_{n+1}, \dots, Z_m\right) \geq E(Z_1, Z_2, \dots, Z_m). \quad (28)$$

So, we permute the $(n + 1)$ th component of the vector at left with each of its first n components to get the vector set:

$$\begin{aligned} \mathbf{Z}^k &= \left(\sum_{i=1}^n \frac{Z_i}{n}, \dots, \sum_{i=1}^n \frac{Z_i}{n}, Z_{n+1}, \dots, Z_m \right), \\ \mathbf{Z}^1 &= \left(Z_{n+1}, \sum_{i=1}^n \frac{Z_i}{n}, \dots, \sum_{i=1}^n \frac{Z_i}{n}, Z_{n+2}, \dots, Z_m \right), \\ \mathbf{Z}^m &= \left(\sum_{i=1}^n \frac{Z_i}{n}, Z_{n+1}, \sum_{i=1}^n \frac{Z_i}{n}, \dots, \sum_{i=1}^n \frac{Z_i}{n}, Z_{n+2}, \dots, Z_m \right), \\ &\vdots \end{aligned}$$

For $\mathbf{Z}^f = \frac{1}{n+1}\mathbf{Z}^k + \frac{1}{n+1}\mathbf{Z}^1 + \dots$, theorem 1 and inequality (28) yield:

$$E \left(\sum_{i=1}^{n+1} \frac{Z_i}{n+1}, \dots, \sum_{i=1}^{n+1} \frac{Z_i}{n+1}, Z_{n+2}, \dots, Z_m \right) \geq E(Z_1, Z_2, \dots, Z_m). \quad (29)$$

Comparing this inequality with (28) we conclude:

$$E \left(\sum_{i=1}^m \frac{Z_i}{m}, \dots, \sum_{i=1}^m \frac{Z_i}{m} \right) = E \left(\frac{N}{m}, \dots, \frac{N}{m} \right) \geq E(Z_1, \dots, Z_m), \quad (30)$$

which proves the corollary.

In this way we have generalized our previous results showing the capabilities of theorem 1. In the same sense this theorem may be used to order the energies of these homonuclear systems:

Corollary 2. The energy of any homonuclear isoprotonic–isoelectronic molecule in its minimum energy configuration increases with the number of nuclei.

Proof. Let us consider the following set of vectors:

$$\begin{aligned} \mathbf{Z}^1 &= \left(\overbrace{\frac{N}{l}, \dots, \frac{N}{l}}^{l \text{ times}}, 0, \dots, 0 \right), \\ \mathbf{Z}^2 &= \left(\overbrace{\frac{N}{l}, \dots, \frac{N}{l}}^{l-1 \text{ times}}, 0, \frac{N}{l}, 0, \dots, 0 \right), \end{aligned}$$

$$\mathbf{Z}^p = \left(0, \overbrace{\left(\frac{N}{l}, \dots, \frac{N}{l} \right)}^{l \text{ times}}, 0, \dots, 0 \right).$$

Note that all those vectors have the same number of components, as they were build by permuting the first null component with each one of the non-null components of the first vector. By construction this vectors correspond to different nuclear configurations of an arbitrary homonuclear system. Now, considering the element $\mathbf{Z}^a = \sum_{k=1}^p \frac{1}{l+1} \mathbf{Z}^k$ in the polyhedron generated by those vectors, theorem 1 yields:

$$E(\mathbf{Z}^a) \geq E(\mathbf{Z}^1)$$

$$E \left(\overbrace{\left(\frac{N}{l+1}, \dots, \frac{N}{l+1} \right)}^{l+1 \text{ times}}, 0, \dots, 0 \right) \geq E \left(\overbrace{\left(\frac{N}{l}, \dots, \frac{N}{l} \right)}^{l \text{ times}}, 0, \dots, 0 \right). \quad (31)$$

Note that vector at left is an homonuclear system isoprotonic–isoelectronic to vector at right and that the first one has one more nucleus; therefore, since l is arbitrary, the corollary is immediately proven. \square

4.2. Functional groups and their energies

Let us consider the following nuclear charge vectors sharing the last q components:

$$\begin{aligned} \mathbf{Z}^A &= (Z_1^a, \dots, Z_p^a, Z_1^c, \dots, Z_q^c) = \mathbf{Z}^a \oplus \mathbf{Z}^c, \\ \mathbf{Z}^B &= (Z_1^b, \dots, Z_p^b, Z_1^c, \dots, Z_q^c) = \mathbf{Z}^b \oplus \mathbf{Z}^c. \end{aligned} \quad (32)$$

