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Total wavefunction refinement and charge density analysis of Z'>1 molecular crystals and cocrystal structures: comparison with neutron structural data

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We report for the first time the total constrained refinement of a quantum mechanical wavefunction to X-ray diffraction data.

This means that the geometrical and atomic displacement parameters (ADP's) used to define the structure factors from the wavefunction are completely refined to the X-ray data by a least-squares procedure, using aspherical atomic form factors derived from the quantum mechanical charge density by Hirshfeld atom partitioning [1]. The electronic variables - the orbital coefficients - are refined subject to the restraint/constraint that they minimise the total quantum mechanical energy because there are more parameters than data. Both geometrical refinement and electronic constraints are applied simultaneously, for the first time, using a "block-diagonal" iterative procedure. In addition, refinement/constraint to the structure factor magnitudes is used for the first time. Furthermore, the procedure is extended to remove the previous restriction to Z'=1 and single-molecule structures. Each unique molecular wavefunction in the unit cell is self-consistently embedded in the multipole field of its neighbours. The technique is reported using DFT-type wavefunctions in a gaussian basis set expansion.

We report results (geometric parameters and other derived properties) for the dipeptide Gly-L-Ala. Geometrical parameters are compared to those from a neutron diffraction analysis. We also report results for a tripeptide L-Alanyl-L-Tyrosyl-L-Alanine cocrystallizing with dimethylformamide.

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Topological partition of the crystal elastic constants

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Previous works have demonstrated the partitioning of the bulk modulus and compressibility of solids into contributions due to each atom [1,2] or even to the core, valence, and lone pair electron regions [3,4]. We discuss in this communication how this partitioning, based on Bader's Quantum Theory of Atoms in Molecules, can be extended to the elastic constants, that represent the energy cost of deforming the crystal under small but arbitrary stress forces.

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New Gapless Dispersion Surface instead of Usual Erroneous Gappy Dispersion One

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In almost all previous works, the hyperbolic dispersion surfaces of the central proper quadrics have been erroneously derived from reduction of the degree from the bi-quadratic equation that could be defined by the existence of the solutions in the homogeneous simultaneous linear propagation equation with two unknowns as follows:

$$\begin{vmatrix} \boldsymbol{k}_0^2 - k^2 & K^2 C\chi_{\bar{g}} \\ K^2 C\chi_g & \boldsymbol{k}_g^2 - k^2 \end{vmatrix} = 0 \qquad (1)$$

$$(\boldsymbol{k}_0 + k)(\boldsymbol{k}_g + k)(\boldsymbol{k}_0 - k)(\boldsymbol{k}_g - k) - K^4 C^2 \chi_g^2 = 0 \qquad (2)$$

By use of some roughly indefinable approximate relation of $k_0 + k \approx 2K \approx 2k$ and $k_g + k \approx 2K \approx 2k$, the roots of eq. (2) from above factorization of eq. (1) can be given by

$$(\boldsymbol{k}_0 + k)(\boldsymbol{k}_g + k) - 4K^2 = 0 \qquad (3a)$$

$$(\boldsymbol{k}_0 - k)(\boldsymbol{k}_g - k) - (K^2 C^2 \chi_g^2 / 4) = 0\,. \quad (3b)$$

Somehow, the big hyperbola in eq. (3a) has not been adopted but the small one in eq (3b) has been drafted for some reason, which means one of the first serious vandalizations of fundamental eq. (1).

The hyperbola in eq. (3b) could be found in the shape of constricted parts of the cocoon-shaped curve in Fig. 1. Then, by neglecting the high symmetry of eq. (3b) in drawings in Fig. 1, both the branches in eq. (3b) have been substituted by the asymmetric surfaces composed of a pair of a central constricted part of the cocoon-shaped curve and a vertex of the oval in Fig. 1 in imitation of the ellipse without presenting reasonable evidence. This misapplication is the second serious vandalization of it.

Further, very small parts of the Laue circles by dotted lines in Fig. 1 could be substituted as the two tangential lines at L_D, that have been used for the asymptotes of the hyperbola of eq. (3b), also. This is the third serious vandalization of it, without the recognition of the difference between the contact point on the line and its line, which is not curve.

A new original gapless dispersion surfaces could be derived from eq. (1) without crude omission of a term by the usual analogy with the band theory of solid state physics as the closest approximation to the truth. This report including [1] is a part of the extended work of our previous works [2-5].

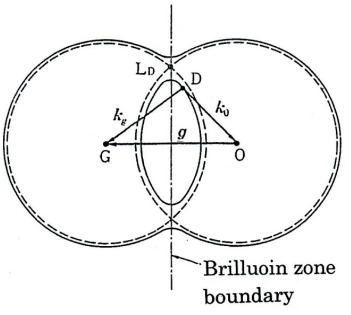

Fig. 1. The conven- tionally familiar gappy dispersion surfaces.