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Concerning virial-based estimations of strength of bonding intermolecular interactions in molecular crystals and supramolecular complexes

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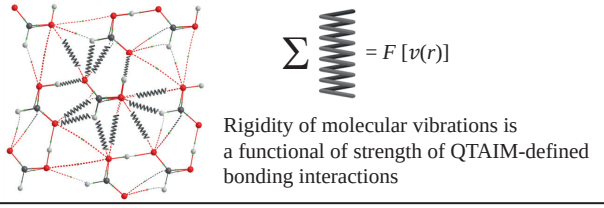
It is shown that the electronic virial-based correlation should be used to estimate bonding contributions to the rigidity of molecular vibrations in crystals.



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This paper is dedicated to the 50th birthday of Dr. Professor K. A. Lyssenko

Any task of theoretical chemistry is often treated in terms of the so-called bonding interactions and their contribution to the stability and properties of the system of interest. The search for bonding interactions between atoms is inherently linked with a real space point of view on the electronic structure which lacks standard protocols of orbital-based methods. Nowadays, the quantum theory of atoms in molecules[1] (QTAIM) is the most popular and almost routine tool for analyzing the electronic structure of polyatomic aggregates in real space. Despite the well-known criticism of QTAIM,[2] it is still very popular, as it provides a number of useful and convenient tools. Namely, using a topological analysis of the electron density function $\rho(r)$, one can rationalize the complex averaged behavior of electrons in terms of simple and chemically significant entities such as atoms, bonding interactions, *etc*. Probably the most controversial features of $\rho(r)$ are the (3,−1) critical point of $\rho(r)$ and the corresponding interatomic surface (IAS) of $\rho(r)$ zero flux, which, although extensively analyzed, are extremely misleading. The topography of $\rho(r)$ in the vicinity of these objects makes them unique indicators of bonding interactions for a pair of so-called topological atoms (hereinafter, topological bonding). However, such a definition of bonding interactions does not necessarily imply the presence of attractive forces between atoms leading to energetically favorable bonding.[3] Nevertheless, this does not prevent the QTAIM applicator community from referring to this critical point as the bond critical point: the desire to confuse bonding interactions thus defined with the concept of chemical bonding is too great to be overcome.[4]

Fortunately, there still exists a physically sound consequence of the phenomenon of topological bonding: an increase in the exchange-correlation contribution to the interaction energy between topological atoms in their *in situ* states.[5] To some extent, this justifies the applicability of topological bonding analysis, at least for studying of interatomic interactions with significant exchange contributions (or covalent contributions, in terms of conventional chemistry). In this respect, one has to note the ability of QTAIM to give insight into the nature of intermolecular interactions, which are classically considered as non-covalent.[6] An enormous number of studies utilize the properties of topological bonding to highlight and analyze the most important reference diatomic interactions for all possible pairs of atoms from different molecules.

Undoubtedly, the correlation scheme developed by Espinosa, Mollins and Lecomte (EML)[7] is one of the most recognizable QTAIM-based methods, matching topological bonding properties with chemically meaningful quantities. Namely, this method suggests that the binding energy of an interaction is proportional to the value of potential energy density [electronic virial field $v(r)$] at the (3,−1) critical point of interest. Developed to estimate the energy of intermolecular hydrogen bonds, EML has been successfully extended to other types of non-covalent interactions[8] and even to some coordination bonds with *f*- and *d*-metals.[9] Here we should especially note the rarely cited works of K. Lyssenko *et al.*[10] who are in fact the pioneers of this application of EML. Moreover, they even suggested using EML to estimate bonding contributions to the crystal lattice energy,[10(*d*),(*e*)] which was extremely helpful for studying polymorphs and self-assembly phenomena.[9(*b*),11]

