

A CONVEXITY RELATION FOR THE ENERGIES OF CERTAIN POLYMERS OF UNIT CELLS OF DIFFERENT SIZES

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Abstract

A simple rule in the form of total energy inequalities is proposed for special polymers of very large unit cells, in terms of some related polymers of small unit cells. If energy data can be calculated for the latter regular polymers, these energy values lead to energy constraints on the polymers of very large unit cells. The actual evaluation of these constraints involves only a simple inspection of the nuclear charges and elementary calculations.

1. Introduction

Disordered polymers such as biopolymers and doped, highly conducting polymers with randomly distributed impurities are of major importance in a wide variety of fields, ranging from DNA research to industrial applications (new types of batteries, etc.). Whereas the theoretical-computational methods for the elucidation of the electronic structure of periodic systems are well developed (see, for example, reviews [1,2]), the theoretical analysis of aperiodic systems is a much less straightforward task. In periodic systems, the very periodicity can be exploited to reduce the complexity of the computational task; however, there is no apparent shortcut for the accurate numerical calculation of the total energies of large aperiodic systems.*

*It should be pointed out, however, that in quasi one-dimensional aperiodic systems the negative factor counting technique [2] gives quite reliable one-electron level distributions (density of states).

The available options seem to be very limited indeed, either to a statistical model or to "brute force" calculation of large aperiodic clusters, with a sacrifice of either numerical accuracy or computational feasibility.

One may, however, set a much less ambitious goal of providing some *constraints*, e.g. lower bounds of energies of *aperiodic* systems, using results obtained for some related *periodic* systems. Such constraints do not yield precise values; nonetheless, they can provide some information on the electronic stability of some aperiodic systems, in comparison with some periodic ones. These constraints can also be used in simple tests for the reliability of various methods for direct energy band structure calculations and, as one of our examples indicates, they can reveal the lack of reliability of some numerical results.

In this paper, we shall describe a simple technique for obtaining energy inequalities (energy bounds) for some polymers of very large unit cells (representing a "random" system) in terms of periodic polymers of small unit cells. Whereas the technique is quantum-mechanically rigorous (within the Born–Oppenheimer approximation), it is applicable only in special cases. The energy-ordering, when applicable, is necessarily valid for the exact energies and also for all approximate energies which are obtained within a consistent variational framework, e.g. for energies at the Hartree–Fock limit. Such energy inequalities naturally lead to energy bounds; however, these energy bounds are in most cases rather loose. It is noteworthy that the testing of these energy inequalities in actual cases requires only elementary, back-of-the-envelope calculations, even for systems involving several hundred (or in the extreme case, infinitely many) atoms.

2. Total energy constraints for some related polymers

2.1. ELECTRONIC ENERGIES

The proposed energy-ordering is based on the application of a convexity property of molecular electronic energy functionals in the abstract nuclear charge space wZ [3,4]. Convexity properties in Coulomb systems have been used in studies on the jellium model and also in deriving the general result that the electronic energy is minimum for the united atom [5–7]. More general relations, based on convexity and other geometrical-topological properties of *molecular* electronic energy functionals in the abstract nuclear charge space Z , have led to various nuclear geometry-dependent and some geometry-independent results for a variety of molecular families [3,4,8,9]. In the present study, we shall use the following result: if M_1, M_2, \dots, M_{n+1} are isoelectronic molecular systems of the same nuclear geometry, all in the lowest electronic states of the same manifold, and if their nuclear charge vectors z_1, z_2, \dots, z_{n+1} fulfill the condition

$$\sum_{i=1}^n \alpha_i z_i = z_{n+1}, \quad (1)$$

where the α_i scalars satisfy the relations

$$\sum_{i=1}^n \alpha_i = 1 \quad (2)$$

$$\alpha_i \geq 0, \quad i = 1, \dots, n \quad (3)$$

then for the *electronic* energies E_1, E_2, \dots, E_{n+1}

$$\sum_{i=1}^n \alpha_i E_i \leq E_{n+1} \quad (4)$$

holds. (The components of the nuclear charge vector z_i are the nuclear charges of species M_i , listed in arbitrary but fixed order.) Whereas the proof of the above result is valid only for common nuclear geometries of all molecular systems M_1, \dots, M_{n+1} , minor geometry differences do not invalidate inequality (4), and in fact the strong inequality ($<$) applies in all but some pathological cases.

