

## Original Investigations

# Electronic Energy Inequalities for Isoelectronic Molecular Systems

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Within the Born–Oppenheimer approximation an inequality relation is derived between points of electronic energy hypersurfaces of pairs of isoelectronic molecules. The inequality is directly applicable to point pairs fulfilling a symmetry criterion for the nuclear frameworks and it may be extended to coordinate domains on both hypersurfaces. The result is applied to special examples of conformational problems, dissociation reactions and impurity–vacancy centres in solid clusters.

**Key words:** Electronic energy – Potential energy surfaces – Isoelectronic molecules – Upper and lower bounds for energy.

### 1. Introduction

In the Born–Oppenheimer approximation the electronic energy  $E_e$  of a molecular system of  $k$  electrons and  $N$  nuclei, in a given electronic state, is a function of the nuclear positions and nuclear charges:

$$E_e = E_e(\mathbf{z}, \mathbf{r}) = \langle \Psi(\mathbf{z}, \mathbf{r}) | \hat{H}_e(\mathbf{z}, \mathbf{r}) | \Psi(\mathbf{z}, \mathbf{r}) \rangle. \quad (1)$$

Here components  $z_i$  and  $r_j$  of  $N$  and  $3N$  dimensional vectors  $\mathbf{v}$  and  $\mathbf{r}$  correspond to the nuclear charge of nucleus  $i$  and nuclear position coordinate  $j$ , respectively. For fixed  $\mathbf{z}$ ,  $E_e(\mathbf{z}, \mathbf{r})$  is a  $3N$  dimensional hypersurface over the space of nuclear coordinates. (Although for a general polyatomic molecule this dimension may be reduced to  $3N - 6$  by eliminating degrees of freedom corresponding to translation and rotation of the molecule as a whole, for convenience we shall consider  $3N$  cartesian coordinates throughout this study). Alternatively, by generalizing our model and allowing components of  $\mathbf{z}$  to take any non-negative real value, for a

fixed  $\mathbf{r}$  the electronic energy  $E_e(\mathbf{z}, \mathbf{r})$  becomes an  $N$  dimensional hypersurface over a segment of  ${}^N R$ .<sup>1</sup> This segment (formally one  $2^N$ -th of  ${}^N R$ ) is constrained by the non-negativity of the  $z_i$  components for all the allowed  $\mathbf{z} \in {}^N R$ . Whereas only those points on this hypersurface may correspond to chemical structures where all  $z_i$  components are integers, one may expect that certain relations between various chemical structures can be derived by utilizing properties of a continuous hypersurface.

In the expression for the electronic Hamiltonian  $\hat{H}_e$  it is convenient to collect the  $r_j$  components according to the  $i$  nucleus index:

$$\hat{H}_e(\mathbf{z}, \mathbf{r}) = -\frac{1}{2} \sum_t^k \Delta_t - \sum_i^N \sum_t^k \frac{z_i}{|\mathbf{r}_i - \mathbf{r}'_t|} + \sum_{t < t'}^k \frac{1}{|\mathbf{r}'_t - \mathbf{r}'_{t'}|} \quad (2)$$

where  $\mathbf{r}_i$  and  $\mathbf{r}'_t$  refer to position vectors of nucleus  $i$  and electron  $t$ , respectively.

For fixed nuclear framework the nuclear component

$$E_n = \sum_{i < i'}^N \frac{z_i z_{i'}}{|\mathbf{r}_i - \mathbf{r}_{i'}|} \quad (3)$$

of the total energy

$$E_t = E_e + E_n \quad (4)$$

may be calculated easily by applying Coulomb's Law and it is the electronic energy component that requires a more elaborate treatment. Whereas variations of  $E_n$  in the course of a conformational process or chemical reaction are easy to visualize and to correlate with the classical, intuitive concepts of steric effects, the variations of the electronic component  $E_e$  usually have an equally important influence on such processes. In fact,  $\Delta E_n$  and  $\Delta E_e$  nearly cancel out along many reaction paths [1]. The fine variations in the slope and curvature properties of  $E_n$ , important in analysing the chemically relevant "reactive domains" of potential energy hypersurfaces [2], are often dominated by the behaviour of  $E_e$ .

