The PAW/GIPAW approach for computing NMR parameters: A new
dimension added to NMR study of solids

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ABSTRACT

In 2001, Mauri and Pickard introduced the gauge including projected augmented wave (GIPAW) method that enabled for the first time the calculation of all-electron NMR parameters in solids, i.e. accounting for periodic boundary conditions. The GIPAW method roots in the plane wave pseudopotential formalism of the density functional theory (DFT), and avoids the use of the cluster approximation. This method has undoubtedly revitalized the interest in quantum chemical calculations in the solid-state NMR community. It has quickly evolved and improved so that the calculation of the key components of NMR interactions, namely the shielding and electric field gradient tensors, has now become a routine for most of the common nuclei studied in NMR. Availability of reliable implementations in several software packages (CASTEP, Quantum Espresso, PARATEC) make its usage more and more increasingly popular, maybe indispensable in near future for all material NMR studies. The majority of nuclei of the periodic table have already been investigated by GIPAW, and because of its high accuracy it is quickly becoming an essential tool for interpreting and understanding experimental NMR spectra, providing reliable assignments of the observed resonances to crystallographic sites or enabling a priori prediction of NMR data. The continuous increase of computing power makes ever larger (and thus more realistic) systems amenable to first-principles analysis. In the near future perspectives, as the incorporation of dynamical effects and/or disorder are still at their early developments, these areas will certainly be the prime target.

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1. Introduction

During the last decade, solid state NMR spectroscopy has seen many major complementary developments in hardware design (i.e. ultra-high magnetic field and ultra-high sample spinning frequency), pulse sequence design [1–3] and even in the theoretical framework [4,5]. These developments offer a wealth of methodologies to gain insight into the structure and the dynamics of a wide range of solid materials, from inorganic [6–8] to organic [9,10] and to hybrid materials [11]. From those achievements, ever more precise information on the local environment of atoms can be obtained, as being characterized by the four major NMR interactions that can be measured in (diamagnetic) solids: the chemical shift tensor $\sigma$, the quadrupolar or equivalent electric field gradient tensor $Q$, the J coupling tensor $J$ and the dipolar coupling tensor $D$. This yields the NMR spin Hamiltonian (or sometimes referred to as the effective Hamiltonian in quantum chemistry) as

$$H = -\sum_{k} \gamma_k I_k (1-\sigma_k) B_0 + \sum_{k < l} I_k (D_{kl} + J_{kl}) I_l + \sum_{k} J_{kQ} I_k$$

(1)

The summations run all over nuclear spins with gyromagnetic ratio $\gamma_k$. Due to their direct dependence upon geometrical factors, dipolar couplings have received much of the attention in the last decades as a probe of spatial proximities or for a direct evaluation of interatomic distances. Through bond connectivities are given by J couplings and are more and more popular. For the spectroscopic parameters $\sigma$, $Q$ and $J$ which characterize the NMR spectral signature, sophisticated quantum chemical calculations are required because of their intrinsic link with the electronic fundamental state. Putting $a$ priori a spectrum on a structure has been a long-standing problem in solid-state NMR. Since recently, most of these quantum calculations were exclusively performed using cluster approximations of the local surrounding of the atoms of interest, making use of localized atom-centered basis sets or molecular orbitals (MO), as recently reviewed in [12,13]. Such an approach has clearly proven its usefulness in getting more (quantitative) insight into relationships between NMR parameters and local structural features (typically bond angles or bond lengths) [14–17]. However, they are many circumstances where the cluster approximation is by far too much limited for the description of realistic solids, for example accounting for the long range intermolecular or electrostatic interactions, the cationic chemical disorder in ceramics or the structural disorder in glasses. Being all-electron calculations (the wave function near the nucleus is needed to compute the NMR properties), the computational cost of MO approaches becomes prohibitive with the size of the system increasing. Therefore, there was a clear need for NMR spectroscopists of an alternative method, accounting for the main features of the solid state (periodic boundary conditions, long range interactions, etc.). Quantum chemical calculations using plane wave expansion within the numerically efficient pseudopotential DFT formalism had reached a level of high maturity [18]. This was therefore the theoretical framework of choice for the introduction of the GIPAW method. Other periodic methods have been devised such as Linear Augmented Plane Waves (LAPW), an accurate all-electron approach (implemented in the popular WIEN2K package) that includes only the computation of the Electric Field Gradient (EFG) tensor [19].

Here, we summarize the successive progress and extension made in devising the GIPAW method. We first describe the main ideas underlying the PAW/GIPAW approach within the plane wave pseudopotential DFT formalism. An overview of how a typical calculation proceeds and of the main parameters for the end-user is also given. A general view of the nuclei that have been investigated with GIPAW is presented in the second section, pointing out the successes and current limitations of the method. The third section outlines the first applications of GIPAW in the context of NMR crystallography: importance of structure optimization, spectral assignment and structure refinement, hydrogen bonds in organic solids, $a$ priori prediction of NMR parameters. The last sections describe the methodologies developed to account for dynamics and finite temperature effects, chemical disorder in crystalline materials and structural disorder in glasses, respectively.

2. The PAW/GIPAW method

2.1. A brief overview of plane-wave pseudopotential DFT formalism

The plane wave pseudopotential formalism of density function theory (DFT) is now well established and its detailed description is out of the scope of the present review [18]. For our purpose, it is sufficient to say that it provides an efficient theoretical and computational route to determine the ground state energy $E_0$ of any system of electrons. This energy was demonstrated to be determined by the ground state electronic density $n_0(r)$ alone, i.e. through a functional form denoted as $E_0[n_0(r)]$. In other words, it is sufficient to determine $n_0(r)$ to compute the ground state energy from which most of the fundamental properties of the solid can be computed such as lattice parameters or mechanical properties. Within the Kohn–Sham formalism, one defines a set of non-interacting one-electron orbitals $\phi_i(r)$ allowing the computation of $n_0(r)$ as

$$n_0(r) = \sum_{\text{occ}} |\phi_i(r)|^2$$

(2)

where the summation runs over the occupied orbitals. Those orbitals are obtained from Schrödinger-like Kohn–Sham equations

$$\left\{ \frac{1}{2} \nabla^2 + V_0[n_0(r)] + V_{\text{ext}}(r) + V_{\text{xc}}[n_0(r)] \right\} \phi_i(r) = \varepsilon_i \phi_i(r)$$

(3)

where the first term is the kinetic energy, $V_0[n_0(r)]$ is the Hartree potential (electron–electron repulsion), $V_{\text{ext}}(r)$ is the external potential (electron–nuclei interactions) and $V_{\text{xc}}[n_0(r)]$ is the so-called exchange-correlation (XC) potential. The first two contributions are Coulombic interactions and possess analytical expressions. Accordingly, their computation from $n_0(r)$ is straightforward, at least formally. It should be remembered that the Kohn–Sham orbitals correspond to a fictitious non-interacting system with the same electron density as the correct many-body function. The quantum mechanics lies in the XC potential which is the (functional) derivative of the XC energy with respect to the density $n_0(r)$ (and small compared to other terms). If in principle it incorporates exchange energy and all electron correlations effects, its exact form is still unknown. One has therefore to resort to approximations, which are an intensive area of research. Many functionals have been devised that can perform very differently with respect to the calculated
property. In the scope of the present review on the DFT computation of NMR parameters, the most popular functional are the Generalized Gradient Approximation from Perdew–Brueck–Ernzerhof (GGA-PBE) [20] and the GGA-PW91 from Perdew–Wang [21]. It must be emphasized that only a few comparisons of the performance between different functionals have been reported so far in GIPAW contexts [22,23].

Eq. (3) is solved iteratively, starting from an approximated \( n(r) \) (generally built from atomic orbitals) until self-consistency of \( n(r) \) or convergence of the total energy \( E_0 \) is achieved to the required precision (as specified by the user).

