Upper and Lower Bonds for Molecular Energies

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We have revisited the molecular Hamiltonian to emphasize its nuclear charge dependence. We have studied the variations in Ψ due to changes in these charges, and we have related them variationally to isoelectronic isoprotonic molecular systems in the nuclear charge space, through simplicial complexes. We built a general way of comparing B–O energies for these kind of molecules, and we are able to generate an order between them. Up to the case of $Z = 3$, we have shown that the energy of the united atom of nuclear charge $z = N$ and that corresponding to a cluster of N hydrogen atoms play the role of upper and lower bounds for the energy of any molecular system between them.

1. INTRODUCTION

The usual treatment of wave functions and molecular Hamiltonians of supermolecules considers them to be dependent only on the nuclear and electronic spatial–spin coordinates. Some authors have made efforts to consider nuclear charges explicitly as another variable.[1-6] We believe that a complete study of chemical structure should make explicit the dependence of the wave function and its Hamiltonian on nuclear charges.

For the spinless, nonrelativistic Hamiltonian we have to consider, as carrier space, the product space whose factors are the space of nuclear and electronic spatial coordinates, $^{3N}R \times {}^{3m}r$, and the nuclear charge space ^{N}Z.

$$\Theta = {}^{N}Z \times {}^{3N}R \times {}^{3m}r \qquad (1)$$

Generally, ^{N}Z is treated apart from $^{3N}R \times {}^{3m}r$, which is justified if one realizes that, in the differential operators of the Hamiltonian, derivatives are taken with respect to electronic and nuclear spatial coordinates but not with respect to nuclear charges.

In the framework of the Born–Oppenheimer approximation, that separates ^{3N}R and ^{3m}r, it is usual to define an "electronic Hamiltonian"

$$\mathcal{H}_e = -\frac{1}{2}\sum_{u=1}^{m}\nabla_i{}^2 - \sum_{u=1}^{m}\sum_{i=1}^{N}\frac{z_i}{|r_u - R_i|} + \sum_{u=1}^{m}\sum_{v>u}^{m}\frac{1}{|r_u - r_v|} \qquad (2)$$

whose lowest expectation value

$$E_e: \; {}^{N}Z \times {}^{3N}R \to {}^{1}R \qquad (3)$$

gives rise to the "potential energy function":

$$E(z,R) = E_e + V_{NN}$$

$$E(z,R): \; Z^N \times R^{3N} \to R^1 \qquad (4)$$

where V_{NN} is the energy of internuclear repulsion

$$V_{NN} = \left\langle \sum_{i=1}^{J}\sum_{j<i}^{N}\frac{Z_iZ_j}{|R_i - R_j|} \right\rangle \qquad (5)$$

and to the "potential energy hypersurface"

$$\mathcal{E} \subset {}^{N}Z \times {}^{3N}R \times {}^{1}R \qquad (6)$$

In spite of the fact that $z \in {}^{N}Z$ is usually taken as a fixed parameter, we shall try to make explicit that dependence to find some relationships between the energies of isoelectronic systems.[7]

2. NUCLEAR CHARGE SPACE ^{N}Z

We may consider, following the ideas proposed by Mezey,[4-6] a formal vector space ^{N}Z of N-dimensional vectors z with the component z_i defined as the nuclear charge of the ith nucleus 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. (For previous studies on the abstract nuclear charge space, see, for instance, refs 5 and 6 and others quoted therein.)

$$^{N}Z = \{z, z: \; z_i \text{ is the nuclear charge of the } i\text{th nucleus}\} \qquad (7)$$

The points in ^{N}Z can be "added" and "multiplied by a scalar" according to the usual definitions:

$$z^{(k)} = (z_1^{(k)}, z_2^{(k)}, ..., z_N^{(k)}) \quad \text{and} \quad z^{(l)} = (z_1^{(l)}, z_2^{(l)}, ..., z_N^{(l)})$$

$$z^{(k)} \text{ and } z^{(l)} \in {}^{N}Z$$

$$z^{(k)} + z^{(l)} = (z_1^{(k)} + z_1^{(l)}, z_2^{(k)} + z_2^{(l)}, ..., z_N^{(k)} + z_N^{(l)})$$

$$\alpha z^{(k)} = (\alpha z_1^{(k)}, \alpha z_2^{(k)}, ..., \alpha z_N^{(k)}) \qquad (8)$$

We will be constrained to vectors with norm $|z|$ given by

$$|z| = \sum z = N \qquad (9)$$

that is, we will work in a subset defined in the positive orthant of an Euclidean space, whose elements are isoelectronic-isoprotonic molecular systems, if m is constant. Evidently, any molecule must be represented by a vector belonging to a subset of ^{N}Z, of suitable dimension N.