We shall consider polymers which are built from similar but not necessarily identical monomeric units. The formal "length" of a given segment, e.g. of the unit cell, will be characterized by the number m of monomeric units it contains.

Owing to the logarithmic divergence of electronic and nuclear repulsion energy components of the total unit cell energy of an infinite polymer (vide infra), the method is directly applicable only to *finite* (although arbitrarily long) polymer chains *with periodic boundary conditions*, or where the chain-end effects are negligible. However, by taking the $n' \rightarrow \infty$ limit for the number n' of unit cells, the final total energy relations are valid for infinite polymers as well.

In order to apply the above convexity relation (4) to our present problem, consider polymers M_1, \dots, M_{n+1} of unit cell lengths m_1, \dots, m_{n+1} , respectively, with the following properties: There exist integers k_1, \dots, k_n such that

$$k_i m_i = m_{n+1} \quad (i = 1, 2, \dots, n). \quad (5)$$

Hence, all these polymers are periodic by the "large" period m_{n+1} although the first M_1, \dots, M_n polymers have typically several of their actual unit cells contained in the large cell of common length m_{n+1} . We choose $w = sm_{n+1}$ as the dimension of nuclear charge space wZ , where s is the number of nuclei in a monomer.

Assume that m_{n+1} is much larger than any of the other m_i numbers, $i \leq n$, that is, all the k_i integers are large. Furthermore, assume that all large m_{n+1} cells of M_1, \dots, M_n, M_{n+1} are isoelectronic. Hence, if conditions (1)–(3) are fulfilled for the sm_{n+1} dimensional z_i nuclear charge vectors, then one obtains the following generalization of energy constraint (4) for a polymer M_{n+1} of long unit cell in terms of energies of polymers M_1, \dots, M_n of short unit cells:

$$\sum_{i=1}^n k_i \alpha_i E_i \leq E_{n+1}. \quad (6)$$

Implicit in the above model is the assumption that the definition of unit cell energy within each polymer fulfills a natural proportionality condition: taking k_i unit cells of M_i as a "large" new unit cell, the energy is $k_i E_i$. *Energy is an extensive physical property and any correct definition of an energy quantity must reflect this property.* Such proportionality condition for total unit cell energies is necessary for any reliable numerical comparison between calculated stabilities of polymers having unit cells of different sizes, or for comparisons between experimental and calculated relative stabilities of polymers. As follows from the original formulations of the Kármán–Born boundary conditions, an energy per unit cell concept within an exact or any approximate quantum mechanical model should fulfill the following limit condition:

$$\begin{aligned} E_{\text{tot}}(\text{unit cell}) &\equiv \lim_{n' \rightarrow \infty} \{E_{\text{tot}}(n')/n'\} \\ &= \lim_{n' \rightarrow \infty} \{[E_{\text{nuc}}(n') + E(n')]/n'\}. \end{aligned} \quad (7)$$

Here, $E_{\text{tot}}(n')$, $E_{\text{nuc}}(n')$ and $E(n')$ are the total, nuclear repulsion and electronic energies, respectively, of a polymer chain of n' unit cells with periodic boundary conditions. The monomeric units far from each other along the chain are also assumed to be far from each other in space, that is, there is no folding of the chain. These conditions ensure proper additivity of unit cell energies for infinite polymers and also for large enough finite polymers if ∞ in the above expression is replaced by a large enough finite N' . This is, of course, also valid for open (that is, non-circular) polymers, whenever the chain-end effects are negligible as compared to the energy contributions from the intermediate portion of the chain.

