### UNIVERSITA' DEGLI STUDI DI PARMA Dottorato di ricerca in Fisica XXVII Ciclo

## $Ab \ initio \ modelling \ of \ positive \ muon \ implantation \ sites \ in \ crystalline \ solids$

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## Abstract

In this thesis, a computationally efficient method for identifying interstitial muon sites in crystalline solids is presented. An accurate determination of muon embedding positions and effects is important for muon spin rotation and relaxation experiments since it can significantly widen the capabilities of this experimental technique. Indeed, these information are usually unknown to the experimenter and in most cases it is not possible to characterize the muon sites and the muon induced perturbation from experimental knowledge.

The approach proposed in this thesis is based on *ab initio* Density Functional Theory (DFT) simulations and it was designed to provide a companion tool to assist muon spin rotation data analysis. The first principles determined muon stopping site(s) and the expected perturbation produced by the muon implantation have been compared to muon spin rotation and relaxation results in a series of textbook cases that have been extensively characterized experimentally.

It is also highlighted that the estimation of the ground state energy of the muon (also referred to as zero point motion energy) is crucial in order to distinguish between trapping and non-trapping muon sites. In order to keep the computational load of the *ab initio* simulations within the bounds of standard computer clusters capacities, we approximate the total Hamiltonian of the system introducing a Born-Oppenheimer separation between the degrees of freedom of the muon and those of the nuclei and of the electrons. This approach has been referred to as double adiabatic approximation in literature. The method is found to be sufficiently accurate as well as computationally feasible when an algorithmic procedure to efficiently perform the simulations is introduced.

The successful results obtained so far include the identification of muon sites in iron pnictide superconductors, the study of  $F-\mu$ -F cen-

tres in fluorides, muon diffusion in Copper and the recent identification of muon sites in MnSi and T'-La<sub>2</sub>CuO<sub>4</sub>. All these cases confirm the validity of the DFT approach and emphasize the importance of accurate muon site predictions.

## Acknowledgements

My sincere gratitude goes to my advisor, Prof. Roberto De Renzi. His quick and enlightening physical intuition provided the fundamental guidance for all the work hereby presented. However, it would be unfair to avoid mentioning how the inspiring discussions, the effective ideas, his humor and positive attitude in general made working in Parma amazing. In brief, having Roberto De Renzi as advisor has been an honour and a pleasure.

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Part of the work discussed in this thesis arises from the discussion and the excellent work of a number of collaborators that I will not list here because, for sure, I would forget someone. To mention but a few, it has been a pleasure to meet and discuss with doctors Gwendolyne Pascua, Johannes Möller, Franz Lang, Hubertus Luetkens, Alex Amato and Rustem Khasanov.

Finally, I cannot refrain from expressing my grateful acknowledgements to the ping pong people, to Michela for her unbelievable patience and to my parents for being my parents!

## List of papers

The papers published during the Ph.D. are divided in two sections. This thesis is based on the work collected in articles from section A which deal partially or entirely with the identification of muon sites. Other results concerning superconducting and magnetic materials are reported in papers listed in section B. Pre-prints and submitted papers are listed in section C.

### Section A

1. "Ab initio strategy for muon site assignment in wide band gap fluorides".

F. Bernardini, P. Bonfà, M. Massidda, R. De Renzi Physical Review B DOI:10.1103/PhysRevB.87.115148

2. "A magnetic glassy phase in  $\operatorname{Fe}_{1+y}\operatorname{Se}_x\operatorname{Te}_{1-x}$  single crystals".

G. Lamura, T. Shiroka, P. Bonfà, S. Sanna, F. Bernardini, R. De Renzi, R. Viennois, E. Giannini, A. Piriou, N. Emery, M.R. Cimberle, M. Putti Journal of Physics-Condensed Matter DOI:10.1088/0953-8984/25/15/156004

 "Common effect of chemical and external pressures on the magnetic properties of RCoPO (R = La, Pr)".
 G. Prando, P. Bonfà, G. Profeta, R. Khasanov, F. Bernardini, M. Mazzani, E.M. Bruning, A. Pal, V.P.S. Awana, H.J. Grafe, B. Buchner, R. De Renzi, P. Carretta, S. Sanna Physical Review B DOI:10.1103/PhysRevB.87.064401

- Understanding the μSR spectra of MnSi without magnetic polarons
   A Amato, P Dalmas de Réotier, D Andreica, A Yaouanc, A Suter, G Lapertot, IM Pop, E Morenzoni, P Bonfà, F Bernardini, R De Renzi
   Physical Review B
   DOI:10.1103/PhysRevB.89.184425
- 5. "Effect of external pressure on the magnetic properties of LnFeAsO (Ln = La, Ce, Pr, Sm)".

R. De Renzi, P. Bonfà, G. Prando, P. Carretta, R. Khasanov,
A. Amato, H. Luetkens, M. Bendele, F. Bernardini, S. Massidda,
A. Palenzona, M. Tropeano and M. Vignolo
Superconductor Science and Technology
DOI:10.1088/0953-2048/25/8/084009

6. "Playing quantum hide-and-seek with the muon: localizing muon stopping sites".

