

QE-CONVERSE: An open-source code for Quantum ESPRESSO package to compute Orbital Magnetization by first principles

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Abstract

In this paper, we present a revised implementation of the converse method for computing orbital magnetization from first principles. This new version, developed for the Quantum ESPRESSO package, replaces the outdated previous version and makes extensive use of modern libraries for linear algebra computation, including scaLAPACK and ELPA, enhancing the efficiency of calculations, especially in the context of supercells. Orbital magnetization calculation holds significant importance as it allows for the ab-initio calculation of the EPR g tensor and NMR chemical shift in a non-perturbative manner, providing valuable insights into the magnetic properties of materials. Our QE-CONVERSE code is well-suited for investigating these properties in periodic systems.

Keywords: EPR, NMR, Ab-initio, Orbital Magnetization, Quantum ESPRESSO

Program summary

Program Title: qe-converse

CPC Library link to program files: (to be added by Technical Editor)

Developer's repository link: <https://github.com/SFioccola/QE-CONVERSE>

Code Ocean capsule: (to be added by Technical Editor)

Licensing provisions(please choose one): GNU General Public Licence 3.0

Programming language: Fortran 90

Supplementary material:

Journal reference of previous version:

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Does the new version supersede the previous version?: yes

Reasons for the new version: The previous code was integrated into an obsolete version of the PW code in the Quantum ESPRESSO package. The new version is compatible with the modern package and utilizes modern libraries for linear algebra computation.

Summary of revisions: The code underwent a process of refactoring.

Nature of problem: Ab-initio calculation of the EPR g tensor and the NMR chemical shift in solid state.

Solution method: Compute the Orbital Magnetization through

a non-perturbative method.

Additional comments including restrictions and unusual features (approx. 50-250 words):

1. Introduction.

Orbital magnetization, a fundamental property arising from the orbital motion of electrons, plays a crucial role in determining the magnetic behavior of molecules and solids. Alongside spin magnetization, it contributes significantly to the total magnetization observed in various materials. The origin of orbital magnetization is connected in the breaking of time-reversal (TR) symmetry, which is induced by spin-orbit (SO) coupling. This phenomenon occurs spontaneously in ferromagnetic materials or can be triggered in nonmagnetic materials by explicit perturbations. The calculation of orbital magnetization allows ab-initio computation of macroscopic properties like the Nuclear Magnetic Resonance (NMR) chemical shifts and the Electronic Paramagnetic Resonance (EPR) g tensor through a non-perturbative approach known as the "converse" method. This method can be highly superior to existing and widely spread used linear response (LR) method [1], especially in systems where spin-orbit coupling cannot be described as perturbation or the g tensor exhibits a large deviation from the free electron value [2, 3]. While the calculation of the orbital magnetization in finite systems is

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straightforward, it becomes challenging in periodic systems due to the ill-defined position operator in Bloch representations and the contribution of itinerant surface current [4, 5]. Over the past two decades, this challenge has been addressed in the modern theory of orbital magnetization [6, 7] by reformulating the problem in the Wannier representation, similar to the approach used for electric polarization. This reformulation enables the computation of orbital magnetization in the thermodynamic limit, employing a formula reminiscent of the Berry-phase formula.

Recently, the converse approach has been implemented [2] in the Quantum ESPRESSO [8] plane wave code, extending the ab-initio calculation of orbital magnetization via the Berry formula [5] from simple tight-binding models to molecules and periodic systems. In this paper, we present a novel implementation of the converse method that, building upon the foundation of the previous version, continues to rely on first-principle DFT calculations of orbital magnetization using the Berry phase formula. However, a notable enhancement lies in the integration of modern linear algebra libraries, including scalAPACK [9] and ELPA [10]. These advanced libraries significantly improve the efficiency of matrix diagonalization processes especially for larger-scale systems, where computational resources are often a limiting factor. By leveraging these libraries, our upgraded approach enables researchers to tackle the computation of properties such as the EPR g tensor or the NMR chemical shift in larger and more complex systems with improved efficiency and accuracy. This enhancement represents a significant step forward in the practical utility of ab-initio calculations for studying the magnetic properties of materials. This paper is organized as follows. In Section 2, we briefly review the theoretical background of converse method. In Section 3 and 4 we explain the implementation, the installation and usage of QE-CONVERSE code. Finally we provide a couple of applications: one concerning the EPR g tensor calculation for the substitutional Nitrogen defect in Silicon (N_{Si}), and another one concerning the NMR chemical shift of ^{27}Al in alumina (Al_2O_3).

2. Theoretical background.

2.1. Converse EPR

The converse method for calculating the EPR g tensor has been introduced in Ref.[2] and can be summarized as follows. The basic starting point is an independent particles Kohn-Sham Hamiltonian having the translation symmetry of the crystal but breaking Time-Reversal (TR) symmetry. Within the density-functional theory (DFT) and the all-electron (AE) formalism, the Hamiltonian in atomic units is:

$$H_{AE} = \frac{1}{2}[\mathbf{p} + \alpha A(\mathbf{r})]^2 + V(\mathbf{r}) + \frac{\alpha^2 g'}{8} \sigma \cdot [\nabla V(\mathbf{r}) \times \mathbf{p} + \alpha A(\mathbf{r})] \quad (1)$$

where $A(\mathbf{r})$ is the symmetric gauge equal to $\frac{1}{2}\mathbf{B} \times \mathbf{r}$, $\alpha = \frac{1}{c}$ is the fine structure constant, $g' = 2(g_e - 1)$ and σ are Pauli matrices. In contrast to the linear response approach, the converse method bypasses the perturbation of the Hamiltonian: the spin-orbit coupling (SO) term is explicitly incorporated into the self-consistent field calculations while the spin other orbit (SOO) term, that in general has a small contribution to the g tensor, is neglected. The orbital magnetization is formally given by the Hellmann-Feynman equations as:

$$\mathbf{M} = f_n \sum_n \langle \psi_n | -\frac{\partial H_{AE}}{\partial \mathbf{B}} | \psi_n \rangle \quad (2)$$

where f_n is the occupation of the eigenstate n where the expectation values is taken on ground-state spinor ψ_n . Eq. 2 provides a direct evaluation of orbital magnetization in finite systems. However, extending this formula to periodic systems poses a challenge due to the undefined nature of the position operator in such systems. To overcome this limitation, the equation has been reformulated in the Wannier representation, which allows for the computation of orbital magnetization in the thermodynamic limit using the Berry-phase formula:

$$\mathbf{M} = -\frac{\alpha N_c}{2N_k} Im \sum_{n,\mathbf{k}} f_{n,\mathbf{k}} \langle \partial_{\mathbf{k}} u_{n,\mathbf{k}} | \times (H_{\mathbf{k}} + \epsilon_{n,\mathbf{k}} - 2\epsilon_F) | \partial_{\mathbf{k}} u_{n,\mathbf{k}} \rangle \quad (3)$$

where $H_{\mathbf{k}}$ is the crystal Hamiltonian with $\mathbf{B} = 0$, $\epsilon_{n,\mathbf{k}}$ and $u_{n,\mathbf{k}}$ are its eigenvalues and eigenvectors, ϵ_F is the Fermi level, N_c is the number of cells and N_k is the number of \mathbf{k} points. The $|\partial_{\mathbf{k}} u_{n,\mathbf{k}}\rangle$ is \mathbf{k} the derivative of the Bloch wave function for n occupied states. In the context of an all-electron method, Eq. (3) is valid for both normal periodic insulators and metals, as well as Chern insulators with a non-null Chern invariant. In the norm-conserving pseudopotential framework, instead, where the core regions of all-electron wave functions are replaced by smoother pseudo waves (PS), the application of the gauge including projection augmented wave (GIPAW) transformation (see Ref. [11]) is necessary to derive the pseudo GIPAW Hamiltonian. At zero order of the magnetic field this transformation yields the following terms:

$$H_{GIPAW}^{(0,0)} = \frac{1}{2} \mathbf{p}^2 + V_{loc(r)} + \sum_{\mathbf{R}} V_{\mathbf{R}}^{NL} \quad (4)$$

$$H_{GIPAW}^{(1,0)} = \frac{g'}{8} \alpha^2 \left[\sigma \cdot (\nabla V_{loc}(\mathbf{r}) \times \mathbf{p}) + \sum_{\mathbf{R}} F_{\mathbf{R}}^{NL} \right] \quad (5)$$

where $V_{loc(r)}$ is the local Kohn-Sham potential and $V_{\mathbf{R}}^{NL}$ is the nonlocal pseudopotential in the separable Kleinmann-Bylander (KB) form:

$$V_{\mathbf{R}}^{NL} = \sum_{nm} |\beta_{\mathbf{R},n}\rangle v_{\mathbf{R},nm} \langle \beta_{\mathbf{R},m}| \quad (6)$$

while $F_{\mathbf{R}}^{NL}$ is the separable nonlocal operator accounting the so-called paramagnetic contribution of the atomic site \mathbf{R} , that given the set of GIPAW projectors $|\tilde{\rho}_{\mathbf{R},n}\rangle$ can be written as:

$$F_{\mathbf{R}}^{NL} = \sum_{\mathbf{R},nm} |\tilde{\rho}_{\mathbf{R},n}\rangle \sigma \cdot \mathbf{f}_{\mathbf{R},nm} \langle \tilde{\rho}_{\mathbf{R},m}| \quad (7)$$

The expression $f_{\mathbf{R},nm}$ refer to the paramagnetic GIPAW integral and is given by Eq. 10 of Ref.[1]. At the first order in the magnetic field, the GIPAW transformation yields the two terms:

$$H_{\text{GIPAW}}^{(0,1)} = \frac{\alpha}{2} \mathbf{B} \cdot \left(\mathbf{L} + \sum_{\mathbf{R}} \mathbf{R} \times \frac{1}{i} [\mathbf{r}, V_{\mathbf{R}}^{NL}] \right) \quad (8)$$

$$\begin{aligned} H_{\text{GIPAW}}^{(1,1)} = & \frac{g'}{16} \alpha^3 \mathbf{B} \cdot \left(\mathbf{r} \times (\sigma \times \nabla V_{loc}) + \sum_{\mathbf{R}} E_{\mathbf{R}}^{NL} \right. \\ & \left. + \sum_{\mathbf{R}} \mathbf{R} \times \frac{1}{i} [\mathbf{r}, F_{\mathbf{R}}^{NL}] \right) \end{aligned} \quad (9)$$

where $E_{\mathbf{R}}^{NL}$ similar to $F_{\mathbf{R}}^{NL}$, is the separable nonlocal operator accounting the diamagnetic contribution which use the GIPAW integral $e_{\mathbf{R},nm}$ given by Eq. 11 of Ref.[1]:

$$E_{\mathbf{R}}^{NL} = \sum_{\mathbf{R},nm} |\tilde{\rho}_{\mathbf{R},n}\rangle \cdot e_{\mathbf{R},nm} \langle \tilde{\rho}_{\mathbf{R},m}| \quad (10)$$