Despite the successful use of EML correlation in solving many practical tasks, its universality and accuracy have been discredited several times. For instance, different proportionality coefficients have been proposed for different types of non-covalent interactions,[12] while the accuracy of corresponding estimations has been called into question even in the case of H-bonds.[13] However, some of us have been able to show that the properties of topological bonding in terms of the $v(r)$ function should be used to estimate not the plastic deformation of an interaction (its binding energy), but the elasticity of its stretching.[14] Namely, it was found that the effective force constant (eFC)[15] of the stretching vibration of any two

topologically bonded atoms is proportional to the integral of $v(r)$ over the corresponding IAS divided by the corresponding internuclear distance:

$$\partial^2 E/\partial R^2 \sim (1/R)\int_{\mathrm{IAS_i}} v(r)\mathrm{d}S(r). \quad (1)$$

Here, R is the internuclear distance corresponding to the bonding interaction of interest. This proportionality is of universal character, suggesting that the workability of the EML estimations of binding energy observed in some systems should be just a special case of the eFC trend for interactions with similar exponents of the Morse potential.[16]

This rationalization of EML raises the question of an integral property that is estimated by the electronic virial at bond critical points or corresponding surfaces for molecular crystals and supramolecular clusters, the main scope of EML applications. Indeed, if the strength of topological bonding in terms of the $v(r)$ function does not correspond to the bonding contribution to the crystal lattice energy, then what integral quantity does it approximate?

To answer this question, we assumed that the stretching of the bonding interactions formed by a molecule in a crystal completely determines its elastic translational vibrations as a rigid unit in the mean field of its environment. In this case, the Cartesian coordinates of the vibrations can be reformulated into the coordinates of the stretching of topological bonding to give the same trace of the matrix of second derivatives (if the harmonic approximation is used):

$$\sum_{\mathrm{i}} \left\{(1/R_{\mathrm{i}})\int_{\mathrm{IAS_i}} v(r)\mathrm{d}S(r)\right\} \sim \partial^2 E/\partial x^2 + \partial^2 E/\partial y^2 + \partial^2 E/\partial z^2. \quad (2)$$

Recall that the summation in the left-hand side is performed over all bonding interactions formed by a molecule with its environment, while the right-hand side is invariant against the rotation of the coordinate system.

To verify assumption (2), we performed DFT calculations for several molecular crystals and their fragments at the PBE0-D3BJ/def2TZVP level.[17] The range of objects was balanced to consider crystals with different types and different strengths of intermolecular interactions. It should be noted here that proportionality (1) was observed for equilibrium molecular structures,[14] that implies the same to be true for proportionality (2). Therefore, complete relaxation was first carried out for the selected crystal structures (the CRYSTAL17 software[18]). To some extent, assumption (2) is equivalent to the Einstein model of heat capacity: all molecules in a crystal are considered as independent harmonic oscillators. Then, to simulate parameters of their dynamics, it suffices to estimate the derivatives at the maximum of the density of vibrational states, *i.e.*, at the center of the corresponding first Brillouin zone. This was done by performing unrelaxed scans for the molecular clusters cut from each optimized crystal structures using the Gaussian 09 program.[19] Additional optimization steps were taken for the central molecules to account for the absence of a periodic potential. These structures were further used to calculate the $\rho(r)$ and $v(r)$ functions and perform integration procedures using a home modified version of the MultiWFN program[20] and the AIMAll program.[21] Next, the central molecule of each cluster was translated along the Cartesian axes (standard orientation) with a step of 5×10^{-4} Å to obtain five points on the potential energy surface in each direction. The central finite difference scheme from the textbook was then used to calculate the second derivatives. To test the applicability of $v(r)$-based quantities to calculate the crystal lattice energy, the latter was approximated by the energy of cohesion (E_{coh}) between the central molecule and its cluster environment. The cohesion energy was calculated as the difference between the Interacting Quantum Atoms (IQA) energy[22] of the central molecule in a cluster and the energy of an isolated molecule with the same geometry (the AIMAll program). The IQA scheme was used because the virial theorem was not satisfied for molecular clusters having fixed positions of non-central molecules. Optimized fractional coordinates and cell parameters for model crystals, Cartesian coordinates for molecular clusters and plots of atomic connectivity graphs obtained using topological analysis of electron density are listed in Online Supplementary Materials. The sum values of the second derivatives, cohesion energies and integral descriptors of bonding are given in Table 1.