Lower and upper bounds for  $E_e$  are very useful in obtaining approximations to wavefunctions and in estimating total energy differences [3]. Upper bounds may easily be obtained by the variational theorem for the lowest electronic state of atomic or molecular systems. Lower bounds of energy expectation values may be used to estimate the differences between approximate and exact wavefunctions via Eckart's theorem [4]. At least in principle both lower and upper bounds may be obtained as close to the exact value as desired, e.g. by applying the theorem of Mazziotti and Parr [5]. However, the actual calculation of reasonably accurate bounds involves optimizations that are just as (or more) tedious as the direct optimization of the wavefunction itself.

Most optimization methods applied to wavefunctions and some of the techniques used to derive upper and lower energy bounds, are based on the continuity of  $E_e$

<sup>1</sup> In deviation from the common custom, we shall use left superscript rather than right superscript to indicate the dimension of the space.

and some of its derivatives with respect to various parameters. Some of the differentiability conditions, however, may be replaced by convexity conditions [6, 7]. Convexity properties of energy expectation values are easier to establish than analyticity and arguments based on convexity properties are also free from some of the ambiguities associated with Taylor expansion methods [6, 7]. Convexity properties in relation with the variational theorem have been used to obtain various inequalities for atoms, jellium and for special molecular problems, one of the interesting results for molecules being a rigorous proof that the electronic energy of a molecular system is minimum when all nuclei are at the same point [7, 8] ("United atom").

Convexity relations are often not properly appreciated, although they may be expected to provide information on some more general problems of molecular physics, such as energy relations between isoelectronic molecules, conformational behaviour and chemical reaction paths. In this study, an attempt is made to establish inequality relations for a class of chemical problems of the above types. In particular, relations between special points on the electronic energy hypersurfaces  $E_e(z, r)$ , belonging to different but isoelectronic molecular systems, are investigated. Detailed proof is given only for special nuclear configurations, although it is expected that similar inequalities are valid for a much broader variety of nuclear configurations.

## 2. Discussion

Consider a set  $A$  of nuclei,  $A = \{A_i\}_{i=1}^l$  and a set  $R_A$  of arbitrary points,  $R_A = \{r_i\}_{i=1}^l$  in the three dimensional space. Let us assume that nucleus  $A_i$  is at point  $r_i$  and that the number  $k$  of electrons is fixed. The entire nuclear arrangement and any extension of it will be referred to as "molecule", even if its geometry does not resemble that of any stable molecule. Furthermore, consider a set  $R_B$  of points,  $R_B = \{p_j\}_{j=1}^m$  in three space, fulfilling the following condition:

For an arbitrary nucleus  $X$ , placed at points  $p_j \in R_B$ , ( $j = 1 \cdots m$ ) the isomeric molecules composed from nuclei  $\{A_i\}_{i=1}^l$  and  $X$ , i.e.

$$\{A_i\}_1^l X(p_1), \{A_i\}_1^l X(p_2), \dots, \{A_i\}_1^l X(p_m) \quad (i = 1 \cdots l) \quad (5)$$

are either superimposable or may be derived from each other by an improper rotation.

The fulfillment of condition (5) depends both on the mutual spatial arrangements of points in  $R_A$  and  $R_B$ , and on the nature of nuclei  $A_i$ , e.g. on the presence of identical nuclei and in general on the symmetry of the entire nuclear arrangement.

A set of  $n$  "molecules"  $\{M^a\}_{a=1}^n$  of  $k$  electrons may be constructed by combining nuclei  $\{A_i\}_1^l$  at positions  $\{r_i\}_1^l$  with  $n$  possibly but not necessarily different sets of nuclei  $B^a = \{B_j^a\}_{j=1}^m$ ,  $a = 1, \dots, n$ , in positions  $\{p_j\}_{j=1}^m$ . For fixed  $R_A$  and  $R_B$  the first, second and  $n$ -th of these molecules may be represented as

$$M^1 = \{A_i\}_1^l \{B_j^1\}_1^m, \quad M^2 = \{A_i\}_1^l \{B_j^2\}_1^m, \dots, M^n = \{A_i\}_1^l \{B_j^n\}_1^m \\ i = 1, \dots, l, j = 1, \dots, m, \quad (6)$$

respectively. Some positions of set  $R_B$  may be unoccupied, i.e. the formal nuclear charge of  $B_j^a$  may be zero for certain  $j$  and  $a$ , and in special cases sets  $R_A$  and  $A$  may be empty. In such special cases condition (5) is trivially fulfilled for any point set  $R_B$ . By allowing for zero nuclear charges, "molecules"  $M^a$  differ only in the nuclear charges.