Inserting the Hamiltonian first order terms, $H_{\text{GIPAW}}^{(0,1)} + H_{\text{GIPAW}}^{(1,1)}$, into Eq. (2) we obtain the final expression of orbital magnetization in the presence of nonlocal pseudopotential:

$$\mathbf{M} = \mathbf{M}_{bare} + \Delta\mathbf{M}_{NL} + \Delta\mathbf{M}_{para} + \Delta\mathbf{M}_{dia} \quad (11)$$

$$\mathbf{M}_{bare} = \frac{\alpha}{2} \sum_{\mathbf{R}} \langle \mathbf{r} \times \frac{1}{i} [\mathbf{r}, H_{\text{GIPAW}}^{(0,0)} + H_{\text{GIPAW}}^{(1,0)}] \rangle \quad (12)$$

$$\Delta\mathbf{M}_{NL} = \frac{\alpha}{2} \sum_{\mathbf{R}} \langle (\mathbf{R} - \mathbf{r}) \times \frac{1}{i} [\mathbf{r} - \mathbf{R}, V_{\mathbf{R}}^{NL}] \rangle \quad (13)$$

$$\Delta\mathbf{M}_{para} = \frac{g' \alpha^3}{16} \sum_{\mathbf{R}} \langle (\mathbf{R} - \mathbf{r}) \times \frac{1}{i} [\mathbf{r} - \mathbf{R}, F_{\mathbf{R}}^{NL}] \rangle \quad (14)$$

$$\Delta\mathbf{M}_{dia} = \frac{g' \alpha^3}{16} \sum_{\mathbf{R}} \langle E_{\mathbf{R}}^{NL} \rangle \quad (15)$$

where $\langle \dots \rangle$ stands for $\sum_{n,k} f_{n,k} \langle \psi_n | \dots | \psi_n \rangle$. The \mathbf{M}_{bare} can be easily computed by the modern theory of orbital magnetization of Eq. (3) where H_k is the GIPAW Hamiltonian, and $\epsilon_{n,k}$ and $u_{n,k}$ are its eigenvalues and eigenvectors. The $\Delta\mathbf{M}_{NL}$, $\Delta\mathbf{M}_{para}$ and $\Delta\mathbf{M}_{dia}$ are respectively the nonlocal, paramagnetic and diamagnetic correction and their expression in the framework of Bloch functions can be found in Appendix B of Ref.[12]. In the converse approach, for the sake of simplicity, the orbital magnetization is computed using a collinear approach where the total spin is aligned along an "easy axis" denoted as \mathbf{e} , which is typically one of three crystallographic directions. The choice of \mathbf{e} affects the spin-orbit coupling within

the system. Since the spin-orbit coupling is dependent on the orientation of the spin axis \mathbf{e} , the computed orbital magnetization is a function of \mathbf{e} . Therefore, to obtain a comprehensive understanding of the orbital magnetization within the system, it is necessary to compute the orbital magnetization as a function of the three different orientations of \mathbf{e} . Finally, from the orbital magnetization the deviation of the g tensor $\Delta g_{\mu\nu}$ from the free electron values ($g_e = 2.002319$) is obtained by the variation in \mathbf{M} with a spin flip:

$$\Delta g_{\mu\nu} = -\frac{2}{\alpha} \mathbf{e}_\mu \cdot \frac{\mathbf{M}(\mathbf{e}_\nu) - \mathbf{M}(-\mathbf{e}_\nu)}{S - (-S)} = -\frac{2}{\alpha S} \mathbf{e}_\mu \cdot \mathbf{M}(\mathbf{e}_\nu) \quad (16)$$

where $\mu\nu$ are Cartesian directions of the magnetic field, and S is the total spin.

2.2 Converse NMR The formulation of the converse method for the calculation of NMR chemical shielding is very similar to the formulation presented above for the calculation of EPR, except that an additional vector potential term corresponding to a magnetic dipole \mathbf{m}_s centered at the atom s and coordinates \mathbf{r}_s is included:

$$A_s(\mathbf{r}) = \frac{\mathbf{m}_s \times (\mathbf{r} - \mathbf{r}_s)}{|\mathbf{r} - \mathbf{r}_s|^3} \quad (17)$$

The AE Hamiltonian now become:

$$H_{\text{AE}} = \frac{1}{2} \{ \mathbf{p} + \alpha [A(\mathbf{r}) + A_s(\mathbf{r})] \}^2 + V(\mathbf{r}) \quad (18)$$

Applying the GIPAW transformation to the latter, similarly to what was done for the EPR, at zeroth order in the external magnetic field, we obtain a term $H_{\text{GIPAW}}^{(0,0)}$ that is equal to Eq. (4), while the term $H_{\text{GIPAW}}^{(1,0)}$ become:

$$H_{\text{GIPAW}}^{(1,0)} = \frac{\alpha}{2} [\mathbf{p} \cdot A_s(\mathbf{r}) + A_s(\mathbf{r}) \cdot \mathbf{p}] + \sum_{\mathbf{R}} K_{\mathbf{R}}^{NL} \quad (19)$$

where $K_{\mathbf{R}}^{NL}$ addressing the paramagnetic contribution of the magnetic dipole and it has the form of a nonlocal operator:

$$K_{\mathbf{R}}^{NL} = \frac{\alpha}{2} \sum_{\mathbf{R},nm} |\tilde{\rho}_{\mathbf{R},n}\rangle \mathbf{k}_{\mathbf{R},nm} \langle \tilde{\rho}_{\mathbf{R},m}| \quad (20)$$

where $k_{\mathbf{R},nm}$ refers to the GIPAW paramagnetic integrals that take into account the effect of the additional vector potential. These integrals, obtained from a set of AE partial waves $|\phi_{\mathbf{R},n}\rangle$ and pseudopotential partial waves $|\tilde{\phi}_{\mathbf{R},n}\rangle$, can be written as:

$$\begin{aligned} k_{\mathbf{R},nm} = & \langle \phi_{\mathbf{R},n} | \mathbf{p} \cdot A_s(\mathbf{r}) + A_s(\mathbf{r}) \cdot \mathbf{p} | \phi_{\mathbf{R},n} \rangle \\ & - \langle \tilde{\phi}_{\mathbf{R},n} | \mathbf{p} \cdot A_s(\mathbf{r}) + A_s(\mathbf{r}) \cdot \mathbf{p} | \tilde{\phi}_{\mathbf{R},n} \rangle \end{aligned} \quad (21)$$