J. S. Möller, P. Bonfà, D. Ceresoli, F. Bernardini, S. J. Blundell, T. Lancaster, R. De Renzi, N. Marzari, I. Watanabe, S. Sulaiman, M. I. Mohamed-Ibrahim Physica Scripta DOI:10.1088/0031-8949/88/06/068510

### Section B

- 7. Poisoning effect of Mn in  $LaFe_{1-x}Mn_xAsO_{0.89}F_{0.11}$ : Unveiling a quantum critical point in the phase diagram of iron-based superconductors F Hammerath, P Bonfa, S Sanna, G Prando, R De Renzi, Y Kobayashi, M Sato, P Carretta Physical Review B DOI:10.1103/PhysRevB.89.134503
- 8. Tuning the magnetic and structural phase transitions of PrFeAsO via Fe/Ru spin dilution

Yuen Yiu, Pietro Bonfà, Samuele Sanna, Roberto De Renzi, Pietro Carretta, Michael A. McGuire, Ashfia Huq, and Stephen E. Nagler

Physical Review B DOI:10.1103/PhysRevB.90.064515

- 9. **75As NQR signature of the isoelectronic nature of ruthenium for iron substitution in \text{LaFe}\_{1-x}\text{Ru}\_x\text{AsO}** Marcello Mazzani, Pietro Bonfà, Giuseppe Allodi, Samuele Sanna, Alberto Martinelli, Andrea Palenzona, Pietro Manfrinetti, Marina Putti, Roberto De Renzi physica status solidi (b) DOI:10.1002/pssb.201350237
- 10. "s-wave pairing in the optimally-doped LaO<sub>0.5</sub>F<sub>0.5</sub>BiS<sub>2</sub> superconductor".
  G. Lamura, T. Shiroka, P. Bonfà, S. Sanna, R. De Renzi, C. Baines, H. Luetkens, J. Kajitani, Y. Mizuguchi, O. Miura, K. Deguchi, S. Demura, Y. Takano, and M. Putti Physical Review B (R) DOI:10.1103/PhysRevB.88.180509
- 11. "Role of in-plane and out-of-plane dilution in CeFeAsO: Charge doping versus disorder".

G. Prando, O. Vakaliuk, S. Sanna, G. Lamura, T. Shiroka, P. Bonfà, P. Carretta, R. De Renzi, H.-H. Klauss, C. G. F. Blum,
S. Wurmehl, C. Hess, and B. Büchner
Physical Review B
DOI:10.1103/PhysRevB.87.174519

- 12. "Onset of magnetism in optimally electron-doped LFe<sub>1-x</sub>Ru<sub>x</sub>AsO<sub>1-y</sub>F<sub>y</sub> (L = La, Nd, or Sm) superconductors around x =<sup>1</sup>/<sub>4</sub>".
  S. Sanna, P. Carretta, R. De Renzi, G. Prando, P. Bonfa, M. Mazzani, G. Lamura, T. Shiroka, Y. Kobayashi, M. Sato, R. De Renzi Physical Review B DOI:10.1103/PhysRevB.87.134518
- 13. Crossover between magnetism and superconductivity in LaFeAsO with low H-doping level G Lamura, T Shiroka, P Bonfà, S Sanna, R De Renzi, F Caglieris, MR Cimberle, S Iimura, H Hosono, M Putti Journal of Physics: Condensed Matter DOI:10.1088/0953-8984/26/29/295701

### Section C

- 14. Efficient and reliable strategy for identifying muon sites based on the Double Adiabatic Approximation P Bonfà, R De Renzi submitted to: The Journal of Chemical Physics C
- DFT assisted muon embedding site assignment: the case of T'-La<sub>2</sub>CuO<sub>4</sub> P. Bonfà, F. Bernardini, R. De Renzi, G. Pascua, H. Luetkens in preparation

**Comments on my participation** In paper 1) I have carried out the developments, all the calculations and I have written the manuscripts. In papers 2), 3) and 4) I have carried out the DFT simulations and written part of the manuscript. In paper 5) I have taken part to the analysis of the muon site. In paper 6) I have done part of the DFT simulations and written part of the manuscript. Paper 7) is the sum of NMR and  $\mu$ SR measurements. I analysed an discussed the  $\mu$ SR part. Paper 8) is the sum of neutron scattering and  $\mu$ SR measurements. I analysed an discussed the  $\mu$ SR part. In paper 9) I have done the DFT simulations and I took part to the NMR measurements and simulations and I wrote part of the manuscript. In papers 14) and 15) I have done/developed all the DFT simulations as well as written the manuscripts.

## Acronyms

- $\mu {\bf SR}$  Muon Spin rotation and Relaxation spectroscopy. 3–5, 7, 99, 106, 111
- **AFM** antiferromagnetic. 22, 63, 65, 101, 111
- **APW** Augmented Plane Waves. 49, 50
- **BO** Born Oppenheimer. 36, 43, 44, 56, 98
- DAA Double Adiabatic Approximation. 57, 77, 86, 87, 89, 90, 92, 97, 105, 110, 111, 118, 121, 129
- **DBO** Double Born Oppenheimer. 58, 90, 91, 94–96, 117, 129
- **DFT** Density Functional Theory. 4, 5, 29–32, 34, 38, 40, 45, 51, 53, 55, 60, 61, 68, 69, 75, 78–87, 89, 99, 101, 104, 106, 109–111, 113, 117, 118
- **DMFT** Dynamical Mean Field Theory. 101, 118
- **FM** Ferromagnetic. 66, 68, 71, 116
- **FP** Full Potential. 49, 60, 61, 101, 113–116
- **GGA** Generalized Gradient Approximation. 41, 101, 113, 116, 118, 119
- **GSE** Ground State Energy. 54, 56, 57, 63, 65, 72, 77–79, 81, 85, 87, 97, 105, 110
- **HF** Hartree Fock. 4, 29