Theorem 1 states that $E(\mathbf{Z}^B) \geq E(\mathbf{Z}^A)$ if the linear equations system

$$\begin{aligned} \sum_i \alpha_i Z_1^{ai} &= Z_1^b \\ &\vdots \\ \sum_i \alpha_i Z_p^{ai} &= Z_p^b \\ \sum_i \alpha_i Z_1^c &= Z_1^c \\ &\vdots \\ \sum_i \alpha_i Z_q^c &= Z_q^c \end{aligned} \quad (33)$$

is solved by a set of real numbers $\{0 \leq \alpha_i \leq 1\}$. Equations corresponding to the common components Z_j^c are solved by any set of positive real numbers whose sum is equal to one. For the sets we are considering, i.e. polyhedra in \mathbb{Z}^N , this is always the case; thus, the condition for $E(\mathbf{Z}^B) \geq E(\mathbf{Z}^A)$ is determined by the first p equations of the system. Since those are the equations that determine the energy relation $E(\mathbf{Z}^a) \geq E(\mathbf{Z}^b)$, we conclude:

Corollary 3. If $E(\mathbf{Z}^a) \geq E(\mathbf{Z}^b)$ then $E(\mathbf{Z}^a \oplus \mathbf{Z}^c) \geq E(\mathbf{Z}^b \oplus \mathbf{Z}^c)$, $\forall \mathbf{Z}^c \in \mathbb{Z}^N$.

This is a quite interesting result, as it resembles the functional group concept, i.e. the idea of a transferable molecular fragment with some invariable properties associated; in this case, an energetic property.

This resemblance appears clearly in the following example: it is easily verified, by means of theorem 1, that:

$$E(CH_3) \geq E(NH_2) \geq E(OH) \geq E(F). \quad (34)$$

Corollary 3 states that one can paste a vector \mathbf{Z}^c to each one of the charge vectors above without altering the inequalities. Such vector \mathbf{Z}^c corresponds to a common molecular fragment R , so we have:

$$E(R - CH_3) \geq E(R - NH_2) \geq E(R - OH) \geq E(R - F). \quad (35)$$

In an isoprotonic–isoelectronic series, the energy of the hydrocarbon is greater than the that of the amine, the energy of the amine is greater-than the energy of the alcohol, which is greater than the energy of the halide. When there exist isomers of any of this molecules, the ordering holds for the less energetic isomer as were required by the theorem. We have not specified the number of electrons, as it is constant but arbitrary.² Thus, the energetic order we have found holds for neutral, cationic and anionic species, e.g.:

$$\begin{aligned} E(\varphi - CH_3) &\geq E(\varphi - NH_2) \geq E(\varphi - OH) \geq E(\varphi - F), \\ E(CH_4) &\geq E(NH_3) \geq E(H_2O) \geq E(HF), \\ E(CH_3^-) &\geq E(NH_2^-) \geq E(OH^-) \geq E(F^-), \\ E(CH_4^+) &\geq E(NH_4^+) \geq E(H_3O^+) \geq E(H_2F^+). \end{aligned}$$

More relevant cases of this type of relations can be found, e.g. the results found by Stankevich [8] concerning the stability of $B - N$ substituted carbon nanotubes are just a particular case of theorem 1–corollary 3, since the substituted pair $C - C$ can be as: $(6, 6) = \frac{1}{2}(7, 5) + \frac{1}{2}(5, 7)$.

²Isoelectronic character of equation (4) was discussed in [7]. The number of electrons is held constant and it is not related to the nuclear charge or spatial variables, so it remains arbitrary.

Taking into account theorem 1 we have:

$$E(B - N) \leq E(C - C), \quad (36)$$

Even more, corollary 3 states that the former inequality implies:

$$E(R - B - N) \leq E(R - C - C). \quad (37)$$

If we take $R = C_n$ we conclude that substituting a $C - C$ group by a $B - N$ group in a carbon structure, as a nanotube, causes a decrease in the energy of the molecular system. As stated before this is just one particular case, as (37) states that any substitution of a $C - C$ group by a $B - N$ group in any bounded molecular system causes a decrease in its energy.

There is a difference between our result and those found by Stankevich. Here we are considering molecules in minimum energy configurations, so we do not have to assume that the substitution happens in a “isostructural” way, i.e. with minimal changes in nuclear geometry. This is important because a constant geometry approximation is very reasonable in the context considered by Stankevich, but if the number of substituted groups increases the approximation will be greater. Therefore, the flexibility afforded by allowing configurational changes achieved in this work can not be overlooked. As stated by our theorem, Stankevich’s results are fortunately held anyway.