At first order in the external magnetic field, we obtain a term $H_{\text{GIPAW}}^{(0,1)}$ that is equal to Eq. (8), while the term $H_{\text{GIPAW}}^{(1,1)}$ become:

$$H_{\text{GIPAW}}^{(1,1)} = \frac{\alpha}{2} \mathbf{B} \cdot \left(\mathbf{r} \times A_s(\mathbf{r}) + \sum_{\mathbf{R}} J_{\mathbf{R}}^{\text{NL}} + \sum_{\mathbf{R}} \mathbf{R} \times \frac{1}{i} [\mathbf{r}, K_{\mathbf{R}}^{\text{NL}}] \right) \quad (22)$$

where $J_{\mathbf{R}}^{\text{NL}}$ is the nonlocal operator:

$$J_{\mathbf{R}}^{\text{NL}} = \sum_{\mathbf{R},nm} |\tilde{\rho}_{\mathbf{R},n}\rangle \mathbf{j}_{\mathbf{R},nm} \langle \tilde{\rho}_{\mathbf{R},m}| \quad (23)$$

and the $\mathbf{j}_{\mathbf{R},nm}$ its GIPAW integrals addressing the diamagnetic contribution:

$$\begin{aligned} \mathbf{j}_{\mathbf{R},nm} = & \langle \phi_{\mathbf{R},n} | (\mathbf{r} - \mathbf{R}) \times A_s(\mathbf{r}) | \phi_{\mathbf{R},n} \rangle \\ & - \langle \tilde{\phi}_{\mathbf{R},n} | (\mathbf{r} - \mathbf{R}) \times A_s(\mathbf{r}) | \tilde{\phi}_{\mathbf{R},n} \rangle \end{aligned} \quad (24)$$

As in the case of EPR, solving the Hellmann-Feynman equation using the first-order in magnetic field Hamiltonian terms, yields the orbital magnetization as the sum of \mathbf{M}_{bare} , $\Delta\mathbf{M}_{\text{NL}}$, $\Delta\mathbf{M}_{\text{para}}$ and $\Delta\mathbf{M}_{\text{dia}}$ terms like the Eq. 11. However, in the calculation of NMR, the $\Delta\mathbf{M}_{\text{para}}$ and $\Delta\mathbf{M}_{\text{dia}}$ terms are defined by replacing the nonlocal operators $E_{\mathbf{R}}^{\text{NL}}$ and $F_{\mathbf{R}}^{\text{NL}}$, respectively, with $K_{\mathbf{R}}^{\text{NL}}$ and $J_{\mathbf{R}}^{\text{NL}}$:

$$\Delta\mathbf{M}_{\text{para}} = \frac{\alpha}{2} \sum_{\mathbf{R}} \langle (\mathbf{R} - \mathbf{r}) \times \frac{1}{i} [\mathbf{r} - \mathbf{R}, K_{\mathbf{R}}^{\text{NL}}] \rangle \quad (25)$$

$$\Delta\mathbf{M}_{\text{dia}} = \frac{\alpha}{2} \sum_{\mathbf{R}} \langle J_{\mathbf{R}}^{\text{NL}} \rangle \quad (26)$$

Finally, the chemical shielding tensor $\sigma_{s,\alpha\beta}$ is obtained form the derivative of the orbital magnetization \mathbf{M} with respect to a magnetic point dipole \mathbf{m}_s , placed at the site of atom s :

$$\sigma_{s,\alpha\beta} = \delta_{\alpha\beta} - \Omega \frac{\partial \mathbf{M}}{\partial \mathbf{m}_s} \quad (27)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta and Ω is the volume of the simulation cell.

3. Implementation.

In the QE-CONVERSE code to compute the EPR g tensor or the NMR chemical shift, a special-purpose norm-conserving pseudopotential with GIPAW reconstruction is employed. These pseudopotentials, apart from the standard norm-conserving pseudopotentials, incorporate a complete set of AE core wavefunctions as well as AE ($\phi_{\mathbf{R},n}$) and PS ($\tilde{\phi}_{\mathbf{R},n}$) partial waves. Both AE and PS partial waves are utilized to calculate the GIPAW integrals ($f_{\mathbf{R},nm}$, $e_{\mathbf{R},nm}$, $k_{\mathbf{R},nm}$ and $j_{\mathbf{R},nm}$) and the GIPAW projectors ($\tilde{\rho}_{\mathbf{R},n}$) at the beginning of the calculations. In the reference [12], detailed information on how norm-conserving pseudopotentials with GIPAW reconstruction are constructed are provided. A non-exhaustive library

of GIPAW pseudopotentials can be found in Ref.[13]. In principle, the calculation of EPR g tensor or NMR shielding involves incorporating the SO coupling term for EPR, or the vector potential corresponding to the magnetic dipole in the case of NMR, into the Hamiltonian. The Kohn-Sham equation is then solved self-consistently under this Hamiltonian to converge to a new ground state. In the second step, the \mathbf{k} derivative of the Bloch wave function is evaluated in order to determine the \mathbf{M}_{bare} using the Eq. 3. In QE-CONVERSE this derivative is obtained using a covariant finite difference formula, which corresponds to:

$$|\tilde{\partial}_i u_{nk}\rangle = \frac{1}{2} (|\tilde{u}_{n,k+\mathbf{q}}\rangle - |\tilde{u}_{n,k-\mathbf{q}}\rangle) \quad (28)$$

where is $|\tilde{u}_{n,k+\mathbf{q}}\rangle$ the gauge-invariant "dual" state in mesh direction i constructed as a linear combination of the occupied state $|u_{n,k+\mathbf{q}}\rangle$ at neighboring mesh point \mathbf{q} :

$$|\tilde{\partial}_i u_{nk}\rangle = \sum_{n'} (S_{k+\mathbf{q}}^{-1})_{n'n} |u_{n',k+\mathbf{q}}\rangle \quad (29)$$

where $(S_{k+\mathbf{q}})_{nn'}$ is the overlap matrix defined as:

$$(S_{k+\mathbf{q}})_{nn'} = \langle u_{n,k} | u_{n',k+\mathbf{q}} \rangle \quad (30)$$

The diagonalization of the Hamiltonian, undertaken by both the routines dedicated to SCF calculations and those executing the \mathbf{k} derivative of the Bloch functions, employs the Davidson method, addressed by the `csgtorg` routine of Quantum ESPRESSO (Fig.1).