3. UNDERLYING SPACE OF ISOELECTRONIC–ISOPROTONIC MOLECULES IN Z

In order to formalize the condition on the norm given by expression 9 and to obtain some scheme to organize those systems, we shall use some early definitions of algebraic topology.[9-11]

Definition 1: A set of points $\{z^{(0)}, z^{(1)}, ..., z^{(n)}\}$, $z^{(k)} \in {}^N Z$, is in *general position* if the set of vectors

$$\{z^{(1)} - z^{(0)}, z^{(2)} - z^{(0)}, ..., z^{(n)} - z^{(0)}\}$$

is linearly independent.

Therefore, any two distinct points are in general position. Three distinct points are in general position if and only if they are the vertices of a triangle. Four points in general position must be the vertices of a tetrahedron and so forth.

Definition 2: A set $\mathbf{M} \subset {}^N Z$ is called *convex* if $z^{(k)}, z^{(l)} \in \mathbf{M}$ and $0 \leq \alpha \leq 1$ imply that $\alpha z^{(k)} + (1 - \alpha)z^{(l)} \in \mathbf{M}$.

Definition 3: Given a set of points $\{z^{(0)}, z^{(1)}, ..., z^{(p)}\}$, a subset of ${}^N Z$, in general position, the set

$$S_p = \{z: z = \sum_{k=0}^{p} \alpha_k z^{(k)}, \sum_{k=0}^{p} \alpha_k = 1, \alpha_k > 0, k = 0, 1, ..., p\}$$

is the *geometric simplex* spanned by the points $z^{(0)}, z^{(1)}, ..., z^{(p)}$. These points are the *vertices* of S_p. The number p is the *algebraic dimension* of the simplex S_p.

Since we are interested in molecular systems with norm equal to N, we may use as vertices the points corresponding to an atom of nuclear charge $z = N$ located on every one of the N-coordinate axes. Hence, any simplex S_p, $p \leq N$, allows us to build a family of molecules fulfilling the condition of isoprotonicity (9).

The collection of all isoprotonic molecules will be given by the union of the families defined by the S_p simplexes.

Definition 4: A *complex* K is a finite collection of geometric simplexes in ${}^N Z$ subject to the following conditions:

if $S_p \in K$ and S_q is a face of S_p, then $S_q \in K$

if $S_p \neq S_q$, then $S_p \cap S_q = \varnothing$

The *polyhedron* $|K|$ of a complex K is the union of its simplexes. The complex K is called a *triangulation* of the polyhedron $|K|$, so that the whole family of isoprotonic molecules will be associated with a complex K.

As stated before, we are interested in the properties of the Born–Oppenheimer energy in the nuclear charge space under consideration. Therefore, we need a concept more general than that of a geometric complex.

Definition 5: Given a geometric complex K in ${}^N Z$ and homeomorphism, e.g. the potential energy function $E(z)$,

$$E: {}^N Z \rightarrow \mathscr{E}$$

where $\mathscr{E}$ is a topological space. The collection of images of the simplexes of K forms a *simplicial complex*.

All concepts that were introduced in definition 4 for a geometric complex have analogous definitions for a simplicial complex. Thus the polyhedron will be the underlying space of a simplicial complex.

Now, if we fix the total number of negative charges, we will have the means to explore the energy hypersurfaces of the elements of a family of isoelectronic–isoprotonic molecular systems.

