as the S^2_{hkl}(calc) ones. It is understandable that such an iterative process requires starting cell and profile parameters as good as the Rietveld method itself. The process is easier to incorporate within an existing Rietveld code than the Pawley method, so that most Rietveld codes now include structure-factor amplitudes extraction as an option (generally multiphase), with the possibility of combining Rietveld refinement(s) together with Le Bail fit(s).

A non-exhaustive list of programs applying this method (either exclusively or added within a Rietveld code) includes *MPROF* (Jouanneaux *et al.*, 1990), later renamed *WinMPROF*; *FULLPROF* (Rodriguez-Carvajal, 1990); *EXTRACT* (Baerlocher, 1990); *EXTRA* (Altomare *et al.*, 1995); *EXPO* (Altomare *et al.*, 1999), which is the integration of *EXTRA* and *SIRPOW.92* for solution and refinement of crystal structures; and *RIETAN* (Izumi & Ikeda, 2000). Then followed most well known Rietveld codes (*BGMN*, *GSAS*, *MAUD*, *TOPAS etc.*) or standalone programs (*AJUST* by Rius *et al.*, 1996). In the work of the Giacovazzo group, many modifications of the $|F_{hkl}|$ values for SDPD purposes were applied before or after the extraction and were integrated in *EXPO2011* (Altomare *et al.*, 2011): obtaining information about the possible presence of preferred orientation by statistical analysis of the normalized structure-factor moduli; using the positivity of the Patterson function in the decomposition process, this having been considered previously (David, 1987; Estermann & Gramlich, 1993); characterization of pseudotranslational symmetry used as prior information in the pattern-decomposition process; multiple Le Bail fits with random attribution of intensity to the overlapping reflections, instead of equipartition, followed by application of direct methods to large numbers of such data sets; use of a located structure fragment for improving the pattern-decomposition process; and use of probability (triplet-invariant distribution functions) integrated with the Le Bail algorithm. Another approach for solving the overlapping problem was proposed by using maximum-entropy coupled with likelihood evaluation (Dong & Gilmore, 1998). The list of structure solutions made from intensities extracted by using the Pawley and Le Bail methods is too long to be given here; a partial list (>1000 first cases, including those using $|F_{hkl}|$ values extracted by other methods) can be found on the web (Le Bail, 2007). The first application of the Le Bail method was to the structure solution of $LiSbWO_6$ (Le Bail *et al.*, 1988) using the *ARITB* software.

3.5.3. Pitfalls in the extraction of accurate $|F_{hkl}|$ values using the Pawley and Le Bail methods

In the Rietveld refinement guidelines published by the IUCr Commission on Powder Diffraction (McCusker *et al.*, 1999), it is said that the Rietveld R_{wp} value should approach the value obtained in a structure-free refinement (*i.e.* using WPPD methods). Such a refinement is recommended for the estimation of initial values of the Rietveld profile parameters. Consequently, $|F_{hkl}|$ values extracted by WPPD can be used to make a good reproduction of the experimental powder pattern if the cell is correct (which is ultimately only proven if the structure is solved and refined). Pitfalls can occur during post-treatment and application of the $|F_{hkl}|$ data if one neglects the possible errors that are inherently present due to exact or accidental overlap, preferred orientation effects or wrong background estimations, citing only three of the main possible causes of errors in these $|F_{hkl}|$ values.

3.5.3.1. *Consequences of (exact or accidental) overlap*

The uncertainties of the $|F_{hkl}|$ values of overlapped reflections cannot be overcome in a single powder-diffraction experiment. This problem has led to various approaches, all being more or less inefficient: equipartition, non-equipartition by random distribution *etc*. If direct methods are applied, the trend is to multiply the number of solution attempts, trying to identify the most convincing one by using structural arguments (such as atoms in chemically reasonable positions). When applying real-space methods (which require chemical knowledge, such as the three-dimensional molecular structure or the presence of definite polyhedra) one generally chooses to work either directly on the raw powder pattern or on a pseudo pattern built from the extracted $|F_{hkl}|$ values, so that wrong individual values are less of a problem, since only the sums of the contributions in overlapping regions are checked during the search for the molecule, polyhedra or atom positions. Indeed, working on the raw powder pattern does not need reduction to $|F_{hkl}|$ values in theory, but in practice either the Pawley or Le Bail methods are applied first in order to fix the zero point, background, cell and profile parameters which will then be applied during the structure model checking, and to speed the calculations. The extracted $|F_{hkl}|$ values can be used in mathematical expressions defining correlations induced by the overlap. These equations were developed by David *et al.* (1998) for the Pawley method in the real-space structure solution program *DASH* and by Pagola *et al.* (2000) for the Le Bail method in *PSSP*. Regenerating a powder pattern from the extracted $|F_{hkl}|$ values was carried out in the *ESPOIR* real-space computer program (Le Bail, 2001) using a simple Gaussian peak shape whose width follows the Caglioti relation established from the raw pattern. With such a pseudo powder pattern (without profile asymmetry, background *etc*.), the calculations are much faster than if the raw pattern is used. When using direct methods instead of real-space methods, the approaches are different, because direct methods require a more complete data set (up to d = 1 Å) of accurate $|F_{hkl}|$ values. However, removing up to half of them (those with too much overlap, *i.e.* where the overlap is greater than half the FWHM, for instance) can lead to success with direct methods. One can even remove up to 70–80% of the data if the Patterson method is applied and if only a small number of heavy atoms are to be located.