The nonlocal, paramagnetic, and diamagnetic correction terms are then computed starting from the converged ground state and using the nonlocal operators $E_{\mathbf{R}}^{\text{NL}}$, $F_{\mathbf{R}}^{\text{NL}}$, and $K_{\mathbf{R}}^{\text{NL}}$, $J_{\mathbf{R}}^{\text{NL}}$ respectively for the EPR g tensor and for the NMR chemical shielding. All the magnetization terms are summed as specified by Eq. 11 to yield the total orbital magnetization \mathbf{M} . At the end, once \mathbf{M} is obtained, the deviation $\Delta g_{\mu\nu}$ is calculated according to Eq. 16. Alternatively, in the case of NMR, it is derived with respect to the magnetic dipole according to Eq. 27.

4. Installation and usage.

The repository of our code is released at GitHub (<https://github.com/SFioccola/QE-CONVERSE>). A Fortran 90 compiler and the Quantum ESPRESSO package must be previously installed. To take advantage of the enhancements in linear algebra operations, the scalAPACK package or the ELPA library are required. To install the code, the source files and the `Makefile` must be copied in the `/PP/` directory of Quantum ESPRESSO and typing `$ make` the executable binary `qe-converse.x` is compiled. To execute a converse calculation with the QE-CONVERSE, the first step is to perform a SCF calculation using the `PW` code of Quantum

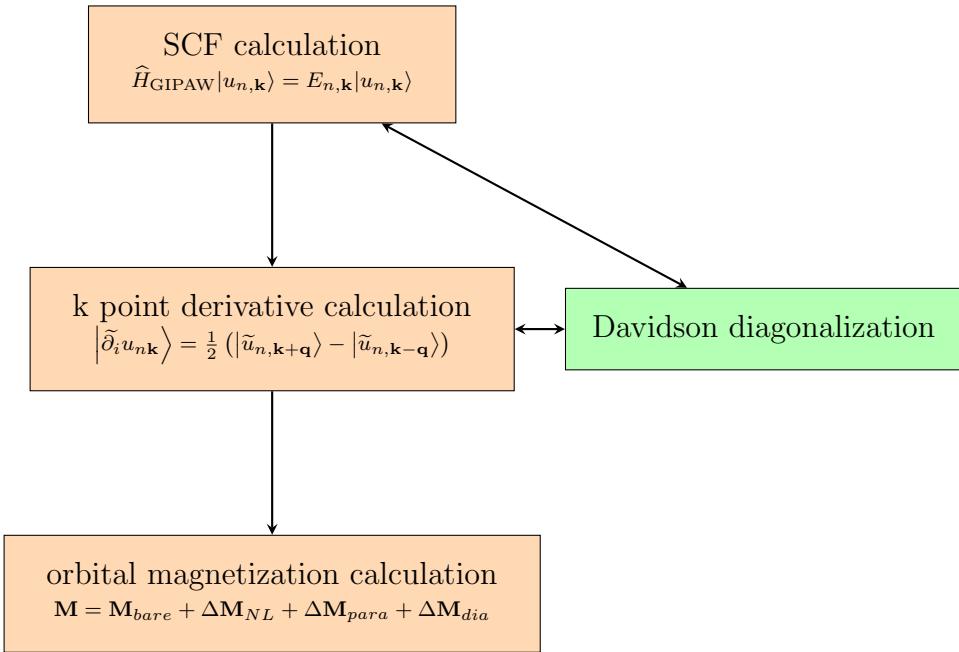


Figure 1: Schematic view of the process to calculate the orbital magnetization in QE-CONVERSE code.

ESPRESSO on a geometrically optimized structure. The SCF calculation must be spin-polarized inserting the flag `nspin=2` in the input for `PW` code. The \mathbf{k} -points grid mesh should be set up without applying symmetry operations to the crystal, and given that the Kohn-Sham Hamiltonian breaks time-reversal symmetry, it is necessary to assume that the k points and $-k$ points are not equivalent. This grid construction can be easily implemented including the flags `nosym=.true.` and `noinv=.true.` in the input for the SCF calculation. In the same directory where the calculation with the `PW` program is executed, the `QE-CONVERSE` code is launched with `./qe-converse.x` using an input file (an example for EPR and NMR calculation is provided in Appendix A). It is essential that the `prefix` and `outdir` flags match those used in the SCF calculation with the `PW` program. This is because the `QE-CONVERSE` code reads essential data such as atomic coordinates, ground state function, pseudopotentials, and the \mathbf{k} -points grid from the XML file in the `outdir` directory of a preceding spin-polarized SCF calculation. The flag `q` in the input file refers to the small vector used for the covariant derivative. Since its value influences the accuracy of the derivative, it is suggested to keep its default value of 0.01. To compute the EPR g tensor, the flag `lambda_so(1, ..., 3)` must be included in the input file to incorporate the SO term into the Hamiltonian. The integer value within the parentheses indicates the direction in which the orbital magnetization is calculated. When calculating the NMR chemical shift instead, it is necessary to introduce into input file the nuclear dipole moment flag, `m_0(1, ..., 3)` and the index of the atom carrying the dipole moment using the designated flag `m_0_atom`.