Unfortunately, in actual *ab initio* polymer calculations the above additivity condition is not automatically satisfied. Additivity (proportionality) of unit cell energies requires the application of somewhat cumbersome truncation criteria [10], necessitated by a logarithmic divergence of the electronic energy expansion in the Hartree–Fock and related models of an infinite polymer. (Actually, the divergence of the negative infinite sum of electron-nuclear attraction terms are compensated only

by the positive infinite sum of nuclear-nuclear repulsion terms in the total energy per unit cell expression of an infinite polymer.) These truncation criteria, however, are seldom applied in practice and in most polymer calculations, actual energy comparisons between different unit cells are routinely performed, without recourse to such criteria [10]. Electronic energy is of fundamental importance within any variational treatment where the very determination of the wave function, hence that of *any* related physical property, is based on energy minimization. Consequently, incorrect (e.g. non-additive) unit cell energies, when involved in variational energy minimization, cast some doubt on the reliability of all other calculated properties. Whereas the rather common practice of comparing formal *ab initio* unit cell energies obtained by an incorrect lattice sum truncation is known to be a very questionable approximation, the resulting error in *relative* energies has often been assumed to be minor. This practice may be justified in many instances; nonetheless, in most cases it is difficult to judge the error involved, without actually applying the correct truncation criteria. The technique described in this study offers a simple diagnostic tool for detecting severe inconsistencies. In some special cases (see, for example, (iv) below), these inequalities can clearly indicate that two formal unit cell energies obtained by incorrect truncation are not at all comparable.

Our proposed inequalities are strictly valid only for correct, i.e. *additive*, energies per unit cell within any given approximation that is variational and involves a Hamiltonian depending linearly on the nuclear charges. (Hence, the technique is not applicable to certain semi-empirical methods of assumed Hamiltonians with no direct Z -dependence.) As follows from the above considerations, a formal violation of these inequalities may also serve as a diagnostic tool to indicate gross violations of the additivity condition of energies per unit cell within the actual approximation. In all such severe cases, very little physical meaning can be attached to the concept of direct, *ab initio* energies per unit cell obtained by incorrect truncation of the lattice sums.

Assuming that correct additive energy values (calculated or experimental) are available for the polymers M_1, \dots, M_n of short unit cells, these values constrain the electronic energy (give a *lower* energy bound) for the polymer M_{n+1} of long unit cell according to relation (6). The latter polymer may *formally* represent a random polymer, or, a polymer with randomly distributed impurities. Note, however, that even within a very large unit cell of length m_{n+1} , the distribution of nuclei is far from random, since relations (1)–(3) imply that \mathbf{z}_{n+1} is fully determined by the nuclear charge vectors $\mathbf{z}_1, \dots, \mathbf{z}_n$ of the first n polymers M_1, \dots, M_n . In fact, using a given set of M_1, \dots, M_n polymers one can “design” a formal “random” polymer using relations (1)–(3) and utilizing the following observation: in order to obtain a constraint for a “random” polymer of *large* cell length m_{n+1} , it is advantageous to choose the m_1, \dots, m_n cell lengths as relative primes. In general, in the

$$m_{n+1} = p_1^{a_1} p_2^{a_2} \dots p_j^{a_j} \dots p_r^{a_r} \quad (8)$$

prime factorization of m_{n+1} , each prime p_j occurs with an exponent a_j that is the largest exponent p_j appears with in any of the m_1, \dots, m_n numbers.

In order to establish relation (6) for actual polymers, only elementary additions and multiplications are required, which calculations can, indeed, be carried out on the back of an envelope. However, actual *numerical* lower bounds for electronic energy E_{n+1} require calculated or experimental estimates for the E_i values of the M_i ($i = 1, \dots, n$) polymers of short unit cells. Nevertheless, direct calculations for those simpler polymers are a much easier computational task than that for polymer M_{n+1} (the latter task may very well fall far beyond current computational possibilities).