4. RELATIONSHIPS BETWEEN ELEMENTS IN THE COMPLEX K

We shall consider first isoelectronic–isoprotonic molecular systems with a fixed nuclear geometry $\mathbf{R} = (R_1, R_2, ..., R_N)$ and make the z_i dependence explicit, denoting the energy simply by $E(z)$. We will state a relationship between the

Born–Oppenheimer energy of any point in a simplex S_p and that of its generatrices by means of a decomposition of the molecular Hamiltonian and the variational principle.[11]

4.1. Simplex S_1. The Edge. Given two points $z^{(k)}$ and $z^{(l)} \in {}^N Z$ satisfying condition 9, the points in the simplex expanded by them will be $z = \alpha_k z^{(k)} + \alpha_l z^{(l)}$, with $\alpha_k + \alpha_l = 1$ and $0 < \alpha_k, \alpha_l < 1$, so that its molecular Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\sum_{i=1}^{m}\nabla_i^2 + \sum_{v>l}^{m}\sum_{u=1}^{m}\frac{1}{r_{uv}} -$$

$$\sum_{u=1}^{m}\sum_{i=1}^{N}\frac{z_i}{|R_i - r_u|} + \sum_{j>i}^{N}\sum_{i=1}^{N}\frac{z_i z_j}{|R_i - R_j|}$$

$$\mathcal{H} = K_e + V_e - \sum_{u}^{m}\sum_{i}^{N}\frac{z_i}{|R_i - r_u|} + \sum_{j>i}^{N}\sum_{i}^{N}\frac{z_i z_j}{R_{ij}} \quad (10)$$

can be decomposed in the following way

$$\mathcal{H} = K_e + V_e - \sum_{u}^{m}\sum_{i}^{N}\frac{\alpha_k z_i^{(k)} + \alpha_l z_i^{(l)}}{|R_i - r_u|} +$$

$$\sum_{j>i}^{w}\sum_{i}^{w}\frac{(\alpha_k z_i^{(k)} + \alpha_l z_i^{(l)})(\alpha_k z_j^{(k)} + \alpha_l z_j^{(l)})}{R_{ij}} \quad (11)$$

$$\mathcal{H} = \alpha_k\left(K_e + V_e - \sum_{u}^{m}\sum_{i}^{N}\frac{z_i^{(k)}}{|R_i - r_u|} + \sum_{j>i}^{N}\sum_{i}^{N}\frac{z_i^{(k)}z_j^{(k)}}{R_{ij}}\right) +$$

$$\alpha_l\left(K_e + V_e - \sum_{u}^{m}\sum_{i}^{N}\frac{z_i^{(l)}}{|R_i - r_u|} + \sum_{j>i}^{N}\sum_{i}^{N}\frac{z_i^{(l)}z_j^{(l)}}{R_{ij}}\right) +$$

$$\alpha_k\alpha_l\left(\sum_{j>i}^{N}\sum_{i}^{N}\frac{(z_i^{(k)} - z_i^{(l)})(z_j^{(l)} - z_j^{(k)})}{R_{ij}}\right) \quad (12)$$

and its corresponding energy can be written as

$$E(z) = \alpha_k\langle\Psi|\mathcal{H}(z^{(k)})|\Psi\rangle + \alpha_l\langle\Psi|\mathcal{H}(z^{(l)})|\Psi\rangle +$$

$$\alpha_k\alpha_l\left\langle\Psi\left|\sum_{j>i}^{N}\sum_{i}^{N}\frac{(z_i^{(k)} - z_i^{(l)})(z_j^{(l)} - z_j^{(k)})}{R_{ij}}\right|\Psi\right\rangle \quad (13)$$

where Ψ is the normalized wave function for the z problem.

Ψ can be used as a trial function for both $z^{(k)}$ and $z^{(l)}$ molecular systems. Consequently, invoking the variational principle we obtain

$$E(z) \geq \alpha_k\langle\Psi^{(k)}|\mathcal{H}(z^{(k)})|\Psi^{(k)}\rangle + \alpha_l\langle\Psi^{(l)}|\mathcal{H}(z^{(l)})|\Psi^{(l)}\rangle +$$

$$\alpha_k\alpha_l\sum_{j>i}^{N}\sum_{i}^{N}\frac{(z_i^{(k)} - z_i^{(l)})(z_j^{(l)} - z_j^{(k)})}{R_{ij}} \quad (14)$$

$$E(z) \geq \alpha_k E(z^{(k)}) + \alpha_l E(z^{(l)}) +$$

$$\alpha_k\alpha_l\sum_{j>i}^{N}\sum_{i}^{N}\frac{(z_i^{(k)} - z_i^{(l)})(z_j^{(l)} - z_j^{(k)})}{R_{ij}} \quad (15)$$

It is important to point out that this inequality is independent of the choice of the geometry because it considers the internuclear repulsion term. Note that this inequality is analogous to the one developed earlier by Mezey for the electronic energy,[6,12] when the third term is positive.

