

Non-Spherical Form Factors in Crystallographic Refinement

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1. MOTIVATION

The crystallographic refinement process relies on form factors which describe the scattering power of an atom. This scattering power is proportional to the Fourier transform of the electron density (with the atomic location at the origin).

$$f_j = \int_{\mathbb{R}^3} \rho_j(\mathbf{x}) e^{2\pi i \mathbf{h} \cdot \mathbf{x}} d\mathbf{x} \quad (1)$$

This has generally been taken from spherically symmetric representations of atoms, but this is not necessary – with newer methods of computational quantum mechanical calculations or other modelling, they can be calculated more accurately for a specific structure.

2. THEORY

Whilst much of the refinement process remains the same as with the spherical assumption, some parts require adjustment:

Assumption 1: f_j is a function of the size of \mathbf{h} , $|\mathbf{h}|$

For spherical electron densities $\rho_j(\mathbf{x}) = \rho_j(|\mathbf{x}|)$, $f_j(\mathbf{h}) = f_j(|\mathbf{h}|)$. This is used to simplify the refinement process by collation of identical f_j . This cannot be used for non-spherical distributions.

Assumption 2: f_j is a real number

In the spherical case, symmetry causes complex components of f_j to cancel out. In the non-spherical case, this is not so, and f_j can be a complex number. For refinement software, this especially can require adjustment to deal with as complex values do not typically appear until later.

Assumption 3: Atoms of the same type have identical f_j

Atoms of the same type are no longer assumed to have identical electron density distributions, so each atom requires its own form factors calculated from its electron density, affected highly by its neighbouring atoms.

Simplification 1: Symmetries (and twins) still have relations

In the spherical case, f_j for an atom and its symmetry equivalents are identical. For symmetry equivalent atoms related by the rotation R , their non-spherical form factors are related by $f_1(\mathbf{h}) = f_2(\mathbf{h}R)$. Translation components are dealt with identically to the spherical case. For twins, the peaks remain at the same integer points, so the transformations as used in the spherical case still hold.

Simplification 2: We require only values at integer \mathbf{h}

The spherical form factors are approximated by equations describing their value for any $|\mathbf{h}| \in \mathbb{R}$. It is the case that constructive interference can only occur for integer-values \mathbf{h} , leading to the simplification of calculation that f_j need only be calculated at these integer points.

Complication 1: A value for every atom, for every $\mathbf{h} \in \mathbb{Z}^3$

Non-spherical form factors do not typically give rise to a simple analytical solution, and the form factors must be calculated individually for every \mathbf{h} with a F_o (or a symmetry equivalent F_o) recorded, for each atom. This is much more information than with the prior form factors, and unique to the specific crystal being worked on, so this information must be recalculated and potentially transferred to refinement software. Olex2 uses a *.tsc* file to transfer this information.

Complication 2: Recalculate frequently

Non-spherical form factors are derived from the calculated electron density. Any change to the positions of atoms within the molecule will cause a shift to this electron density, resulting in a shift to these form factors. Thus, the calculated form factors are only entirely accurate when there is no shift (i.e. when it has settled), and they should certainly have been calculated from the settled model.

4. CONCLUSION

The adjustments required in refinement, subject to the verification of the assumptions listed in ‘3. Further Considerations’, are relatively easy to implement into the standard crystallographic process. It can be more difficult to make these adjustments within written software if code optimisation has been done which takes advantage of spherical rules which no longer apply.

Stewart [1] said “By necessity, if not by choice, crystallographers have treated bonded atoms as point nuclei with a spherically symmetrical distribution of electron charge” when carrying out similar processes for bonded hydrogen atoms. We may now have passed beyond this necessity, but the re-evaluation of choice is only just beginning.

3. FURTHER CONSIDERATIONS

The refinement process contains deductions and assumptions which require re-consideration for non-spherical form factors.

The refinement process relies on the use of the first derivative of F_c with regards to every refinement parameter. This arises from a Taylor expansion, along with the assumption that any higher order derivative (multiplied by its respective Δx) is much less than $\partial F_c / \partial x \Delta x$, which will hold for sufficiently small Δx .

