Bananas, pears and other fruitful discussions: modelling atomic motions in molecules

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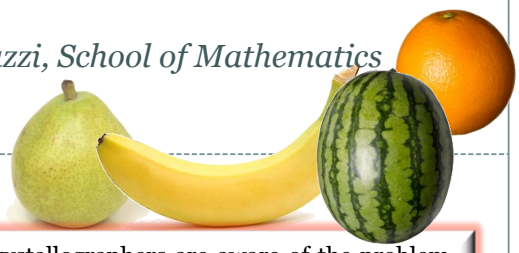
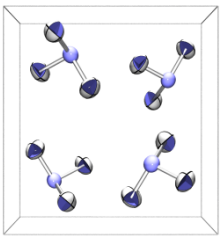
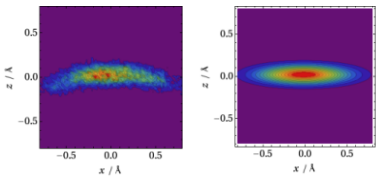


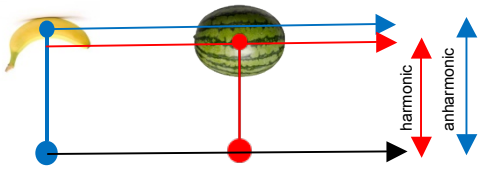
The gold-standard technique that allows chemists to characterise new compounds is crystallography. The output of this technique is, quite literally, a picture, such as the one shown below.



Thus crystallography allows not just the atomic identity and connectivity to be identified, but also geometric information such as bond lengths, angles etc to be obtained.

Atomic vibrational motion must be accounted for when crystal structures are solved, which is represented by the ellipsoids in the above diagram. We believe that current methods should now be improved. For instance, the left-hand image below represents a probability density function (PDF) for an atom that follows a curved trajectory; the right hand PDF is how the current crystallographic software would interpret this atomic vibrational motion.



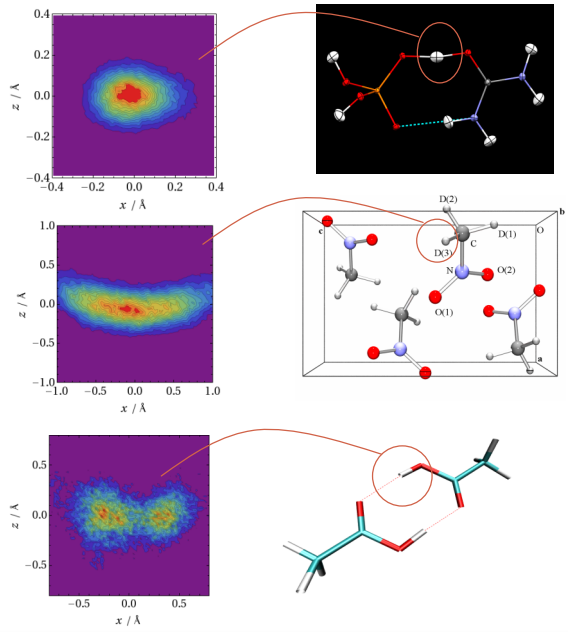


The diagram above shows that poor modelling of the atomic PDF will give rise to a bond distance that is too short. And it matters – in this case the distance correction amounts to x 3 the experimental uncertainty.

Of course, crystallographers are aware of the problem. The current solution is based on an expansion of Hermite polynomials, which are very parameter intensive and the results are rather non-intuitive. Unsurprisingly the scheme is hardly ever used.

We seek an alternative solution. We use simulation (molecular dynamics) to generate numerical atomic PDFs. We then seek simple parametric models that will fit these shapes. The ideal solutions should be analytical, require a minimal number of additional parameters beyond that needed to describe the standard ellipsoid model, and we should be able to obtain the mean position of the distribution in a straightforward fashion. This forms the basis of the project funded through the Informatics IDEAS lab initiative. If successful our new PDFs will be incorporated into public-domain crystallographic software packages.

Below are some examples of numerical atomic PDFs that we recently obtained in our simulations:



IDEA Lab Proposal #09: Parametric models of anharmonic structures