For numerical implementation, it is necessary to expand the Kohn–Sham orbitals using a set of basis functions. From Bloch’s Theorem arising from the periodic boundary conditions and crystal symmetries (the analog of the popular Floquet theorem in the NMR community), one has

\[
\phi_j(r) = \sum_k \alpha_{j,k} \exp(-i\mathbf{k}\mathbf{r}) u_{j,k}(r)
\]

where the summation runs over the reciprocal vectors \( \mathbf{k} \), usually chosen as an equidistant mesh in the first Brillouin zone defined the crystallographic unit cell. \( u_{j,k}(r) \) are periodic functions with respect to the real space lattice vectors. Among many possible choices, it is therefore natural to expand the latter in terms of plane waves as

\[
u_{j,k}(r) = \sum_G c_{j,k}(G) \exp(-i\mathbf{G}\mathbf{r})
\]

The plane waves basis has several advantages: simplicity, efficiency, independence from atomic positions (in contrast to localized orbitals basis sets) and an easy parallel implementation of matrix–vector products through the fast Fourier transform. Another advantage is the fact that the quality of this basis set is adjusted through a single and variational parameter: the cutoff (kinetic) energy \( E_{\text{cut}} \) restricting the summation in Eq. (5) to wavelengths fulfilling the condition

\[ |k + G_{\text{max}}|^2 < 2E_{\text{cut}} \]

However such calculations will be still computationally prohibitive because of the number of electrons and the nodal properties of the orbitals which require a high plane wave cutoff \( E_{\text{cut}} \). The pseudopotential method aims at a drastic reduction of the number of electrons keeping explicitly only the valence electrons. The core electrons are frozen in their atomic configuration or in any other relevant reference configuration depending on the system of interest. The core-valence interactions are replaced by an effective potential, namely the pseudopotential. Valence electrons can then be represented by a nodeless (i.e. smooth) pseudo-wave function which significantly reduces the number of plane waves in the expansion Eq. (5). By construction, the pseudopotential model reproduces exactly the valence state properties in the reference state and its close vicinity; it treats the valence electrons as moving in a background of ionic cores. The most popular form of the pseudopotential is the so-called norm-conserving pseudopotential which follows the Martin–Troullier recipe [24] in the Kleinman–Bylander form [25]. However, the so-called ultrasoft pseudopotentials which use a generalized formalism [26] (which is a close cousin of the PAW approach [27]), are now more common as they increase the efficiency of the DFT calculations for the whole periodic table (see Section 3). The use of a reliable pseudopotential is crucial in DFT calculations. As constructed numerically from an atomic calculation, its transferability to other chemical environments has to be checked. In general, the accuracy of the predictions of properties of simple structures (such as the lattice parameters) is used as an assessment of the pseudopotential quality, and now NMR properties can be part of it as well. Pseudopotentials are generally available in libraries delivered along with most of DFT software packages. Availability of reliable pseudopotentials has certainly greatly contributed to the quick widespread usage of the GIPAW method.

2.2. Computation of NMR parameters

As a direct function of the ground state, the computation of the electric field gradient (EFG) tensor is, in principle, straightforward. \( x, \beta \) denoting the Cartesian coordinates, its components \( V_{x,y}(r) \) can be calculated from the charge density \( n(r) \) as

\[
\overline{\mathbf{B}}_{\text{ind}}(r) = \int dr \frac{\mathbf{m}(r)}{|r-r'|} \left\{ \frac{\delta_{x,y} - 3(r_x r_x - r_y r_y)}{|r-r'|^3} \right\}
\]

Eq. (7) highlights the fact that the EFG tensor depends upon the charge density close to the nucleus. As the pseudo-valence density has a non-physical form in the core region, one has to reconstruct the true density, i.e. all-electron, in that region. This is the purpose of the projector augmented wave (PAW) method [28–31]. It introduces a linear transformation that uses predefined functions, i.e. the projectors, to reconstruct the true all-electron wave function in the core region from the pseudo-wave function. Computationally the calculation of the EFG tensor is very short, once the charge density of the ground state has been determined (i.e. converged). The simple dependence of the electric field gradient upon \( n(r) \) in Eq. (7) was recently outlined as providing a simple mean for extending its computation to the case of paramagnetic materials [32].

The magnetic shielding tensor is defined through the response of the system to an external uniform magnetic field. It relates the magnetic shielding tensor to the applied external magnetic field \( \mathbf{B}_0 \) according to

\[
\overline{\mathbf{B}}_{\text{ind}}(r) = -\sigma(r) \cdot \mathbf{B}_0
\]

In the GIPAW method [33], the determination of \( \overline{\mathbf{B}}_{\text{ind}}(r) \) proceeds through the calculation of the first-order induced current density \( \mathbf{j}^{(1)}(r) \) which reads

\[
\mathbf{j}^{(1)}(r) = \sum_j \langle \mathbf{J}^{(0)}(r) \cdot \mathbf{V} \rangle \phi_j^{(1)}(r) + \phi_j^{(1)}(r) \cdot \mathbf{V} \phi_j^{(0)}(r) - \frac{\mathbf{e}}{\mathbf{C}_0} \mathbf{n}(r) \mathbf{A}(r)
\]

The summation runs over the occupied states and \( \mathbf{n}(r) \) is the unperturbed charge density. \( \phi_j^{(0)}(r) \) are the unperturbed Kohn–Sham orbitals and \( \phi_j^{(1)}(r) \) their first order perturbed counterpart due to the external magnetic field. The latter make the determination of the shielding tensor much more computationally demanding than the EFG tensor. In Eq. (9) is given the decomposition of the induced current into the so-called paramagnetic term \( \mathbf{j}^{(1)}(r) \) (involving the first-order perturbed orbitals) and the diamagnetic term \( \mathbf{j}_d^{(1)}(r) \) (which only depends on the unperturbed charge density). \( \mathbf{A}(r) \) is the vector potential connected to \( \mathbf{B}_0 \) through

\[
\mathbf{A}(r) = \frac{1}{2} \times \mathbf{B}_0 \times (r-r_0)
\]

where \( r_0 \) is the so-called gauge origin. The main theoretical issue is that if \( \mathbf{j}^{(1)}(r) \) is independent of the gauge (i.e. \( r_0 \) in Eq. (10)), \( \mathbf{j}^{(1)}(r) \) and \( \mathbf{j}_d^{(1)}(r) \) are individually dependent on it. One has to address this carefully in practical implementation in order to avoid divergences in the calculations of \( \mathbf{j}^{(1)}(r) \). \( \overline{\mathbf{B}}_{\text{ind}}(r) \) is finally obtained from the Biot–Savart law which reads

\[
\overline{\mathbf{B}}_{\text{ind}}(r) = \frac{1}{\mathbf{C}} \int dr' \frac{\mathbf{j}^{(1)}(r') \times (r-r')}{|r-r'|^3}
\]
The first elements of the GIPAW theory, i.e. the calculation of the response to a uniform magnetic field using periodic boundary conditions in the plane wave pseudopotential formalism, were introduced by Mauri et al. [34] and Mauri and Louie [35]. Theoretically, they considered the response to a periodic magnetic field with a finite wavelength q, subsequently extrapolated in the limit q → 0 to compute the magnetic shielding. Their formalism could manage the numerical instabilities associated with the summation of the two individually divergent terms: diamagnetic and paramagnetic. This first approach was referred to as the MPL approach. Nevertheless, it was only an approximation as it neglected the contribution of the core electrons and valence electrons in the core region (with no reconstruction of the all-electron wave function in that region). An important subsequent step was the demonstration that the core electrons contribute to the chemical shielding in a way independent of the chemical environment [36]. Thus, the core contribution needs only to be evaluated once, typically from a simple atomic calculation. 

In 2001, Mauri and Pickard extended MPL, combining it with the projector augmented wave (PAW) approach [33], deeming in fact the theoretical basis for computing the all-electron response to a uniform magnetic field. To this aim, they introduced projectors fulfilling the theoretical requirement of gauge invariance. This led to the gauge invariant projector augmented wave (GIPAW) method. Its outstanding accuracy was quickly recognized in silicates [31] and confirmed afterwards for a wide class of nuclei and materials as reviewed below. It should be stressed again that in comparison to standard all-electron approaches, the use of the pseudopotential approximation allows a significant reduction of the computational cost as only the valence electron functions are explicitly treated. Equations involved for the evaluation of \( j^{11}(r) \) are too lengthy to be reproduced here, it is only necessary to note that the GIPAW method outputs the absolute shielding \( \sigma \) in terms of four components as

\[
\sigma = \sigma_{\text{core}} + \sigma_{\Delta d} + \sigma_{\Delta p} + \sigma_{\text{bare}}
\]

\( \sigma_{\text{core}} \) is the (isotropic) contribution of the core electrons (calculated once on an isolated atom), \( \sigma_{\text{bare}} \) is the contribution from the pseudo-valence wave function. \( \sigma_{\Delta d} \) and \( \sigma_{\Delta p} \) account for its deviation from the all-electron wave function close to the nucleus, referred to as the augmentation diamagnetic and paramagnetic terms. It is worth noting that the shielding tensor is an asymmetric tensor which can therefore be decomposed into a symmetric and antisymmetric part. The latter part can be ignored as it only affects the NMR spectrum to second order [37]. Nevertheless, GIPAW has recently revitalized the interest in the anti-symmetric components as discussed in Ref. [38].

In order to improve its efficiency but also to widen its range of applicability in terms of atomic species, the GIPAW formalism was extended to permit the use of a generalized form of pseudopotential named as ultra-soft pseudopotential [39]. This form was introduced by Vanderbilt [26] and allows an increase of the core region radius without loss of accuracy. In comparison to a norm-conserving pseudopotential, the obtained pseudo-wave functions are smoother thus reducing the size of the basis sets that is the value of the cutoff energy (Eq. (6)). Such an optimization turned out to be crucial for calculations on transition elements such as titanium and vanadium [40].