Linear approximation of the data demonstrates that proportionality (2) is indeed fulfilled with a relatively high accuracy (m.a.e. 0.0066 atomic units) [Figure 1(*a*)]. In general, the performance of the resulting trend does not show a pronounced dependence on the nature of the system. The rigidity of molecular vibrations can be reasonably predicted both for hydrocarbon crystals stabilized only by dispersion interactions and for carboxylic acid crystals stabilized by H-bonds with a pronounced charge transfer component. The largest discrepancy is observed for ethene and butane crystals: although this could be a manifestation of a more complex (power-like) dependence, technical problems with zero-flux surfaces of $\rho(r)$ in its flat regions can also be the reason. Finally, the sum of $v(r)$ values at the (3, –1) critical points of $\rho(r)$ (the EML metric) satisfactorily correlates with the right-hand side of proportionality (2) (m.a.e. 0.0116 atomic units) [Figure 1(*b*)].

Table 1 Selected integral quantities (atomic units) for the calculated crystal fragments.

Crystal	Rigidity of molecular vibrations[a]	E_{coh}	$\sum_{\mathrm{i}} -v(r_{\mathrm{i}})$	Sum of virial integrals over IAS[b]
Acetic acid	0.1988	0.0395	0.1625	0.3869
Aminomethane	0.0961	0.0187	0.0600	0.2185
Butane	0.0527	0.0112	0.0599	0.1847
Ethane	0.0370	0.0115	0.0368	0.1232
Ethene	0.0403	0.0025	0.0327	0.0989
Formic acid	0.1985	0.0415	0.1588	0.3796
Formaldehyde	0.1055	0.0145	0.0688	0.2222
Formamide	0.1674	0.0505	0.1235	0.3259
H_2O_2	0.2475	0.0464	0.2028	0.4571
Me_2O	0.0558	0.0064	0.0507	0.1662
MeOH	0.1467	0.0262	0.1167	0.3100
Methylhydrazine	0.1392	0.0289	0.0941	0.2881
Propane	0.0479	0.0056	0.0572	0.1558

[a] Calculated according to the right-hand side of proportionality (2). [b] Calculated according to the left-hand side of proportionality (2).

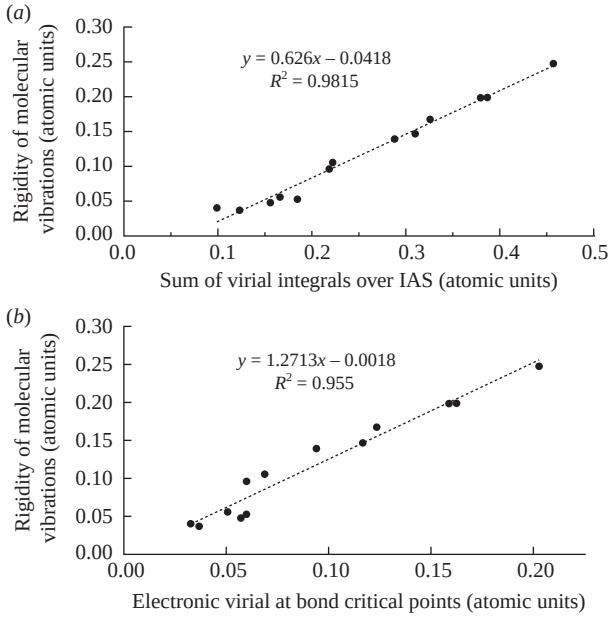

Figure 1 Linear trends approximating the dependences between the rigidity of molecular vibrations [the right-hand side of proportionality (2)] and the integral strength of QTAIM topological bonding: (*a*) in terms of the virial integrals over intermolecular surface and (*b*) in terms of the electronic virial at bond critical points.

