

in the way predicted by Mills and Nixon, divided by the sum of all Kekulé structural weights. Thus defined, this index takes the values 0.142, 0.140, 0.106, and 0.019 for BCP, BCB, NCP, and NCB, respectively. It appears from these considerations that the MN effect is drastically reduced from benzene to naphthalene, when the annelating ring is cyclobutane, while it remains significant with a fused cyclopropane.

As in the case of BCP and BCB, we also performed calculations on distorted unannulated naphthalenes, having the geometries of the naphthalene fragments in NCP and NCB. The results, displayed in the third and fifth rows of Table III, indicate that the MN effect due to pure geometrical distortions is very small in NCB, as expected; on the other hand, it looks surprisingly significant in NCP, and this seems to be contrary to our assumption that the effect of geometrical distortions should gradually collapse as the aromatic ring gets bigger. It should however, be noted that the results of the latter calculations can be taken as a measure of the purely geometrical effect of σ -bond distortions, due to the neighboring strained ring, only in the case when the electronic effect of the CH_2 group(s) on the naphthalene π -MOs is negligible, i.e., in the case of NCB. Otherwise, the distortions of the naphthalene ring can be due, in part, to the MN effect itself, of which they are a secondary consequence rather than a cause. Secondly, the geometric distortions are more favorable to a MN effect in NCP than they are in BCP; the reason for this is that the small ring is attached to a long C-C bond of naphthalene (1.415 vs. 1.364 Å for the neighboring ones, while all are 1.40 Å long in benzene), therefore the shortening of the junction bond in NCP leaves it longer than the two adjacent ones, while the reverse was true in BCP, thus neatly favoring structure 11.

V. Conclusion

Our results support the effectiveness of the Mills-Nixon effect as it was originally proposed, i.e., a π -bond-localization effect on strained-ring-annelated benzenes. The geometric distortions of the benzene frame, induced by the strained fused ring at the level

of the σ bonds, are the only cause of the MN effect in BCB, while this factor is less important in BCP where a direct polarization of the π -electron cloud by the CH_2 group is at least as much effective. As discussed above, it is difficult to quantify the importance of the pure geometrical effect when it is not the only effective factor. Yet, the fact that half the MN effect is already present in BCP with a standard geometry suggests that it is caused, for the most part, by the direct electronic effect of the CH_2 group.

Our results also indicate that the MN effect is much larger for NCP than it is for NCB, while examination of geometrical distortions alone, with respect to naphthalene, would suggest a smaller difference between these derivatives. These results are coherent with the idea that the effect of a cyclobutane ring is purely locally geometric, and depends strongly on the geometry of the parent molecule, while the polarization of the π -electron cloud induced by a fused cyclopropane ring might still be effective in large systems. The extension to larger annulenes may not be straightforward since naphthalene is a benzo(6)annulene rather than a bridged (10)annulene. However, we can tentatively predict that the π -electron effect of a cyclopropane ring would increase in larger annulenes, as a result of stronger pseudo-Jahn-Teller mixing. On the other hand, the effect of the σ distortion induced by a cyclobutane ring is difficult to predict without any knowledge of the geometries of the annelated as well as non-annelated molecules, and might well vary from one compound to another. Thus, although we find a rather small MN effect in BCB, and Mitchell found almost no effect in cyclobutane-annelated dihydropyrene, it would be unwise to attempt any generalization of these results to cyclobutane-annelated large systems.

Registry No. 2b, 95842-00-5; benzocyclopropane, 4646-69-9; tricyclo[4.1.0.0^{1,4}]hepta-2,5-diene, 95841-96-6; tricyclo[3.2.0.0^{2,4}]hepta-1-(6),3-diene, 95841-97-7; benzocyclobutane, 694-87-1; tricyclo[4.2.0.0^{1,4}]octa-2,5-diene, 95841-98-8; tricyclo[4.2.0.0^{2,5}]octa-2(5),7-diene, 95841-99-9; naphtho[b]cyclopropane, 286-85-1; naphtho[b]cyclobutene, 6827-31-2.

A Simple Relation between Nuclear Charges and Potential Surfaces

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Abstract: The nuclear charges in a molecular system have a major role in determining most chemical properties. This fact is well recognized; however, this dominant influence of the nuclear charges has not yet been fully exploited in establishing simple rules for polyatomic molecules. In particular, various molecular energy components are often *concave functions* of the nuclear charges. This fact can be used for the derivation of trends in the relative stabilities of different molecules and to prove that an entire potential surface of one molecule lies above that of another molecule. In several recent studies concavity properties of molecular electronic energy functionals have been used to derive various local and global bounds for *electronic energy hypersurfaces* of isoelectronic molecules and chemical reactions. Since the nuclear repulsion energy is *not* in general a concave functional of the nuclear charges, the extension of the above local and global energy constraints to the molecular *total energy* functional (to potential energy surfaces) has met with difficulties. In the present study a simple sufficient and necessary criterion is given for the existence and for the evaluation of such constraints for total energy functionals. These constraints lead to rules for the energy ordering of different chemical species and to an ordering of potential energy surfaces. The applications of these rules require only a simple inspection of the nuclear charges and elementary calculations on a pocket calculator. Several examples are given.

Molecular properties and chemical reactions are fundamentally influenced by the magnitude of nuclear charges present in a given chemical system. In a formal sense the molecular total energy may be regarded as a function $E(\mathbf{z}, \mathbf{r})$ of both the nuclear charges \mathbf{z} and the nuclear geometry \mathbf{r} , where \mathbf{z} is a formal vector variable

containing the nuclear charges as components, whereas vector \mathbf{r} represents the collection of internal coordinates for the molecule. Within this model one may obtain energy relations between two molecules by analyzing the dependence of this function on variables \mathbf{z} and \mathbf{r} , as they change their values from $\mathbf{z}(1)$ and $\mathbf{r}(1)$ of molecule

1 to $\mathbf{z}(2)$ and $\mathbf{r}(2)$ of molecule 2. Function $E_t(\mathbf{z},\mathbf{r})$ is rather complicated, and it is useful to restrict our analysis (i) to iso-electronic species, (ii) to changes in \mathbf{r} while \mathbf{z} is fixed, or (iii) to changes in \mathbf{z} while \mathbf{r} is fixed.

