CrossMark

TECHNICAL ARTICLE

Combined powder X-ray diffraction data and quantum-chemical calculations in EXPO2014

Angela Altomare,[1] Fulvio Ciriaco,[2] Corrado Cuocci,[1,a)] Aurelia Falcicchio,[1] and Flavio Fanelli[1,3]
[1]*Institute of Crystallography (IC), National Research Council, Bari, Italy*
[2]*Department of Chemistry, University of Bari, Italy*
[3]*Department of Pharmacy – Drug Science, University of Bari, Italy*

(Received 14 October 2016; accepted 12 January 2017)

This paper describes new features implemented in the EXPO2014 software and aimed at assisting crystallographers in the use of quantum-chemistry calculations in combination with experimental powder diffraction data. The implemented tools are useful in particular in two important steps of the process of crystal structure determination from powder diffraction data: (1) preparing accurate structural model suitable for crystal structure determination by real-space methods; (2) validating structure determination. The combination of experimental/quantum-chemical methods in EXPO2014 is now managed easily thanks to the following capabilities: (a) converting crystallographic data in input files and reading molecular geometry from output files of a wide variety of computational chemistry packages (GAMESS-US, NWChem, Gaussian, CRYSTAL, ABINIT, QUANTUM ESPRESSO); (b) optimizing the geometry of a molecule using Open Babel's force fields; (c) a graphical interface to run semi-empirical quantum calculation by MOPAC (Molecular Orbital PACkage); (d) producing input file for dispersion-corrected density functional theory. © *2017 International Centre for Diffraction Data.* [doi:10.1017/S088571561700015X]

Key words: structure solution, density functional theory

I. INTRODUCTION

Quantum-chemical calculations have been successfully used to complement the experimental powder X-ray diffraction (PXRD) data at several stages of the crystal structure solution process: (1) Optimization of the molecular geometry in the gas phase to obtain more accurate starting molecular structure models suitable for structure solution by real-space methods. At this stage, different levels of theory can be applied: molecular mechanics (MM), semi-empirical (SE) methods, Hartree–Fock methods, density functional theory (DFT). (2) Minimization of the energy of crystal structure and estimate of reasonable bond distances and angles to be used as chemical restraints in the Rietveld refinement. (3) Energy minimization as the most reasonable approach to compute optimal positions for the H atoms (the accurate location of the H position is a difficult task from PXRD data) to be refined, with unit cell and non-H atomic positions, by the Rietveld method. (4) Selecting the correct structure from a set of potential structures that differ in the torsion angle rotation of functional group (Naelapää *et al.*, 2012) or in the space group, and could not be distinguished on the basis of the PXRD data alone. (5) Geometry optimization with dispersion-corrected DFT (DFT-D) approach in the solid state for refining crystal structure and providing results whose accuracy is comparable with that of single crystal, especially when, the Rietveld refinement yields inaccurate molecular geometry (Smrcok *et al.*, 2013). (7) Assessment of the correctness of experimental crystal structures (van de Streek and Neumann, 2010).

Many packages for quantum-chemistry calculations support the application to periodic systems, expanding the electron orbitals in crystalline solid either in periodic combination of atomic orbital basis sets modulated with plane waves [e.g., GAUSSIAN (Frisch *et al.,* 2013), CRYSTAL (Dovesi *et al.*, 2014)] or in plane wave basis sets alone [e.g., VASP (Kresse and Hafner, 1993), ABINIT (Gonze et al., *2009*), NWCHEM (Valiev *et al.*, 2010), QUANTUM ESPRESSO (Giannozzi *et al.*, 2009), CPMD (CPMD, 1990)]. Several packages are freely available or can be acquired for academic use at relatively low cost. The use of these programs is in general quite easy and requires the preparation of input data files where the user supplies the atomic positions (Cartesian or fractional coordinates), crystallographic data (e.g., unit-cell dimensions, space group, number of atoms per unit cell or in the asymmetric unit), aspects related to the computational method (e.g., density functional, basis set), and type of calculation (e.g., geometry optimization, vibrational analysis, single-point energy). These programs generate output information, which can be analysed, and the final molecular structure, which can be displayed by many programs.