2.2. NUCLEAR REPULSION ENERGY

Let us assume that conditions (1)–(3) are fulfilled, and the additional condition

$$0 \geq \sum_{i=1}^{n-1} \sum_{j>i}^n \alpha_i \alpha_j (z'_i - z'_j) Q(z_i - z_j) \quad (9)$$

is satisfied, where z'_i is the transpose of vector z_i , and the elements of matrix Q are defined as

$$Q_{ii} = 0 \quad (10)$$

$$Q_{ij} = 1/(2 d_{ij}) \quad (i \neq j). \quad (11)$$

Here, d_{ij} is the distance between nuclei i and j . It can be shown that in such a case the convexity condition

$$\sum_{i=1}^n \alpha_i E_i(\text{nuc}) \leq E_{n+1}(\text{nuc}) \quad (12)$$

for the nuclear repulsion energies is also valid [11]. If for the $n + 1$ chemical systems both inequalities (4) and (12) are fulfilled, then for the *total energies* one can write:

$$\sum_{i=1}^n \alpha_i E_i(\text{tot}) \leq E_{n+1}(\text{tot}). \quad (13)$$

If the above inequalities are applied for a disordered chain, then all the considerations concerning lattice sum truncation, as discussed above for the electronic energies, apply in identical form [see text following eq. (7)]. In the applications to polymers, the actual inequalities, analogous to inequality (6), are as follows:

$$\sum_{i=1}^n k_i \alpha_i E_i(\text{nuc}) \leq E_{n+1}(\text{nuc}) \quad (14)$$

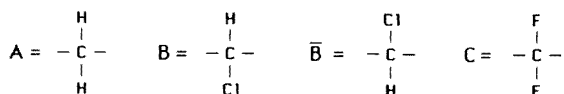
and

$$\sum_{i=1}^n k_i \alpha_i E_i(\text{tot}) \leq E_{n+1}(\text{tot}). \quad (15)$$

EXAMPLES

Example (i)

Consider the following monomeric units:



and the following infinite polymers (only unit cells are indicated):

$$M_1 = A B A B A \bar{B}$$

$$M_2 = A B A B A \bar{B} A \bar{B} A B A \bar{B} A B$$

$$M_3 = A B A B A \bar{B} A C A B A \bar{B} A B A B A C A C A C A C A B$$

$$A C A B A C A \bar{B} A B A C A C$$

of cell lengths

$$m_1 = 6$$

$$m_2 = 14$$

$$m_3 = (m_{n+1}) = 42.$$

Evidently, the prime factorization of $m_{n+1} = 42 = 2 \times 3 \times 7$ follows rule (8), implying $k_1 = 7$ and $k_2 = 3$. Since all of the AB , $A\bar{B}$ and AC moieties are isoelectronic, the same follows for the "long" unit cells of lengths $k_1 m_1 = 7 \times 6$, $k_2 m_2 = 3 \times 14$ and $m_3 = m_{n+1} = 42$. The $sm_{n+1} = w$ dimension of the relevant nuclear charge space wZ is $sm_{n+1} = 3 \times 42 = 126$. Simple inspection of the nuclear charges shows that

$$0.5 z_1 + 0.5 z_2 = z_3,$$

that is, conditions (1)–(3) are fulfilled. Hence, for the unit cell energies of M_1 , M_2 and M_3

$$k_1 \alpha_1 E_1 + k_2 \alpha_2 E_2 \leq E_3,$$

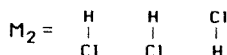
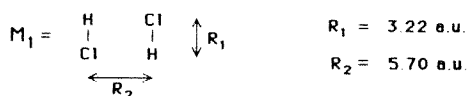
that is,

$$3.5 E_1 + 1.5 E_2 \leq E_3.$$

A lower bound for the electronic energy of "random" polymer M_3 of unit cell length of 42 (the cell containing 126 atoms) is obtained in terms of "regular" polymers M_1 and M_2 of unit cell lengths of 6 and 14, respectively. Whereas direct *ab initio* calculations for infinite periodic polymers M_1 and M_2 are not impossible (only expensive), direct *ab initio* calculation for infinite polymer M_3 is likely to be prohibitively expensive in the foreseeable future.