Acronyms

- **HK** Hohenberg and Kohn. 32–35
- **IPSC** Iron Pnictides Superconductor. 60, 61, 64, 73–75, 89, 109
- **KKR** Korringa-Kohn-Rostocker. 51, 52
- **KS** Kohn and Sham. 32, 35, 37, 39, 40, 43–45, 47, 58
- **LAPW** Linearized Augmented Plane Waves. 44, 49, 50, 113, 114, 116
- LDA Local Density Approximation. 40, 41, 113
- MP Monkhorst and Pack. 42, 94, 114, 116–118
- **NEB** Nudged Elastic Band. 94, 97, 117
- **NMR** Nuclear Magnetic Resonance. 3, 4, 8, 18, 63, 99, 101, 102, 106, 107
- **PAW** Projector Augmented Wave. 48, 77, 114
- PBC Periodic Boundary Conditions. 29, 52, 55, 91, 96
- **PBE** Perdew Burke Ernzerhof. 114, 116–118
- **PW** Plane Wave. 44, 45, 68, 114, 115, 118
- **TDDFT** Time-Dependent Density Functional Theory. 32

## Introduction and motivation

The scope behind the study presented in this thesis is the development of a computational companion tool to assist Muon Spin rotation and Relaxation spectroscopy ( $\mu$ SR) data analysis in a time effective and affordable manner. An efficient, reliable and sufficiently accurate way to study the interstitial sites and perturbations introduced by the positively charged muon in its local neighbourhood in crystalline solids would empower  $\mu$ SR with unprecedented quantitative estimation possibilities.

 $\mu$ **SR** is a powerful experimental technique for all the problems in condensed matter physics which can take advantage of a microscopic magnetometer embedded within the sample, i.e. the muon. Among the many, magnetism and superconductivity are probably the most common, followed by the study of hydrogen-like impurities in semiconductors, their diffusion and reaction kinetics, and studies of quantum diffusion mechanisms [1–3].  $\mu$ SR is often compared to Nuclear Magnetic Resonance (NMR) in providing information on static and dynamic magnetic fields on a local scale, but, unlike NMR, it can easily be performed in zero applied field (since muons can be produced in fully polarised beams), it is applicable to almost any material and removes the requirement for a radio-frequency to activate the probe. The price to pay is a large uncertainty in the muon position inside the sample. In parallel and as a part of the development of the experimental technique, a lot of work has been devoted to the determination of muon sites in crystals. A precise characterisation of the muon interstitial sites was indeed possible from accurate experimental studies of the

### 1. Introduction and motivation

Knight shift, of the level crossing resonance (LCR) and by inspecting asymmetry relaxation rates as a function of applied fields in selected compounds (see for example [4–8]). However, in a large number of cases the muon position and its effect on the hosting system cannot be inferred solely by experimental knowledge and a reliable method to obtain the muon site in condensed matter would be of great value. To this aim, we have selected *ab initio* methods, and especially Density Functional Theory (DFT) based quantum chemistry approaches, as the computational scheme to perform muon site identification simulations and support  $\mu$ SR data analysis.

DFT is a widely accepted framework to solve the Schrödinger equation for an interacting many-body system. Its enormous success is testified by the large set of scientific fields which benefit from the prediction power offered by the computational approaches based on Kohn Sham's auxiliary system method. Developments in electronic structure methods combined with a continuously increasing computing power can deliver unprecedented accuracies in computational experiments on a quantum mechanical perspective. As of today, many experimental techniques rely on DFT to support the data analysis. In the field of condensed matter, DFT can be used to interpret and predict spectroscopic properties like core-level electron energy loss (EELS) spectra, vibrational infra-red and Raman spectra, NMR and electron paramagnetic resonance spectra (EPR), linear and nonlinear optical spectra [9, 10]. This vast collection of successful results promoted DFT simulations as the computational scheme of election for the practical realisation of a tool for  $\mu$ SR data interpretation support.

**Identifying muon sites** with *ab initio* approaches is not a new idea. A lot of attention has been devoted, in the last three decades, to the analysis of muon interactions in solids by means of Hartree Fock (HF), DFT and other simulation techniques (see for example Ref. [11–15]). The contributions to the development of the experimental technique obtained with computational methods are hardly enumerable. However, in most cases the attention has been mainly devoted to  $\mu$ SR experiments where the interpretation of the experimental data was

elusive or ambiguous. Here we started from the opposite perspective. In this thesis we choose a set of materials where the muon site is known from the experiment or can be easily checked. On this solid grounds we test the accuracy of a DFT based approach to identify muon sites. Accomplishing this ambitious task is of course well beyond the ability of any single researcher or group possibilities. However, the results discussed in this thesis and in literature (among the many, see Ref. [16–25]) are promising and call for further investigations.