Furthermore, within the Born–Oppenheimer approximation it is useful to consider the electronic energy E_e and the nuclear repulsion energy E_n components of total energy E_t separately:

$$E_t(\mathbf{z},\mathbf{r}) = E_e(\mathbf{z},\mathbf{r}) + E_n(\mathbf{z},\mathbf{r}) \quad (1)$$

In studies on potential energy hypersurfaces, restrictions i and ii are applied, leading to a quantum chemical description of vibrational, conformational, and reactive chemical processes (for recent reviews see, e.g., ref 1–5).

A theoretical model applying restrictions i and iii also has some merits, in particular when *comparisons between different molecular species and relations between entire potential surfaces* are the subject of the study. Whereas a continuous variation in the components of the nuclear charge vector \mathbf{z} does not correspond to any real chemical transformation, nonetheless, such a model is useful in establishing various local and global relations among different potential energy hypersurfaces. In the earliest related applications continuous \mathbf{z} dependence in the electronic energy component $E_e(\mathbf{z},\mathbf{r})$, combined with concavity properties of $E_e(\mathbf{z},\mathbf{r})$ for fixed \mathbf{r} have been used to derive energy relations for the jellium model and to obtain an elegant proof that the electronic energy is minimum for the united atom.^{6–8} In subsequent extensions of this model to chemical problems, concavity and other properties of the $E_e(\mathbf{z},\mathbf{r})$ electronic energy functional have been used to obtain simple energy inequalities between molecules, as well as rules on the energy ordering, on various upper and lower bounds, and on local and global energy constraints for isoelectronic (and also for some non-isoelectronic) families of molecules.^{9–12} The application of these energy relations to actual molecular systems is extremely simple, as they require no more than an inspection of the nuclear charges, followed by elementary “back of the envelope” calculations.

A function f is *concave*, that is, “convex from above”, within an interval $[x,y]$ if $f(ax + (1-a)y) \geq af(x) + (1-a)f(y)$ whenever $0 \leq a \leq 1$. For variationally optimum electronic wave functions concavity of the *molecular electronic energy* functional $E_e(\mathbf{z},\mathbf{r})$ in variable \mathbf{z} follows from the linearity of the electronic Hamiltonian $\mathbf{H}_e(\mathbf{z},\mathbf{r})$ in \mathbf{z} .¹⁰ However, the total energy Hamiltonian, $\mathbf{H}_t(\mathbf{z},\mathbf{r})$, is not linear in \mathbf{z} , owing to the quadratic nuclear repulsion term, with the trivial exception of atomic species. Hence, the above concavity relations are not directly applicable for *molecular total energies*. This may appear as an unfortunate limitation, total energy being a most fundamental quantum mechanical observable, responsible for the existence, stability, and transformation properties of molecules. However, the lack of general concavity of $E_t(\mathbf{z},\mathbf{r})$ in variable \mathbf{z} does not exclude the possibility of concavity relations for certain constrained variations in \mathbf{z} . In the present study a simple, sufficient, and necessary condition will be given for such constrained concavity relations that allows one to use a simple inspection of nuclear charges to derive various constraints, lower and upper bounds for *molecular*

total energies. The utility of these relations will be demonstrated by examples.

A Concavity Condition for Molecular Total Energies

Consider two isoelectronic molecular systems characterized by nuclear charge vectors $\mathbf{z}(1)$ and $\mathbf{z}(2)$, respectively. We shall consider a common nuclear geometry for these two systems, $\mathbf{r} = \mathbf{r}(1) = \mathbf{r}(2)$, that is, we shall assume that their energy hypersurfaces are defined over a common nuclear configuration space, and we are interested in the question of how these surfaces are placed with respect to each other. In particular, we shall investigate which energy surface lies above the other at any given nuclear geometry \mathbf{r} . A common nuclear configuration space can always be defined, even for molecules containing different numbers of nuclei, by simply extending the smaller system with “dummy” nuclei of zero nuclear charges.

The nuclear repulsion energy is a quadratic form,

$$E_n(\mathbf{z},\mathbf{r}) = \mathbf{z}'\mathbf{Q}(\mathbf{r})\mathbf{z} \quad (2)$$

where the quadratic matrix $\mathbf{Q}(\mathbf{r})$ is defined as

$$\mathbf{Q}(\mathbf{r})_{ij} = 0 \quad \text{if } i = j \quad (3)$$

$$\mathbf{Q}(\mathbf{r})_{ij} = 1/(2d_{ij}) \quad \text{if } i \neq j \quad (4)$$

and where d_{ij} is the distance between nuclei i and j . Note that in the above quadratic form the geometry dependence is separated from the nuclear charge dependence, as a geometry change affects only $\mathbf{Q}(\mathbf{r})$ and the nuclear charges appear only in \mathbf{z} . This formal separation simplifies the forthcoming analysis. We shall investigate the following problem: under what condition is it true that

$$\mathbf{z}(3) = a\mathbf{z}(1) + (1-a)\mathbf{z}(2) \quad 0 \leq a \leq 1 \quad (5)$$

implies

$$E_n(\mathbf{z}(3),\mathbf{r}) \geq aE_n(\mathbf{z}(1),\mathbf{r}) + (1-a)E_n(\mathbf{z}(2),\mathbf{r}) \quad (6)$$

that is, along which line segments $[\mathbf{z}(1),\mathbf{z}(2)]$ and for which geometries \mathbf{r} is a cross section of the nuclear repulsion energy functional *concave*? An analogous concavity relation does exist¹⁰ for molecular electronic energies $E_e(\mathbf{z},\mathbf{r})$, subject to the same condition 5 and to the conditions that the molecular systems are isoelectronic and are in an electronic state that is the lowest state of any given electronic manifold (e.g., lowest singlet or lowest doublet state, etc.). Consequently, for such molecules a relation of the form of eq 6, if valid, does imply an analogous inequality for *molecular total energies* as well:

$$E_t(\mathbf{z}(3),\mathbf{r}) \geq aE_t(\mathbf{z}(1),\mathbf{r}) + (1-a)E_t(\mathbf{z}(2),\mathbf{r}) \quad (7)$$

Such a total energy relation, in turn, can be used for the energy ordering of different molecular species or for the ordering of sequences of entire potential hypersurfaces, using only a simple inspection of the nuclear charges and elementary calculations.