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The last expression gives the possibility of achieving insight about the energy of any molecular system simply knowing the energy of its possible generatrices. They can be chosen in a proper way to simplify the corresponding calculations, e.g. hydrogen clusters or single atoms bonded to dummy atoms. Some particular examples will be studied below.

4.2. Simplex S_p. Inequality 15 can be extended to a p-dimensional simplex following a similar procedure but considering more than two points to expand it. In such a case the inequality takes the form

$$E(z) \geq \sum_{k=0}^{p} \alpha_k E(z^{(k)}) +$$
$$\sum_{l>k}^{p} \sum_{k}^{p} \sum_{j>i}^{N} \sum_{i}^{N} \alpha_k \alpha_l \frac{(z_i^{(k)} - z_i^{(l)})(z_j^{(l)} - z_j^{(k)})}{R_{ij}} \quad (16)$$

As p may be as large as we want, we can cover all the complex K to set relationships between the energy of different elements of the family of isoelectronic–isoprotonic molecular systems and explore the topology of the simplicial complex. That is, we may build molecules from a set of suitable vertices knowing how its energies are related without making any calculation.

An analogous expression for the third term of inequalities 15 and 16 was found by Mezey considering only the internuclear repulsion contribution to the total energy.[13]

5. UPPER AND LOWER BOUNDS FROM ONE-DIMENSIONAL SIMPLEXES S_1

5.1. Two-Dimensional Nuclear Charge Space, ^2Z. In the following, we shall show some of the capabilities of these simple expressions, starting from the simplest case $N = m = 2$, i.e., studying the two-dimensional nuclear charge space ^2Z. The energy of any diatomic molecule in the simplex expanded by two helium atoms, $z^{(1)} = (2,0)$ and $z^{(2)} = (0,2)$, is related to those of the atoms by

$$E(z) \geq \alpha_1 E(z^{(1)}) + \alpha_2 E(z^{(2)}) + \frac{4\alpha_1\alpha_2}{R_{12}} \quad (17)$$

Since the energy is independent of the position of a single nuclear charge in the ordinary three-dimensional space, it follows that $E(z^{(1)}) = E(z^{(2)})$. Taking into account that the third term is always positive, we obtain

$$E(z) > E(He) \quad (18)$$

Coming back to relationship 17, we may search for critical points of the energy, defined on the nuclear charge space, to find that there is a maximum for the right side of this inequality when $\alpha_1 = \alpha_2 = \frac{1}{2}$, that is, when we have the hydrogen molecule, H_2. Then,

$$E(H_2) > E(He) \quad (19)$$

and we have a proof of the theorem of the united atom[3] for this particular case.

These inequalities imply that the energy of any point in the edge is bounded from below by the united atom value $E(He)$ and from above by the energy of the hydrogen molecule H_2. $E(z)$ is a monotonically increasing function when z spans the edge between $(2,0)$ and $(1,1)$, because the second derivative is negative in this range.

5.2. Three-Dimensional Nuclear Charge Space, ^3Z. We will consider lithium atoms as generative points for the

isoprotonic–isoelectronic molecular system. The Born–Oppenheimer energy on any one of the three edges, S_1, will have the form

$$E(z) \geq \alpha_1 E(z^{(1)}) + \alpha_2 E(z^{(2)}) + \frac{9\alpha_1\alpha_2}{R_{ij}} \quad (20)$$

The subindices of the relative coordinate R_{ij} correspond to those of the nonzero components of the generative points, e.g., considering the points $(3,0,0)$ and $(0,3,0)$ to expand the simplex, the energy will depend only on the internuclear coordinate R_{12}.