### 1.1. Outline of the thesis

In chapter 2 and 3 we introduce the  $\mu$ SR technique and illustrate the basic concepts behind DFT. In chapter 4 we discuss a simple approach to identify muon sites, namely the inspection of the minima of the electrostatic potential of the unperturbed material. This approach is found to be sufficiently accurate for some special cases. However, in general, this crude approximation does not provide satisfying results. Therefore, a better estimation, which takes into account the perturbation introduced by the  $\mu$  embedding, is discussed in chapter 5. In chapter 6 we improve our method by proposing a simple and yet sufficiently accurate approach to evaluate the ground state energy of the muon, whose effect is found to have relevant consequences on the interstitial site determination task. In chapter 7 we discuss how all the above results are used to unveil the magnetic properties of a material of high scientific interest, namely the T' structure of La<sub>2</sub>CuO<sub>4</sub>. Indeed, the knowledge of the muon site, which in this case happens to be in a low symmetry interstitial position, allows to distinguish among the possible long-range magnetic orders and therefore to determine the ground state magnetic structure. In chapter 8 we conclude the thesis and discuss some perspectives for future developments.

# A short introduction to $\mu SR$

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 $\mu$ SR is a spectroscopic technique in which implanted positive muons are used as a nanoscopic magnetometer placed within the sample. This is made possible by two favourable conditions offered by nature: parity violation in the weak decay and the production of spin polarised  $\mu^+$  beams through the decay of the pion. The experimenter is provided



Figure 2.1.: Header of the first  $\mu$ SR newsletter.

with the time evolution of the direction of the muon spin which can be extracted from the collection of each decay positron as a function of the individual muon lifetime spent within the sample.

The name stands, in the words of the first  $\mu$ SR Newsletter (Fig. 2.1), for "Muon Spin Relaxation, Rotation, Resonance, Research, or what have you" intentionally suggesting the analogy with NMR in which nuclei are used for the same scope.

 $\mu$ SR is often utilised to investigate the magnetic and the superconducting properties of a sample, but it finds wide application also in studies of the effect hydrogen-like impurities in semiconductors, quantum diffusion, reaction kinetics and several other fields [2, 26].

In this section, a brief introduction to  $\mu$ SR is presented. For a more detailed description of this technique as well as of the various applications in many field of research, the reader is referred to the several books and review articles [1, 3, 27–29].

### 2.1. Brief history

The muons arising from the secondary radiation of cosmic rays were first observed in 1936 by C. D. Anderson and S. Neddermeyer. However, the breakthrough that allowed the progress toward the modern  $\mu$ SR technique was the discovery of parity violation in weak decay observed experimentally in  ${}^{60}$ Co beta decay by Wu *et al*[30] in 1957 and predicted by Nobel awarded scientists Lee and Yang [31].

The first proton accelerators offering the intense pion (and hence muon) beams which are needed to perform  $\mu$ SR experiments were first produced at the CERN synchrotron, at JINR in Dubna, at SREL in Berkeley and at Nevis Columbia at the end of the 1950s. Starting from the 1970s, new high-intensity intermediate-energy accelerators were built at laboratories in the Schweizerisches Institut für Nuklearphysik (CH), Los Alamos (USA) and TRIUMF Vancouver (Canada). These new accelerators offered continuous beams (vide infra) two orders of magnitude more intense than the previous accelerators. Shortly after, pulsed muon facilities were realised in ISIS at the Rutherford Appleton Laboratory in UK and KEK in Tsukuba, Japan (now replaced by J-PARC in Tokai) and the new continuous beam facility PSI was built in Villigen (CH).

### 2.2. Muon production

High intensity collimated muon beams are produced using accelerated protons in a two step process. The collision of two protons or a proton and a neutron initially produces a pion according to

$$p + p \to \pi^+ + p + n , \qquad (2.1)$$

$$p + n \to \pi^+ + n + n \tag{2.2}$$

or

$$p + n \to \pi^- + p + p \tag{2.3}$$

The first particle in Eq. 2.1, 2.2 and 2.3 comes from the accelerated proton beam while the second is at rest in a muon production target (usually graphite). The kinetic energy  $T = c^2(m - m_0) = m_0(\gamma - 1)$ of the accelerated proton having quadrimomentum  $\bar{P}_{1i}$  for producing a pion at rest in the muon production target where the neutron with quadrimomentum  $\bar{P}_{2i}$  resides is

$$P_{1i} + P_{2i} = P_f$$
  
$$\left(\bar{P_{1i}} + \bar{P_{2i}}\right)^2 = \bar{P_f}^2$$
  
$$2m_p^2 + 2m_p^2\gamma = (2m_p + m_\pi)^2$$

where we have assumed  $m_n = m_p$  (the intended meaning of the symbols should be clear from context). This gives  $\gamma = 1 + \frac{2m_\pi}{m_p} + \frac{m_\pi^2}{2m_p^2} \simeq 1 + \frac{2m_\pi}{m_p}$  and a threshold kinetic energy of about  $(\gamma - 1)m_pc^2 = 2m_\pi c^2 \sim 280$  MeV. However, for sake of efficiency in the pion production, usually proton beams with energies between 500 and 800 MeV are used.

Pion half life time is just 26 ns and from its decay a positive or negative muon is produced via the two-body decay:

$$\pi^+ \to \mu^+ + \nu_\mu \tag{2.4}$$

$$\pi^- \to \mu^- + \bar{\nu}_\mu \tag{2.5}$$

It's worth noting that the negative pion (process in Eq. 2.3) stopping in the production target almost always undergoes nuclear capture before it has a chance to decay. Negative muons may be produced from the in-flight negative pion's decays (see following) but, as for negative pions, the lifetime of negative muons in matter is reduced by nuclear capture. For this reason, and also because surviving  $\mu^-$  fall into atomic orbitals extremely close to atomic nuclei,  $\mu^+$ SR is more commonly used to investigate condensed matter and will be considered in the following.