A set of operators  $\{\hat{Z}_j\}_{j=1}^m$  may be defined, operating on the sets of  $B^a = \{B_j^a\}_{j=1}^m$  by

$$\hat{Z}_j\{B_j^a\}_{j=1}^m = X(\mathbf{p}_j, z^a) = X_j^a \quad (7)$$

where  $X(\mathbf{p}_j, z^a) = X_j$  is a nucleus in position  $\mathbf{p}_j$  with a nuclear charge<sup>2</sup> of  $z^a$ , where

$$z^a = \sum_{j=1}^m z(B_j^a), \quad (8)$$

i.e. the sum of all nuclear charges of set  $\{B_j^a\}_{j=1}^m$ . Operator  $\hat{Z}_j$  then simply eliminates the set of nuclei  $\{B_j^a\}_{j=1}^m$  and replaces it by a single nucleus in position  $\mathbf{p}_j$ , keeping the total nuclear charge constant.

As a consequence of condition (5), the total energy  $E_t$  and its nuclear and electronic components,  $E_n$  and  $E_e$  of molecules

$$\hat{Z}_j M^a = \hat{Z}_j \{A_i\}_1^l \{B_j^a\}_1^m = \{A_i\}_1^l \hat{Z}_j \{B_j^a\}_1^m = \{A_i\}_1^l X_j^a \quad (9)$$

are independent of index  $j$ . That is,

$$E_t(\hat{Z}_j M^a) = E_t^{a,X} \quad (10a)$$

$$E_n(\hat{Z}_j M^a) = E_n^{a,X} \quad (10b)$$

$$E_e(\hat{Z}_j M^a) = E_e^{a,X} \quad (10c)$$

where upper index  $X$  distinguishes these quantities from the respective energy values  $E_t^a$ ,  $E_n^a$  and  $E_e^a$  of the original molecule  $M^a$ . If for two molecules,  $M^a$  and  $M^b$ , Eq. (8) gives

$$z^a = z^b \quad (11)$$

then

$$E_t^{a,X} = E_t^{b,X} \quad (12a)$$

$$E_n^{a,X} = E_n^{b,X} \quad (12b)$$

and

$$E_e^{a,X} = E_e^{b,X}. \quad (12c)$$

Utilizing the fact that the hypersurface  $E_e(z)$  of the lowest electronic state of a given symmetry type is jointly concave in  $z$ , a general property of operators  $\hat{Z}_j$ , with respect to variations in the electronic energy  $E_e$ , may be established. The result is analogous to that obtained for the simplest case of united atom [8],

<sup>2</sup> Throughout the remainder of this paper upper indices will be used as identifying indicies and never as powers.

however, the proof is sufficiently general to give inequality relations for the electronic energies of molecules of the type  $M^a$ . In the special case of  $R_A = \emptyset$ , the theorem reduces to the familiar result that  $E_e$  is minimum for the united atom [8].

*Theorem:* If  $M$  is a molecule of  $k$  electrons and of  $N$  nuclei

$$\{A_i\}_{i=1}^l, \{B_j\}_{j=1}^m, l+m=N, \quad \text{at points } \{r_i\}_{i=1}^l (=R_A), \{p_j\}_{j=1}^m (=R_B)$$

fulfilling condition (5), and  $M$  is in the lowest electronic state of a given symmetry type, then  $E_e(\hat{Z}_{j'}M)$  is independent of  $j'$  and

$$E_e(\hat{Z}_{j'}M) \leq E_e(M), \quad (j' = 1, \dots, m).$$

*Proof:* Consider a set of  $n$  molecules,  $\{M^a\}_{a=1}^n$  with nuclear charges  $\{z^a\}_{a=1}^n$  and geometries specified by sets  $R_A$  and  $R_B$ . Furthermore, consider an additional molecule  $M^\alpha$  of the same geometry, and nuclear charges given by