Inequality 6 is evidently true for any geometry \mathbf{r} if $a = 0$ or 1 , hence we may restrict our analysis to the $0 < a < 1$ open interval. Substitution of quadratic form (2) into eq 6 for $\mathbf{z}(1)$, $\mathbf{z}(2)$, and $\mathbf{z}(3)$, respectively, gives

$$[a\mathbf{z}'(1) + (1-a)\mathbf{z}'(2)]\mathbf{Q}(\mathbf{r})[a\mathbf{z}(1) + (1-a)\mathbf{z}(2)] \geq a\mathbf{z}'(1)\mathbf{Q}(\mathbf{r})\mathbf{z}(1) + (1-a)\mathbf{z}'(2)\mathbf{Q}(\mathbf{r})\mathbf{z}(2) \quad (8)$$

Carrying out the multiplications on the left-hand side, collecting like terms on the right-hand side, and dividing by the *positive* quantity $a(1-a)$ lead to the inequality

$$2\mathbf{z}'(1)\mathbf{Q}(\mathbf{r})\mathbf{z}(2) \geq \mathbf{z}'(1)\mathbf{Q}(\mathbf{r})\mathbf{z}(1) + \mathbf{z}'(2)\mathbf{Q}(\mathbf{r})\mathbf{z}(2) \quad (9)$$

that is, to

$$0 \geq [\mathbf{z}'(1) - \mathbf{z}'(2)]\mathbf{Q}(\mathbf{r})[\mathbf{z}(1) - \mathbf{z}(2)] \quad (10)$$

where the fact that $\mathbf{Q}(\mathbf{r})$ is a symmetric matrix has been used. Inequality 10 is a *sufficient and necessary condition for the validity of concavity relation* 6, subject to condition 5, where the $0 < a < 1$ open interval is considered.

Inequality 10 is valid for any $\mathbf{z}(1)$ and $\mathbf{z}(2)$ pair of nuclear charge vectors if the matrix $\mathbf{Q}(\mathbf{r})$ is negative semidefinite, that

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(9) P. G. Mezey, *Theor. Chim. Acta*, **59**, 321 (1981).

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(11) P. G. Mezey, *Mol. Phys.*, **47**, 121 (1982).

(12) P. G. Mezey, *J. Chem. Phys.*, **80**, 5055 (1984).

is, if it has no positive eigenvalues. However, the trace of $\mathbf{Q}(\mathbf{r})$ is zero for *any geometry* \mathbf{r} by virtue of definition 3, hence $\mathbf{Q}(\mathbf{r})$ is negative semidefinite only if it has no negative eigenvalues either, that is, if it is the zero matrix, representing a formal geometry \mathbf{r} where all nuclei are pairwise infinitely separated. Consequently, with the exception of the above trivial case, no geometry \mathbf{r} exists for which concavity relation 6 would be valid for *all choices* of nuclear charges $\mathbf{z}(1)$ and $\mathbf{z}(2)$.

Whereas for realistic molecular geometries \mathbf{r} condition 10 is *not* necessarily fulfilled for an *arbitrary choice* of $\mathbf{z}(1)$ and $\mathbf{z}(2)$, nonetheless, condition 10 and hence relation 6 are valid for many chemically important combinations of $\mathbf{z}(1)$, $\mathbf{z}(2)$, and \mathbf{r} .

Example 1. That condition 10 is not vacuous can be demonstrated with the simple example of the potential curves of the two diatomics CO and N_2 of nuclear charge vectors

$$\mathbf{z}'(1) = (6,8) \quad (11)$$

$$\mathbf{z}'(3) = (7,7) \quad (12)$$

respectively. Considering a second CO molecule (a formal OC molecule) with the reversed assignment of nuclear charges

$$\mathbf{z}'(2) = (8,6) \quad (13)$$

relation 5 is fulfilled with $a = 0.5$:

$$(7,7) = 0.5(6,8) + 0.5(8,6) \quad (14)$$

The potential energy curves of CO and OC are, of course, identical and can be compared with that of N_2 , by considering molecular total energies at the same bond length values. These molecules are isoelectronic, hence, e.g., for the lowest singlet electronic states the nuclear charge relation 14 implies

$$E_e(\text{N}_2) \geq 0.5E_e(\text{CO}) + 0.5E_e(\text{OC}) \quad (15)$$

that is,

$$E_e(\text{N}_2) \geq E_e(\text{CO}) \quad (16)$$

for any common bond length d , by concavity of the molecular electronic energy, proven earlier.¹⁰

In order to test condition for the *nuclear repulsion energy*, we write matrix \mathbf{Q} as

$$\mathbf{Q}(\mathbf{r}) = (1/(2d)) \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} \quad (17)$$