EXPO2014, the evolution of EXPO2013 (Altomare *et al.*, 2013), is a computer program which is able to carry out almost automatically all the steps of the structure solution by PXRD data. It includes new additional features to automate the process of creation of input files and elaboration of the output files created by the quantum-chemistry packages. Quantum-chemistry programs have parallel computing capabilities and can be run on platforms ranging from modern laptops to supercomputers. A typical not expensive hardware could be a multi-core Linux workstation and the time required for the calculation is in the order of magnitude of 100 h for a DFT-optimization on small molecules on a single CPU.

a)Author to whom correspondence should be addressed. Electronic mail: corrado.cuocci@ic.cnr.it

https://doi.org/10.1017/S088571561700015X Published online by Cambridge University Press

PXRD is a powerful and rapid analytical method used for phase identification of crystalline materials, for providing information about unit cell, space groups (Bergmann *et al.*, 2004), and structure model. Powder diffraction also allows for rapid, non-destructive analysis of multi-component mixtures without needing extensive sample preparations. Unfortunately, some problems (diffraction peak overlap and broadening, preferred orientation, and background) make the structure solution process by PXRD a not straightforward task. *Ab initio* structure solution from powder data is still now a challenge in many cases.

In EXPO2014, either *ab initio* procedures by Direct Methods or real-space techniques can be used to deal with PXRD structure solution (David *et al.*, 2002; Dinnebier and Billinge, 2008). Direct Methods are very effective and fast when high-quality data are available, especially synchrotron radiation data, and heavy atoms are present. Their complexity rises with the number of atoms. On the other hand, real-space methods can be applied on large molecular system with a complexity bound to the number of internal degrees of freedom. One of the drawbacks of the real-space methods is the necessity to input an accurate 3D (three-directional) structural model of the asymmetric unit with bond distances, bond angles and ring conformations that should match as closely as possible that of the correct and unknown crystal structure. A starting model for real-space methods can be prepared following essentially two different approaches: (1) searching for similar crystal structure in database [e.g., Cambridge Structure Database (CSD) (Groom *et al.*, 2016), Inorganic Crystal Structure Database (ICSD) (Belsky *et al.*, 2002), Crystallography Open Database (COD) (Grazulis *et al.*, 2009), Pauling File (Villars *et al.*, 2004), ICDD databases with atomic coordinates: PDF-4 + , PDF-4/Minerals, PDF-4/Organics (Faber and Fawcett, 2002)], (2) performing a geometry optimization by using quantum-chemistry packages on the basis of three different levels of quantum-chemistry theories described on the next section, for each of them EXPO2014 provides a specific support. But the use of theoretical calculations is not limited to this preliminary step and can be applied also in the following steps of the process of crystal structure determination from powders.

Experimental powder diffraction data, especially standard laboratory data, could have low/medium-quality information because of preferred orientation, severe reflection overlap, low-resolution, absence of heavy atoms, and rapid decay of scattering power (organic compounds). The quality of data can be sufficient to locate heavy atoms or significant part of molecule by Direct Methods, or to position all molecular fragments in the cell by real-space techniques, but not enough to refine the structure. The refinement of structure can require the use of restraints and constraints to stabilize the refinement especially when the number of refined parameters is large. The hydrogen atoms are normally placed in calculated positions during structure refinement calculations rather than explicitly refined, leaving a great uncertainty in the position of terminal H-atoms (e.g., hydrogens in methyl group, hydroxyl group, and aminic group), frequently important in the definition of hydrogen bond network. In this scenario, the DFT-optimization can be used as an independent source of information for obtaining accurate bond distances and angles that should be used as restraints in the Rietveld analysis, and in an accurate location of hydrogen atoms. At the end of the structure refinement, the DFT-D method can be used to assess the correctness of the experimental crystal structure.

II. EXPERIMENTAL

A. Geometry optimization through MM force field

In MM, the forces acting on atoms are not described on the basis of a solution of the electron wavefunction, but of a simplified geometrical model responding to chemical knowledge of fragments of the structure, with parameters derived either from experiment or from quantum-chemistry calculations. Such models and their parameters are named "force fields" and are usually specific to compound classes, though a few of them attempt to cope with all the periodic table.

