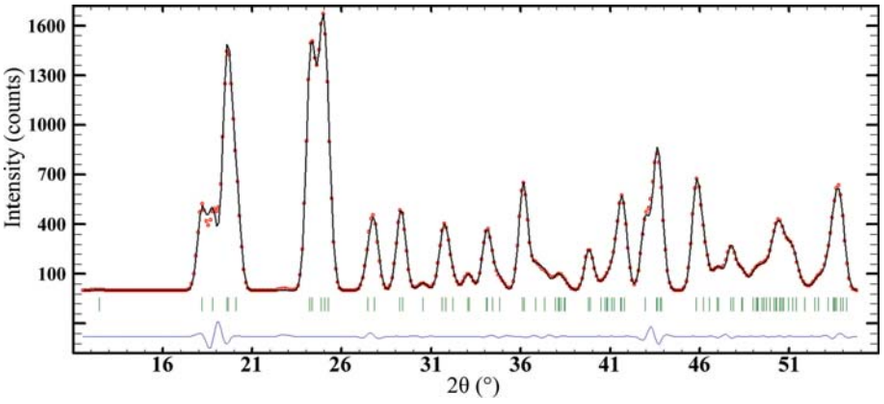

Figure 3.5.1
Data reduction to $|F_{hkl}|$ values for the C_6F_{10} Pawley (1981) test case by the Le Bail method using *FULLPROF*. The neutron powder pattern (4.2 K) was rebuilt (λ = 1.909 Å) from the intensities given in the original paper (*P*2/*m*). The extraction of $|F_{hkl}|$ values was carried out in the space group $P2_1/n$.

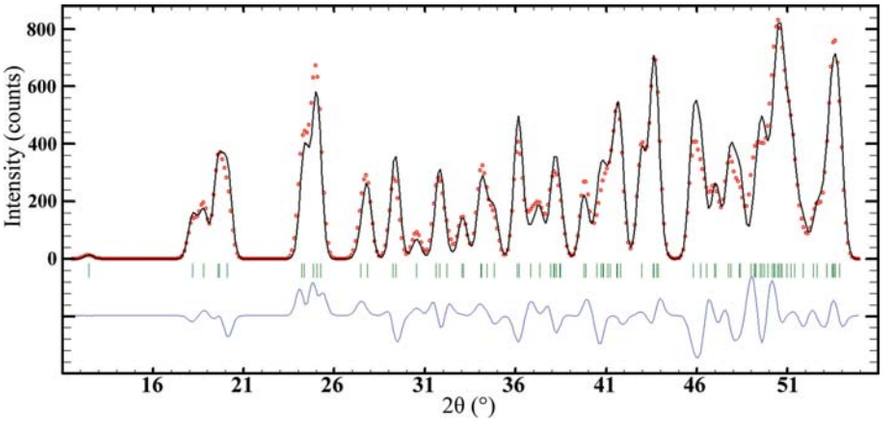

Figure 3.5.2
The C_6F_{10} Monte Carlo molecule positioning by the real-space *ESPOIR* program produces that best fit (R_p = 13.6%) of the pseudo powder pattern built from the previously extracted $|F_{hkl}|$ values (Fig. 3.5.1), overcoming the equipartition problem at the reduction stage. Compared to Fig. 3.5.1, which shows intensities, the multiplicity and geometrical factors are removed, leading to structure-factor amplitudes.

3.5.3.3. *Background-estimation effects*

Logically, a background value will never be higher than the observed intensity at the diffraction angle where it is visually estimated. In the first refinement cycles by the Pawley or Le Bail methods, it is preferable to keep the background fixed as well as the cell parameters, which assumes that the starting values have been carefully estimated or even (in the cell-parameter case) have already been refined from the peak positions that were used for indexing. This is because all refinement processes need to start from parameters close to the final values. Selecting background values leading to negative intensities after background removal could result in negative $|F_{hkl}|$ values if the software does not account for this.

3.5.4. Applications and by-products

The first modern WPPD method with cell restraints was developed for neutron data by Pawley (1981), 12 years after the publication of the paper that described the Rietveld (1969) method. In Le Bail *et al.* (1988) a new WPPD approach was used to extract intensities, making use of iterations of the Rietveld decomposition formula. It is clear that both these WPPD methods are children of the Rietveld method. Today most users of the Rietveld method do not cite the original Rietveld papers, but only refer to the computer program that they used. This is also now increasingly the case for the WPPD methods.

From the Thomson Reuters ISI citation index consulted in May 2015, the papers for the Pawley and Le Bail methods scored 892 and 1425 direct citations, respectively. There are several highly cited papers that then cite these two papers. The most highly cited paper (>5100 times) that cites both WPPD methods concerns use of the Le Bail intensity-extraction method by *FULLPROF* for solving magnetic structures (Rodriguez-Carvajal, 1993). This paper is also given as a reference for *FULLPROF* used in more standard Rietveld refinements. This suggests that the impact of WPPD methods is higher than commonly believed. The list of possible WPPD applications includes phase identification, quantitative phase analysis, measurement of crystallite sizes and strains, creation of Fourier maps for partially solved structures, structure refinement by the two-step method, studies of electron-density distribution, and characterization of pole figures, using either the Pawley or Le Bail methods. All routes to SDPD use at least one of them. WPPD has even entered into the indexing step, with Kariuki *et al.* (1999) using the Le Bail fit for testing cell hypotheses (for which it is faster than the Pawley method) in a new computer program that uses a genetic algorithm. But the main applications of the WPPD methods are to provide support for cell-parameter refinement and the determination of the space group, as a