Example (ii)

Whereas actual numerical results for systems of the size of example (i) are at present not available, nevertheless one may design simpler models of "stacking" polymers of diatomics for which such numerical tests are possible:



All required relations are fulfilled with $m_1 = 2$, $m_2 = 3$, $m_3 = 6$, $k_1 = 3$, $k_2 = 2$, $\alpha_1 = 0.5$, $\alpha_2 = 0.5$ and $s = 2$. The dimension w of the relevant nuclear charge space wZ is 12. Relation (6) gives

$$1.5 E_1 + E_2 \leq E_3.$$

Ab initio crystal orbital calculations [1] using an STO-3G basis set and incorporating only nearest neighbours' interactions between unit cells, give the following results when substituted into the above inequality

$$\begin{aligned} &1.5(-1154.242 \text{ a.u.}) + (-1716.285 \text{ a.u.}) \\ &= -3447.648 \text{ a.u.} < -2957.699 \text{ a.u.} \end{aligned}$$

The prescribed energy-ordering is evidently valid with a very large margin. Whereas the electronic energy bounds are, in general, rather loose, the extremely large electronic energy difference in the above inequality is not typical. It stems from the extreme differences between H and Cl atoms, which are the nuclei compared in this example.

For the nuclear repulsion energies (also calculated in the nearest neighbour interactions approximation), one obtains the following inequality:

$$\begin{aligned} &1.5(186.561 \text{ a.u.}) + 352.261 \text{ a.u.} \\ &= 632.545 \text{ a.u.} < 999.812 \text{ a.u.} \end{aligned}$$

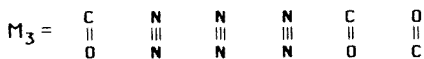
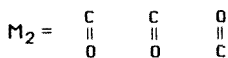
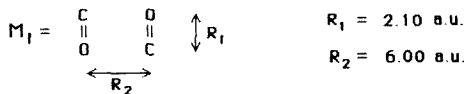
The result agrees with condition (12), leading to an inequality for the total energies:

$$-2815.545 \text{ a.u.} < -1957.887 \text{ a.u.}$$

that is the expected order.

Example (iii)

The differences between nuclei are much smaller, hence the energy bounds are much tighter, in the following example:



All parameters (except nuclear charges) are the same as in example (ii), and one again obtains

$$1.5 E_1 + E_2 \leq E_3.$$

The actual *ab initio* results of the STO-3G basis polymer calculations give

$$E_1 = -448.006 \text{ a.u.}$$

$$E_2 = -672.344 \text{ a.u.}$$

$$E_3 = -1334.775 \text{ a.u.}$$

Substitution into the above inequality gives

$$-1344.353 \text{ a.u.} \leq -1334.775 \text{ a.u.}$$

and the predicted constraint is evidently fulfilled. This energy bound gives an electronic energy difference of 1.6 a.u. per monomeric unit, still a rather large difference, but significantly smaller than that of example (ii).

The corresponding nuclear repulsion energy inequality is also satisfied:

$$1.5(152.455 \text{ a.u.}) + 267.819 \text{ a.u.}$$

$$= 496.501 \text{ a.u.} < 672.142 \text{ a.u.}$$

Adding the electronic components, the total energy relation is also fulfilled:

$$-847.851 \text{ a.u.} < -662.633 \text{ a.u.}$$

Example (iv)

Whereas the energy bounds are too loose to replace numerical calculations, nevertheless they are useful to give an ordering. In particular, they are useful diagnostic tools to assess the reliability of numerical comparisons when the computational models themselves involve some approximations whose effect is difficult to estimate. For example, it is customary in polymer calculations to compare energies of unit cells of various sizes taking into account the *same* number of nearest neighbour's, next-to-nearest neighbour's, etc., interactions. The above condition alone, however, does not guarantee the compatibility of the results [10] and, depending on the differences in the sizes of unit cells, further interaction terms are required to ensure a proper truncation of the lattice sum and the "natural proportionality condition" of unit cell energies,

referred to above. Whereas in the above examples neglecting the truncation criteria did not lead to severe errors causing a violation of inequality (6), this is not the case in our following example.