Substitution of

$$\mathbf{z}'(1) - \mathbf{z}'(2) = (6,8) - (8,6) = (-2,2) \quad (18)$$

into condition 10 gives

$$0 \geq -4/d \quad (19)$$

that is, the condition is fulfilled for any positive bond length d . Consequently, the nuclear repulsion energy is also a concave functional for a linear variation of nuclear charges between $\mathbf{z}(1)$ and $\mathbf{z}(2)$ of CO and OC, respectively. This implies that for any a , $0 \leq a \leq 1$, in particular, for $a = 0.5$, relation 6 holds, that is,

$$E_n(\text{N}_2) \geq 0.5E_n(\text{CO}) + 0.5E_n(\text{OC}) \quad (20)$$

that is,

$$E_n(\text{N}_2) \geq E_n(\text{CO}) \quad (21)$$

Consequently, the molecular total energy E_t , a sum of E_e and E_n , is also a concave function for the nuclear charge variations constrained to the $\mathbf{z}(1)$, $\mathbf{z}(2)$ interval, hence relation 7 is also fulfilled, and

$$E_t(\text{N}_2) \geq E_t(\text{CO}) \quad (22)$$

for any bond length d . That is, *the entire potential energy curve of N_2 must lie above that of CO.*

Some Simpler Rules for Special Cases

Whereas the evaluation of the general condition 10 involves only a simple calculation of a quadratic form, that can be accomplished even for large molecules on any programmable pocket

calculator, further simplifications are possible for special cases.

In most actual problems of comparing different molecular species, there are common molecular fragments which do not participate in the formal nuclear charge variation. We may partition the nuclear charge vectors $\mathbf{z}(i)$ accordingly, assuming that the first m components represent the "variable" nuclei, and the last $n - m$ components are kept constant. This leads to the representation of each vector $\mathbf{z}(i)$ as a direct sum of an m dimensional vector $\mathbf{z}_v(i)$ and an $n - m$ dimensional vector $\mathbf{z}_c(i)$, corresponding to the two sets of components, respectively:

$$\mathbf{z}(i) = \mathbf{z}_v(i) \oplus \mathbf{z}_c(i) \quad (23)$$

Accordingly, matrix $\mathbf{Q}(\mathbf{r})$ is also partitioned into blocks, into two blocks, $\mathbf{Q}_v(\mathbf{r})$ and $\mathbf{Q}_c(\mathbf{r})$, along the diagonal and into two off-diagonal blocks, $\mathbf{Q}_{vc}(\mathbf{r})$ and its transpose, $\mathbf{Q}_{cv}(\mathbf{r})$:

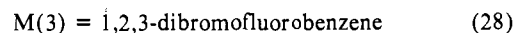
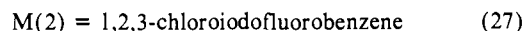
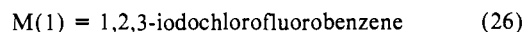
$$\mathbf{Q}(\mathbf{r}) = \begin{vmatrix} \mathbf{Q}_v(\mathbf{r}) & \mathbf{Q}_{vc}(\mathbf{r}) \\ \mathbf{Q}_{cv}(\mathbf{r}) & \mathbf{Q}_c(\mathbf{r}) \end{vmatrix} \quad (24)$$

The nuclear repulsion energy expression 2 becomes

$$E_n(\mathbf{z}(i), \mathbf{r}) = \mathbf{z}_v'(i) \mathbf{Q}_v(\mathbf{r}) \mathbf{z}_v(i) + \mathbf{z}_v'(i) \mathbf{Q}_{vc}(\mathbf{r}) \mathbf{z}_c(i) + \mathbf{z}_c'(i) \mathbf{Q}_{cv}(\mathbf{r}) \mathbf{z}_v(i) + \mathbf{z}_c'(i) \mathbf{Q}_c(\mathbf{r}) \mathbf{z}_c(i) \quad (25)$$

Here the last constant term is a (trivial) concave function of the variable nuclear charges \mathbf{z}_v . The second and third terms depend linearly on the variable nuclear charges \mathbf{z}_v , hence they are also concave functions of \mathbf{z}_v , for any geometry \mathbf{r} and for any choice of the fixed charges \mathbf{z}_c . Consequently, it is sufficient to test the general condition 10 for block $\mathbf{Q}_v(\mathbf{r})$ and for the $\mathbf{z}_v(1) - \mathbf{z}_v(2)$ difference and to establish concavity only for the first term involving $\mathbf{Q}_v(\mathbf{r})$. If the condition is fulfilled, then concavity relation 6 is necessarily true for the complete nuclear repulsion expression $E_n(\mathbf{z}, \mathbf{r})$ when the nuclear charge variations are restricted to the $\mathbf{z}(1), \mathbf{z}(2)$ interval.

Example 2. Let us consider the potential energy hypersurface of the following three molecules, halobenzenes M(1), M(2), and M(3):



These molecules are isoelectronic, and we shall consider their singlet ground states. Their nuclear charge vectors, in partitioned form, can be given as

$$\mathbf{z}_v'(1) = (53,17) \quad (29)$$

$$\mathbf{z}_v'(2) = (17,53) \quad (30)$$

$$\mathbf{z}_v'(3) = (35,35) \quad (31)$$

where the two vector components correspond to the nuclear charges of the two substituents in ring positions 1 and 2, respectively, hence $m = 2$. The total number of nuclei in each molecule is 12, and the dimension of the common constant vector $\mathbf{z}_c = \mathbf{z}_c(1) = \mathbf{z}_c(2) = \mathbf{z}_c(3)$,

$$\mathbf{z}_c' = (9,6,6,6,6,6,1,1,1) \quad (32)$$

is $n - m = 12 - 2 = 10$, where these components correspond to the constant nuclear charges of one fluorine, six carbons of the benzene ring, and three hydrogen atoms. Condition 5 is fulfilled for the $\mathbf{z}_v(i)$ vectors:

$$(35,35) = 0.5(53,17) + 0.5(17,53) \quad (33)$$

The expression for $\mathbf{Q}_v(\mathbf{r})$ is identical with that of $\mathbf{Q}(\mathbf{r})$ of example 1 (eq 17), if one takes d as the distance between substituents 1 and 2. As in example 1, concavity condition 10 is fulfilled, implying that for the nuclear repulsion energies of these halobenzenes