It should be noted that the accuracy of $v(r)$-based estimations of the E_{coh} energy is noticeably worse (Figure 2) that agrees well with previous studies. Although we encourage scientists to use more accurate schemes[16] for estimating bonding energy and related quantities, it may be assumed that the EML scheme will still continue to be used for molecular crystals and other supramolecular aggregates due to its simplicity. In this sense, the estimated accuracy of EML predictions of the crystal lattice energy is also of great interest, since no information on this matter has been published so far. As expected,[16] the determination coefficient is larger for the trend producing the E_{coh} values from the left-hand side of proportionality (2) (0.86 *vs.* 0.82 for the EML metric). At the same time, the EML metric is characterized by a lower m.a.e. value: 0.0052 atomic units (3.25 kcal mol^{-1}) *vs.* 0.0112 atomic units (7.01 kcal mol^{-1}) for the surface integral scheme. This contradiction is removed once the formamide crystal is left from account as the most outlier: the R^2 value is lower, and the m.a.e. value is larger for the EML metric (0.92 and 0.0055 atomic units *vs.* 0.95 and 0.0049 atomic units, respectively, for the surface integral scheme). Taking into account that the formamide cluster is characterized by the largest value of E_{coh}, this is an illustrative example of the insufficiency of the electronic virial field to be an estimator of bonding energies for strong interactions.

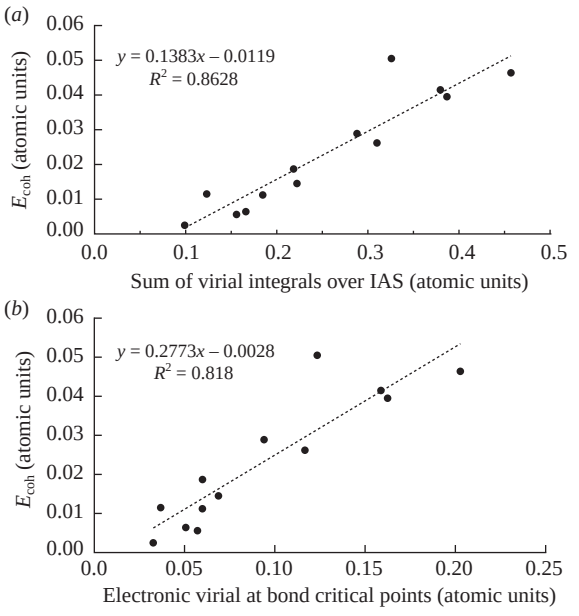

Figure 2 Linear trends approximating the dependences between the cohesion energy of a molecular cluster (as an approximation of the crystal lattice energy) and the integral strength of QTAIM topological bonding: (*a*) in terms of the virial integrals over intermolecular surface and (*b*) in terms of the electronic virial at bond critical points.

In conclusion, the $v(r)$-defined strength of diatomic topological bonding interactions formed between a molecule and its supramolecular environment should be considered as a measure of the bonding contribution to the rigidity of molecular translational vibrations. This opens up new possibilities for conventional electron density analysis, which is known to be an important method to get a deep insight into the structure–property relationships in functional materials.[23] Moreover, our results provide a reasonable basis for the well-known yet empirical comparison of the parameters of atomic motion in a crystal (in particular, atomic displacement parameters) and peculiarities of interatomic interactions. For instance, molecular or ionic mobility in solids can be studied and possibly even predicted by carefully examining QTAIM topological bonding using explored trends. In addition, proportionality (2) obviously confirms the ability to formulate the coordinates of a dynamic process in any caged system (at least vibrations in the vicinity of equilibrium for crystals and supramolecular associates) using the parameters of bonding interactions. This allows us to anticipate that other quantities related to the motion of nuclei (for example, the mobility of ions in crystals) may be estimated from real space fields describing the electronic structure and decomposed into bonding contributions. In the limiting case of only one atom in a molecule, it can be assumed that proportionality (2) describes the contribution of a particular atom and its bonding to the zero-point vibrational energy of a polyatomic system. This subject will hopefully be more elaborated in a future publication.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.04.018.

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