Structure solution of real materials: Charge flipping can help

Ab initio phasing of x-ray powder diffraction patterns by charge flipping, *Nature Materials* **5** 647 (2006)

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Knowledge of structure is a prerequisite for calculating properties and understanding the behavior of materials from the simplest to the most complex. We think of structure solution as a largely solved problem, one of the great successes of 20th century physics, and not something that we tend to worry too much about as it just takes care of itself. This is true for well ordered crystals, but increasingly the materials we care about, real materials, aren't quite like that. What happens then?

Luckily crystallography is quite robust against the introduction of defects and imperfect crystals can still be studied in considerable detail. Some situations cause headaches though: the structures of systems with reduced dimensionality, for example, such as surfaces and interfaces. Reducing dimensionality further we have nanoparticles and their Babinet couple, nanoporous (or mesoporous) materials. Also, increasingly in condensed matter physics, we are interested in nanometer scale structures within otherwise well behaved crystals, as are suspected to be important in strongly correlated electron systems like colossal magnetoresistant and high temperature superconducting materials. Methods that go beyond crystallography are needed for these cases, and developing and applying these methods are active areas of Condensed Matter Physics research.

One situation problematic to crystallography occurs when it is not possible to get a single crystal, but only a powder, of a material. Powder diffraction data is relatively easy to acquire and is useful for refining known structure models using the widely known Rietveld refinement method [1]. In the last 10 years or so, progress has been made in *ab initio* structure solution from powder data [2], finding a structure from scratch without a good starting model, but it remains difficult and success is patchy for reasons we describe below. Wu *et al.* describe the application of the recently developed "charge flipping" algorithm [3] in a very novel approach to this problem. Algorithms come, and sometimes go, but this one is worth keeping an eye on. It is remarkably simple in concept, but has already been implemented in a widely used structure-solution-from-powders software program, TOPAS, and is working above all expectations. It also shows great promise beyond the particular problem of *ab initio* structure

solution from powders and has already been applied to the reconstruction of images from diffraction data.

Powder diffraction data are just single-crystal data that have been collapsed onto a 1-D axis with a concomitant loss of information. The magnitudes of the scattering vectors $\mathbf{h}_{hkl}$ are preserved, but the directions lost. Scattering vectors of similar length become overlapped and their intensities cannot be determined unambiguously, challenging structure solution methods. Still, in favorable cases phase reconstruction algorithms such as "Direct Methods" can be used. Alternatively, "Direct space" approaches can be taken where a global optimization is carried out of real-space structural parameters such as atomic positions using the data as a guide. Often this is coupled with the use of prior knowledge in the form of structural constraints such as the known bonding topology of a molecule in question. On the other hand, as explained in Ref. [3] and in Wu et al., charge flipping is a Fourier cycling method where the data are cycled between direct and reciprocal space and densities in real-space modified. It is outrageously simple, and this is part of the attraction, along with the fact that it seems to work outstandingly well.

Charge-flipping solves the phase problem: the fact that in a diffraction measurement the intensity, rather than the amplitude, of the scattered wave is measured. The lost phase information can be reconstructed if sufficient information in addition to the measured intensities is known and can be used as additional constraints. It turns out that the positivity of the density, and the atomicity of the solution (the density is piled up at discrete points in space with very low density in between) provides strong constraints and allows a solution to be found with good uniqueness. Charge flipping makes use of this information in a very direct way. Start with the square-roots of the measured Bragg-peak intensities; assign random phases to each peak; Fourier transform to get a density. Because of the incorrect phases and missing information the calculated charge density will have positive and negative values. Charge-flipping describes how to update the trial solution, and it is simple. Pick a threshold, δ, which is a number greater than, but close to zero (say a few percent of the strongest peak in density). If the intensity in a given pixel is greater than δ then leave it. If it is less than δ, change its sign. After this update step the data are Fourier transformed back to reciprocal space resulting in a new set of amplitudes and phases for the Bragg peaks. Retain the new phases but replace the amplitudes with the measured ones. This process is then iterated. Somewhat remarkably, the system, after a period of latency, converges towards the correct solution. In this process it is not clear what is the cost-function that is being minimized, but just by enforcing the physical reality of charge density positivity (*small* negative deviations are allowed due to the incomplete data-set and this is why a non-zero δ is chosen), whilst retaining the measured scattering factors, the system settles to a steady-state that is the correct structure. The process is quite robust to noise and missing information in the Bragg pattern. The conceptual simplicity matches that of Monte Carlo yet, surprisingly, the computational efficiency

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seems to match, or exceed, much more elaborate existing algorithms for the phase reconstruction. It is actually somewhat surprising that it works at all.

The implementation described by Wu et al. is interesting in that it combines two problematic areas of structure solution from powders, extracting the intensities and the phase reconstruction, into one step (the space-group of the material is not required for a successful solution, in fact the algorithm works better when that information is not given!). It is fast and seems to be robust. Wu et al. also describe a number of tweaks that improve performance and prevent stagnation. It is fun when something as simple, yet so powerful, comes along.

I would like to acknowledge useful comments and feedback from Dr. Chandra Varma and Prof. John Spence

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