The total potential energy is typically taken to be the sum of the bond stretching energy E_{str}, the bending energy E_{bend}, the twisting (or torsion) energy E_{tor}, and the energy of interaction between non-bonded atoms $E_{non\text{-}bond}$. The last contribution includes van der Waals, steric, and electrostatic interactions between atoms not chemically bound.

$$E_{tot} = E_{str} + E_{bend} + E_{tor} + E_{non-bond}. \quad (1)$$

To optimize the molecular geometry and find the most stable conformation, each of the forces f_i acting on a nucleus must vanish:

$$f_i = -\partial E_{tot}/\partial q_i = 0, \quad (2)$$

where q_i are the nuclear coordinates of the ith atom.

In EXPO2014, two MM force fields can be used: (1) the Merck molecular force field (MMFF) for organic molecules and biomolecules (Halgren, 1996); (2) the universal force field (UFF), which accounts for all the periodic table. This is widely used for system containing inorganic elements (Rappe *et al.*, 1992). In EXPO2014, the support for MM is provided using the class OBForceField from the library Open Babel (O'Boyle *et al.*, 2011). The geometry optimization by MM can be carried out by the EXPO2014 menu "Optimize Geometry" (Figure 1). Clicking on "Tools" > "Optimize Geometry" > "Optimize", the MMFF94 force field will be applied and, in case of failure (e.g., inorganic elements), an UFF calculation will be executed. The initial molecular geometry can always be restored clicking on "Modify" > "Undo". The geometry optimization can also be applied only on an atom selection ("Tools" > "Optimize Geometry" > "Optimized Selected Atoms"). For example, if one is interested in optimizing only the position of H atoms and fixing the position of all other atoms you can choose "Select" > "Select Type" > "H atoms" and then "Tools" > "Optimize Geometry" > "Optimize Selected Atoms".

The two salient features of MM calculations on small to medium-sized molecules are that they are fast and they can be very accurate, especially on organic compounds, for which the force fields are very detailed. MM calculations might still take only seconds. MM, even when it does not provide very accurate geometries, can supply reasonably good structures for other kinds of calculations: SE, *ab initio* or DFT; and this is undoubtedly one of its main application.

https://doi.org/10.1017/S088571561700015X Published online by Cambridge University Press

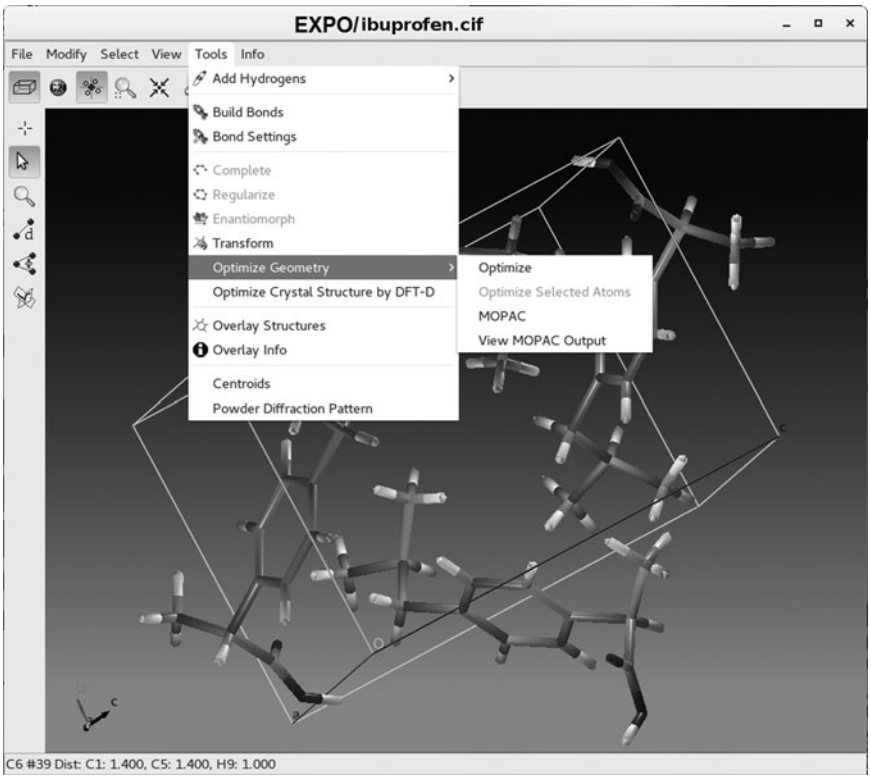


Figure 1. Menu for geometry optimization in EXPO2014.