5. Molecular POSETs

Let us review the methodology we have followed to determine order relations for molecular energies. Given two isoprotonic–isoelectronic molecules with nuclear charge vectors \mathbf{Z}^A and \mathbf{Z}^B , by acting with the group of permutations \mathbb{T} we generate two sets of vectors, $\{\mathbf{Z}^{Ai}\}$ and $\{\mathbf{Z}^{Bi}\}$. Then, we solve the linear equations systems (22) and (23). If the solutions of (22) are all positive, we conclude $E(\mathbf{Z}^B) \geq E(\mathbf{Z}^A)$; conversely, if the solutions of (23) are positive, we conclude $E(\mathbf{Z}^A) \geq E(\mathbf{Z}^B)$.

But it is possible that neither (22) nor (23) have positive solutions; in such a case, we can not reach any conclusion. As we are not always able to determine all the energy order relations existing among the elements of a given set of isoprotonic molecules, it would be laudable to design a proper representation that let us see all the known relations within a molecular set.

From a mathematical perspective, the structure we are facing is a Partially Ordered Set (POSET). A POSET is a set endowed with a binary relation \geq that fulfills [13]:

- (i) $a \geq a \forall a$, Reflexive,
- (ii) $a \geq b \wedge b \geq a \Rightarrow a = b$, Antisymmetric,

(iii) $a \geq b \wedge b \geq c \Rightarrow a \geq c$, Transitive.

It should be noted that it is not required that, for each pair of elements a and b in the POSET, either $a \geq b$ or $b \geq a$

The POSETs are commonly represented by Hasse diagrams in which every element of the set is represented by a different point. The existence of an order relation $a \geq b$ is represented by a line ascending from b to a . Nevertheless, if a point c appears above a point d , it does not necessarily mean that $c \geq d$. In fact, c and d are not related unless there is a sequence of lines (a path) ascending from one point to the other.

Let us consider a complete set of isoelectronic molecules with total nuclear charge 10, \mathcal{Z}^{10} (figure 1). We determined all the energy order relations between elements of this set that can be derived from theorem 1 and put them into the corresponding Hasse diagram. There is a total of 1722 possible order relations, two for each molecular pair. Apparently, it means that the corresponding 1722 linear equations systems should be solved. However, by a progressive construction of Hasse diagram, it is easily seen that most of this relations are associated by transitivity, so that by solving about 50 systems – most of which can be solved by simple inspection – one can gather all the information available.

This diagram is completely connected, besides there is a general lower bound (the null element) corresponding to the united atom and a general upper bound (the universal element) corresponding to the hydrogen cluster. A POSET with these characteristics has an interesting property which ensures that given any subset, it is always possible to find a greater lower bound and a lower upper bound for all the elements in the subset [13]. In this way, we are now able to determine narrower bounds within sets of isoprotonic–isoelectronic molecules than those previously known.

From the inspection of Hasse diagram it can be noted that the greater lower bound for each subset of molecular systems having the same number of nuclei are – at least for the subsets of systems with five or less nuclei – those molecules well known by its abundance in nature.

6. Final remarks

Summarizing, starting from a decomposition of the BO Hamiltonian, we have defined particular sets of molecules (polyhedra), having the property of being both isoprotonic and isoelectronic. Afterwards, we have shown how to find particular sets of vertices such that the energy of any element of the polyhedron is related to the energies of these vertices by a linear inequality (lemma 1). From this simplified relation, we have derived an inequality that allows us to compare energies of any pair of bounded isoprotonic–isoelectronic molecules in nuclear configurations of minimal energy (theorem 1). From this result, we derived some