$$E_n(\text{M}(3)) \geq 0.5E_n(\text{M}(1)) + 0.5E_n(\text{M}(2)) \quad (34)$$

The nuclear charge relation 33 for the \mathbf{z}_v vectors implies a similar relation for the full, 12-dimensional nuclear charge vectors,

$$\mathbf{z}(3) = 0.5\mathbf{z}(1) + 0.5\mathbf{z}(2) \quad (35)$$

hence for these isoelectronic molecules in the lowest singlet electronic states the electronic energies fulfill the relation

$$E_e(M(3)) \geq 0.5E_e(M(1)) + 0.5E_e(M(2)) \quad (36)$$

Inequalities 34 and 36 imply for the total energies

$$E_i(M(3)) \geq 0.5E_i(M(1)) + 0.5E_i(M(2)) \quad (37)$$

Since this result is valid for any geometry \mathbf{r} , we conclude that the potential energy hypersurface of 1,2,3-dibromofluorobenzene lies above the average of potential energy hypersurfaces of 1,2,3-iodochlorofluorobenzene and 1,2,3-chloriodofluorobenzene. The same derivation applies if the fluorine atom is replaced with a hydrogen in all three compounds, then $M(1)$ is identical with $M(2)$, and one obtains that for all conformations where $M(1) = M(2)$ the entire potential energy hypersurface of 1,2-dibromobenzene ($M(3)$) must lie above that of *o*-iodochlorobenzene ($M(1) = M(2)$).

In the above example it is sufficient to evaluate the concavity condition only for those nuclei which are subject to replacement. Nevertheless, the resulting energy relation is *global*, valid for the entire potential surfaces of the given molecules. In the following we shall consider special relations, valid only for certain restricted domains of potential surfaces.

Consider a special case, where matrix $\mathbf{Q}_v(\mathbf{r})$ can be written in a simple form:

$$(\mathbf{Q}_v(\mathbf{r}))_{ij} = (1 - \delta_{ij})/(2d) \quad (38)$$

that is, it is the constant $1/(2d)$ times a matrix containing zeros in the diagonal and ones in all other positions. This $\mathbf{Q}_v(\mathbf{r})$ represents a geometry where all variable nuclei are at the same d distance from one another, e.g., they form a regular tetrahedron or an equilateral triangle. The case of example 2 also belongs to this class, being the simplest possibility for such $\mathbf{Q}_v(\mathbf{r})$. Using the notations

$$\mathbf{x} = \mathbf{z}_v(1) - \mathbf{z}_v(2) \quad (39)$$

and

$$y = \sum_i x_i \quad (40)$$

concavity condition 10 becomes

$$\mathbf{x}'\mathbf{Q}_v(\mathbf{r})\mathbf{x} = (1/(2d))\sum_i x_i \sum_{j(j \neq i)} x_j = (1/(2d))\sum_i x_i (y - x_i) \leq 0 \quad (41)$$

The inequality holds in an important special case when no term in the sum is positive,

$$y x_i \leq x_i^2 \quad (42)$$

for each component x_i , that is, when $y \leq x_i$ for positive x_i and $x_i \leq y$ for negative x_i . This condition is certainly valid for the case of $y = 0$, that is, when the sum of nuclear charges in the two molecules is the same.

Example 3. Consider an adamantane derivative $M(1)$ in which four alternating carbon positions bear the substituents Cl, Cl, I, H and the remaining substituents are arbitrary, but fixed. For this molecule $M(1)$ the four-dimensional $\mathbf{z}_v(1)$ vector is

$$\mathbf{z}'_v(1) = (17, 17, 53, 1) \quad (43)$$

In two additional adamantane derivatives $M(2)$ and $M(3)$

$$\mathbf{z}'_v(2) = (53, 1, 17, 17) \quad (44)$$

$$\mathbf{z}'_v(3) = (35, 9, 35, 9) \quad (45)$$

that is, the variable four substituents are I, H, Cl, Cl in $M(2)$ and Br, F, Br, F in $M(3)$, respectively, whereas all the remaining nuclei are kept unchanged. Consider any geometry \mathbf{r} for these three molecules where the four distinguished substituents are arranged such that they form a regular tetrahedron. Note that there is no further restriction on the common geometry \mathbf{r} and there are infinitely many nuclear geometries fulfilling this constraint. The result we shall obtain will be valid for all these \mathbf{r} points of the respective potential surfaces. The sum y of the components of difference vector $\mathbf{x} = \mathbf{z}_v(1) - \mathbf{z}_v(2)$ is zero, hence (41) applies, and

concavity relation 6 is valid for any a , $0 \leq a \leq 1$. These molecules are isoelectronic, and in the lowest singlet (or lowest triplet, etc.) electronic states

$$\mathbf{z}_v(3) = 0.5\mathbf{z}_v(1) + 0.5\mathbf{z}_v(2) \quad (46)$$

implies concavity for the electronic energies as well,¹⁰ hence one obtains

$$E_i(M(3)) \geq 0.5E_i(M(1)) + 0.5E_i(M(2)) \quad (47)$$

for the molecular total energies, that is the result we wanted to prove.

Molecules $M(1)$ and $M(2)$ are not in general identical. However, for some choices of the fixed substituents on the remaining positions of the adamantane skeleton, molecules $M(1)$ and $M(2)$ are identical and in such cases

$$E_i(M(3)) \geq E_i(M(1)) \quad (48)$$

A Generalization of Total Energy Concavity Condition for Simplexes Involving Several Molecules

In general only very few nuclear charge vectors fall on a straight line defined by two such vectors, and it is useful to extend the above concavity relations from the interiors of line segments to the interiors of triangles, tetrahedra, or higher dimensional polyhedra. Evidently, within suitably chosen triangles or polyhedra there are many \mathbf{z} vectors representing real molecular systems (necessarily of integer nuclear charges), and a general concavity relation for such polyhedra gives a constraint for the total energies of *all of these molecules*, in terms of the total energies of molecules defining the vertices of these polyhedra.