Inclusion of relativistic effects through the simple scalar formalism of zeroth-order regular approximation (ZORA) has been described in Ref. [41]. It was reported that the influence of relativity on the valence electrons in the core region results in an increase of the absolute chemical shielding. It was nevertheless recognized that the differences in chemical shifts (the quantity of interest for the experimentalist) cancel out between a relativistic and non-relativistic calculation. This suggests that the contribution of relativity to the NMR shifts treated at the ZORA level of approximation is independent of the chemical environment, as shown in Fig. 1. This method has not yet been made available to the end-user (to the best of our knowledge) for further investigations. To date, the standard (and only available) practice for introducing relativity in GIPAW is through the use of relativistic or scalar relativistic pseudopotentials. The latest developments in the GIPAW are those related to the computation of the J coupling tensor [42,43]. However they are not yet available to the end-user so that only a few studies have

\Fig. 1. GIPAW versus experimental \( \text{Se} \) and \( \text{Te} \) isotropic magnetic shielding values (data extracted from Ref. [41]). Solid lines represent linear regressions with a slope given in legends. These data suggests that accounting for relativistic effects within the scalar ZORA approximation induces only a uniform shift, i.e. independent of the chemical environment (the slopes of the two respective (with and without ZORA) linear regressions are indeed almost identical).
been reported [38,44–46]. It is certain that this NMR interaction will play a crucial role in near future as indeed it is at the heart of most of the latest significant development in solid state NMR [6]. It is worth noting that the GIPAW formalism can be applied as well for the computation of the EPR g tensor of paramagnetic species [47,48] and the NMR shifts in metallic systems [Knight shifts and orbital shifts] [49–51]. Those aspects are out of the scope of the present review (and yet unexplored). At the present level of the GIPAW theory, only diamagnetic systems have been considered for computation of NMR parameters. Paramagnetic solids (computation of the so-called paramagnetic NMR shifts) are in sight, but require a deeper understanding of the effective interactions between the nuclear and electronic spins [52–56].

Concerning available software packages, three plane-wave DFT packages implement the GIPAW method for magnetic shielding tensor (and EFG) calculations. The PARATEC code [57] was the first implementation (limited to norm-conserving pseudopotentials) but, to the best of our knowledge, the code is no more maintained. CASTEP [58] is the most popular, implementing GIPAW with either ultra-soft or norm-conserving pseudopotentials, as well as J-coupling tensors calculations but for developers only. Quantum Espresso [59], which is the only free software, does only support norm-converging pseudopotential but implements g-tensor calculations. An overview of the influence of the many parameters involved in the computation of the NMR parameters (i.e. convergence of the NMR parameters with the electronic structure, influence of the structure optimization and DFT functionals, choice of a reference for the chemical shift scale, etc.) can be found in a recent work [60]. Through the two tensors as provided by a GIPAW calculations, namely the EFG tensor Eq. (7) and the shielding tensor Eq. (12), one can determine the NMR values which are experimentally measured from their diagonalization as well documented in most of papers and using different conventions (up to the choice of the end-user). For a description of the most commonly used conventions see Ref. [61]. There are in fact two important parameters that need to be supplied by the end-user for converting the outputs into experimental values, i.e. shielding to chemical shift tensor and EFG to quadrupolar tensor.

The first parameter is the absolute isotropic shielding reference \( \sigma_{iso}^{calc}(ref) \) which defines the chemical shift tensor \( \delta \) as

\[
\delta_{ii} = \sigma_{iso}^{calc}(ref) - \sigma_{ii} \tag{13}
\]

In general, Eq. (13) is approximated as \( \delta_{ii}^{calc} \approx \sigma_{iso}^{calc}(ref) - \sigma_{ii} \) giving the isotropic chemical shift (the most important quantity in the context of high-resolution NMR) as

\[
\delta_{iso}^{calc} = \sigma_{iso}^{calc}(ref) - \sigma_{iso} \tag{14}
\]

Several methods have been described to define \( \sigma_{iso}^{calc}(ref) \). Most frequent practices follow two ways. The first is by imposing a single reference compound with known (and trusted) NMR shift values. The second approach is by fitting the calculated values for the set of studied systems to the experimental values using Eq. (14). This second approach seems to become the standard practice. The constraint of a unity slope in Eq. (14) is sometimes relaxed for the linear relationship

\[
\delta_{iso}^{calc} = a(\sigma_{iso}^{calc}(ref) - \sigma_{iso}) \tag{15}
\]

but this seems not to be the preferred approach. A significant deviation of the parameter \( a \) from unity is often considered as an evidence of the deficiency of the DFT GIPAW method. Most important is the fact that the linearity of Eq. (15) ensures that the spectral assignment can be done without any ambiguity. More discussion about the choice of \( \sigma_{iso}^{calc}(ref) \) can be found, to name but a few, in Refs. [62,60]. Notably, the contribution of the bulk macroscopic susceptibility (which depends on the shape of the sample) has been discussed in the case of carbon nanotubes [63].

A similar question arises regarding the value of the quadrupolar moment value \( Q \) (the second parameter) that relates the electric field gradient principal value \( V_{zz} \) (the largest in magnitude eigenvalue of the tensor Eq. (7)) to the quadrupolar coupling constant:

\[
C_Q = eQ V_{zz}/h \tag{16}
\]

A first choice is to consider it as a constant value, generally extracted from the Pyykkö table [64]. A second choice is to treat it as an adjustable parameter by fitting the calculated \( V_{zz} \) values to experimental \( C_Q \) values with Eq. (16). In that case, the obtained \( Q \) value is obviously a parameter dependent upon the level of DFT theory involved in the calculations. An appealing feature of GIPAW is the determination of the relative orientation of shielding and EFG tensors with respect to the crystallographic axes (or molecular frame), as well as the computation of their relative orientation. To date, software has been developed to facilitate the detailed analysis of the outputs [65], as well for more general analysis and direct simulations of NMR spectra [66].

### 3. A GIPAW tour of the periodic table

This section aims at briefly reviewing most of the nuclei which have been studied by the GIPAW method. We have chosen to classify the nuclei according to how easy or difficult they can be amenable to a GIPAW study. The first group presented here comprises the nuclei which are now known as well suited for DFT calculations and well established nuclei for NMR studies (NMR established nuclei). The second group contains nuclei which are inherently insensitive to NMR, such as nuclei with low gyromagnetic ratio (low-\( g \)) and/or low natural abundance (Less NMR sensitive nuclei). Quadrupolar halogen nuclei are characterized by a sizable nuclear quadrupole moment and have been in the focus of several recent studies [67]. They are in the third group (Halogen nuclei). Transition elements for which the implementation of the DFT theory itself can be more demanding or clearly exhibited deficiencies, are described in a fourth group. Last group (Other nuclei) will encompass all other nuclei.

#### 3.1. NMR established nuclei

This first set of nuclei comprises the common nuclei which are now well established as standard nuclear probe for structural NMR studies and also involved in the most advanced GIPAW-NMR methodologies as discussed in the next sections. Those are mainly proton (\( ^1H \)), boron-11, carbon-13, nitrogen-14, nitrogen-15, oxygen-17, sodium-23, aluminum-27, silicon-29 and phosphorous-31 which electronic properties can be well described with the standard DFT level of theory. Several studies have shown that GIPAW provides from good to excellent predictions in a wide range of materials: silicates [31], sodo-silicates [68], aluminosilicates [69], magnesium silicates [70], borates [71], boron carbides [72], sodium perovskites [73], sodium niobate [74], organic solids [75–77], calcium phosphates [78], sodium phosphates [79,80], aluminum oxides [80] and molecular solids [81], tungsten oxides [82]. Today, the above nuclei can now be considered as a routine implementation of the DFT GIPAW method. Most important is the fact that the linearity of Eq. (15) ensures that the spectral assignment can be done without any ambiguity. More discussion about the choice of \( \sigma_{iso}^{calc}(ref) \) can be found, to name but a few, in Refs. [62,60]. Notably, the contribution of the bulk macroscopic susceptibility (which depends on the shape of the sample) has been discussed in the case of carbon nanotubes [63].
or safe practice for GIPAW analysis, using the most popular DFT GGA functional, namely PBE [20] and PW91 [21]. For an illustrative example of the comparison between these functionals, see Ref. [60].

