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)].