Concavity condition 10 is based on a linear variation of nuclear charges within a one-dimensional simplex, the $(\mathbf{z}(1), \mathbf{z}(2))$ interval, defined by the nuclear charges of two molecules, $M(1)$ and $M(2)$. For truly concave functions, like for the electronic energy, such relations are easily generalized for the case of the interior of a higher dimensional simplex defined by the nuclear charges of several molecules $M(1), \dots, M(k)$, e.g., for a triangle defined by three nuclear charge vectors $\mathbf{z}(1), \mathbf{z}(2)$, and $\mathbf{z}(3)$ of three molecules $M(1), M(2)$, and $M(3)$. However, in the case of functions such as the nuclear repulsion energy, which functions are not in general concave only under special conditions, it is somewhat more cumbersome to generalize the results for simplexes which are higher dimensional than the simplest nontrivial simplex: the $(\mathbf{z}(1), \mathbf{z}(2))$ interval.

Consider a sequence

$$M(1), M(2), \dots, M(k), M(k+1) \quad (49)$$

of isoelectronic molecules in the lowest electronic state of some electronic manifold. We shall assume that the nuclear charge vector $\mathbf{z}(k+1)$ lies within the $k-1$ dimensional closed simplex defined by the first k nuclear charge vectors, that is,

$$\mathbf{z}(k+1) = a_1\mathbf{z}(1) + a_2\mathbf{z}(2) + \dots + a_k\mathbf{z}(k) \quad (50)$$

for some constants a_1, a_2, \dots, a_k , constrained by

$$a_1 + a_2 + \dots + a_k = 1; a_i \geq 0 \text{ for every } i \quad (51)$$

These conditions imply¹⁰ for the electronic energy $E_e(M(k+1))$ at any common nuclear geometry \mathbf{r} that

$$E_e(M(k+1)) \geq a_1E_e(M(1)) + a_2E_e(M(2)) + \dots + a_kE_e(M(k)) \quad (52)$$

Our task is to find out what additional conditions are necessary for the fulfillment of an analogous relation for the nuclear repulsion energies, hence for the total energies, that is, for domains of potential energy hypersurfaces. The relation

$$E_n(M(k+1)) \geq a_1E_n(M(1)) + a_2E_n(M(2)) + \dots + a_kE_n(M(k)) \quad (53)$$

for which we want to find sufficient and necessary conditions can be written as

$$(\sum_i a_i \mathbf{z}'(i))\mathbf{Q}(\mathbf{r})(\sum_i a_i \mathbf{z}(i)) \geq \sum_i a_i \mathbf{z}'(i)\mathbf{Q}(\mathbf{r})\mathbf{z}(i) \quad (54)$$

Carrying out the multiplication for the terms in the sums on the left-hand side, and collecting all pure quadratic terms on the right-hand side, one obtains

$$\sum_i \sum_{j(j \neq i)} a_i a_j z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(j) \geq \sum_i a_i (1 - a_i) z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(i) \quad (55)$$

Since according to (51)

$$1 - a_i = \sum_{j(j \neq i)} a_j \quad (56)$$

one may write

$$\begin{aligned} 0 \geq & \sum_i \sum_{j(j \neq i)} a_i a_j \{z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(i) - z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(j)\} = \\ & \sum_i \sum_{j(j > i)} a_i a_j \{z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(i) - z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(j)\} + \\ & \sum_i \sum_{j(j < i)} a_i a_j \{z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(i) - z'(i) \mathbf{Q}(\mathbf{r}) \mathbf{z}(j)\} = \\ & \sum_i \sum_{j(j > i)} a_i a_j z'(i) \mathbf{Q}(\mathbf{r}) [\mathbf{z}(i) - \mathbf{z}(j)] + \\ & \sum_i \sum_{j(j < i)} a_i a_j z'(i) \mathbf{Q}(\mathbf{r}) [\mathbf{z}(i) - \mathbf{z}(j)] \quad (57) \end{aligned}$$

where the $j > i$ and $j < i$ terms are collected in separate sums. By interchanging the i and j indices in the last double sum the index constraints become identical in both double sums and one may write

$$\begin{aligned} 0 \geq & \sum_i \sum_{j(j > i)} a_i a_j z'(i) \mathbf{Q}(\mathbf{r}) [\mathbf{z}(i) - \mathbf{z}(j)] + \\ & \sum_j \sum_{i(i < j)} a_i a_j z'(j) \mathbf{Q}(\mathbf{r}) [\mathbf{z}(j) - \mathbf{z}(i)] = \\ & \sum_i \sum_{j(j > i)} a_i a_j z'(i) \mathbf{Q}(\mathbf{r}) [\mathbf{z}(i) - \mathbf{z}(j)] - \\ & \sum_i \sum_{j(j > i)} a_i a_j z'(j) \mathbf{Q}(\mathbf{r}) [\mathbf{z}(i) - \mathbf{z}(j)] \quad (58) \end{aligned}$$

that is,

$$0 \geq \sum_i \sum_{j(j > i)} a_i a_j [z'(i) - z'(j)] \mathbf{Q}(\mathbf{r}) [\mathbf{z}(i) - \mathbf{z}(j)] \quad (59)$$

This is the general form of a sufficient and necessary condition for the validity of nuclear repulsion energy relation 53. Note that the function $E_n(\mathbf{z}, \mathbf{r})$ does not have to be concave for the entire simplex defined by vectors $\mathbf{z}(1)$, $\mathbf{z}(2)$, ..., $\mathbf{z}(k)$ in order to have a valid relation 53 for certain specific values of constants a_1 , a_2 , ..., a_k . In particular, some of the quadratic forms in inequality 59 may very well be positive, hence along the corresponding $(\mathbf{z}(i), \mathbf{z}(j))$ intervals the one-dimensional concavity relation may be invalid, but this does *not* exclude the possibility for a negative sum in general relation 59 for some special values of the a_i coefficients. Hence, for some points within the $k - 1$ dimensional simplex, relation 53 may hold even if concavity does not hold along some of the edges of the simplex.