Because of its growing importance for both inorganic [83] and organic solids [84,85], oxygen–17 has probably been the most (GIPAW) investigated nucleus, with recent studies pointing out the importance of the sensitivity of both the EFG and CSA tensor to H-bonding motifs [86–90] or metal–oxygen interactions [91]. In these works, it has been clearly recognized that the use of ab-initio calculations is essential to input constraints on NMR parameters for spectral deconvolution. The clear advantage of GIPAW is to provide the full EFG and shielding tensors, as well as their orientations with respect to the molecular or crystallographic frame and their relative orientation. Despite its successful application for oxygen–17 in both organic and inorganic solids, surprisingly GIPAW calculations enabled to put in evidence some unexpected deficiencies of the DFT theory in calcium silicates [92]. Using standard parameters as assessed on silicates and despite the prediction of good structural and vibrational properties, the NMR parameters of the non-bridging oxygen (bonded to only one silicon atom) involved in Ca–O bonds were found to be in a strong disagreement with the experimental data. This discrepancy was identified as a clear deficiency of the DFT theory for the description of the partially covalent Ca–O bond (because of the low-lying Ca 3d orbital hybridized with the O 2p orbital). But more interestingly, it was shown that through a simple empirical modification of the Ca pseudopotential (shift of the unoccupied Ca 3d energy level), an excellent agreement between experimental and calculated values could be recovered. Satisfactorily, this energy shift was found to be consistent the values predicted with more advanced calculations accounting for the correlations between the electrons.

Concerning fluorine–19, a comparison between PBE and a semi-empirical GGA functional (KT3) [93] was reported for octa-fluoronaphtalene [23]. Of interest was the fact that the KT3 was specifically designed to improve the prediction of shielding constants. However, as a result of the referencing for the chemical shift calculation (Eq. (14)), a uniform deviation between the two functional was obtained, thus independent of the chemical environment. Despite the poor predictions, the correct ordering of the chemical shift values allowed a spectral assignment. It was therefore suggested that electronegative atoms could be more challenging for GIPAW calculations so that the assignment cannot be made confidently on the basis of calculations alone. Similar conclusions were drawn from a study of a metal fluorides series [94] (using PBE functional), indeed reporting a slope of experimental versus calculated values of 0.86 (much less than 1).

3.2. Less NMR sensitive nuclei

Another group of nuclei for which the GIPAW method has been recognized as crucial for spectral interpretation is the NMR insensitive nuclei. This is typically the case for sulfur–33, calcium–43 and magnesium–25 which are low–γ nuclei with low natural abundance. The two latter possess moderate quadrupolar moment that makes them probably more accessible than the former.

Two recent studies provided an extensive measurement of magnesium–25 NMR parameters for simple compounds, using an ultra-high magnetic field (21.1 T) in inorganic compounds [95] or within a multiple fields approach in organic and inorganic compounds [96]. Significant increase of the sensitivity could be achieved with the help of signal enhancement techniques (QCPMG, VOCS, see references in Ref. [6]). It should be noted that most of the works cited in this section are also well illustrative of the increasingly popular enhancement techniques, enabling the acquisition of good quality data for a valuable benchmark of the GIPAW method. The agreement between the calculations and experiments was found to be very good for the quadrupolar coupling constant, reasonable for the isotropic chemical shifts but only semi-qualitative for the asymmetry parameter.

Calcium–43 has been in the focus of many recent studies in the field of biomaterials. NMR was used for probing its binding environment beyond the first coordination sphere which could be essential for the understanding of biological mechanisms underlying the biocompatibility. To this aim, exciting perspectives were recently demonstrated using 43Ca–13C TRAPDOR NMR measurements, supported by GIPAW calculations [97]. The reliability of GIPAW predictions for calcium–43 has been assessed recently for a very large number of inorganic compounds [98,99].

For calcium and magnesium, a good correlation between the isotropic chemical shift and the average Ca–O or Mg–O bond distance was confirmed [100,101], with a dependence upon the nature of the associated oxo-anion. From those works the high potentials of combined DFT–25Mg and/or 43Ca NMR approach for biomaterials studies was clearly established, as confirmed by a recent investigation of magnesium incorporation in hydroxyapatite [102].

Following the same approach, i.e. use of ultra-high magnetic field combined with signal enhancement pulse sequences, GIPAW was shown to predict values only in semi-quantitative agreement with experiment for sulfur–33 in potassium-sulfates salts [103]. Interestingly, it was observed that the isotropic chemical shift was relatively insensitive to the local environment, on the contrary, the quadrupolar interaction coupling constant highly correlated to the symmetry of the SO4– anion and the S–O bond lengths.

3.3. Halogen nuclei

These nuclei have recently received a renewed interest for NMR studies [104]. The common NMR characteristic of 35,37Cl, 79,81Br and 127I is their relatively high gyromagnetic ratio but their very large nuclear quadrupole moment which has been for a long time prohibitive for the study of solids with non symmetric environments. Thanks to the availability of ultra-high magnetic fields and robust signal enhancement techniques for wideline studies (such as VOCS and QCMPG), benchmark of high quality experimental data have been recently acquired on alkaline earth metal bromides [105], chlorides [106], alkaline earth chloride hydrates [107] and metal iodides and their hydrates [108]. In those studies a particular emphasis was put on the extraction of structural information through the use of GIPAW calculations. For the three nuclei, the quadrupolar interaction parameters were well predicted whereas the isotropic chemical shifts were found to be systematically overestimated, as a probable evidence of relativistic effects not (yet) included in GIPAW implementations. However this semi-quantitative agreement (i.e. deviation of the linear slope in Eq. (15) from unity) was found to be sufficient for providing some essential if not crucial information for the interpretation or the assignment of the experimental spectra. It was also noticed that the quadrupolar coupling constant was particularly sensitive to the hydration level of the compounds. It was suggested that the vibrational motions of the water molecule could induce a dynamical averaging effect on the NMR parameters and could therefore explain the discrepancies between calculated and experimental values.

In the specific case of iodine–127, higher-order quadrupolar effects, as induced by a very large quadrupolar interaction (no longer negligible with respect to the Zeeman interaction), were evidenced on static NMR spectra. Independent NQR
measurements were performed to confirm the quadrupolar coupling constants. It was clearly shown that the consideration of these higher order effects using an exact (i.e. non-perturbative) simulation of the NMR spectrum [109] was required to extract the correct chemical shifts in the regime of a dominant quadrupolar interaction. This study highlights some of the novel opportunities brought by the availability of the full tensorial description of the NMR interactions (with respect the crystallographic frame); performing more reliable (here non perturbative) spectral simulations. As a prospect, a better characterization of such higher-order effects can be expected from GIPAW calculations, as well as those arising from the interplay of multiple interactions or crystallographic equivalence versus magnetically non-equivalence [110].

3.4. Transition elements

As formalized within the norm-conserving pseudopotential NCPP (i.e. the pseudo-wave function reproduces the electronic charge of the all-electron wave function inside the core region), transition elements such as typically Ti, V or Cu are well known to be difficult elements to deal with the DFT theory [111,112]. This is because of the so-called semi-core states which overlap with the d-valence states. Having these semi-core states treated as valence states would require a prohibitive increase of the basis set size (the cutoff energy) because of a small core region radius. The ultra-soft pseudopotential USPP formalism adds the necessary flexibility with devising the pseudopotential by relaxing the norm conservation constraint (but at the cost of a generalized eigenvalue problem to be solved). Specifically the valence orbitals are pseudized with the help of two or more atom like pseudo-wave functions (instead of one for a NCPP), allowing the use of larger cut-off radii which reduces therefore the basis set size. This improvement was demonstrated as a crucial step to make the transition elements amenable to the GIPAW approach, as clearly demonstrated in the pioneering works on vanadium-51 and titanium-47/49 [113,114] (Fig. 2). It was reported that the prediction of the isotropic chemical shift was more successful than the full shielding tensor eigenvalues. It was suggested that discrepancies could be masked by the average isotropic chemical shift but magnified by the anisotropy and asymmetry parameters. Molybdenum-95 was recently also found to be suitable for a GIPAW analysis for an extensive set of alkaline and alkaline earth molybdates [115]. The performances in term of accuracy of several Mo pseudopotentials were compared and it was concluded that on-the-fly pseudopotentials (internally generated within the CASTEP code with default parameter setup) were suitable.

Similar success was reported for niobium-93 in a complete set of oxide compounds with niobium involved in Nb2O5 and NbO2 units [61], and with high quality data acquired at multiple fields. This led the authors to significantly correct the previous published experimental values. This work nicely illustrates the difficulties in separating the effects of the CSA and EFG tensors from fitting the spectra without the recourse to the analysis of spectra at multiple field strengths. Surprisingly, GIPAW was found to give good predictions for the chemical shift anisotropy but not for isotropic chemical shifts as shown in Fig. 3. The GIPAW EFG values compare well with experiments and periodic all-electron calculations (WIEN2k) whereas the cluster approach (Gaussian basis set) was clearly recognized as deficient. Such data would certainly be of great importance in future as providing a benchmark of quality to assess any further improvement in GIPAW.

Other nuclei were shown as valid candidates for the GIPAW method are zirconium-91 (in layered phosphates [116] and zircon ceramics [117]), yttrium-89 [118] (this work will be discussed in more detail in the last section as illustrative of cationic disorder in ceramics) and scandium-45 in scandium sulfate pentahydrate [119] (but only a qualitative agreement was reported).

In passing, it should be mentioned that USPP are the default choice within the CASTEP package, whereas only NCPP are supported in the Quantum Espresso package (stable release). For the latter this may be considered presently as a limitation for its usage for a wide range of nuclei. These works on transition elements point out the importance in the development of efficient pseudopotentials for competing with all-electron approaches.