In the process in Eq. 2.4, since the neutrino has negative helicity and the pion is a spin-less particle, the conservation of momentum implies that muon spin is aligned antiparallel to its momentum in the pion's rest frame. As a consequence, polarised muon beams are produced in two distinct pion momentum regimes

• selecting muon that arise from  $\pi^+$  at rest near the surface of the muon production target. This method produces a 100% polarised muon beam with kinetic energies of about 4.1 MeV and a maximum momentum of 29.8 MeV/c. This is the so called



Figure 2.2.: Flow chart showing the processes involved in the slowing down of high-energetic muons in matter.

"surface" or "Arizona" beam. The low momentum characterising these beams is suited for studying thin samples and tiny single crystals of about  $1 \text{ mm}^2$ .

By collecting muons from in-flight pion's decays in a long superconducting solenoid. Typical muon beams with a polarisation < 100% and energies of ~40-50 MeV are produced after momentum selection by bending magnets. As a consequence, muons have appreciably longer stopping ranges in matter and this can be used to overcome thick cryostat walls or pressure cells, thus allowing the exploration of extreme temperature or pressure conditions.</li>

### 2.3. Implantation and decay

As already discussed,  $\mu^+$  are directed at the sample as a fully polarised beam. They slow down loosing energy primarily by ionisation, vacancy formation and bremsstrahlung emission [32]. During the deceleration, the muon may form a bound state, called muonium, with an electron. The bound state can dissociate during the deceleration and the formation and dissociation process may take place repeatedly. The muon eventually reaches an interstitial position where it may reside with the collected electron or (partially) lose it as a consequence of chemical interactions with the electrons of the hosting material. In several cases muons end up in multiple final states, with different probabilities.

A sketch of the processes involved in the deceleration is shown in Fig. 2.2. Muonium interacts with the host by collisions with the atoms

#### 2. A short introduction to $\mu$ SR

and radiation damage is produced during the deceleration. However, when muon's energy eventually drop below the threshold for vacancy production, it still travels ahead for  $\sim 100-600$  Å [33]. For this reason, the muon usually probes a region of the sample which is far from the initial part of the deceleration path which suffered from radiation damage.

The interactions between the muon and the sample during the deceleration process most often preserve the muon's polarisation [34]. The deceleration time depends on the density of the material and ranges from 100 ps in condensed matter to 10 ns in gases. This time interval is too short to allow a significant loss of polarisation coherence during the early stages of the thermalization in non-magnetic metallic samples where muonium formation is rare. The situation is different in insulators and molecular materials. In this case a discrepancy between the initial muon beam polarisation and the polarisation at the earliest measurable time is not uncommon. This is possibly due to the formation of a muonium precursor that may give rise to a prompt depolarisation usually referred as "missing fraction". It's important to mention that, in high field experiments, the initial polarisation of the muons can be slightly different from that of the muon beam, but, in this case, the coherence between the initial polarisation of all incoming muons is preserved.

### **2.4.** The $\mu$ SR observable: the asymmetry

The average lifetime of the muon is  $\tau_{\mu} = 2.2 \ \mu s$  and the decay probability follows the well known exponential law  $e^{-t/\tau_{\mu}}$ . The weak decay of the muon is a three body process

$$\mu^+ \to e^+ + \nu_e + \bar{\nu}_\mu \tag{2.6}$$

where  $e^+$  is a positron and  $\nu_e$  and  $\bar{\nu}_{\mu}$  are neutrinos. Parity violation in the weak decay and the conservation of angular momentum imply an asymmetry in the positron emission direction. This is the result on which the entire  $\mu$ SR technique is based. In the weak decay the positron emission probability as a function of its energy is given by



Figure 2.3.: In (a), the probability of emitted positron energy and the relative asymmetry function a are shown (see Eq. 2.4). In (b), the angular distribution of the positron emission probability for various positron energies is depicted.

[35]

$$\frac{dP(\epsilon^*,\theta)}{d\epsilon^* d\Omega} = \frac{1}{2\pi} p(\epsilon^*) \left(1 + a(\epsilon^*)\cos\theta\right)$$
(2.7)

where  $\epsilon^* = \epsilon/\epsilon_{max}$  ( $\epsilon_{max} = 52.8 \text{MeV}$ ),  $\theta$  is the angle between muon's spin and positron emission direction and  $p(\epsilon^*)$  and  $a(\epsilon^*)$  are the relative emission number and the asymmetry functions, given by:

$$a(\epsilon^*) = \frac{2\epsilon^* - 1}{3 - 2\epsilon^*}$$
$$p(\epsilon^*) = (\epsilon^*)^2 (3 - 2\epsilon^*).$$

Both functions are plotted in Fig. 2.8. Averaging over all positron energies gives

$$\tilde{A} = \langle a(\epsilon^*) \rangle = \int_0^1 a(\epsilon^*) p(\epsilon^*) \, d\epsilon^* = \frac{1}{3}$$
(2.8)

Substituting  $\tilde{A}$  from Eq. 2.8 into Eq. 2.7 and integrating over all positron emission energies one finds that the positrons are emitted predominantly in the direction of the muon spin. Thus, collecting the



Figure 2.4.: A simple diagram of the detector's geometry in a typical  $\mu$ SR experimental setup. Black and orange arrows indicate particles' spin and momentum direction, respectively. The detectors are identified by capital characters U, L, F, B respectively for upper, lower, forward and backward.

positron counts in a detector at a given direction as a function of time, it is possible to follow the muon spin dynamics.