B. Geometry optimization with Molecular Orbital PACkage (MOPAC)

MM force fields do not include an explicit treatment of the electrons and therefore do not well account for a variety of effects. In particular, the molecular potential energy cannot always be well described as a sum of bond and angles terms, and the parametrization of forces for elements with a wide variance of nearest-neighbour geometries or bond lengths may be unfeasible.

The determination of the electron structure is typically a quantum problem, the solution of which is numerical and subject to different possible levels of approximation. As usual, in quantum mechanics, it starts with the Schrödinger equation:

$$H\Psi = E\Psi, \tag{3}$$

where H, the Hamiltonian operator, summarizing the kinetic energy, all the particle–particle interactions inside a molecule and interaction with the external field (usually because of other molecules, like in the condensed state). The lowest energy state can be estimated by the minimization of the energy associated with the wave function. The wavefunction is a complicated many particle function, usually described in terms of orbitals, single-particle functions composed to yield a correct form for the wavefunction. Nowadays, the most profitable descriptions of the molecular energy, in the context of geometry resolution are two: (1) a model simplified Hamiltonian with parameters derived from experimental datasets and quantum calculations of high accuracy, denoted as SE, fast, and especially accurate for compounds belonging to the same classes as those found in the experimental datasets. (2) The density functional energy, describing all the energy in terms of the orbitals and their associated electron density, much slower than SE methods but covering all molecules.

MOPAC (MOPAC2016, 2016) is one of the most widely used semi-empirical software packages and is designed for a wide range of functionality. We tested version 2012 and 2016. MOPAC is not distributed with EXPO2014, so a copy of the software needs to be separately downloaded. For more information or to obtain a copy, please visit http://www.openmopac.net/MOPAC2016.html, the software is currently free for academic use.

An interface to MOPAC is provided in EXPO2014 and allows users to perform a gas-phase geometry optimization. This approach is useful to generate molecular models with accurate angles and bond lengths, suitable as a starting model for structure solution by real-space methods. The advantage of SE calculations is that they are much faster than self-consistent field method (SCF) or DFT methods and can be applied routinely to large system. A MOPAC optimization is performed selecting "Tools" > "Optimize Geometry" > "MOPAC" from the principal menu. The calculation is performed by choosing some options in the MOPAC dialogue window (Figure 2). This dialogue window allows the user to: (1) define the title of the calculations, e.g., the name of molecule. It is then reported in the second line of the MOPAC input file. (2) Specify the SE Hamiltonian used in the electronic part of the calculation to obtain molecular orbitals and the associated energy. Not all chemical elements are supported by every selected Hamiltonian. (3) Write the charge of the system under study. (4) Allow the user to specify the number of singly occupied orbitals. Singlet is the default, and specifies a closed shell (most organic and low atomic weight molecules); doublet specifies one singly occupied orbital (e.g., organic radicals); triplet specifies two singly occupied orbitals; and so on. If the multiplicity is unknown, trying each sensible case is advisable. (5) Specify if the molecular geometry is described using the Cartesian coordinate definition or the Gaussian *Z*-matrix format. The position of molecule in the cell unit will be lost if the geometry is defined

https://doi.org/10.1017/S088571561700015X Published online by Cambridge University Press