$$z(\alpha) = \sum_{a=1}^n \alpha_a z^a \quad (13)$$

$$\sum_{a=1}^n \alpha_a = 1, \quad \alpha_a \geq 0. \quad (14)$$

Here the first  $l$  components of all  $z^a$  vectors and vector  $z(\alpha)$  are common. For a fixed  $R_A, R_B$  and  $k$  the  $z$  dependence of  $E_e$  may be made explicit

$$E_e = E_e(z). \quad (15)$$

If  $\Psi$  is the wavefunction of molecule  $M^\alpha$  with nuclear charges  $z(\alpha)$  then  $\Psi$  is a good trial function for any of the  $M^a$  molecules with nuclear charges  $z^a$ . By applying Eq. (14), the variational theorem and the fact that  $\hat{H}_e$  is linear in  $z$ , we may write for a normalized  $\Psi$

$$\begin{aligned} \sum_a \alpha_a E_e(M^a) &= \sum_a \alpha_a E_e(z^a) \leq \sum_a \alpha_a \langle \Psi | \hat{H}_e(z^a) | \Psi \rangle \\ &= \langle \Psi | \sum_a \alpha_a \hat{H}_e(z^a) | \Psi \rangle = \langle \Psi | \hat{H}_e\left(\sum_a \alpha_a z^a\right) | \Psi \rangle \\ &= \langle \Psi | \hat{H}_e(z(\alpha)) | \Psi \rangle = E_e(z(\alpha)) = E_e(M^\alpha), \end{aligned} \quad (16)$$

that is

$$\sum_a \alpha_a E_e(M^a) \leq E_e(M^\alpha), \quad (17a)$$

or more explicitly

$$\sum_a \alpha_a E_e(M(z^a)) \leq E_e\left(M\left(\sum_a \alpha_a z^a\right)\right). \quad (17)$$

Inequality (17) is a rather general form of the convexity property of Coulomb systems and is an important property of the  $E_e(z)$  electronic energy hypersurface.

Consider now a molecule  $M = \{A_i\}_{i=1}^l \{B_j\}_{j=1}^m$  and the corresponding  $z$  vector with components

$$z_i = z(A_i) \quad i \leq l \quad (18)$$

$$z_{l+j} = z(B_j) \quad (19)$$

and define chemical structures  $\{M^j\}_{j=1}^m$  by

$$M^j = \hat{Z}_j M, \quad (j = 1, \dots, m), \quad (20)$$

where operator  $\hat{Z}_j$  is defined in Eq. (7).

Here in each  $M^j$  the first  $l$  nuclei, hence the first  $l$  components of each vector  $z$  are the same as in  $M$ .

Let us choose components of  $\alpha$  as

$$\alpha_j = \frac{z_{l+j}}{z^{j'}} \quad (21)$$

where  $z^{j'}$  is given by (8), then

$$\sum_{j=1}^m \alpha_j = 1 \quad (22)$$

that is equivalent to condition (14), since in this case  $m = n$ . Note however, that  $z_{l+j} = 0$ , that is,  $\alpha_j = 0$  is possible for some (but not simultaneously all) indices  $j$ . Due to the properties of operators  $\hat{Z}_j$  and to the construction of set  $\{M^j\}$  the constant  $z^{j'}$  is independent of index  $j'$ . Consequently, inequality (17) takes the special form

$$\frac{1}{z^{j'}} \sum_{j=1}^m z_{l+j} E_e(M^j) \leq E_e(M). \quad (23)$$

Due to the definition of point set  $R_B$  and condition (5), in the absence of external fields all the  $M^j$  molecules are equivalent in energy and  $E_e(M^j)$  too, is independent of index  $j$ . Consequently,

$$E_e(M^j) \frac{1}{z^{j'}} \sum_{j=1}^m z_{l+j} \leq E_e(M)$$

that is

$$E_e(M^j) \leq E_e(M). \quad \text{Q.E.D.} \quad (24)$$

It is always possible to establish lower and upper bounds for the electronic energy of a molecular system at any point of the  $E_e(z, r)$  hypersurface ( $z$  fixed), either by the main result of the theorem (inequality 24) or by convexity relation (17). The  $z$  vector of a molecule may always be derived from  $z$  vectors of isoelectronic molecules either by applying operators  $\hat{Z}_j$  or by generating linear combinations fulfilling conditions (13) and (14).