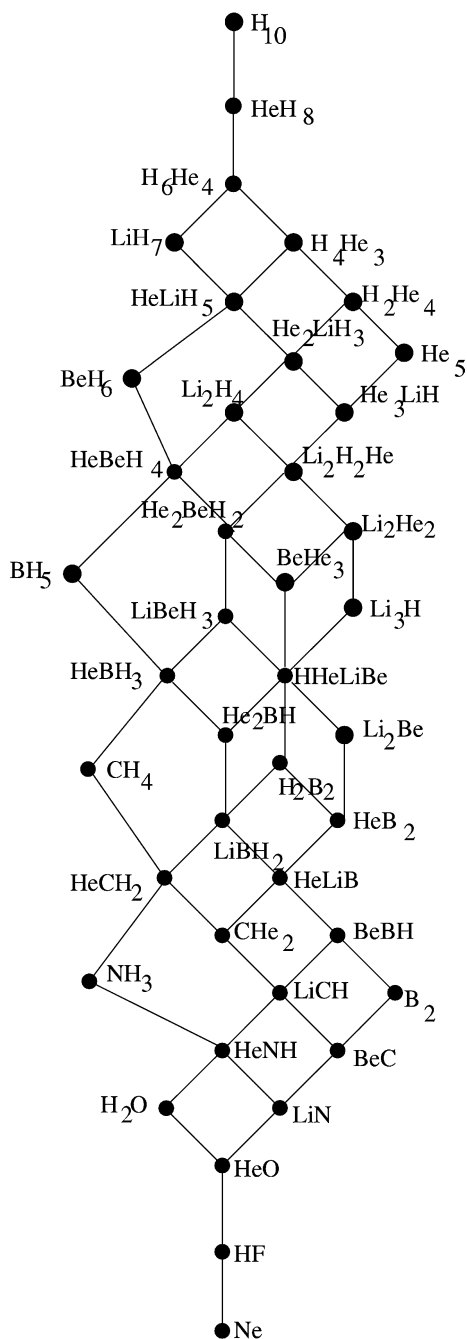


Figure 1. Elements of the POSET \mathcal{Z}^{10} . This Hasse diagram shows how molecular energies are ordered, the lowest energy corresponds to the atom of neon and the highest to the hydrogen cluster.

bounds for the energies of elements in the polyhedron; in particular, we have shown that the polyhedron is bounded from above by the energy of the corresponding homonuclear system (corollary 1) and that the energy of homonuclear systems in the polyhedron increases with the number of nuclei (corollary 2). We also found that energy relations derived from (theorem 1) can be extended to new molecules by the addition of any fixed group of atoms to every element in the polyhedron (corollary 3). At the end we discussed the POSET structure endowed to sets of isoprotonic–isoelectronic molecules by all this energy order relations.

We want to emphasize that results presented here are due to algebraic properties of the Born Oppenheimer Hamiltonian, instead of the behavior of the electronic wave function or electron density of each molecular system. Actually we have not evaluated any wave function to derive the energetic inequalities we have proposed. When we compared families of Born–Oppenheimer operators we considered nuclear charges as variables and from this approach it has been possible to show how operators of different molecular systems may be related. From this considerations, an strong condition to generate sets of molecules whose energies can be compared has been stated.

This alternative approach, in which emphasis has been done on nuclear charges as variables, let us manage sets of molecules instead of individual systems. The fundamental idea behind this proposal is that, in order to grasp a better concept of chemical structure it is necessary to study sets of molecules, instead of focusing in one molecule at time. The structure of the POSET of isoprotonic–isoelectronic molecules, as well as the invariability of energy order relations including constant atomic groups – suggesting the functional group idea – show that in fact this broader perspective is giving us additional insight into the concept of chemical structure. We hope that this ideas can be extended to cover other properties and help to formalize a concept whose usual definitions are elusive and that recently has been recognized to be a diffuse concept [14,15].

References

- [1] E.B. Wilson, *J. Chem. Phys.* 36 (1962) 2232.
- [2] P. Politzer and R.G. Parr, *J. Chem. Phys.* 61 (1974) 4258.
- [3] P. Politzer, *J. Chem. Phys.* 64 (1976) 4239.
- [4] P.G. Mezey, *Theor. Chim. Acta* 59 (1981) 321.
- [5] P.G. Mezey, *Int. J. Quant. Chem. Quant. Chem. Symp.* 15 (1981) 279.
- [6] P.G. Mezey, *J. Am. Chem. Soc.* 107 (1985) 3100.
- [7] E.E. Daza and J.L. Villaveces, *J. Chem. Inf. Comp. Sci.* 34 (1994) 309.
- [8] I.V. Stankevich and R. Seto, *Phys. Solid State* 43 (2001) 1995.
- [9] I.V. Stankevich, E.G. Gal'pern and R. Seto, *Russian J. Phys. Chem.* 77 (2003) 768.
- [10] P.G. Mezey, *Int. J. Quant. Chem.* 22 (1982) 101.
- [11] E.E. Daza, Un concepto más flexible de estructura química basado en las variables espaciales y de carga asociadas con los núcleos, Doctoral Thesis, Universidad Nacional de Colombia, Bogotá (2000).

- [12] R. Carbó-Dorca, *J. Molec. Struct. (Theochem)* 451 (1998) 11.
- [13] D.E. Rutherford, *Introduction to lattice theory* (Oliver & Boyd, Edinburg, 1966).
- [14] E.E. Daza and J.L. Villaveces, in: *Concepts in Chemistry*, ed. D.H. Rouvray (Wiley, Newyork 1997) pp. 101–129.
- [15] P.G. Mezey, *Shape in Chemistry: An Introduction to Molecular Shape and Topology* (VCH, 1993).