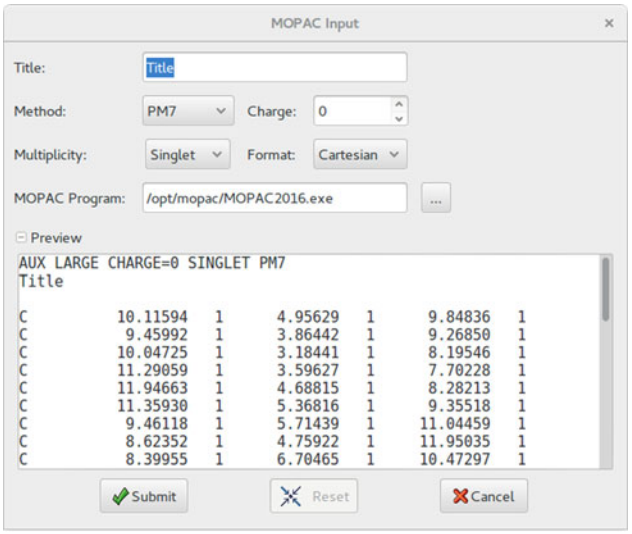


Figure 2. (Colour online) Dialogue for generating input file for MOPAC.

in *Z*-matrix format. (6) Specify the folder where the MOPAC executable file is located. EXPO2014 automatically locates the position where MOPAC exists if MOPAC is installed in a standard directory (C:/Program Files/MOPAC/on Windows, /opt/mopac/on Linux) or the environment variable PATH includes the installation directory; otherwise the MOPAC executable must be specified directly by the user. By selecting *Submit*, MOPAC will be started and at the end of the geometry optimization, the new geometry will be displayed and an output file will be produced in the working directory. The output file can be viewed inside EXPO: ("Tools" > "Optimize Geometry" > "View MOPAC Output"). Previously generated MOPAC output files can be read and the molecular geometry can be displayed through the menu "File" > "Import Structure" and selecting "MOPAC Output File (*.out)" in the file extension menu.

It is important to note that these calculations require the inclusion of hydrogen atoms that are normally excluded in structure solution calculations from PXRD. Selecting "Add Hydrogens" in the menu "Tools", it is possible to assign sensible positions of H-atoms. Wrong starting geometry, missing hydrogens or wrong multiplicity are possible causes of incorrect result. In this situation, the use of "Modify" > "Undo Optimize Geometry" to restore the initial geometry is suggested. Then the output file can be read to find a possible cause of error. Additional calculations can be performed by clicking the *Preview* button and changing the input file. For example, the keyword *NOOPT* can be used to perform only an energy calculation; the calculated energy will be written in the output file. The use of the keyword *NOOPT OPT-H* is devoted to optimize the positions of hydrogen atoms while freezing the positions of all other atoms.

C. Geometry optimization by DFT

An approach that has gained increasing prominence in recent years is DFT, in particular in the Kohn–Sham formulation (Kohn, 1999; Sholl and Steckel, 2009). This is the only formulation for which there is ample coverage in the mentioned quantum-chemistry programs. The electron density is expressed in terms of a set of orbitals, and the energy is obtained from functionals of the density matrix (kinetic energy) or of the electron density alone. Some part of this, usually denoted $E_{XC}[\rho]$, is fruit of approximation and several prescriptions for it can be found in the DFT literature. The correct choice of the density functional is important to the calculation of several molecular properties, but not so much in the geometry optimization, except when two geometries must be distinguished which differ in energy by a small value, typically <20 kJ mol^{-1}.