In the latter case, however, it may be necessary to involve a large number of isoelectronic molecules and to include all the corresponding  $z$  vectors in the linear

combination. Before considering examples for the application of the theorem, we shall investigate a special case of such linear combinations. For any conformation  $(R_A, R_B)$  of an arbitrary molecule  $M$  of nuclear charges  $z$ , and total nuclear charge

$$z = \sum_{i=1}^N z_i, \quad (25)$$

a simple linear combination, fulfilling (13) and (14) may be constructed in the following way. It is always possible to find an isoelectronic molecule  $M^n$  of nuclear charges  $z^n$ , of total nuclear charge

$$z^n = z \quad (26)$$

where

$$z^n = \sum_{i=1}^N z_i^n, \quad (27)$$

and of nuclear positions corresponding to  $R_A, R_B$ . Since no  $\hat{Z}_i$  operations are needed to arrive at convexity relation (17), point set  $R_B$  may be empty. Furthermore,  $n-1 = N$  identical atoms of nuclear charge  $z$  and of  $k$  electrons are included in the linear combination, as "molecules"  $M^1, \dots, M^{n-1}$ . It is always possible to find a small enough  $\alpha_n, 1 > \alpha_n > 0$ , for which

$$z_i - \alpha_n z_i^n \geq 0 \quad (28)$$

for every index  $i$ , since each element of point sets  $R_A, R_B$  is assumed to be occupied in  $M$  and all nuclear charges are finite. Since the position of a single atom in vacuum may be chosen arbitrarily, one may select a  $z^a$  vector for "molecule"  $M^a$  as

$$z_i^a = z \delta_{ia} \quad (a = 1, 2, \dots, n-1). \quad (29)$$

A linear combination

$$\sum_{a=1}^n \alpha_a z^a = z \quad (30)$$

with a fixed  $\alpha_n$ , having property (28), and with

$$\alpha_a = (z_a - \alpha_n z_a^n) / z, \quad (31)$$

$$a = 1, 2, \dots, n-1 \quad (31a)$$

fulfills both conditions (13) and (14). Consequently, for isoelectronic molecules  $M, M^n$  and atom  $M^1$  convexity relation (17) holds and takes the special form:

$$(1 - \alpha_n) E_e(M^1) + \alpha_n E_e(M^n) \leq E_e(M). \quad (32)$$

For any molecule  $M$  in any conformation one may find  $M^n$  and  $M^1$  fulfilling the above conditions. For a given  $M$  and  $M^n$  pair inequality (32) gives the sharpest result for the largest value of  $\alpha_n$  that is permitted by (28).

The theorem itself is directly applicable to those points of electronic energy hypersurfaces of isoelectronic molecules where condition (5) is fulfilled. Several simple examples are given in Fig. 1.