Considering only nearest neighbour's interactions and no further corrections, the same set of polymers of example (iii), with a somewhat more crowded arrangement of $R_2 = 4.00$ a.u., gives the following numerical results:

$$E_1 = -477.332 \text{ a.u.}$$

$$E_2 = -698.969 \text{ a.u.}$$

$$E_3 = -1590.340 \text{ a.u.}$$

Substitution into the inequality gives

$$-1414.967 \text{ a.u.} \not\leq -1590.340 \text{ a.u.},$$

that is, the constraint is violated, indicating a severe incomparability of the results on these three polymers, the energy discrepancy being at least 29.23 a.u. per constituent molecule. The proposed energy bounds are evidently useful to point out such an incompatibility, which is expected to be particularly severe at shorter bond distances.

Whereas the inconsistencies in the comparison of the formal unit cell electronic energies in this example lead to a violation of the inequality, this is not the case for the nuclear repulsion energies:

$$1.5(202.406 \text{ a.u.}) + 362.188 \text{ a.u.}$$

$$= 665.797 \text{ a.u.} \leq 928.200 \text{ a.u.}$$

In fact, the above inequality for the nuclear repulsion energies is fulfilled with a large enough margin to compensate for the violation of the electronic energy inequality, leading to the expected inequality for the total energies:

$$-749.170 \text{ a.u.} \leq -662.140 \text{ a.u.}$$

Example (iv) shows that in a disordered chain with strongly coupled units (the distance between subsequent molecules being 4 a.u. = 2.12 Å), one can not expect that nearest neighbour interactions (and most probably even second nearest neighbour interactions) provide sufficient numerical accuracy to fulfill all the inequalities.

3. Summary

We may conclude that for weakly coupled units (e.g. for H-bonded or stacked units) in a disordered chain, the proposed energy relations are expected to be fulfilled even using inaccurate, e.g. one- or a few-neighbour's interactions approximation. On the other hand, for strongly coupled units (e.g. in a covalently bonded chain), the calculation of unit cell energy components sufficiently accurate to fulfill the energy inequalities evidently requires the evaluation of many more neighbour interactions and a careful application of truncation criteria. The proposed inequalities can serve as a diagnostic tool for pointing out severe discrepancies and to indicate the need for more consistent truncation. In some cases, as in example (iv), the inequality is not violated for total energies, only for the electronic energy components. This indicates that unsatisfactory truncation of lattice sums may not manifest itself in the total energy relations, when it is already severe enough to cause a violation of the electronic energy relations. Hence, for diagnosing severe truncation errors, an investigation of energy components is a more sensitive test than that of the total energies.

Acknowledgements

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References

- [1] J.J. Ladik, in: *Electronic Structure of Polymers and Molecular Crystals*, ed. J.-M. Andre and J.J. Ladik (Plenum Press, London – New York, 1975) p. 23.
- [2] J.J. Ladik, *Int. J. Quant. Chem.* 23(1983)1073.
- [3] P.G. Mezey, *Theor. Chim. Acta* 59(1981)321.
- [4] P.G. Mezey, *Int. J. Quant. Chem.* 22(1982)101.
- [5] W. Thirring, *Acta Phys. Aust. Suppl.* 14(1975)631.
- [6] H. Narnhofer and W. Thirring, *Acta Phys. Aust.* 41(1975)281.
- [7] E.H. Lieb and B. Simon, *J. Phys.* B11(1978)L537.
- [8] P.G. Mezey, *Mol. Phys.* 47(1982)121.
- [9] P.G. Mezey, *J. Chem. Phys.* 80(1984)5055.
- [10] S. Suhai, Quantum mechanical investigations of quasi-one-dimensional solids, Habilitation Thesis, University Erlangen-Nürnberg, Erlangen (1983).
- [11] P.G. Mezey, *J. Amer. Chem. Soc.* 107(1985)3100.