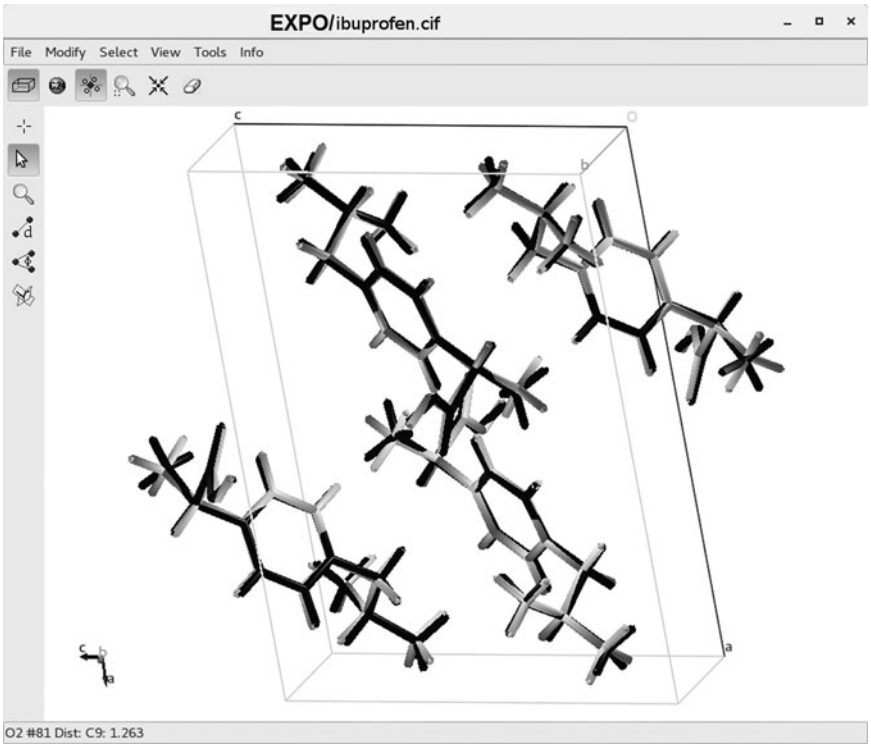


Figure 3. Example of overlaid between experimental (black) and optimized (grey) crystal structures of ibuprofen. The optimization was performed by using DFT-D3 in NWChem.

https://doi.org/10.1017/S088571561700015X Published online by Cambridge University Press

DFT is rather efficient; the computational suites optimize the code to scale almost linearly with the number of electrons, so as to make affordable computations with a large number of electrons on modern hardware. It can be used for crystalline solids with hundred atoms per unit cell, which is a sufficient number for the application in the field of powder diffraction. EXPO2014 is able to create input files for well-known quantum-chemistry programs, selecting "File" > "Import Structure" from its main menu. Input files for GAMESS-US (Schmidt *et al.*, 1993) and NWChem contain keywords for geometry optimization by DFT calculations to perform using the B3LYP functional (Stephens *et al.*, 1994) and a standard 6–31G* basis set (Hehre *et al.*, 1972).

One of the most widely used applications of the DFT is the validation of experimental molecular crystal structures. This type of calculation is generally performed by using plane-wave DFT with GGA (generalized gradient approximation) functionals such as PBE (Perdew *et al.*, 1996) and PW91 (Perdew and Wang, 1992). The long-range dispersive interactions (London or attractive van der Walls forces), which play an incredibly important role in determining the structure and the properties of molecular crystal and are not included in the DFT Hamiltonian, are described applying specific correction schemes such as DFT-D3 (Grimme *et al.*, 2010) and TS (Tkatchenko and Scheffler, 2009). The procedure is simple: a geometry optimization is performed using, as starting molecular geometry, the experimentally determined coordinates of the crystal structure. The final calculated crystal structure is compared with the experimental one. By using "Tools" > "Optimize Crystal Structure by DFT-D", EXPO2014 can create input files for the optimization of crystal structure by DFT-D3 with functional PBE. Currently, the supported software are NWChem, ABINIT, CRYSTAL, and QUANTUM ESPRESSO. The input files generated for these software can be directly used to run the crystal structure validation or can require only minor modifications. At the end of the DFT-optimization, the output file generated by the quantum-chemistry software can be imported in EXPO2014 and the calculated crystal structure can be visually compared with the experimental one by using "Tools" > "Overlay Structures" to generate an overlaid (Figure 3). The quality of the agreement between the experimental and the theoretical structure can be evaluated in terms of root-mean-square displacement (RMSD) calculated for all non-H atoms. According to a recent paper (van de Streek and Neumann, 2010), the value of RMSD never exceeds 0.25 Å for correct crystal structure. RMSD information is also available in EXPO2014 by "Tools" > "Overlay info".