When immersed in a magnetic field **B** forming an angle with the initial muon polarisation  $\mathbf{s}_{\mu}(t_0)$  the muon will *precess* around it with an angular frequency  $\omega_{\mu}$  given by

$$\omega_{\mu} = \gamma_{\mu} |\mathbf{B}| \tag{2.9}$$

where  $\gamma_{\mu} = \frac{e}{2m_{\mu}}g_{\mu}$  is the gyromagnetic ratio of the muon. The experimental values [36]  $g_{\mu} = -2.0023318418(13), m_{\mu} = 1.883531475(96) \times 10^{-28}$  kg give  $\gamma_{\mu}/2\pi = -135.538817(7)$  MHz/T.

The time dependent count of detected positrons can be written as:

$$N_{e^+}^{(i)}(t) = N_0^{(i)} \left\{ e^{-t/\tau_{\mu}} \left[ 1 + \tilde{A} P^{(i)}(t) \right] + B_0^{(i)} \right\}$$
(2.10)

where *i* is a label enumerating the detectors and, with reference to the scheme shown in Fig. 2.4, ranges from 1 to 4 and refers to the Upper, Lower, Backward and Forward detectors,  $B_0$  is a time-independent background of uncorrelated counts and  $N_0$  is a normalizing rate constant. The decreasing exponential accounts for the decay of the  $\mu^+$ 



Figure 2.5.: Schematic illustration of a  $\mu$ SR acquisition histogram. The figure shows the exponential decay of the muons (dotted line) as collected by an appropriate couple of opposite detectors in the presence of a local magnetic field forming an angle with the initial muon spin (for example the forward and backward scintillators reported as  $N_F$  and  $N_B$  in the figure). The signal will overshoot or stay under the standard exponential decay during the  $\mu^+$  lifetime reflecting the time dependence of the muon polarization.

and  $P^{(i)}(t)$  is the time evolution of the muon polarisation in the direction of the *i*-th detector.

If the muons stop in equivalent sites within the lattice and experience a unique perpendicular magnetic field (either internal or applied) with respect to the detector i and the initial beam polarization, the spins precess around the field and the emission in the i direction is given by inserting

$$P^{(i)}(t) = \cos(\omega_{\mu}t + \theta^{(i)}) \tag{2.11}$$

in Eq. 2.10, where  $\theta^{(i)}$  is the initial phase of the muon relative to the *i*-th detector. The signal coming from opposite detectors shows the typical decay plus oscillation sketched in Fig. 2.5.

It's possible to remove the dependence from the exponential decay

by introducing the asymmetry function:

$$A(t) = \frac{N^{(i)}(t) - N^{(j)}(t)}{N^{(i)}(t) + N^{(j)}(t)}$$
(2.12)

where i and j are couples of opposite detectors, for example backward and forward or upper and lower. Substituting Eq. 2.11 and Eq. 2.10 into Eq. 2.12 and disregarding the constant background one gets

$$A(t) = \frac{(\alpha - 1) + \tilde{A} \left( \alpha P^{(i)} - P^{(j)} \right)}{(\alpha + 1) + \tilde{A} \left( \alpha P^{(i)} + P^{(j)} \right)}$$
(2.13)

where  $\alpha = N_0^{(i)}/N_0^{(j)}$ . This last parameter takes into account the differences in finite detectors' geometry, efficiency between *i* and *j* detectors and not perfect initial beam polarisation. In general  $\alpha$  takes values close to 1. Once the differences among the detectors that influence the asymmetry have been corrected using

$$A^{*}(t) = \frac{\alpha N^{(i)}(t) - N^{(j)}(t)}{\alpha N^{(i)}(t) + N^{(j)}(t)}$$
(2.14)

by substituting Eq. 2.11 into Eq. 2.14 one gets

$$\max(A^*(t)) = \tilde{A}. \tag{2.15}$$

Practically,  $\max(A^*(t)) \simeq 0.25$  due to lower relative efficiency in the detection of high energy large asymmetry positrons and to the finite size of the detector array.

### 2.4.1. Continuous and pulsed puon beams

Muon spectroscopy facilities offer two kind of muon beams: continuous and pulsed. These two approaches offer complementary potentialities. In continuous- $\mu$ SR, muons arrive nearly continuously and are detected by muon's detector one by one (see Fig. 2.4). Each muon hitting the muon detector starts the electronic clock and the system awaits for the decay event to be detected in one of the positron detectors. It may happen anyway that two muons reach the sample before a decay event is detected. This prevents the association of the decayed positron to its parent muon. This fact constitutes the main source of background noise in continuous- $\mu$ SR and limits the maximum incident muon rate. On the other hand, one of the main advantages of the continuous beam facilities is the excellent time resolution, which can be of a few tenths of ps.