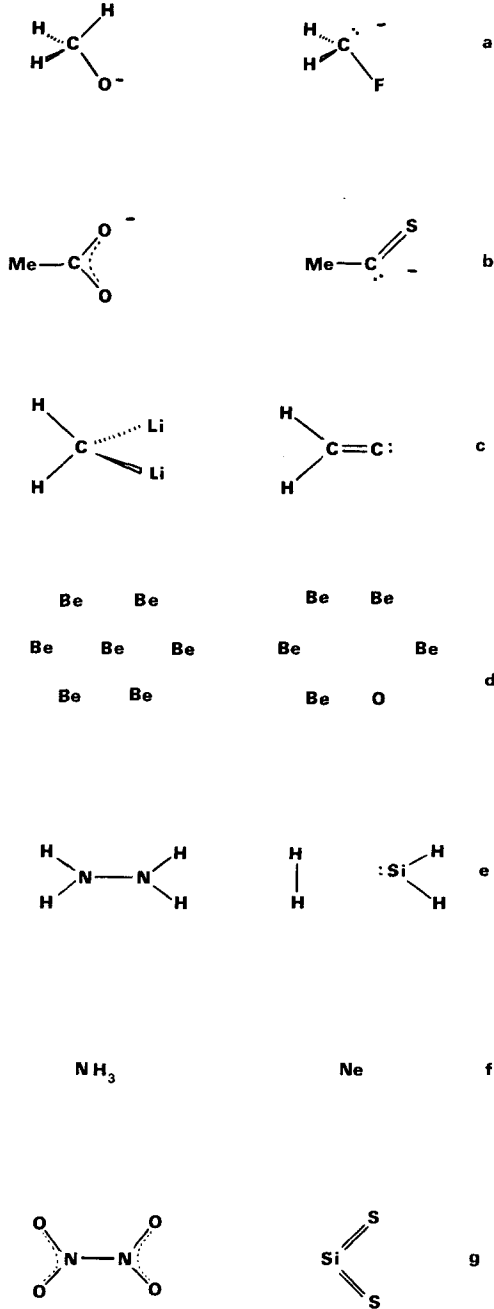


Fig. 1. Examples (a)-(g) for isoelectronic molecule-pairs  $M, \hat{Z}M$



In example (a), the two sets of nuclei are the following:  $A = \{C, H_1, H_2\}$ ,  $B = \{O, H_3\}$  and  $X = F^3$ . Those point pairs on the respective electronic energy hypersurfaces are directly comparable where nuclear coordinates belonging to point set  $R_A$  are common, and condition (5) is fulfilled for nuclear coordinates belonging to  $R_B$  and  $X$ . That is, the two  $CH_1H_2$  moieties have the same geometry, and the out of plane angles for the  $H_3$ , O, and F atoms as well as the C— $H_3$ , C—O and C—F distances are the same.

There are infinitely many such point pairs along the two electronic energy hypersurfaces where these conditions are fulfilled, and at such points at least one of these molecules must be distorted with respect to their equilibrium geometries. According to the theorem for any such point pair

$$E_e(CH_2F^-) \leq E_e(CH_3O^-). \quad (33)$$

Similarly, by choosing the set of nuclei  $A$  as those in the  $H_3C-C$  moiety and taking  $B = \{O, O\}$ ,  $X = S$ ,

$$E_e(H_3C_2S^-) \leq E_e(H_3C_2O_2^-) \quad (34)$$

is valid in example (b), subject to geometric conditions (5).

Although condition (5) appears quite restrictive, in some special cases the theorem gives useful results for nuclear configurations that do not fulfill (5).

If condition (5) applies for a geometry  $r$  of molecule pair  $M_j(r)$  and  $M(r)$ , then

$$E_e(M_j(r)) \leq E_e(M(r)). \quad (35)$$

If, however,  $r^{(1)}$  and  $r^{(2)}$  are two geometries that do not necessarily fulfill condition (5) but

$$E_e(M_j(r^{(1)})) \leq E_e(M_j(r)) \quad (36)$$

and

$$E_e(M(r)) \leq E_e(M(r^{(2)})) \quad (37)$$

then, clearly

$$E_e(M_j(r^{(1)})) \leq E_e(M(r^{(2)})) \quad (38)$$

is also valid. For a given  $r$  entire coordinate domains  $R^{(1)}$ , ( $r^{(1)} \in R^{(1)}$ ) and  $R^{(2)}$ , ( $r^{(2)} \in R^{(2)}$ ) may fulfill (36) and (37) respectively, and then point  $r$  may provide the link between the two hypersurfaces.

Particularly important are those cases, where  $r^{(1)}$  and  $r^{(2)}$  are equilibrium geometries. In such cases inequalities (36) and (37) reflect conditions on the relaxation processes  $r \rightarrow r^{(1)}$  and  $r \rightarrow r^{(2)}$  of molecules  $M_j$  and  $M$ , respectively, provided that the common  $r$  geometry fulfills condition (5). In the special case

$$r = r^{(2)} \quad (39)$$

<sup>3</sup> Nuclei  $H_1$  and  $H_2$  are in a plane perpendicular to that of the paper.

it suffices to show that in the  $\mathbf{r} \rightarrow \mathbf{r}^{(1)}$  relaxation process of  $M_j$

$$\Delta E_n \geq 0 \quad (40)$$

since then  $\Delta E_e \leq 0$  follows from  $\Delta E_t \leq 0$ , valid in any relaxation process. That is, in such a case both (36) and (37) are fulfilled and inequality (38) applies.