5. Applications.

5.1 the EPR g tensor for substitutional Nitrogen in Silicon

The following section presents the EPR g tensor calculation for the substitutional Nitrogen defect in Silicon (N_{Si}). This defect has recently garnered significant theoretical and experimental attention due to its potential role as a spin donor in silicon-based quantum devices [14, 15]. It is characterized by the presence of two stable states, where the Nitrogen atom transitions from the tetra-coordinated on-center (T_d) configuration site to a tri-coordinated off-center configuration (with C_{3v} symmetry) along one of the $\langle 111 \rangle$ crystal directions, through a Jahn-Teller mechanism [16]. In this example, we focus solely on the off-center configuration (Figure 2), referred as SL5 in experimental EPR signals. Regarding the g tensor in SL5, g_1 corresponds to the component aligned with the principal axis parallel to the $\langle 111 \rangle$ crystal direction (or $g_{||}$), while g_2 and g_3 represent the isotropic perpendicular components to the $\langle 111 \rangle$ crystal direction (or g_{\perp}).

All ab-initio calculations were performed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [17], together with norm-conserving Trouiller-Martins pseudopotentials with GIPAW reconstruction and employing a plane wave basis set with a kinetic energy cutoff of 84 Ry. To model the (N_{Si}) off-center point defect we used a 512 atoms supercell in which a substitutional nitrogen atom is embedded within a silicon cell. Geometry optimization

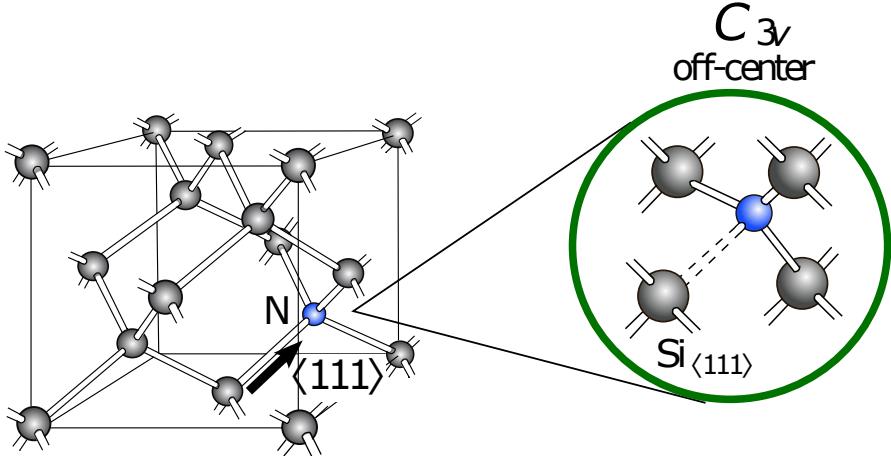


Figure 2: Graphic representation of the off-center configuration for (N_{Si}) defect.

Table 1: The EPR g tensor for the substitutional nitrogen point defect in silicon (N_{Si}) calculated in this work using the QE-CONVERSE code compared to the values of Ref. [16], in which a linear response approach is implemented. Results are compared to experimental data of Ref. [14].

Ref.	g_1	g_2	g_3
This work	2.00209	2.00860	2.00860
Ref. [16]	2.00200	2.00890	2.00780
Exp. [14]	2.00219	2.00847	2.00847

was conducted by sampling at the Γ point and setting the ionic convergence threshold to $0.026 \text{ eV}/\text{\AA}$. In the subsequent SCF and EPR g tensor calculation, we ensured convergence of the parameters by sampling \mathbf{k} -points on a $3 \times 3 \times 3$ mesh grid without considering symmetry, resulting in the integration of the Brillouin zone over a total of 54 \mathbf{k} -points. The convergence threshold was set to $1 \cdot 10^{-8} \text{ Ry}$.

The Table 1 presents the values of the g tensor calculated using the QE-CONVERSE code, compared with experimental results [14] and the g tensor calculated by Simha et al.[15] where the linear response method was implemented [1]. Our results demonstrate good agreement with the experimental data. Moreover, our calculations yield a g tensor that is fully consistent with the axial symmetry along the $\langle 111 \rangle$ crystal directions, as predicted by experiments, thus improving upon the results previously computed by the linear response method of Ref.[15].

5.2 ^{27}Al NMR chemical shifts in alumina

Corundum ($\alpha\text{-Al}_2\text{O}_3$) represents the most thermodynamically stable crystalline form of alumina and it can be synthesized through the calcination process starting from unactivated gibbsite (Al(OH)_3), which transforms into corundum via γ and $\theta\text{-Al}_2\text{O}_3$ at temperatures exceeding 400°C . Determining the structure and the temperature at which transitions phase occur is crucial and it has applications in various industrial fields. For example, $\gamma\text{-Al}_2\text{O}_3$ is used as a catalyst in the petrochemical industry. The most useful technique for this purpose is solid-state NMR of ^{27}Al which detailed interpretation of the experimental spectra remains, however, a challenge. In this study, we apply the QE-CONVERSE code to perform ab-initio calculations of the NMR chemical shift of ^{27}Al in θ phase of alumina (Figure 3). In this phase, the experimental spectra of ^{27}Al exhibit two distinct signals: one corresponding to the aluminum atoms octahedrally coordinated (Al_{oct}), and the other to those tetrahedrally coordinated (Al_{tet}) by oxygen atoms [18]. Implementing the Eq. 27 we computed the absolute chemical shift tensors of ^{27}Al nuclei that we converted into isotropic chemical shieldings using $\sigma_{\text{iso}} = \text{Tr}[\sigma_s/3]$. Finally, we compared this last one with experimental isotropic chemical shifts by using the expression: $\delta_{\text{iso}} = \sigma_{\text{ref}} - \sigma_{\text{iso}}$, where σ_{ref} in this work is the isotropic shielding of ^{27}Al in α phase, used as reference. We performed DFT calculations with the PBE generalized gradient approximation and using the norm-conserving Trouiller-Martins pseudopotentials with GIPAW reconstruction. We used a cutoff energy of 70 Ry. We first relaxed a 200 atoms $\theta\text{-Al}_2\text{O}_3$ supercell sampling at the Γ point and setting the ionic convergence threshold to $0.026 \text{ eV}/\text{\AA}$. We then computed the SCF and NMR calculation setting the \mathbf{k} -points on a $2 \times 2 \times 2$ mesh grid without symmetric constraint. We converged the ground-state to $1 \cdot 10^{-9} \text{ Ry}$. In Table 2 below, we present the chemical shifts of ^{27}Al obtained in this work, compared to experimental [18] and theoretical

data from Ref. [19], where a linear response method was implemented. Our results show very close agreement with both the experimental and previous theoretical results.