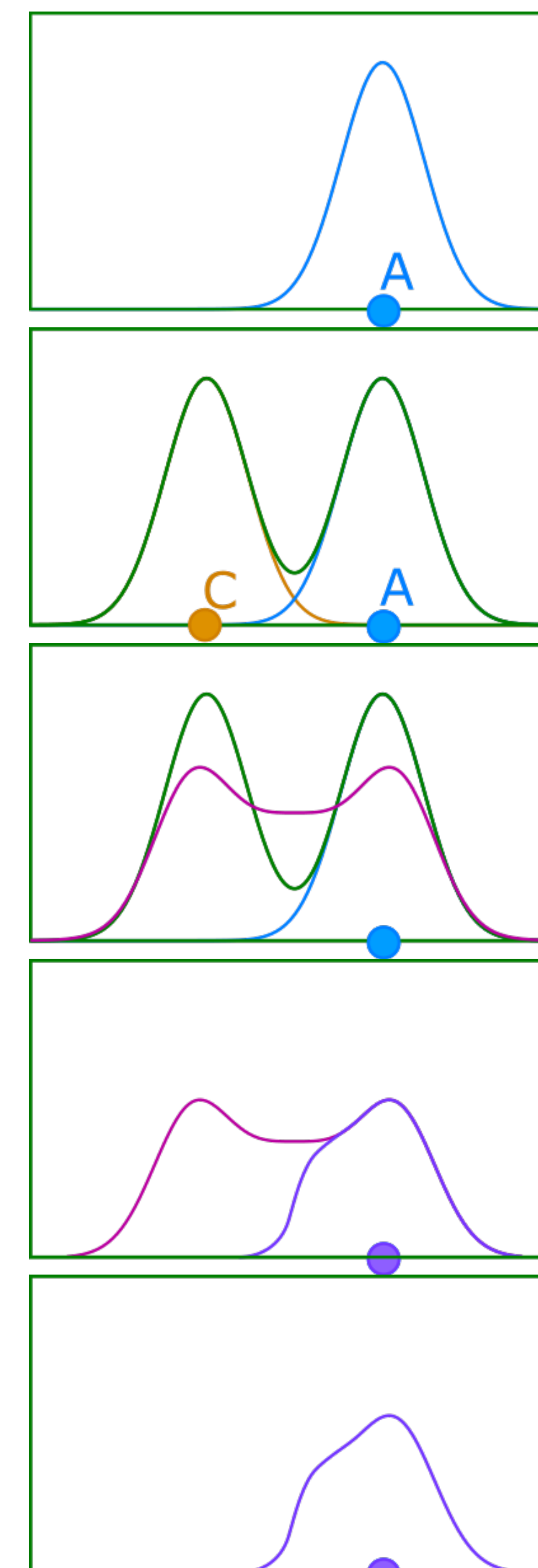
Through the fact that $F_c(\mathbf{h}) = \sum_{j=1}^N f_j(\mathbf{h}) G_j(\mathbf{h})$, with G_j representing considerations of location and ADPs as in the spherical case, this can be divided into the derivatives of $f_j(\mathbf{h}) G_j(\mathbf{h})$. In the spherical case, f_j is constant with respect to the refinement parameters, so this derivative results in $f_j(\mathbf{h}) \times \partial G_j(\mathbf{h}) / \partial x$. However, in the non-spherical case, there is an extra term $\partial f_j(\mathbf{h}) / \partial x \times G_j(\mathbf{h})$. If this term is small compared to the first, it can be neglected, and we take it to be 0 to allow the refinement process to match the spherical case. If this is not valid, it would have a significant impact on the sparse matrices and optimisations thereof within the refinement process, but so long as an estimation of $\partial f_j(\mathbf{h}) / \partial x$ could be made, it could be accounted for.

ASIDE: HIRSHFELD PARTITIONING

One example of splitting an electron density calculation into individual atom densities is the process of *Hirshfeld Partitioning* [3].

For this process, one requires both an electron density function for the entire structure (this can be simply defined across the asymmetric unit) and the previously-used spherical approximations. Then these are adjusted by a weighting scheme $w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r}-\mathbf{r}_A)}{\sum_B \rho_B^0(\mathbf{r}-\mathbf{r}_B)}$ (where B runs over all atoms, A represents the atom under consideration, and ρ^0 is the spherical electron density), taking $\rho_A(\mathbf{r}) = w_A(\mathbf{r}) \rho_{\text{mol}}(\mathbf{r})$ as the ‘true’ electron density of the atom.

In the images below, we show this process for a simple two-atom structure.



We begin with a single standard atom **A** at \mathbf{r}_A with $\rho_A^0(\cdot - \mathbf{r}_A)$

We bring in a second non-interacting atom **C**, and the resultant density $\rho_A^0(\cdot - \mathbf{r}_A) + \rho_C^0(\cdot - \mathbf{r}_C)$.

We then consider this in comparison to the calculated density ρ_{mol} . Note that this has a higher density between the atoms, and lower on their ‘centers’.

We finally adjust the electron density of the chosen atom such that all atomic densities sum to the calculated density, whilst remaining proportionally the same in contribution as the independent atom prediction,

$$\rho_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r} - \mathbf{r}_A)}{\sum_B \rho_B^0(\mathbf{r} - \mathbf{r}_B)} \rho_{\text{mol}}(\mathbf{r})$$

This results in an atomic density function which better models the electron density around the atom.

This new atomic function can then have the transform (1) applied to generate its form factor, which can then be used in the refinement process.

ACKNOWLEDGEMENTS & REFERENCES

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- [1] Robert F Stewart, Ernest R Davidson, and William T Simpson. Coherent x-ray scattering for the hydrogen atom in the hydrogen molecule. *The Journal of Chemical Physics*, 42(9):3175–3187, 1965.
- [2] Luc J. Bourhis, Oleg V. Dolomanov, Richard J. Gildea, Judith A. K. Howard, and Horst Puschmann. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment – Olex2 dissected. *Acta Crystallographica Section A*, 71(1):59–75, Jan 2015.
- [3] F. L. Hirshfeld. Bonded-atom fragments for describing molecular charge densities. *Theoretica Chimica Acta*, 44:129–138, 1977.