III. CONCLUSIONS

EXPO2014 has recently added features to support the increasing application of quantum-chemistry calculations as complementary tools to the structure determination from powder diffraction data. EXPO2014 can assist the user in preparing input files for quantum codes such as MOPAC, GAMESS-US, NWChem, GAUSSIAN, ABINIT, CRYSTAL, and QUANTUM ESPRESSO. Input files can be directly run for geometry optimization of molecules or to automate the procedure of crystal structure validation. Only for MOPAC a graphic dialogue has been developed and present the basic features required to run basic quantum calculations. In addition, a quick optimization through the force fields provided by the Open Babel can be performed.

ACKNOWLEDGEMENTS

The authors thank Dr. Caterina Chiarella of the Institute of Crystallography (Bari, Italy) for technical support.

Altomare, A., Cuocci, C., Giacovazzo, C., Moliterni, A., Rizzi, R., Corriero, N., and Falcicchio, A. (**2013**). "EXPO2013: a kit of tools for phasing crystal structures from powder data," J. Appl. Crystallogr. **46**, 1231–1235.

Belsky, A., Hellenbrandt, M., Karen, V. L., and Luksch, P. (**2002**). "New developments in the Inorganic Crystal Structure Database (ICSD): accessibility in support of materials research and design," Acta Crystallogr. B **58**, 364–369.

Bergmann, J., Le Bail, A., Shirley, R., and Zlokazov, V. (**2004**). "Renewed interest in powder diffraction data indexing," Z. Kristallogr. **219**, 783–790.

CPMD (**1990**). http://www.cpmd.org/, Copyright IBM Corp 1990–2015, Copyright MPI für Festkörperforschung Stuttgart 1997–2001.

David, W. I. F., Shankland, K., McCusker, L. B., and Baerlocher, Ch. (**2002**). *Structure Determination from Powder Diffraction Data* (Oxford University Press, New York). IUCr Monograph on Crystallography 13.

Dinnebier, R. E. and Billinge, S. J. L. (**2008**). *Powder Diffraction: Theory and Practice* (RCS Publishing, Cambridge).

Dovesi, R., Orlando, R., Erba, A., Zicovich-Wilson, C. M., Civalleri, B., Casassa, S., Maschio, L., Ferrabone, M., De La Pierre, M., D'Arco, P., Noel, Y., Causa, M., Rerat, M., and Kirtman, B. (**2014**). "CRYSTAL14: a program for the *ab initio* investigation of crystalline solids," Int. J. Quantum Chem. **114**, 1287–1317.

Faber, J. and Fawcett, T. (**2002**). "The Powder Diffraction File: present and future," Acta Crystllogr. B **58**, 333–337.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J. (**2013**). Gaussian 09, Revision D.01 (Computer Software), Gaussian, Inc., Wallingford, CT, United States.

Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G. L., Cococcioni, M., Dabo, I., Dal Corso, A., Fabris, S., Fratesi, G., de Gironcoli, S., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzari, N., Mauri, F., Mazzarello, R., Paolini, S., Pasquarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Sclauzero, G., Seitsonen, A. P., Smogunov, A., Umari, P., and Wentzcovitch, R. M. (**2009**). "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials," J. Phys.: Condens. Matter. **21**, 395502–395520.

Gonze, X., Amadon, B., Anglade, P. M., Beuken, J.-M., Bottin, F., Boulanger, P., Bruneval, F., Caliste, D., Caracas, R., Cote, M., Deutsch, T., Genovese, L., Ghosez, Ph., Giantomassi, M., Goedecker, S., Hamann, D., Hermet, P., Jollet, F., Jomard, G., Leroux, S., Mancini, M., Mazevet, S., Oliveira, M. J. T., Onida, G., Pouillon, Y., Rangel, T., Rignanese, G.-M., Sangalli, D., Shaltaf, R., Torrent, M., Verstraete, M. J., Zérah, G., and Zwanziger, J. W. (**2009**). "ABINIT : first-principles approach to material and nanosystem properties," Comput. Phys. Commun. **180**, 2582–2615.