As before, the right side of inequality 20 shows a maximum in the middle, $\alpha_1 = \alpha_2 = \frac{1}{2}$; in this case it means the virtual molecule Bisesquile, which has as components two atoms of nuclear charge $\frac{3}{2}$. Again the energy function $E(z)$ increases its value from the vertices to the maximum.

$$E\left(\frac{3}{2},\frac{3}{2},0\right) > E(Li) \quad (21)$$

Besides, in each of the edges there are some other points corresponding to natural chemical species. In the case we are considering, helium hydride (HeH), is a point of the S_1 simplex. Consequently we may expect to find upper and lower bounds for its energy using relationship 15. A possible approach may be to consider two points symmetrical to the maximum. Thus, using the points $(2,1,0)$ and $(1,2,0)$, we obtain

$$E(z) \geq \alpha_1 E(HeH) + \alpha_2 E(HHe) + (\alpha_1\alpha_2)/R_{12}$$

$$E(z) > E(HeH) + (\alpha_1\alpha_2)/R_{12} \quad (22)$$

The maximum is reached when $\alpha_1 = \alpha_2 = \frac{1}{2}$. Consequently we may assert that

$$E\left(\frac{3}{2},\frac{3}{2},0\right) > E(2,1,0) \quad (23)$$

since $1/(4R_{12})$ is always positive.

With regard to these results it can be easily seen that the maximum energy always takes place at the middle of the edge and then we may state the following theorem.

Theorem 1:
Every set of isoelectronic–isoprotonic diatomic molecules has a maximal lower bound for the energy in the case of the homonuclear molecule in the set.

Consider any two vertices in an N-dimensional nuclear charge space, i.e., atoms with nuclear charge $z = N$. The energy on the simplex spanned by them is

$$E(z) \geq \alpha_1 E(z^{(i)}) + \alpha_2 E(z^{(j)}) + \frac{\alpha_1\alpha_2 N^2}{R_{ij}}$$

the maximum appears when

$$\alpha_1 = \{E(z^{(i)}) - E(z^{(j)})\}\frac{R_{ij}}{2N^2} + \frac{1}{2} = \frac{1}{2}$$

with an energy given by

$$E(z) > E(z^{(i)}) + \frac{N^2}{4R_{ij}} \quad (24)$$

To complete the relationships between the energies of the chemical systems in the edges we use as generative points those corresponding to the maximum and the united atom so

that

$$z(\text{HeH}) = \frac{1}{3}z(\text{Li}) + \frac{2}{3}z(\text{bisesquile})$$

$$E(2,1,0) \geq \frac{1}{3}E(3,0,0) + \frac{2}{3}E\left(\frac{3}{2},\frac{3}{2},0\right) + \frac{1}{2R_{12}} \quad (25)$$

As $E(3,0,0) < E(^3/_2,^3/_2,0)$ and $1/2R_{12} > 0$, then $E(\text{HeH}) > E(\text{Li})$, and we may write

$$E(3,0,0) < E(2,1,0) < E(^3/_2,^3/_2,0) \quad (26)$$

to set explicitly the upper and lower bounds along the edges.

5.3. Four-Dimensional Nuclear Charge Space, ^4Z. Theorem 1 provides us with the first family of upper bounds. For example, considering the vertices $(4,0,0,0)$ and $(0,4,0,0)$, we find that the maximum for the energy occurs at $\alpha_1 = \alpha_2 = {}^1/_2$, i.e., for the molecular helium, He_2. Next, using $(3,1,0,0)$ and $(1,3,0,0)$ as generative points, we find a maximum for the same molecular system, so we may state that

$$E(\text{Be}) < E(\text{He}_2)$$

$$E(\text{LiH}) < E(\text{He}_2)$$

As before, taking one vertex and the maximum in the edge as generative points, we may complete the sequence of meaningful chemical species:

$$\text{LiH} = (3,1,0,0) = {}^1/_2(2,2,0,0) + {}^1/_2(4,0,0,0)$$

From (15), $E(\text{LiH}) > E(\text{Be})$, therefore

$$E(\text{Be}) < E(\text{LiH}) < E(\text{He}_2) \quad (27)$$

5.4. N-Dimensional Nuclear Charge Space, ^NZ. This approach may be used in an N-dimensional charge space to set an ordering relationship between all molecules in the edges in the following way:

First, using theorem 1, we may assert that

$$E(0,...,z_i^{(M)},...,0,...,z_j^{(M)},...,0) > E(0,...,z_i^{(k)},...,0,...,z_j^{(k)},...,0)$$

with

$$z_i^{(M)} = z_j^{(M)} = \frac{N}{2}$$

$$z_i^{(k)} = \frac{N}{2} - a$$

$$z_j^{(k)} = \frac{N}{2} + a \quad (28)$$

When N is an even integer and a spans the integer values between 0 and $N/2$, we obtain the whole series of molecules. When N is an odd integer, half-integer values of a correspond to chemically significant molecules. As a goes from $1/2$ to $N/2$ we obtain the whole series. We may then call M_a the particular molecule for which $z_i^{(k)} = (N/2) - a$ and $z_j^{(k)} = (N/2) + a$. Next, we may build relationships between the energies of molecules in the edge starting from the homonuclear one M_0 to generate with a molecule M_b some molecule M_a, such that $b > a$. That is, for all M_a and M_b

$$M_a = \alpha_1 M_0 + \alpha_2 M_b$$

from (15)

$$E(M_a) \geq \alpha_1 E(M_0) + \alpha_2 E(M_b) + \frac{\alpha_1\alpha_2 a^2}{R_{ij}}$$

as $E(M_0) < E(M_b)$

$$E(M_a) > E(M_b) \quad (29)$$

Systematically used, this approach leads us to a complete ordering of all diatomic molecules in the edges.

6. UPPER AND LOWER BOUNDS FROM ONE-DIMENSIONAL SIMPLEXES S_1, IN OTHER SUBDIVISIONS

Now that we know how to move about any edge, we may get into the higher dimensional faces of the polyhedron, without increasing the dimension of the working simplex. To achieve this, we may use one-dimensional simplexes, S_1, generated by some other *subdivision* of the complex K, defined as

Definition 6: Let K and L be two complexes. L is called a subdivision of K if the following conditions are satisfied:

$$|K| = |L|$$

to every simplex $S' \in L$, there is a
simplex $S \in K$ such that $S' \subset S$

This concept has been used implicitly in the previous section to find relationships between meaningful chemical systems in the edges. Now it may be used to find relationships for chemical systems not being necessarily in the edges.

6.1. Barycentric Subdivision. One possibility is to use a barycentric subdivision and consider as generative points a vertex and the middle point of its opposite edge, i.e., the points $z^{(1)} = (0,0,...,z_j,0,...,z_k,0,...,0)$ and $z^{(1)} = (0,0,...,z_l,0,...,0)$ with $z_j = z_k = N/2$, $z_l = N$, and $l \neq j \neq k$.

In such a case the energy in the simplex will be

$$E(z) \geq \alpha_1 E(z^{(1)}) + \alpha_2 E(z^{(2)}) +$$
$$\alpha_1\alpha_2\left\{\frac{N^2}{2R_{jl}} + \frac{N^2}{2R_{kl}} - \frac{N^2}{4R_{jk}}\right\} \quad (30)$$

the maximum for the right side of the inequality occurs when

$$\alpha_1 = \frac{E(z^{(1)}) - E(z^{(2)})}{2\{(N^2/2R_{jl}) + (N^2/2R_{kl}) - (N^2/4R_{jk})\}} + \frac{1}{2} \quad (31)$$

using the lower limit of the difference from relationship 24 and assuming that the relative coordinates are equal; that is, if we have an equilateral triangle in ^{3N}R, the value of α_1 will be $^2/_3$.

This result for ^3Z lead us to

$$\frac{2}{3}\left(0,\frac{3}{2},\frac{3}{2}\right) + \frac{1}{3}(3,0,0) = (1,1,1) = \text{H}_3$$

$$E(3,0,0) < E(2,1,0) < E\left(\frac{3}{2},\frac{3}{2},0\right) < E(1,1,1) \quad (32)$$

showing that the hydrogen cluster is an upper bound for the energy for all its isoelectronic–isoprotonic molecular systems.