3.5. Other nuclei

Gallium-69/71 predictions were assessed across various oxides and gallates [62] allowing for varying coordination for gallium sites, including the unusual GaO5 site. This work also presents a detailed discussion about the choice of the chemical shift reference. As illustrative of the potentials of GIPAW applied to nuclei with sizable nuclear quadrupole moment, first results on bismuth-209 [120] and barium-135,137 [121] should be mentioned. Application to heavier elements such as the exemplar lanthanum-139 [122] will certainly appear soon. Successful applications for selenium-77 in GeSe2, GeSe4, and GeSb crystals [123] and ZnSe nanoparticles [124] as well as tin-119 [125] in pyrochlore were reported.

4. Applications to ordered systems

In this section, we first discuss some important issues regarding the optional structure optimization prior to the NMR calculations together with the structural trends of NMR parameters as provided by GIPAW. Its integration into structure refinement and spectral assignment procedures as developed within the emerging NMR crystallography framework [126,127,143] is then reviewed. Emphasis will be put on the improved analysis enabled by GIPAW of intermolecular and long-range interaction contributions to NMR shifts (hydrogen and halogen bonds, aromatic π–π interactions). Finally, we describe applications of GIPAW used as
a predictive tool, such as for foreseen experiments or their optimization.

4.1. The structure optimization

Since its early applications [31,68,75], questions quickly arise regarding the DFT optimization of the structure (overall or partial relaxation of the atomic positions and possibly the unit cell parameters) prior to GIPAW calculations. Indeed, as a result of the high sensitivity of NMR shifts to slight structural modifications (to some extent rediscovered in solids by the introduction GIPAW), often combined to relatively high error limits in experimental structures (most of them determined from powder X-ray diffraction which is more representative of a thermal average than the true local environment), the agreement between the calculated and experimental NMR parameters is generally found to be significantly improved after a DFT optimization of the structure geometry. This problem is well known for hydrogen atoms, it was generally observed in most of the subsequent works for a wide range of nuclei and materials and posed the question: To relax or not to relax? [128]

Fig. 3. Left panel: multiple fields static \(^{93}\)Nb NMR spectra. Right panel: comparison between GIPAW and experimental NMR parameter values. EFG parameters (b, d) are well predicted (and well agree will all-electron calculations using WIEN2k), whereas an unusual behavior is observed for the chemical shift values: the good agreement for the chemical shift anisotropies (c) contrasts with the poor one for the isotropic chemical shift values (e). Adapted from J.V. Hanna, K.J. Pike, T. Charpentier, T.F. Kemp, M.E. Smith, B.E.G. Lucier, R.W. Schurko, L.S. Cahill: A \(^{93}\)Nb Solid-State NMR and Density Functional Theory Study of Four- and Six-Coordinate Niobate Systems. Chemistry A–European Journal. 2010. Volume 16. Pages 3222–3239. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

[129] It is certainly a good practice to let this choice concerning the structure optimization determined from the best agreement between the NMR calculations and experiment. In these respects, the significant increase in the quality and accuracy of experimental NMR data will certainly deserve new acquisitions of high quality diffraction data for some reference systems.

In the case of DFT optimization of structures, it is worth noticing that intrinsic errors inherent in the chosen XC functional exist. They are nevertheless generally well identified and systematic. For example, GGA functional such as PBE or PW91 are well known to overestimate the bond length [68] (under-binding effect) yielding increased cell dimensions. In the case of silicates [68,130], it was shown that the PBE optimization resulted in an expansion of the unit cell volume between 4% and 4.5%. This overestimation of the bond length can be afterwards compensated by an isotropic scaling of the unit cell, and even confirmed by the improved predictions of the NMR parameters, especially oxygen-17. Similarly, there are known deficiencies of most of pure XC DFT functional in describing van der Waals (or dispersion) interactions. A recent proposed method to work around this problem consists in adding a semi-empirical dispersion energy term to the conventional Kohn–Sham DFT energy [131].

Another important point is the fact that the computations are effectively carried out on a frozen structure (at zero degrees if forces are relaxed), whereas NMR data are generally collected around room temperature (though low temperature NMR measurements can be performed). Directions to accounting for the finite temperature and/or motions in NMR computations will be presented below but in this context, GIPAW is a field still in its
infancy. Taking this issue from the experimental point of view, an interesting alternative was recently proposed through the use of linearly extrapolated values to 0 K from variable temperature measurements. This was found to yield predicted experimental values in a clear better agreement with the calculated ones [132]. Such works will certainly promote the use of variable temperature NMR in near future.

4.2. Structural trends of NMR parameters

Firmly establishing the correlations linking the observed NMR parameters to their originating environments is a long-standing problem in solids. This question has been extensively addressed, for example in silicates and aluminosilicates [133] either using a database approach (deriving empirical rules from extensive set of data) or using cluster calculations [16,17,14,134]. The search for relationships between local structural features (bond angle, distances, and nearby species) and NMR values is a common exercise in most of the GIPAW studies dedicated to the assessment of the method, as reviewed Section 3. If GIPAW permits the effects of the wider periodic (or crystalline) environment to be included in the NMR parameter calculation, it must be recognized that the cluster approach is more flexible: structural parameters can be easily varied independently from each other as well illustrated in recent works on the J-coupling tensors [14,134].

Besides the fact that GIPAW can treat large clusters as well (using a super-cell approach, i.e. the cluster is placed in a vacuum box), implementation of a systematic variation of a structural parameter is more difficult, due to the geometrical constraints of the periodic crystal structure and the often limited range or variety of experimental values available in reference crystalline compounds. To overcome these limitations, it has been proposed to use the variation of the NMR parameter of interest as induced under compressive and/or tensile pressure (with geometry optimization for each pressure value). This was done to establish the correlation between 29Si isotropic chemical shift and Si–O–Si bond angles in silicates [135], and more recently to follow the variation of the 27Al isotropic chemical shift with respect to the mean Al–O bond length in aluminum oxides [80]. An attempt to formalize the variations of NMR parameters upon stress tensor has been described (relating second-order tensors yields a fourth-rank tensor as a result), [136] but yet not fully explored. To address the question of NMR versus local geometry relationships, the use of molecular dynamics in the context of glass studies has been shown to be a valuable approach [130] and this will be detailed in section 24.

One weakness of GIPAW formalism, as currently implemented in DFT packages, is the lack of interpretative tools, even approximate, giving insights into the electronic properties underlying the NMR parameters, as recently proposed using localized basis set frameworks [137,138,139,140]. This is one of the drawbacks of the DFT Kohn–Sham formalism in periodic systems that delocalizes the electronic density throughout the whole simulation cell, preventing straightforward extraction of the individual electronic properties of a specific atom. At this stage, the only decomposition available is those as provided by Eq. (12) but is rather limited. To the best of our knowledge, this has not been yet really investigated. In a recent 45Sc NMR study, it was shown that simple electrostatic point charge calculations yielded a sufficient approximation of the EFG tensors to provide a valuable mean to assign the NMR spectra [141].

Concepts to capture the short- versus long-range interactions contribution to NMR shifts have been explored, especially for investigating the hydrogen bonds [142], and they will be discussed later. In general, the quality of correlation of NMR parameters with local features is taken as a measure of their local character. This is typically the case for oxygen-17 which EFG tensor which can be well predicted by the Si–O–Si linkage geometry whereas its isotropic chemical shift is hardly so well correlated to local features [16,130]. To the best of our knowledge, no attempt has been made to develop some decomposition (such as projection onto local orbitals), even in an approximate manner, of the rather synthetic GIPAW expressions of the NMR shifts. If feasible, this could be useful for end-users, either to gain insight in the underlying chemistry of the NMR shifts or to build semi-quantitative approaches.

4.3. NMR crystallography

The general idea behind the emerging NMR crystallography field is to incorporate the wide variety of information as provided by solid-state NMR experiments into the process of crystal structure determination or refinement. This is done typically with diffraction characterization methods combined to computational chemistry. Investigated materials are particularly those for which it is difficult to obtain suitably large single crystals for single-crystal diffraction experiments [143]. In the scope of the present review is the type of crystallographic information that can be obtain from chemical shift information [144]. GIPAW will undoubtedly become a major component of NMR crystallography as it enables for the first time to put a spectrum on a structure with an accuracy and efficiency that outperform all previous approaches.