The relaxation process in example (c) has the above property. If  $A = \{\text{H}, \text{H}, \text{C}\}$ ,  $B = \{\text{Li}, \text{Li}\}$  and  $X = \text{C}$ , then there are infinitely many geometries  $\mathbf{r}$  that fulfill condition (5), and thus the theorem is applicable. By choosing  $\mathbf{r}$  as the equilibrium geometry [9] of the Li compound, ( $=M$ ), condition (36) is trivially fulfilled. The Li—C bond length is calculated as 2.128 Å [9]. The equilibrium C—C bond length in carbene  $\text{H}_2\text{C}_2$  ( $=M_j$ ) is *much* shorter, being a formal double bond [10]. Although the Li—Li repulsion is missing in  $M_j$ , this is more than compensated for by an increased C··C repulsion at the shorter bond distance, consequently  $\Delta E_n > 0$  in the  $\mathbf{r} \rightarrow \mathbf{r}$  [1] relaxation process of  $M_j$ . That is,

$$E_e(\text{H}_2\text{C}_2) < E_e(\text{H}_2\text{CLi}_2) \quad (41)$$

is valid for the equilibrium geometries as well. The relaxation process may be very general and may even involve intermediate energy barriers as long as for the net process  $\Delta E_t < 0$  and  $\Delta E_n > 0$ . In example (c), an  $M_j(\mathbf{r}) \rightarrow \text{H}-\text{C}\equiv\text{C}-\text{H}$  proton shift and formation of the equilibrium geometry of acetylene is also associated with  $\Delta E_t < 0$  and  $\Delta E_n > 0$ , consequently inequality (41) applies for acetylene as well as for carbene  $\text{H}_2\text{C}=\text{C}$ .

In microclusters or crystal lattices, where the relaxation is constrained by the lattice itself, an impurity-vacancy pair may take the role of  $X$ . In example (d),  $M$  is a Be cluster with a regular hexagonal close-packed lattice, whereas  $M_j$  contains a vacancy–Oxygen pair, with the Oxygen replacing a Beryllium. In this example the rest of the cluster corresponds to nucleus set  $A$ , and  $B = \{\text{Be}, \text{Be}\}$ ,  $X = 0$ . As long as the translational symmetry in the neighbourhood  $A$  of set  $B$  is preserved (i.e. the cluster is large and there are no deformations), condition (5) hence the theorem applies, indicating lower electronic energy for the cluster with the impurity-vacancy pair, than for the “pure” cluster.

Whereas most of the above examples with non-equilibrium geometries represent distorted conformations that may arise in large amplitude vibrations or conformational changes, the theorem may also be applied for certain points of electronic energy hypersurfaces along reaction paths involving distinct reactants. In example (e),  $A = \{\text{H}, \text{H}, \text{H}, \text{H}\}$ ,  $B = \{\text{N}, \text{N}\}$  and  $X = \text{Si}$ . The electronic energies of various  $\text{H}_2\text{N}-\text{NH}_2$  structures, having at least a point of inversion or a reflection plane perpendicular to the N—N bond, represent upper bounds for the electronic energy of the corresponding arrangements of molecules  $\text{H}_2 + \text{SiH}_2$ , that may arise in the fragmentation reaction of  $\text{SiH}_4$ .

In example (f), set  $A = \emptyset$ , empty, consequently condition (5) is fulfilled for any geometry and

$$E_e(\text{Ne}) \leq E_e(\text{NH}_3) \quad (42)$$

that is, the theorem reduces to the inequality for the united atom case [7, 8].

It is possible to generalize the main result of the theorem by considering  $3s$  dimensional  $\mathbf{p}'_j$  vectors in set  $R'_B$ , of condition (5), representing the cartesian coordinates of  $s > 1$  nuclei, rather than that of individual nuclei ( $s = 1$ ). In this case both  $X'$  and the  $B'_j$  elements of  $B' = \{B'_j\}_{j=1}^m$  correspond to sets of  $s$  nuclei. Similarly, in the definition of operators  $\hat{Z}'_j$ , Eqs. (7) and (8), scalars  $z^a$  and  $z(B'_j)$  are replaced by  $s$ -dimensional vectors  $\mathbf{z}'^a$  and  $\mathbf{z}'(B'_j)$ , respectively. Since  $\mathbf{a}'^a$  is the vector sum of the  $\mathbf{z}'(B'_j)$  nuclear charges at positions  $\mathbf{p}'_j$ , operator  $\hat{Z}'_j$  generates a set of  $X'(\mathbf{p}'_j, \mathbf{z}'^a)$  nuclei of nuclear charges  $\mathbf{z}'^a$  at  $s$  points specified by  $\mathbf{p}'_j$ , replacing all nuclei in the entire set  $B'$  and preserving the total nuclear charge of the molecule:

$$\hat{Z}'_j \{B'_j\}_{j=1}^m = X'(\mathbf{p}'_j, \mathbf{z}'^a) = X_j'^a. \quad (43)$$

With these generalizations the entire proof may be repeated and an analogous conclusion of form (24) may be obtained.

In example (g) in Fig. 1 this generalized form of the theorem may be applied. Sets  $A$  and  $R_A$  are empty and there are only two elements in set  $B' = \{B'_1, B'_2\}$ , both corresponding to an  $\text{NO}_2$  moiety ( $s = 3$ ) whereas set  $X'$  is  $\text{SiS}_2$ , a monomeric unit of polymer  $(\text{SiS}_2)_n$ . For a distorted (bent)  $\text{SiS}_2$  "molecule" the conditions (5), as generalized above, are fulfilled and the theorem yields

$$E_e(\text{SiS}_2) \leq E_e(\text{O}_2\text{NNO}_2). \quad (44)$$

As an extreme generalization of the  $E_e(\mathbf{r}, z)$  electronic energy hypersurface concept, any such surface of fixed total nuclear charge  $z$  and fixed number of electrons  $k$ , may be regarded as a particular crosssection of a hypersurface  $E_e^H(\mathbf{r}^H, \mathbf{z}^H)$  of  $z$  nuclei and  $k$  electrons, where the arguments are a  $3z$  dimensional  $\mathbf{r}^H$  vector and a  $z$  dimensional  $\mathbf{z}^H$  vector. That is, the  $E_e^H(\mathbf{r}^H, \mathbf{z}^H)$  hypersurface is embedded in a  $4z + 1$  dimensional space  ${}^{4z+1}R$ , and is defined over the product space  ${}^{3z}R \otimes {}^zR$ . In the special case of  $z$   $H$  nuclei (referred to by the  $E_e^H$  notation) the components of vector  $\mathbf{z}^H$  are

$$z_i^H = 1 \quad \text{for all } i. \quad (45)$$

By allowing the cartesian coordinates of some of the  $H$  nuclei to become identical, the  $E_e(\mathbf{r}, z)$  hypersurface of any isoelectronic molecule with the same total nuclear charge may be obtained as a crosssection of  $E_e^H(\mathbf{r}^H, \mathbf{z}^H)$ . This model allows for the simplest interpretation of the main result of the theorem: inequality (24) gives upper or lower bounds for "degenerate" nuclear arrangements of coincident nuclear positions on the  $E_e^H(\mathbf{r}^H, \mathbf{z}^H)$  electronic energy hypersurface.

### 3. Conclusions

An inequality relation is derived for special points  $\mathbf{r}$  (restricted by symmetry, condition (5)) on the electronic energy hypersurfaces of pairs of isoelectronic molecules. If two additional inequalities, (36) and (37) are verified for some  $R^{(1)}$  and  $R^{(2)}$  coordinate domains of their respective electronic energy hypersurfaces, a comparison at point  $\mathbf{r}$  may establish inequality (24) for any point pair from  $R^{(1)}$  and  $R^{(2)}$ , even if no numerical energy values are available. In special cases (Eq.

39) these inequalities are extended to equilibrium geometries, provided that the variation of the nuclear repulsion term during the relaxation process fulfills condition (40).

A special form (Eq. 32) of convexity relation of  $E_e(z)$  hypersurfaces, not restricted by condition (5) is derived, that gives a lower bound for the electronic energy of a general molecule of arbitrary geometry.

An analysis of simplicial complexes and convex polyhedra in the abstract charge space  $Z$  is given elsewhere [11].

Further work on the topological properties of  $E^H(\mathbf{r}^H, \mathbf{z}^H)$  hypersurfaces is now in progress.

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