On the other hand, one can easily show that a *sufficient and necessary* condition for concavity for the *entire* $k - 1$ dimensional simplex is the non-positivity of *each quadratic form* in inequality 59. Since each product $a_i a_j$ is non-negative, the sum is non-positive if each quadratic form is non-positive. Conversely, in order to have concavity for the entire (closed) simplex, concavity must also apply along *each edge* $(\mathbf{z}(i), \mathbf{z}(j))$, for which the non-positivity of the quadratic form $[z'(i) - z'(j)] \mathbf{Q}(\mathbf{r}) [\mathbf{z}(i) - \mathbf{z}(j)]$ is a necessary condition, according to relation 10.

Example 4. In Figure 1 a two-dimensional simplex, the triangle defined by the nuclear charge vectors of isoelectronic species $M(1) = \text{CO}$, $M(2) = \text{FC}^+$, and $M(3) = \text{F}_2^{4+}$, is shown. These nuclear charge vectors are $\mathbf{z}'(1) = (6, 8)$, $\mathbf{z}'(2) = (9, 6)$, and $\mathbf{z}'(3) = (9, 9)$, respectively. Some nuclear charge vectors of further isoelectronic species, O_2^{2+} , and NO^+ (equivalent to ON^+) fall within this simplex. For all these species matrix $\mathbf{Q}(\mathbf{r})$ is given by eq 17. By substitution of the actual $\mathbf{z}(i)$ vectors into the quadratic forms one finds that

$$[z'(1) - z'(2)] \mathbf{Q}(\mathbf{r}) [\mathbf{z}(1) - \mathbf{z}(2)] = -6/d \leq 0 \quad (60)$$

$$[z'(1) - z'(3)] \mathbf{Q}(\mathbf{r}) [\mathbf{z}(1) - \mathbf{z}(3)] = +3/d > 0 \quad (61)$$

$$[z'(2) - z'(3)] \mathbf{Q}(\mathbf{r}) [\mathbf{z}(2) - \mathbf{z}(3)] = 0 \leq 0 \quad (62)$$

that is, concavity is assured along edges $(\mathbf{z}(1), \mathbf{z}(2))$ and $(\mathbf{z}(2), \mathbf{z}(3))$ but is violated along edge $(\mathbf{z}(1), \mathbf{z}(3))$. According to condition 59 this also implies that global concavity is not valid for the entire triangle of Figure 1, e.g., it is not valid for fictitious "species" of fractional nuclear charges along the interior of edge $(\mathbf{z}(1), \mathbf{z}(3))$. In general, concavity is violated along any edge of positive slope

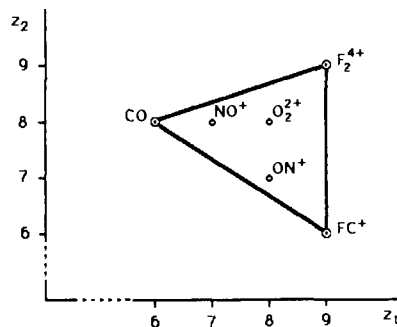


Figure 1. Triangle (two dimensional simplex) defined by the nuclear charges z_1 and z_2 of isoelectronic molecular species CO , FC^+ , and F_2^{4+} . The sets of nuclear charges can be represented as two-dimensional vectors $(6, 8)$, $(9, 6)$, and $(9, 9)$, respectively. For any isoelectronic species of nuclear charge vector falling within this triangle the total energy is larger than the linear combination $a_1 E_i(\text{CO}) + a_2 E_i(\text{FC}^+) + a_3 E_i(\text{F}_2^{4+})$ of total energies of CO , FC^+ , and F_2^{4+} . The linear coefficients in this expression are the same as those needed to express the nuclear charge vector as a linear combination of the nuclear charge vectors of CO , FC^+ , and F_2^{4+} . For example, the nuclear charge vector of ON^+ can be written as $(8, 7) = (3/9)(6, 8) + (5/9)(9, 6) + (1/9)(9, 9)$, hence for the total energy of ON^+ $E_i(\text{ON}^+) \geq (3/9)E_i(\text{CO}) + (5/9)E_i(\text{FC}^+) + (1/9)E_i(\text{F}_2^{4+})$.

in a two-dimensional problem. Nevertheless, there are linear combinations of nuclear charges $\mathbf{z}(1)$, $\mathbf{z}(2)$, and $\mathbf{z}(3)$ with certain special values of coefficients a_1 , a_2 , and a_3 , for which condition 59 holds. Take the following three vectors

$$z'(\text{ON}^+) = (8, 7) = (3/9)z'(1) + (5/9)z'(2) + (1/9)z'(3) \quad (63)$$

$$z'(\text{NO}^+) = (7, 8) = (6/9)z'(1) + (1/9)z'(2) + (2/9)z'(3) \quad (64)$$

$$z'(\text{O}_2^{2+}) = (8, 8) = (3/9)z'(1) + (2/9)z'(2) + (4/9)z'(3) \quad (65)$$

for isoelectronic species ON^+ , NO^+ (equivalent to ON^+), and O_2^{2+} , respectively. Substituting the values of the relevant quadratic forms from eq 60–62 and the values of the respective linear coefficients for ON^+ , NO^+ , and O_2^{2+} into condition 59, one obtains the numbers