The spectral assignment capabilities (i.e. connecting each of the observed resonance to an atomic position in the crystal structure) of GIPAW have been explored and assessed in numerous studies, among others: MgSiO₃ [145], NaNbO₃ perovskites [146], glutamic acids [75], testosterone [147] and polydiacetylene polymers [148]. The identification of phase transitions occurring in (MoO₂)₂P₂O₇ [149] which was made possible with the help of GIPAW supported analysis of 17O NMR data. GIPAW was quickly recognized as perfectly complementing the use of sophisticated two-dimensional NMR techniques (as recently reviewed for spin 1/2 [9] and quadrupolar nuclei [83,6]) generally aiming at determining spatial or through bond connectivities between the resonances to help assign and/or geometrical constraints (such as interatomic distances). The GIPAW calculations then provide either a support of the complete or assessment of the assignment of the NMR spectra, generally based on the isotropic chemical shift values, as extensively studied in organic solids for 1H and 13C NMR [128,150–152,132]. In case of small isotropic chemical shift values dispersion, 13C chemical shift anisotropies were shown to be also valuable information for spectral assignment [153].

In the context of NMR crystallography, GIPAW has therefore been quickly integrated in several protocols for structural determination. It was shown that combination of the proton spin diffusion (PSD) and molecular modeling (MM) (the so-called MM/PSD-NMR method) could be improved by GIPAW 1H and 13C chemical shifts [154,155], as yielding additional accurate restraints to further refine trial structures (Fig. 4). This was even pushed forward by showing that comparison between calculated and experimental 1H chemical shifts was sufficient to identify the structure of powder from among the set of potential candidates based on energy criteria [156].

Combination of GIPAW with multidimensional correlation experiments for spectral assignment and structure validation were also successfully applied for a wide range of inorganic materials: calcium phosphates (31P NMR) in the context of biomaterials [Fig. 5] [157], for a very detailed analysis of 43Ca NMR lineshape in calcium benzoate trihydrate Ca(C6H5-COO)2·3H2O and in the support of remarkable 13C–43Ca correlation experiments enabling carbon resonances to be discriminated
according to their calcium environment (offering exciting perspectives for the NMR analysis of calcium sites in biological materials) [97]; microporous alumino-phosphates [129] (AlPO-14 with nice experiments such as 31P–27Al MQ-J-HETCOR NMR), layered Ti 

\[ \text{Ti(HPO}_4\text{)(PO}_4\text{)}_2 \] 

intercalates [158] (extensive set of NMR experiments, interlayer hydrogen bonds could be evidenced), carbon-nitride polymers [159] and (SCN)\(x\) polymers [160], in scandium sulfate pentahydrate [119] (45Sc MQMAS NMR and response of the resonances to proton decoupling, the need to compute NMR parameters using an energy-optimized crystal structure was once again demonstrated), in the complex decavanadate cluster

\[ \text{Cs}_4[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O} \] 

(\(^{51}\text{V}\) MQMAS NMR and investigation of the influence of the H-bond network) [161]. These studies clearly demonstrate that NMR has entered as a standard tool in the structure resolution process [162].

The NMR crystallography methodology has been pushed forward in zeolites [163,164], combining 29Si DQ NMR build-up curves to probe inter-nuclear silicon distances and full 29Si chemical shift tensors calculated on clusters extracted from the structure. In a subsequent study, GIPAW calculations were recognized as superior in terms of accuracy and efficiency [165]. Determining an atomic position in a structure from the NMR parameters only was demonstrated for a quadrupolar nuclei in the

![Fig. 4](image-url) Within the NMR crystallography framework, here applied to thymol powder crystals, state-of-the-art of NMR methodologies are combined with Molecular Modeling, diffraction data and DFT/GIPAW calculations to refine or determine structures. E. Salager, R.S. Stein, C.J. Pickard, B. Elena, L. Emsley, Physical Chemistry Chemical Physics 11 (2009) 2610. Reproduced by permission of the PCCP Owner Societies. [http://dx.doi.org/10.1039/B821018G](http://dx.doi.org/10.1039/B821018G).

![Fig. 5](image-url) Left panel: experimental and calculated \(^{31}\text{P}\) MAS NMR spectra of \(\beta\)-Ca(PO\(_3\))\(_2\) and \(\gamma\)-Ca(PO\(_3\))\(_2\). Right panel: 2D double quantum (DQ) \(^{31}\text{P}–^{31}\text{P}\) through-bond correlation spectrum (MAS-J-INADEQUATE). Off diagonal peaks indicate DQ resonances of a spin pair belonging to a P–O–P linkage. Adapted with permission from F. Pourpoint, A. Kolassiba, C. Gervais, T. Azais, L. Bonhomme-Coury, C. Bonhomme, C. Maury, Chemistry of Materials 19 (2007) 6367–6369. Copyright 2007 American Chemical Society.
case of MgBr₂ [166] (using the variation of the ⁷⁹Br quadrupolar coupling constant) and for Na⁺ in calix[4]arene guanosine [77].

In many of these works on organics solids, emphasis was put on the examination of the nature of the hydrogen bonding and its influence on the NMR parameters of the involved nuclei. Yates et al. showed that strength of weak C–H···O hydrogen bonding [142] can be quantified by determining the differences in chemical shifts between calculations for the periodic crystal structure and for an isolated molecule extracted from the crystal structure. ¹H and ¹³C chemical shift differences from 1 to 2 ppm and –3 to –5 ppm, respectively, were predicted. Such chemical shift changes can represent a valuable alternative to proximity measurements (as done in crystallography) which do not guarantee the existence of an effective hydrogen bond. This analysis also providing insights in the crystal packing effect was applied to other organic solids [159,167–170] as well as for ¹⁹F [128] in flurbiprofen (with a discussion on the use of XRD structures).

A similar approach was applied to the study of the hydrogen-bond mediated J coupling [171] (a study that clearly shows that calculations of J couplings will also find widespread applications). An estimate of effects of the crystal–lattice (as induced by the long-range electrostatic and packing interactions) was obtained by comparing the results of the full crystal structures and an extracted single molecule, either keeping the initial geometry (first model) or fully relaxed in a vacuum supercell (second model). These two models were built in order to distinguish the contributions that may arise from the local structural effects and crystal–lattice interactions, whereas the comparison between the crystal and the first model should account for the long-range electrostatic contributions. Analysis of the results confirmed the expected strong local character of J coupling in a solid, but nevertheless affected by changes in both structural and electrostatic interactions inherent to the solid state. Again, this study nicely showed the importance of correctly accounting for long-range electrostatic interactions in solids for accurate predictions. It was also emphasized the advantage of the simpler comparison between calculated and experimental in the solid state, avoiding the difficult account for the solvent effects in the liquid state.

Several other examples of the effects of the hydrogen bonds on ¹⁷O NMR parameters (which turn out to markedly affected by small variations) have been described in amino acids [172] (as well as on ³⁵Cl parameters in this work), glutamic acids [75] or ¹⁴N in amino acids [173] to name but a few. In all those works it was possible to find good correlations between NMR parameters and the strength of the hydrogen bonding. A recent study also reported the influence of halogen (N–I) bonds [174].

For the complete assignment of ¹H proton [132] in beta-maltose, the question of accounting for finite temperature effects (thermal averaging) was pointed out. This is currently considered as the explanation of the residual discrepancies between calculations and experiment. In that work, a simple procedure consisting in extrapolating the variations with respect to temperature of the ¹³C and ¹H shifts to 0 K was used to obtain the values to compare with the calculations. This was shown to improve significantly the agreement between the GIPAW calculations and experiment. This nicely shows that, if one can resort to more complex theory (see Section 5), experiments can also be adapted to facilitate the comparison with theoretical calculations.

4.4. A priori prediction

In this section, we are concerned with GIPAW calculations in support of the design or assessment of foreseen experiments. For example, the ¹⁷O NMR responses in various crystalline samples (calcium phosphates) were calculated to assess their resolution in MQMAS experiments [78]. Similarly, the relevance of ¹⁷O MQMAS NMR for distinguishing O [3] (tricluster) and O [4] oxygen sites in Si₃Al₂O₇ aluminosilicates was investigated. Overlap of O(AlSi₃) with bridging oxygen was predicted and only OA₄ was identified as a good candidate to be easily distinguished [69].

Carbon nanotubes have also been extensively studied, addressing some long standing questions such as the influence on ¹³C NMR parameters of the tube diameter [175], (also including a detailed discussion about the choice of the reference shift), research of NMR finger prints of functionalization [177], fluorinated nanotube [178] and the study of nanotube defects (Wales Stone) [179].

5. Dynamical and finite temperature effects

The role of finite temperature and related dynamics in GIPAW calculations is still an open question. These effects are highly system dependent and they are thought to be the main contribution to the residual discrepancies between calculated and experimental results. Indeed, theoretical calculations are most performed considering one particular configuration of the system (theoretically at 0 K). Local dynamics may average partially or completely the NMR interactions (here, we are concerned with the chemical shift and quadrupolar interaction) leading to an apparent contradiction between the calculated and experimental measurements (performed usually at room temperature).