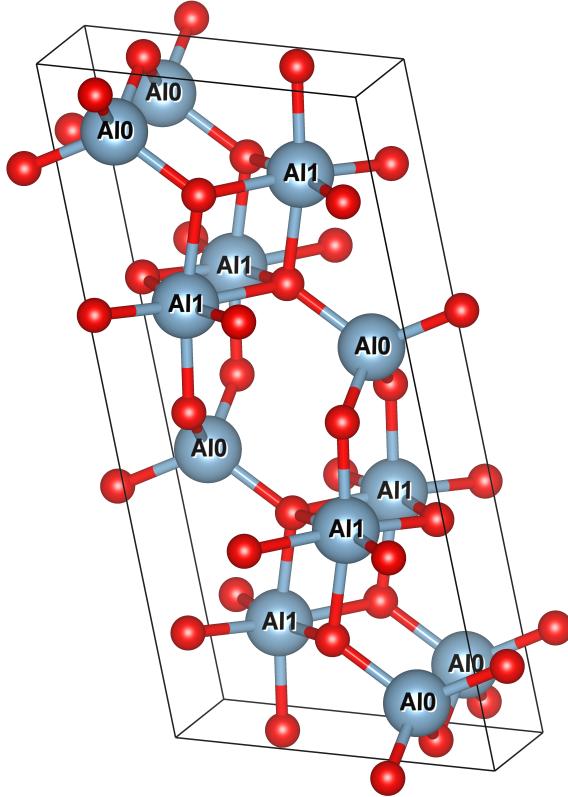


Figure 3: Unit cell of θ -alumina. **AI1** refers to the octahedrally coordinated aluminum atoms (Al_{oct}) while **AI0** are the tetrahedrally coordinated (Al_{tet}).

Table 2: Comparison of chemical shifts calculated in this work and experimental and theoretical data from the literature.

structure	δ_{iso} (ppm)		this work
	previous		
Al site	Exp.	Th.	
$\theta\text{-Al}_2\text{O}_3$			
Al _{oct}	-3.0 (1.0) ^a	-4.9 ^b	-6.3
Al _{tet}	66.5 (1.0) ^a	62.6 ^b	61.0

^a Reference [18]

^b Reference [19]

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Appendix A.

Example of input for EPR g tensor calculation. \$DIR is an integer from 1 to 3 that denotes the spin-orbit coupling direction.

```
&input_qeconverse
prefix = 'example_EPR'
outdir = './scratch/'
diagonalization = 'david'
verbosity = 'high'
q_gipaw = 0.01
dudk_method = 'covariant'
diago_thr_init = 1d-4
conv_threshold = 1e-8
mixing_beta = 0.5
lambda_so(${DIR}) = 1.0
/

```

Example of input for NMR calculation. \$DIR is an integer from 1 to 3 that refers to nuclear dipole moment direction while \$i indicates the atoms that brings the dipole.

```
&input_qeconverse
prefix = 'example_NMR'
outdir = './scratch/'
diagonalization = 'david'
verbosity = 'high'
q_gipaw = 0.01
dudk_method = 'covariant'
diago_thr_init = 1d-4
conv_threshold = 1e-8
mixing_beta = 0.5
m_0(${DIR}) = 1.0
m_0_atom = ${i}
/

```

References

- [1] C. J. Pickard, F. Mauri, [First-principles theory of the epr g tensor in solids: Defects in quartz](#), Phys. Rev. Lett. 88 (2002) 086403. doi:[10.1103/PhysRevLett.88.086403](https://doi.org/10.1103/PhysRevLett.88.086403). URL <https://link.aps.org/doi/10.1103/PhysRevLett.88.086403>
- [2] D. Ceresoli, U. Gerstmann, A. P. Seitsonen, F. Mauri, [First-principles theory of orbital magnetization](#), Phys. Rev. B 81 (2010) 060409. doi:[10.1103/PhysRevB.81.060409](https://doi.org/10.1103/PhysRevB.81.060409). URL <https://link.aps.org/doi/10.1103/PhysRevB.81.060409>
- [3] U. Gerstmann, A. P. Seitsonen, D. Ceresoli, F. Mauri, H. J. von Bardeleben, J. L. Cantin, J. Garcia Lopez, [sic_c antisite pairs in sic identified as paramagnetic defects with strongly anisotropic orbital quenching](#), Phys. Rev. B 81 (2010) 195208. doi:[10.1103/PhysRevB.81.195208](https://doi.org/10.1103/PhysRevB.81.195208). URL <https://link.aps.org/doi/10.1103/PhysRevB.81.195208>