$$-1/d \leq 0 \quad (\text{for } \text{ON}^+) \quad (66)$$

$$0 \leq 0 \quad (\text{for } \text{NO}^+) \quad (67)$$

$$0 \leq 0 \quad (\text{for } \text{O}_2^{2+}) \quad (68)$$

Condition 59 is fulfilled, hence inequality 53 applies for all three of these molecular species, in spite of the lack of a general concavity relation within the triangle. Since all these species are isoelectronic, in the lowest state of any electronic manifold the electronic energy is a concave function at any common geometry \mathbf{r} , and the following inequalities are valid for the *total energies*:

$$E_i(\text{ON}^+) \geq (3/9)E_i(\text{CO}) + (5/9)E_i(\text{FC}^+) + (1/9)E_i(\text{F}_2^{4+}) \quad (69)$$

$$E_i(\text{NO}^+) \geq (6/9)E_i(\text{CO}) + (1/9)E_i(\text{FC}^+) + (2/9)E_i(\text{F}_2^{4+}) \quad (70)$$

$$E_i(\text{O}_2^{2+}) \geq (3/9)E_i(\text{CO}) + (2/9)E_i(\text{FC}^+) + (4/9)E_i(\text{F}_2^{4+}) \quad (71)$$

This result is valid along the *entire potential energy curve* of ON^+ , NO^+ (equivalent to ON^+), and O_2^{2+} , respectively.

The same set of molecular species also may serve as an example for a two-dimensional simplex (triangle) for which a general concavity condition holds. The triangle defined by the nuclear charges of CO , FC^+ , and O_2^{2+} fulfills the edge-concavity relations for all three of its edges (that is, all three quadratic forms on the right-hand side of condition 59 are non-positive), hence concavity relation for total energies applies for *any nuclear charge vector*

\mathbf{z} within this (closed) triangle. If \mathbf{z} is expressed as a linear combination of the nuclear charge vectors at the three vertices, then the total energy of the molecule of charges \mathbf{z} is larger than or equal to the linear combination of total energies of molecules defining the three vertices, if the same linear coefficients are taken.

It is interesting to note that similar relations may also be obtained in some more exotic applications of the above results to hypothetical "quarkonium molecules", present perhaps in the early stages of the universe, i.e., to formal molecules with fractional nuclear charges of multiples of $1/3$. However, the relations derived above are of primary interest in studying potential surface problems of real molecules of integer nuclear charges, e.g., in providing energy bounds for the fundamental group Π_1 of reaction

mechanisms of a family of reactions confined to a given potential energy hypersurface.^{13,14} These groups (one-dimensional homotopy groups, independent of molecular symmetry groups or permutation groups) depend on an upper bound for energy, as well as on the topology of the hypersurface, and may serve as aids to synthesis design.

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Linear Solvation Energy Relationships. 29. Solution Properties of Some Tetraalkylammonium Halide Ion Pairs and Dissociated Ions

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Abstract: Free energies of transfer of tetramethyl- and tetraethylammonium chloride, bromide, and iodide ion pairs (IP) and dissociated ions (DI) are well correlated through equations of the form

$$\Delta G_t^\circ = (\Delta G_t^\circ)_0 + s\pi^* + a\alpha + h\delta_H^2$$

Inclusion of a $b\beta$ term shows only a minimal dependence on β and no improvement in the statistical goodness of fit, which indicates that there is no significant association between the solvents and the R_4N^+ ions acting as Lewis acids. The s , a , and h coefficients are significantly smaller in magnitude for IP's than for their corresponding DI's. The $-a$ values increase significantly, as expected, for both IP's and DI's in the sequence $I^- < Br^- < Cl^-$. These and other smaller structural effects are discussed.

In Part 13 of this series,¹ we reported that free energies of solution of nondipolar solutes (rare gases, alkanes, tetramethyltin) in nonpolychlorinated non-hydrogen bonding aliphatic solvents² were well correlated through equations of the form of eq 1a. The

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + h\delta_H \quad (1a)$$

$$\delta_H = [(\Delta H_v - RT)/V]^{1/2} \quad (2)$$

δ_H term in eq 1a, the Hildebrand solubility parameter,³ is defined by eq 2 (where ΔH_v is the molar heat of vaporization to a gas at zero pressure and V is the molar volume) and is the solvent property which measures the work necessary to separate the solvent molecules (disrupt and reorganize solvent/solvent interactions) to create a suitably sized cavity for the solute. Accordingly, $h\delta_H$ has been characterized as the *cavity term*, but the results do not exclude the possibility that the term also includes contributions from solute/solvent dispersion interactions.

It has since been pointed out to us⁴ that, rather than the first power of δ_H , regular solutions theory requires that the linear regressions of ΔG_s° be with δ_H^2 as in eq 1b. However, since the correlation coefficient of δ_H with δ_H^2 is 0.992 over the 7.27–13.0 range considered, correlations by eq 1a and 1b are of comparable statistical quality.

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + h\delta_H^2 \quad (1b)$$

In accordance with our practice of treating sequentially interactions of progressively increasing complexity, we next con-

sidered free energies of solution and of transfer of dipolar solutes under conditions where neither solutes nor solvents were hydrogen bond donors,² i.e., hydrogen-bonding effects were excluded. In Part 19 of this series,⁵ we reported that such cases are well correlated by equations of the form of eq 3a, where the π^* term is

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* + h\delta_H \quad (3a)$$

the solvatochromic parameter that measures the ability of the solvent to interact with a dipolar solute by virtue of dipole/dipole or dipole/induced dipole interactions. For dipolar solutes, the solute/solvent dipolar interaction is exoergic (negative sign of s) and the cavity term is endoergic (positive sign of h). As before, for the 41 solutes considered, correlations with the square of the Hildebrand solubility parameter (eq 3b) were of similar quality to correlations by eq 3a.

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* + h\delta_H^2 \quad (3b)$$

In the present paper we consider multiple solvation interactions of next greater complexity, the case of free energies of solution and of transfer of anionic hydrogen bond acceptor (HBA) solutes in both hydrogen bond donor (HBD) and non-HBD solvents. Here

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