Grazulis, S., Chateigner, D., Downs, R. T., Yokochi, A. F. T., Quiros, M., Lutterotti, L., Manakova, E., Butkus, J., Moeck, P., and Le Bail, A.

https://doi.org/10.1017/S088571561700015X Published online by Cambridge University Press

(**2009**). "Crystallography Open Database – an open-access collection of crystal structures," J. Appl. Crystallogr. **42**, 726–729.
Grimme, S., Antony, J., Ehrlich, S., and Krieg, H. (**2010**). "A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu," J. Chem. Phys. **132**, 154104–154119.
Groom, C. R., Bruno, I. J., Lightfoot, M. P., and Ward, S. C. (**2016**). "The Cambridge Structural Database," Acta Crystallogr. B **72**, 171–179.
Halgren, T. A. (**1996**). Merck molecular force field. I. Basis, form, scope, parameterization, and performance of MMFF94," J. Comput. Chem. **17**, 490–519.
Hehre, W. J., Ditchfield, R., and Pople, J. A. (**1972**). "Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type basis sets for use in molecular orbital studies of organic molecules," J. Chem. Phys. **56**, 2257–2261.
Kohn, W. (**1999**). "Nobel lecture: electronic structure of matter-wave functions and density functionals," Rev. Mod. Phys. **71**, 1253–1266.
Kresse, G. and Hafner, J. (**1993**). "Ab initio molecular dynamics for liquid metals," Phys. Rev. B **47**, 558–561.
MOPAC2016 (**2016**). *James J. P. Stewart, Stewart Computational Chemistry* (Colorado, CO, USA, Springs). http://OpenMOPAC.net.
Naelapää, K., van de Streek, J., Rantanen, J., and Bond, A. D. (**2012**). "Complementing high-throughput X-ray powder diffraction data with quantum-chemical calculations: application to piroxicam form III," J. Pharm. Sci. **101**, 4214–4219.
O'Boyle, N. M., Banck, M., James, C. A., Morley, C., Vandermeersch, T., and Hutchison, G. R. (**2011**). "Open Babel: an open chemical toolbox," J. Cheminf. **3**, 33.
Perdew, J. P. and Wang, Y. (**1992**). "Accurate and simple analytic representation of the electron-gas correlation energy," Phys. Rev. B **45**, 13244–13249.
Perdew, J. P., Burke, K., and Ernzerhof, M. (**1996**). "Generalized Gradient approximation Made simple," Phys. Rev. Lett. **77**, 3865–3868.
Rappe, A. K., Casewit, C. J., Colwell, K. S., Goddard, V. A. III, and Skiff, W. M. (**1992**). "UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations," J. Am. Chem. Soc. **114**, 10024–10035.
Stephens, P., Devlin, F., Chabalowski, C., and Frisch, M. (**1994**). "Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields," J. Phys. Chem. **98**, 11623–11627.
Sholl, D. S. and Steckel, J. A. (**2009**). *Density Functional Theory: A Practical Introduction* (John Wiley & Sons, Inc., Hoboken).
Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M., and Montgomery, J. A. (**1993**). "General atomic and molecular electronic structure system," J. Comput. Chem. **14**, 1347–1363.
Smrcok, L., Mach, P., and Le Bail, A. (**2013**). "Decafluorocyclohex-1-ene at 4.2 K – crystal structure and theoretical analysis of weak interactions," Acta Crystallogr. B **69**, 395–404.
Tkatchenko, A. and Scheffler, M. (**2009**). "Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data," Phys. Rev. Lett. **102**, 73005–73008.
Valiev, M., Bylaska, E. J., Govind, N., Kowalski, K., Straatsma, T. P., van Dam, H. J. J., Wang, D., Nieplocha, J., Apra, E., Windus, T. L., and de Jong, W. A. (**2010**). "NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations," Comput. Phys. Commun. **181**, 1477–1489.
van de Streek, J. and Neumann, M. A. (**2010**). "Validation of experimental molecular crystal structures with dispersion-corrected density functional theory calculations," Acta Crystallogr. B **66**, 544–558.
Villars, P., Berndt, M., Brandenburg, K., Cenzual, K., Daams, J., Hulliger, F., Massalski, T., Okamoto, H., Osaki, K., Prince, A., Putz, H., and Iwata, S. (**2004**). "The PAULING FILE, Binaries Edition," J. Alloys Compd. **367**, 293–297.

https://doi.org/10.1017/S088571561700015X Published online by Cambridge University Press