In the pioneering contribution by Rossano et al. [180], the principles of the account for the finite temperature (through vibrations) in GIPAW calculations were presented in a study of the temperature dependence of ¹⁷O and ⁵²Mg NMR in solid MgO. These principles are quite general for any response of the system, see for example EPR in liquids [55] [181]. A time-independent and time-dependent approach can be adopted. In the former, normal modes and frequencies of the vibrations are calculated within a harmonic approximation (second-order perturbation theory is necessary for anharmonic effects). Then a vibrational averaging with respect to these normal modes populated according to the Boltzmann distribution at the temperature of interest yields the finite temperature NMR parameters. It is worth noting that such averaging yields a contribution even at T=0 K, referred as zero-point vibrational (ZPV) averaging. In the time-dependent approach, a set of configurations is extracted from a snapshot of a molecular dynamics (MD) simulation at the temperature of interest. Average of the NMR parameters computed on each of these configurations yield the results. The time spacing and the number of configurations have to be large enough to ensure that they are uncorrelated and yield converged average NMR parameters values (Fig. 6). If MD intrinsically accounts for anharmonic effects, it should be remembered that nuclear motion is classical and this can be an issue for light elements such as protons, known to be affected by quantum effects.

In a comparison between the two strategies, the ZPV and motional averaging were shown to be both an important component of chemical shift calculations in organic solids [182]. Time-dependent strategies based on time averaging has been further refined in a study of a peptide [183]. Specifically, first-principles MD (i.e. atomic forces are computed at the quantum level) were carried over to characterize the molecular motions and the induced fluctuations of the NMR parameters. In order to overcome their time-scale limit, typically several picosecond far below the NMR shifts time scale (typically the Larmor period), classical MD (using classical force field) simulations were performed to average over much longer time scales (5 μs). This enabled to identify most populated configurations (rotameric states) and accuracy of the resulting averaged NMR values was found to be improved. Combination of classical and first-principles MD represents therefore a promising approach for predicting
NMR shifts accounting for the dynamical and conformational disorder. In a similar work, the authors proposed to use MD but with classical force fields fitted to reproduce the quantum forces [184]. Langevin dynamics simulations were performed in order to increase the efficiency of the configuration space sampling, by reducing the time spacing between each extracted configuration. This time interval was chosen longer than the correlation times of the NMR shifts. Size effects were also shown to be important.

Besides these fully integrated computational approaches, GIPAW can also be employed in a more empirical way, in support or assessment of a model of motions [185], by providing as inputs the static NMR tensors. Low temperature measurements would be required to determine them. Such an approach was applied for example to investigate tensor reorientations around the P–H bond in phenylphosphonic acid C6H5PO(OH) and could explain the discrepancies between the experimental and calculated 31P CSA tensors. GIPAW calculations could also help characterize the dynamics in tungstate oxides [186]. For such studies, the key feature of GIPAW is to provide the full tensorial information, i.e. including the relative orientation with respect to the molecular or crystallographic frame. Knowing the geometrical factors (and possibly time constants of the motion can be determined as well), the averaged tensor can be determined straightforwardly. The tensorial averaging approach was also successfully applied in revisiting the 29Si and 13C NMR data of octameric silsesquioxanes (RSiO1.5)8 giving a nice illustration of the powder lineshape modification upon several reorientation geometries [187]. Similarly, proton dynamics have been evidenced and characterized in hydrous magnesium silicates through its impact on isotropic 17O shifts in MQ-MAS and line-broadening in ST-MAS experiments [188] (Fig. 7).

Recently, low-energy vibration modes were used to account for the slight static disorder observed in polycrystalline bisphosphinoamine. This disorder as well as its local character could be evidenced by the elongation of the 31P–31P chemical shift correlation observed in 2D NMR experiments, as shown in Fig. 8 [189]. In order to determine its origin, a set of molecular configurations was generated with local distortions along the low-energy vibration modes. From the GIPAW NMR calculations transformed into 31P–31P chemical shift correlation lines, the distortions that likely contribute to the elongation could be identified as illustrated in Fig. 8.

6. Disordered systems

NMR has long been used for the study of disordered materials, since it allows the observation of the local chemical environment independently of the existence of long-range order, unlike many diffraction approaches [190]. This distinct advantage has made NMR as a unique tool to investigate structural disorder, be it compositional (chemical disorder) or geometrical (positional disorder) in nature, within a solid. However, the associated inhomogeneous broadening often leads to partial or complete overlap between the resonances of the chemically different sites. This can significantly complicate the processing and interpretation of the NMR spectra. Therefore GIPAW calculations quickly appeared as valuable means for establishing the missing link between the variations of the local structure associated with disorder and experimental distributions of NMR parameters [191,68]. The periodic boundary conditions and good computational scalability...
with the system size were two of the essential features of the GIPAW method that enabled a reasonably realistic disorder to be simulated through the use of supercells. The usefulness of GIPAW is all the more evident as from recent advances in multidimensional NMR techniques, the characterization of the local short-range order in non-crystalline materials can be achieved up to the nanometer scale, allowing the differentiation of the diverse molecular motifs [192,8]. Thus, it can be envisioned that NMR crystallographic strategies could be adapted for structure refinement of non-crystalline materials in the near future.

6.1. Chemical disorder

Only a few investigations of compositional disorder (cationic disorder) have been recently reported: a $^{89}$Y and $^{119}$Sn NMR investigation of the Ti/Sn substitutional disorder in Y$_2$Ti$_2$SnO$_7$ pyrochlores [193,125] and a study of the incorporation mechanisms of magnesium in hydroxyapatite [102]. The principle of such calculations is to replicate the unit cell of the defect-free structure for creating a supercell. This allows retaining the original three-dimensional structure but different cationic configurations can be built and then studied. The most probable configurations are generally identified based on energy criteria. Structure optimization allows to investigate how the structure, locally but also globally through the lattice parameters, accommodate to the compositional variations. For very different chemical environments such a change in the coordination number, the NMR shift differences are generally large enough to enable the number and nature of environments to be determined (resonances can be resolved). Those changes can be smaller for less significant change in environment such as occupancy of neighboring or next nearest neighboring sites or more remote, thus making the analysis more complex and the use of GIPAW calculations valuable (see Fig. 9). More distant substitutions were shown to have small effects but responsible for the broadening of the resonances [193]. A similar methodology was applied in a theoretical investigation of the NMR signature of point defects as induced under irradiation in the crystalline phase of ZrSiO$_4$ ceramics [117].

6.2. Surfaces

Surfaces have seen only recently appearing the first applications of the GIPAW method, despite a previous investigation of the signature of surfaces on NMR shifts with the MPL approach [194]. As exemplar of the NMR of surfaces, the case of hydroxyl groups was the first to be studied. A representative model of

Fig. 7. Comparison between experimental (a) and calculated (b, c) isotropic MQMAS spectra of hydroxyl-chondrodite (top) and hydroxyl-clinohumite (bottom). In (b) spectra are calculated using static structures, here considering four proton arrangements around each oxygen thus yielding four lines. In (c) the dynamical effects are reproduced through averaging the isotropic shifts of these four lines. Reprinted with permission from J.M. Griffin, S. Wimperis, A.J. Berry, C.J. Pickard, S.E. Ashbrook, Journal of Physical Chemistry C 113 (2009) 465–471. Copyright 2009 American Chemical Society.

Fig. 8. (a) $^{31}$P MAS NMR spectrum of bisphosphinoamine. The two-dimensional $^{31}$P–$^{31}$P correlation experiment (proton-driven spin diffusion using a short mixing time) in (b) shows that correlation peaks have an elongated lineshape that can be attributed to slight local structural disorder. Chemical shift trajectories followed by correlated $^{31}$P–$^{31}$P spin pairs can be calculated for distortions along different low-frequency vibrational modes (solid line). Comparisons with the experimental axis of elongation (dashed line) can then be used to determine the contribution of the considered distortion to the local structural disorder. Adapted with permission from S. Cadars, A. Lesage, C.J. Pickard, P. Sautet, L. Emsley, Journal of Physical Chemistry A 113 (2009) 902–911. Copyright 2009 American Chemical Society.
hydroxylated surface [195] was constructed from a vitreous silica structure by cutting bonds, allowing building a large amount of different Si–OH groups with various proximities and interacting with variable hydrogen bonds strength. The calculated $^1$H isotropic chemical shifts were found to be well correlated to $\text{OH} - \text{C1/C1/C1}$ distances but only up to 2.2 Å, thus placing some upper limits on the distance for effective hydrogen bonds. Used as a model of bone surfaces, the hydroxyapatite surface was used to predict $^{31}$P, $^1$H and $^{17}$O NMR signatures [196]. GIPAW was also found to help the interpretation of NMR data in studies of surface adsorption mechanisms: xylitol on boehmite nanoparticles surface [197] and hydrogen on Ru nanoparticles. [198]. Strategies were also developed for identification and quantification of phase formed during weathering of phosphates [199].