6.2. Chemical Subdivision. Another possibility is to choose as generative points chemical species present in the edges. For example, we may use the two closest chemical systems to one

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vertex, i.e., the points $z^{(1)} = (0,...,z_i,...,z_j,0,...,0)$ and $z^{(2)} = (0,...,z_i,...,z_k,0,...,0)$ with $z_i = (N-1)$, $z_j = z_k = 1$, and $j \neq k \neq i$.

The corresponding energy will be

$$E(z) \geq \alpha_1 E(z^{(1)}) + \alpha_2 E(z^{(2)}) + \frac{\alpha_1 \alpha_2}{R_{jk}} \qquad (33)$$

Note that the only internuclear coordinate that appears is that corresponding to the hydrogen atoms j and k. Hence it is always possible to chose one of the relative coordinates R_{ij} or R_{ik} as the equilibrium geometry to take advantage of the symmetry in Z and write

$$E(z) > E(z^{(1)}) + \frac{\alpha_1 \alpha_2}{R_{jk}} \qquad (34)$$

which present for its right side a maximum when $\alpha_1 = \alpha_2 = {}^1/_2$.

Also it is possible to consider the closest parallel segment to any of the edges, e.g., the opposite to the vertex i, that is, the simplex spanned by the points $z^{(1)} = (0,...,z_i,...,z_j,0,...,0)$ and $z^{(2)} = (0,...,z_i,...,z_k,0,...0)$ with $z_i = 1$, $z_j = z_k = (N-1)$, and $j \neq k \neq i$. In this case we obtain

$$E(z) \geq \alpha_1 E(z^{(1)}) + \alpha_2 E(z^{(2)}) + \frac{\alpha_1 \alpha_2 (N-1)^2}{R_{jk}} \qquad (35)$$

As in the previous case we may chose R_{ij} and R_{ik} in such a way that we may obtain the desired geometry R_{jk}. Without loss of generality we may suppose that $E(z^{(1)}) < E(z^{(2)})$ so that

$$E(z) > E(z^{(1)}) + \frac{\alpha_1 \alpha_2 (N-1)^2}{R_{jk}} \qquad (36)$$

with a maximum for the right side when $\alpha_1 = \alpha_2 = {}^1/_2$, that is, for the element $z = (0,0,...,z_j,...,z_i,...,z_k,0,...,0)$ with $z_i = 1$ and $z_j = z_k = (N-1)/2$.

In the particular case of $N = 3$, we obtain that the maximum occurs for the hydrogen cluster H_3 independently of the geometry. So that we have a generalization of the inequality 32 and may assert that the order proposed always holds.

Up to this point, the results suggest that the energy of any molecular system may lay between the energy of the cluster of N hydrogen atoms and the energy of an atom of nuclear charge N. If this is true, we would have a lower bound for all the elements in the complex K, easily calculable, and a minimal upper bound, given by the cluster of hydrogen atoms, in principle of lower computational complexity.

7. CONCLUDING REMARKS

In this paper we have proposed, using the symmetry properties of the nuclear charge space, a scheme to classify

isoprotonic molecules, as defined by eq 9. This lets us build the whole family from simplexes of increasing dimension. In principle, the vertices for these simplexes may be isolated atoms of nuclear charge equal to the dimension of the charge space considered.

This collection of simplexes make up mathematically a complex, K, encompassing, in the case of integer components for its points, every one of the isoprotonic–isoelectronic molecules that can be built with N nuclear charges. It means that given any molecule, it may be considered as a point of integer coordinates belonging to a complex of suitable dimension "p".

Also, using nuclear charges as variational parameters and taking into account the convexity properties of the simplicial complex, defined by considering the Born–Oppenheimer energy as a continuous function in Z, we have found two simple relationships (eqs 15 and 16). They relate the energy of any molecule in a isoelectronic–isoprotonic family with the corresponding energy of molecules in the set that may be used as its generative points (vertices) in a p-dimensional simplex. Further capabilities of these relationships are being explored by our group, and the results will be reported later on.

Up to now, using these expressions to set upper and lower bounds for molecules in spaces of dimension $N \leq 3$, we have developed an algorithm to order the members of the families, independently of the molecular geometry, achieving insight in the product space $R \times Z$.

Finally, we want to point out the possibility of reaching a full ordering of the set of diatomic isoelectronic–isoprotonic molecules, having a well-defined upper and lower bounds given by theorem 1.

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