In pulsed- $\mu$ SR a bunched beam of muons (up to more than  $10^3$ muons per pulse, at ISIS) reaches the sample and the zero time reference is synchronised with the beam pulses' extraction. Two constraints apply to the time structure of the pulsed beam: the time length of the pulses must be considerably shorter than the muon lifetime, while the repetition time must be much longer than the muon lifetime. The first condition constitutes the main disadvantage of this kind of facilities. The time resolution of the  $\mu$ SR signal is limited by the muon pulse width and, for example, a band width of about 10 MHz (pulse width of 70 ns) will result in a maximum detectable local field of about 600 G. The pulsed muon technique has the advantage of using all muons entering the sample (contrary to continuous  $\mu$ SR where many muons are discarded due to multiple decay events in a single acquisition time window) and provides a signal almost free from background counts. Asymmetry measurements up to  $10\tau_{\mu}$  are possible due to both the negligible background and the possibility of using a higher rate of incoming muons with respect to continuous beams.

### 2.4.2. Experimental setup

For sake of simplicity, in the next section we will introduce the typical experimental setup of a continuous beam facility.

The muon coming from the beam-line and its decay positron are usually detected by fast plastic scintillation and fast phototube detectors (Fig. 2.4). The muon detector is thin enough to let the muon pass through and allows to set the t = 0 reference. After its detection an electronic timer is started and the time between implantation and the positron emission is recorded. The positrons are detected by an array of detectors and  $\mu$ SR data are acquired as a set of time-series histograms.

Three experimental configurations are possible depending on the



Figure 2.6.: LF- $\mu$ SR experimental setup. Red lines represent external field flux lines. Black and orange arrows indicate particles' spin and momentum direction, respectively.

direction of the applied field relative to the initial muon spin polarisation:

**Zero-field configuration (ZF-\muSR)** This experimental setup is characterised by the absence of external magnetic fields. Due to the extreme sensitivity of the  $\mu$ SR technique, usually cancellation of the Earth's magnetic field is also required. This approach is particularly useful in materials with spontaneous magnetic properties since  $\mu$ SR can be used to probe samples without the application of an external field thus providing complementary information with respect to NMR. In magnetic materials, this method offers a measure of the evolution of the order parameter as a function of temperature or pressure since the precession frequency is proportional to the magnetisation (or the staggered magnetisation) of the system.

**Longitudinal-field configuration (LF-\muSR)** In this experimental configuration the magnetic field  $H_{\rm L}$  is applied along the direction of the initial muon polarisation (Fig. 2.6). Longitudinal fields are generally used in combination with zero-field experiments to disclose the nature of the internal magnetic field distribution, the presence of dynamic processes (see Refs. [1, 27] for details) or in Level Crossing Resonance (LCR) experiments.



Figure 2.7.: TF- $\mu$ SR experimental setup. Red lines represent external field flux lines. Black and orange arrows indicate particles' spin and momentum direction, respectively.

**Transverse-field configuration (TF-\muSR)** In this configuration the external field is applied perpendicularly to the initial muon spin direction (Fig. 2.7). The muon spin precesses about the composition of transverse and internal field (if any). The TF- $\mu$ SR configuration can be used to measure the magnetic field distribution of the vortex lattice in a type-II superconductor or the  $\mu$  Knight shift in metallic systems.

### 2.5. Probing magnetic order

Since in this thesis we deal with paramagnetic and magnetically order systems only, in the next section we focus on the description of the interactions which involve the muon spin in a magnetic sample.

### 2.5.1. Contributions to the local field at the muon site

In the semi-classical description of the magnetic field at the muon site, the interaction between the material and the muon spin  $S_{\mu}$  is written as

$$H = \hbar \gamma_{\mu} S_{\mu} \cdot \mathbf{B}_{\mu}, \qquad (2.16)$$

Sample geometry	n factor
Cylinder in parallel field	0
Cylinder in transverse field	1/2
Sphere	1/3
Thin plate in perpendicular field	1

Table 2.1.: The demagnetizing factor n for various geometries.

where  $\mathbf{B}_{\mu}$  is the total field at the muon site.

The main contributions to the total field at the muon site  $\mathbf{B}_{\mu}$  come from the dipolar field, the hyperfine field and the demagnetizing field:

$$\mathbf{B}_{\mu} = \mathbf{B}_{\mathrm{dip}} + \mathbf{B}_{\mathrm{hf}} + \mathbf{B}_{\mathrm{dem}} + \mu_0 \mathbf{H}_{\mathrm{app}} , \qquad (2.17)$$

where  $\mathbf{B}_{\rm hf}$  originates from unpaired electron spin polarization at the muon site and is commonly evaluated as a contact hyperfine field  $\mathbf{B}_{\rm cont}$  and/or a transferred hyperfine field  $\mathbf{B}_{\rm trans}$ . Finally,  $\mathbf{H}_{\rm app}$  is the externally applied field.

The crucial physical parameters governing the size of these contributions are the distance between the  $\mu^+$  and the magnetic ions, the magnetic moments of the ordered magnetic phase, the density of spin polarised electrons at the  $\mu^+$  site and the shape of the sample in the case of ferromagnets or ferrimagnets.