Surfaces are known to play a predominant role in nanoparticles so that their properties can differ significantly from bulk materials with the same composition. An analysis of how the surface influence propagates in the interior of ZnSe nanoparticles was recently presented [124]. The authors investigated the nature and origin of the disorder appearing on the NMR spectra through their shift and broadening with the system size decreasing. The electronic disorder as induced by the abrupt termination of the crystal–lattice was shown to be the predominant factor explaining the NMR shift variations, in contrast to positional disorder. It was even shown that the surface electronic perturbation could propagate in depth (∼1 nm) and thus affecting the NMR shifts of the layers having the exact positional ordering of the bulk material (Fig. 10).

### 6.3. Glass

In glasses, the disorder can manifest itself through both the variety of the chemical bonding of the constituent atoms (chemical disorder) and the distribution of interatomic distances and bond angles (positional disorder). The resulting broadening can make the analysis of the NMR lines rather complex but provides information on the NMR parameter distribution of the identified individual components. In 1D MAS NMR experiments, the extraction of those NMR parameter distributions for spin 1/2 (only affected the isotropic chemical shift, thus characterized by a single parameter distribution) can be by far much simpler than for quadrupolar nuclei (because of the EFG distribution, the...
distribution is three dimensional). In the latter case, one has generally to resort to at least two-dimensional MQMAS [101,200–202] or DAS [203,204] experiments. The derivation of analytical expressions of the EFG distribution in disordered materials (the latter being a tensor, one has to resort to random matrix concepts) has been the focus of several recent theoretical studies either based on electrostatic point charge [205,206] or DFT [207] calculations.

As highlighted very shortly after the introduction of the method, GIPAW represented a major step forward for the investigation of glass structure when combined to molecular dynamics simulations (hereafter referred to as the MD-GIPAW approach) [92,68]. In spite of several previous attempts to correlate NMR to MD simulations, [208,209] GIPAW appeared as the means of establishing the missing link between the variations of the local structure associated with disorder and experimental distributions of NMR parameters. The way these calculations are typically carried out is shown in Fig. 11 and can now deal with typically several hundreds of atoms. In fact, this approach enables several important NMR issues to be addressed at the same time. The first is through the generation of a wealth of reliable self-consistent environments (again because of the account for the long-range electrostatic interactions) as provided by the MD simulations. With sufficient statistics one can seek for the relationships between NMR parameters with local geometries, the range of the latter not being constrained by the crystalline structure. Even if the local character of NMR interactions permit the use of reference crystalline compounds to interpret glass spectra, as done in tellurite [210] and Ge,Se_{1-x} glasses [123], non-crystalline structures can exhibit strong dissimilarities with the crystalline structure of compounds of the same composition. The second is the aforementioned problem of the derivation of analytical representations of the NMR parameter distribution. MD-GIPAW provides direct access to the (multidimensional) NMR parameter distribution. With the help of advanced multivariate statistical tools, analysis and simulation of NMR spectra in the vitreous state could be significantly enhanced [130]. These appealing features are shown in Fig. 12. Combining these capabilities, one can then map the NMR distribution into a structural distribution, typically a bond-angle distribution as shown in Fig. 13 for binary borosilicate glasses [211]. Nevertheless, most important is the fact that MD-GIPAW enabled for the first time the direct comparison between NMR experimental and MD data (through the simulated NMR spectrum), thus allowing further assessment of structural models and of the theoretical parameters (force fields) underlying the MD simulation. As exemplar of this, the structure of vitreous B_2O_3 has been long the subject of controversy regarding the concentration of supramolecular entities, the boroxol rings [212]. GIPAW calculations revealed that diffraction data were in fact not able to discriminate models with a different concentration of boroxol rings. In contrast, the NMR spectra, here because of a greater sensitivity to B–O–B bond angles, could lift the ambiguity.

Because of the large amount of data generated by MD-GIPAW calculations (typically from hundreds to thousands of individual sites must be analyzed), a dedicated software has been developed for treating such data [66]. MD-GIPAW studies of alkali silicate glasses [213] [214] and vitreous GeO_2 [215] glasses have been recently reported. In the context of biomaterials, MD simulations of the 45S5 Bioglass could be assessed with the help of multinuclear NMR [216]. A natural extension of these calculations will be their combination with the aforementioned dynamical strategies, offering appealing perspectives to support NMR of melts [217–219].

7. Summary and outlook

If solid state NMR is now well established for structural studies of a wide range of materials, on the way of becoming a cornerstone technique in many fields, the direct link between a structure and NMR shifts has been a long-standing problem in solids. GIPAW was the first method to treat periodic systems as a whole and to allow the accurate computation of the full NMR information, i.e. in its full tensorial form. Thanks to the plane wave pseudopotential DFT formalism, this can be achieved at a modest computational cost and large system sizes, up to several hundreds of atoms, can now be routinely investigated using standard parallel machines. An impressive amount of information regarding its applicability to a wide range of materials has already been acquired, if there is still yet few nuclei unexplored, the well-established ones can be routinely involved in the most sophisticated methodologies. Combined with the advance NMR pulse sequences methodology, for more challenging nuclei such a large quadrupolar nuclei or in naturally low abundance, GIPAW clearly appears as crucial to complement the interpretation of the data. Even if only semi-quantitative agreement is sometimes observed between the experimental and calculated parameters for heavy nuclei, GIPAW was found as a promising aid in the NMR interpretation.

As a part of the NMR crystallography framework, GIPAW is firmly established as the method of choice to help assign resonances. It can be even push forward to complement the wealth of NMR techniques devoted to distance and connectivities measurements for structure refinement and determination. Because of the (now widely recognized) high sensitivity of NMR parameters to fine structural details, it can even be envisioned that solid-state NMR would supplant other solid-state techniques: structure determination from NMR chemical shifts is clearly in sight. However, some progresses have certainly to be made in providing more chemical insight in NMR parameters as calculated.
by GIPAW calculations for the end-user. Quantifying through NMR shifts the influence of crystal packing on weak interactions such as hydrogen bonds had been emphasized. Understanding how local versus non-local features contributes to the NMR parameters in solids is clearly a question that can be addressed with GIPAW.

Even if yet in their infancy, methodologies to account for the geometrical and/or dynamical disorder are rapidly progressing. NMR has long been used for the study of disorder and dynamics in solids since it allows the observation of the local chemical environment independently of the existence of a long-range order. Vibrational/motional or configurational averaging strategies based on first-principles molecular dynamics (MD) simulations are still limited with respect to accessible time-scale, typically few tens of picosecond. However, combination with classical MD allows to approach the NMR shift time-scale of millisecond. Highly dependent upon the class of materials studied, the question regarding the contribution of the motions as well as zero-point vibrations deserves future theoretical investigations. Via a supercell approach, chemical disorder can be efficiently taken into account. For amorphous systems such as glass, combination of GIPAW and MD simulations has already established as a promising approach, and strategies such as those developed in NMR crystallography can be thought as applicable in a near future. More generally, the wealth of applications reported here are clearly indicative of the growing importance of DFT calculations combined to spectroscopic studies.

Future directions for improvement of the method itself include account for relativistic effects and will follow any progress made in DFT itself, such as designing an improved XC functional or enhancing the efficiency of the computational aspects. The computation of J coupling tensors is one of the major aspects of the progresses that have been accomplished; the next major step could be the treatment of paramagnetic systems. Recently, several alternative DFT methods for periodic systems have been reported: the Gaussian and augmented plane wave method (GAPW) [220], the converse approach [221] which calculates the NMR of a single nucleus without having to resort to the response theory. Implementation of chemical shift calculations within the Linear Augmented Plane Waves (LAPW) [19] would have some great benefits, such as providing an accurate all-electron approach to assess the different approximation made in GIPAW.
Thus, GIPAW combined with MD holds a context, NMR calculations on shorter time-scale have already time scale (on which the experimental NMR shifts report). In this clear need for developing improved computational strategies simulations will clearly play an important role but there is a systems and finite temperature effects. Molecular dynamics

References

Fig. 13. Overview of the MD-GIPAW methodology to extract structural distributions from NMR data, here applied to the 6 B2O3–4 SiO2 glass [211]. The distribution of NMR parameters is extracted from 11B 3QMAS displayed in (a), notably the distribution of isotropic chemical shift (b) for each boron resonance. From GIPAW calculations combined with MD simulations, a correlation can be established and quantified between the 11B isotropic chemical shift and each of the three B–O–B angles, as shown in (c, d). Combining (b) and (c), one can map the NMR parameter distribution into a distribution of the B–O–B angle. For B-ring species, the distribution is bimodal because the two internal angles are highly constrained to a value close to 120°, the third (external) angle describes the B–O–B linkages.

There is still lot of works to be advanced on the disordered systems and finite temperature effects. Molecular dynamics simulations will clearly play an important role but there is a clear need for developing improved computational strategies capable of taking into account motions up the micro/millisecond time scale (on which the experimental NMR shifts report). In this context, NMR calculations on shorter time-scale have already been proven to be valuable for predicting relaxation times from first principles [222]. Thus, GIPAW combined with MD holds a promising prospect for providing both structural and dynamical information in solids.

References*


* Articles of general interest.
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