- [4] R. Resta, **Electrical polarization and orbital magnetization: the modern theories**, Journal of Physics: Condensed Matter 22 (12) (2010) 123201. [doi:10.1088/0953-8984/22/12/123201](https://doi.org/10.1088/0953-8984/22/12/123201). URL <https://dx.doi.org/10.1088/0953-8984/22/12/123201>
- [5] D. Ceresoli, T. Thonhauser, D. Vanderbilt, R. Resta, **Orbital magnetization in crystalline solids: Multi-band insulators, chern insulators, and metals**, Phys. Rev. B 74 (2006) 024408. [doi:10.1103/PhysRevB.74.024408](https://doi.org/10.1103/PhysRevB.74.024408). URL <https://link.aps.org/doi/10.1103/PhysRevB.74.024408>
- [6] D. Xiao, J. Shi, Q. Niu, **Berry phase correction to electron density of states in solids**, Phys. Rev. Lett. 95 (2005) 137204. [doi:10.1103/PhysRevLett.95.137204](https://doi.org/10.1103/PhysRevLett.95.137204). URL <https://link.aps.org/doi/10.1103/PhysRevLett.95.137204>
- [7] T. Thonhauser, D. Ceresoli, D. Vanderbilt, R. Resta, **Orbital magnetization in periodic insulators**, Phys. Rev. Lett. 95 (2005) 137205. [doi:10.1103/PhysRevLett.95.137205](https://doi.org/10.1103/PhysRevLett.95.137205). URL <https://link.aps.org/doi/10.1103/PhysRevLett.95.137205>
- [8] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandri, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. De Gironcoli, P. Delugas, R. Distasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. Nguyen, H.-V. Nguyen, A. Otero-De-La-Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, S. Baroni, **Advanced capabilities for materials modelling with quantum espresso**, Journal of Physics Condensed Matter 29 (46), cited by: 5126; All Open Access, Green Open Access (2017). [doi:10.1088/1361-648X/aa8f79](https://doi.org/10.1088/1361-648X/aa8f79). URL <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85036470554&doi=10.1088%2f1361-648X%2faa8f79&partnerID=40&md5=287986808af5a316774cc3f639b71c06>
- [9] L. S. Blackford, J. Choi, A. Cleary, E. D'Azevedo, J. Demmel, I. Dhillon, J. Dongarra, S. Hammarling, G. Henry, A. Petitet, K. Stanley, D. Walker, R. C. Whaley, **ScaLAPACK Users' Guide**, Society for Industrial and Applied Mathematics, Philadelphia, PA, 1997.
- [10] A. Marek, V. Blum, R. Johann, V. Havu, B. Lang, T. Auckenthaler, A. Heinecke, H.-J. Bungartz, H. Lederer, **The elpa library: scalable parallel eigenvalue solutions for electronic structure theory and computational science**, Journal of Physics: Condensed Matter 26 (21) (2014) 213201. [doi:10.1088/0953-8984/26/21/213201](https://doi.org/10.1088/0953-8984/26/21/213201). URL <https://dx.doi.org/10.1088/0953-8984/26/21/213201>
- [11] C. J. Pickard, F. Mauri, **All-electron magnetic response with pseudopotentials: Nmr chemical shifts**, Phys. Rev. B 63 (2001) 245101. [doi:10.1103/PhysRevB.63.245101](https://doi.org/10.1103/PhysRevB.63.245101). URL <https://link.aps.org/doi/10.1103/PhysRevB.63.245101>
- [12] D. Ceresoli, N. Marzari, M. G. Lopez, T. Thonhauser, **Ab initio converse nmr approach for pseudopotentials**, Phys. Rev. B 81 (2010) 184424. [doi:10.1103/PhysRevB.81.184424](https://doi.org/10.1103/PhysRevB.81.184424). URL <https://link.aps.org/doi/10.1103/PhysRevB.81.184424>
- [13] <https://sites.google.com/site/dceresoli/pseudopotentials>.
- [14] M. Belli, M. Fanciulli, D. Batani, **Electron spin resonance of substitutional nitrogen in silicon**, Phys. Rev. B 89 (2014) 115207. [doi:10.1103/PhysRevB.89.115207](https://doi.org/10.1103/PhysRevB.89.115207). URL <https://link.aps.org/doi/10.1103/PhysRevB.89.115207>
- [15] M. Belli, M. Fanciulli, **Electron spin–lattice relaxation of substitutional nitrogen in silicon: The role of disorder and motional effects**, Nanomaterials 14 (1) (2024). [doi:10.3390/nano14010021](https://doi.org/10.3390/nano14010021). URL <https://www.mdpi.com/2079-4991/14/1/21>
- [16] C. Simha, G. Herrero-Saboya, L. Giacomazzi, L. Martin-Samos, A. Hemeryck, N. Richard, **Deep levels and electron paramagnetic resonance parameters of substitutional nitrogen in silicon from first principles**, Nanomaterials 13 (14) (2023). [doi:10.3390/nano13142123](https://doi.org/10.3390/nano13142123). URL <https://www.mdpi.com/2079-4991/13/14/2123>
- [17] J. P. Perdew, K. Burke, M. Ernzerhof, **Generalized gradient approximation made simple**, Phys. Rev. Lett. 77 (1996) 3865–3868. [doi:10.1103/PhysRevLett.77.3865](https://doi.org/10.1103/PhysRevLett.77.3865). URL <https://link.aps.org/doi/10.1103/PhysRevLett.77.3865>
- [18] L. O'Dell, S. Savin, A. Chadwick, M. Smith, **A ^{27}Al MAS NMR study of a sol–gel produced alumina: Identification of the NMR parameters of the $\theta\text{-Al}_2\text{O}_3$ transition alumina phase**, Solid State Nuclear Magnetic Resonance 31 (4) (2007) 169–173. [doi:<https://doi.org/10.1016/j.ssnmr.2007.05.002>](https://doi.org/10.1016/j.ssnmr.2007.05.002). URL <https://www.sciencedirect.com/science/article/pii/S0926204007000318>
- [19] A. R. Ferreira, E. Küçükbenli, A. A. Leitão, S. de Gironcoli, **Ab initio ^{27}Al nmr chemical shifts and quadrupolar parameters for Al_2O_3 phases and their precursors**, Phys. Rev. B 84 (2011) 235119. [doi:10.1103/PhysRevB.84.235119](https://doi.org/10.1103/PhysRevB.84.235119). URL <https://link.aps.org/doi/10.1103/PhysRevB.84.235119>