defines a domain D and, by taking into account the current limits for the parameters A, B, C and β, a calculated pattern is generated, not in terms of discrete $Q(hkl)$ values but of allowed intervals $\left[Q_-(hkl), Q_+(hkl)\right]$. D is retained only if the observed Q_i values belong to the range $[Q_-(hkl) - \Delta Q_i, Q_+(hkl) + \Delta Q_i]$, where ΔQ_i is the absolute error of the observed lines (*i.e.*, impurity lines are not tolerated). If D has been accepted, it is divided into 2^4 subdomains by halving the original intervals $[A_-, A_+]$, $[B_-, B_+]$, $[C_-, C_+]$ and $[\beta_-, \beta_+]$ and new limits $\left[Q_-(hkl), Q_+(hkl)\right]$ are calculated; if a possible solution is found, the dichotomy method is applied iteratively. In case of triclinic symmetry the expression for $Q(hkl)$ in terms of direct cell parameters is too complicated to be treated *via* the successive-dichotomy method; therefore the basic indexing equation (3.4.2) is used. In this case, the $[Q_-(hkl), Q_+(hkl)]$ intervals are set in reciprocal space according to the A_{ij} parameters of (3.4.2). To reduce computing time the following restrictions are put on the (hkl) Miller indices associated with the observed lines: (1) maximum h, k, l values equal to 2 in case of the first five lines; (2) $h + k + l < 3$ for the first two lines.

The outcome of the successive-dichotomy method is not strongly influenced by the presence of a dominant zone. New approaches have been devoted to overcome the limitations of the method with a strict dependence on data accuracy and on impurities (Boultif & Louër, 2004; Louër & Boultif, 2006, 2007), see Section 3.4.4.2).

3.4.3.2. *Non-traditional indexing methods*

New indexing procedures that provide alternatives to the traditional approaches outlined in Section 3.4.3.1 have recently been proposed.

3.4.3.2.1. *The topographs method*

This method (Oishi *et al.*, 2009) is based on the Ito equation (de Wolff, 1957):

$$Q(\mathbf{h}_1 + \mathbf{h}_2) + Q(\mathbf{h}_1 - \mathbf{h}_2) = 2[Q(\mathbf{h}_1) + Q(\mathbf{h}_2)], \qquad (3.4.9)$$

where $Q(\mathbf{h})$ is the length of the reciprocal vector $\mathbf{r}^*_{hkl}$ corresponding to the Miller index vector $\mathbf{h} = (hkl)$. It uses Conway's topograph (Conway & Fung, 1997), a connected tree obtained by associating a graph to each equation of type (3.4.9) and consisting of infinite directed edges. According to Ito's method, if quadrupoles (Q_1, Q_2, Q_3, Q_4) detected among the observed Q_i values satisfy the condition $2(Q_1 + Q_2) = Q_3 + Q_4$, two Miller-index vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ are expected to exist such that $Q_1 = Q(\mathbf{h}_1)$, $Q_2 = Q(\mathbf{h}_2)$, $Q_3 = Q(\mathbf{h}_1 - \mathbf{h}_2)$ and $Q_4 = Q(\mathbf{h}_1 + \mathbf{h}_2)$. If an additional value Q_5 satisfying the condition $2(Q_1 + Q_4) = Q_2 + Q_5$ is found, the graph of the quadrupole (Q_1, Q_2, Q_3, Q_4) grows *via* the addition of the Q_5 contribution; this procedure is iterated. If topographs share a Q value that corresponds to the same reciprocal-lattice vector, then a three-dimensional lattice is derived containing the two-dimensional lattices associated with the original topographs. Three-dimensional lattices are also obtained by combining topographs. The probability that topographs correspond to the correct cell increases with the number of edges of the graph structure. The method is claimed by the authors to be insensitive to the presence of impurity peaks.

3.4.3.2.2. *Global-optimization methods*

Global-optimization methods, widely adopted for solving crystal structures from powder data, have also been successfully applied to indexing. Among them, we provide brief descriptions of genetic algorithms, and Monte Carlo and grid-search methods.

3.4.3.2.2.1. Genetic-algorithm search method

The use of genetic algorithms (GAs) for solving the indexing problem was proposed by Tam & Compton (1995) and Paszkowicz (1996). Since then, Kariuki and co-workers (Kariuki *et al.*, 1999) have combined GAs with a whole-profile-fitting procedure for indexing powder diffraction patterns. This approach exploits the information of the full powder diffraction pattern. It is inspired by the Darwinian evolutionary principle based on mating, mutation and natural selection of the member of a population that survives and evolves to improve future generations. The initial population consists of a set of trial cell parameters, chosen randomly within a given volume range; a full pattern-decomposition process is performed using the Le Bail algorithm (Chapter 3.5) and the agreement between the calculated and observed profiles is derived and used for assessing the goodness of an individual member (*i.e.*, a set of unit-cell parameters). The most plausible cell is therefore found by exploring a six-dimensional hypersurface $R'_{wp}(a, b, c, \alpha, \beta, \gamma)$ and searching for the global minimum of R'_{wp} (see Section 3.4.4.3.2). In contrast to the main traditional methods, whose outcomes depend on the reliability of a set of peak positions, this procedure has the advantage of being insensitive to the presence of small impurity peaks that have a negligible influence on the agreement factor between the experimental and calculated profiles: the global minimum of R'_{wp} is reached if the majority phase is correctly indexed. The main disadvantage of the method is the computing time required, in particular in the case of low symmetry.

3.4.3.2.2.2. Monte Carlo search method

The Monte Carlo approach has also been applied to indexing powder diffraction patterns (Le Bail, 2004; Bergmann *et al.*, 2004; Le Bail, 2008). It exploits all the information contained in the full pattern, randomly generates and selects trial cell parameters, and calculates peak positions to which it assigns the corresponding Miller indices. An idealized powder pattern consisting of peak positions d and extracted intensities I is considered to test the trial cell. The cell reliability is assessed by suitable figures of merit (*e.g.* R_p and McM_{20}, see Section 3.4.2.1). The main drawback of this approach is the significant computing time required, in particular for triclinic systems.

3.4.3.2.2.3. Grid-search method

This performs an iterated 'step-and-repeat search' in the parameter space. It has the advantage of being flexible, exhaustive and not particularly sensitive to impurities or errors, and the disadvantage of being slow (Shirley, 2003).

3.4.4. Software packages for indexing and examples of their use

The different strategies and methods described in Section 3.4.3 have been implemented in a variety of automatic indexing programs (Bergman *et al.*, 2004). Almost all use one of the two different approaches working in parameter space (*i.e.*, unit-cell parameters) or index space (*i.e.*, reflection indices). Only the *EFLECH/INDEX* program (Bergman, 2007), applying the scan/covariance strategy, works in both spaces: in parameter space from cubic down to monoclinic, switching to index space for triclinic. The different indexing methods are classified according to Shirley (2003) in Table 3.4.3. Alternative classifications can be