3.5.3.2. *Preferred-orientation effects*

One has to ensure that preferred orientation is minimized during the recording of the powder pattern if the extracted $|F_{hkl}|$ values are to be used for structure solution. In transmission geometry with a capillary specimen (provided that it is not composed of long needle-shaped particles that are all aligned), there is generally no problem. But in reflection geometry with samples pressed on the holder, preferred orientation is not rare, even if it is not obvious in the data. Collecting a second pattern from a sample dusted onto the holder through a fine sieve can be informative. However, some WPPD applications may not be sensitive to such a problem. If only the cell parameters have to be accurately estimated for thermal-expansion studies (Evans *et al.*, 1996), it can be much faster to use WPPD rather than the Rietveld method. However, it is not recommended to do this systematically, especially if the structure is complex and the resolution is low [see the warnings in Peterson (2005)].

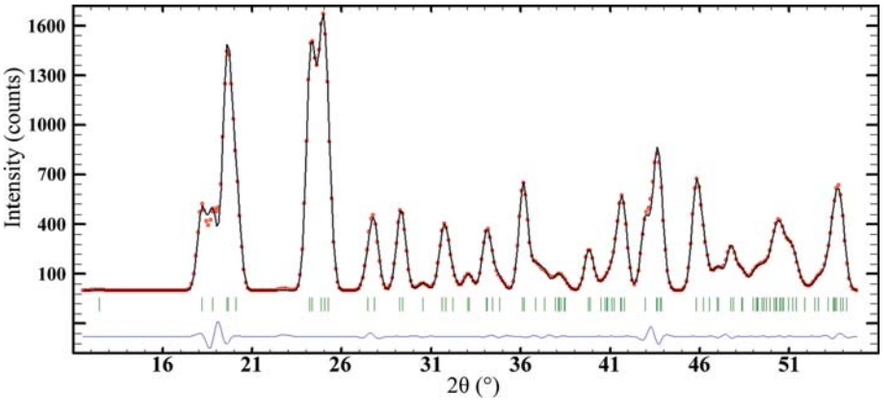

Figure 3.5.1
Data reduction to $|F_{hkl}|$ values for the C_6F_{10} Pawley (1981) test case by the Le Bail method using *FULLPROF*. The neutron powder pattern (4.2 K) was rebuilt (λ = 1.909 Å) from the intensities given in the original paper (*P*2/*m*). The extraction of $|F_{hkl}|$ values was carried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

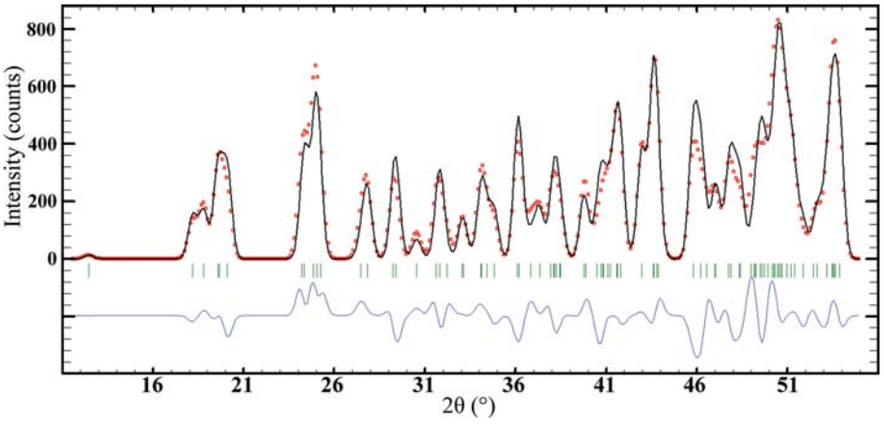

Figure 3.5.2
The C_6F_{10} Monte Carlo molecule positioning by the real-space *ESPOIR* program produces that best fit (R_p = 13.6%) of the pseudo powder pattern built from the previously extracted $|F_{hkl}|$ values (Fig. 3.5.1), overcoming the equipartition problem at the reduction stage. Compared to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