The dipolar field can be written, assuming a classical moment  $\mathbf{m}$  centred at the atomic positions of magnetic atoms, as

$$\mathbf{B}_{\rm dip}(\mathbf{r}) = \frac{\mu_0}{4\pi} \sum_i \left( \frac{3\mathbf{r}_i(\mathbf{m}_i \cdot \mathbf{r}_i)}{r_i^5} - \frac{\mathbf{m}_i}{r_i^3} \right)$$
(2.18)

where  $\mathbf{m}_i$  is the magnetic moment of atom *i* and  $\mathbf{r}_i$  is the distance between atom *i* and the muon site.

The local field at the muon sites are is usually evaluated in direct space by introducing the so-called Lorentz construction. The value  $\mathbf{B}'_{\mu}$  is evaluated for all atoms within a sphere with radius  $r_L$  from the muon site. The sphere is assumed to reside in a single magnetic domain and the magnetic moments outside the Lorentz sphere are regarded as a continuous and homogeneous magnetization density and contribute to an additional field  $\mathbf{B}_L$ . Within a single magnetic domain,  $\mathbf{B}_L = \frac{\mu_0}{3} \mathbf{M}_s$ 

with  $\mathbf{M}_{s}$  being the saturation magnetization of the magnetic domain. The dipolar field at the muon site is then  $\mathbf{B}_{\mu} = \mathbf{B}'_{\mu} + \mathbf{B}_{L}$ . On standard desktop computers, summations of millions of atoms can be performed in a few seconds.

The demagnetizing field  $\mathbf{B}_{dem}$  arises from the dipoles on the surface of the sample. For ellipsoidal samples  $\mathbf{B}_{dem} = -\mu_0 D \mathbf{M}_s$  where Dis the demagnetization tensor and  $\mathbf{M}_s$  is the magnetization of the sample. Of course, both  $\mathbf{B}_{dem}$  and  $\mathbf{B}_L$  vanish in antiferromagnets. In the case of ferro/ferrimagnets, for the special case of ellipsoids, the demagnetization field is linearly related to the magnetization by a geometry dependent constant called the demagnetizing factor n. Its value is reported in Tab. 2.1 for various geometries. For nonellipsoidal samples,  $\mathbf{B}_{dem}$  is inhomogeneous and broadens the local field distribution at the muon site(s).

The contact hyperfine field or contact Fermi field can be written as

$$|\mathbf{B}_{\rm cont}(\mathbf{r}_0)| = -\frac{2}{3}\mu_0 g_e \mu_{\rm B}(n_{up}(\mathbf{r}_0) - n_{dn}(\mathbf{r}_0))$$
(2.19)

for a spherical electronic cloud surrounding the muon in position  $\mathbf{r}_0$  [27].

Two additional contributions are worth citing: in metals with unpaired d or f electrons, a RKKY contribution can take place while in insulators a transferred hyperfine field,  $B_{\text{trans}}$ , can contribute to the local fields at the muon site. The former arises from a second order process which involves the polarisation of conduction electrons by the localised d or f shells having unpaired electrons and a subsequent local field at the muon site is produced by the contact hyperfine interaction. The latter stems from the overlap between the muon wave function and the localised magnetic wave functions.

Finally, a few symmetry considerations apply for the contributions to the local field appearing in Eq. 2.17. In a ferromagnet,  $\mathbf{B}_{\text{cont}}$  lies in the same direction of the domain magnetization. By symmetry considerations  $\mathbf{B}_{\text{dip}}$  vanishes for a muon site in a system of dipoles with cubic point group symmetry (m $\bar{3}$ m).
#### 2.5.2. Static and dynamic local fields

We consider now the effect of a static local magnetic field **B** at the muon site forming an angle  $\theta$  with the initial muon spin direction. In the semi-classical picture, the muon spin precess around the magnetic field forming a cone of half-angle  $\theta$  between the spin and the local magnetic field direction. The muon polarization as a function of time,  $\sigma(t)$ , projected in the direction of the initial spin polarization is

$$\sigma(t) = \cos^2 \theta + \sin^2 \theta \cos(\gamma_\mu |\mathbf{B}| t)$$
(2.20)

Let  $f(\mathbf{B})$  be the magnetic field distribution function at the muon site, then the spin relaxation function G(t) is formally given by

$$G(t) = \int f(\mathbf{B}) \left[ \cos^2 \theta + \sin^2 \theta \cos(\gamma_{\mu} |\mathbf{B}| t) \right] d\mathbf{B} .$$
 (2.21)

If the internal field distribution is only a function of  $|\mathbf{B}|$ , as it is the case, for example, for an antiferromagnetic (AFM) polycrystalline sample, one has

$$G(t) = \int_0^\infty f(|\mathbf{B}|) \left[ \cos^2 \theta + \sin^2 \theta \cos\left(\gamma_\mu |\mathbf{B}| t\right) \right] 4\pi B^2 dB \qquad (2.22)$$

By integrating over angular variables, G(t) can be written as

$$G(t) = \frac{1}{3} + \frac{2}{3} \int f(|\mathbf{B}|) \cos(\gamma_{\mu} |\mathbf{B}| t) \ 4\pi B^2 dB$$
(2.23)

If the local magnetic field has a well defined modulus and randomly distributed directions, i.e.

$$f(|\mathbf{B}|) = \delta(B - B) \tag{2.24}$$

substituting Eq. 2.24 and integrating gives

$$G(t) = \frac{1}{3} + \frac{2}{3}\cos(\gamma_{\mu}\bar{B}t)$$
 (2.25)

This is what would be observed in ideal powdered magnetic samples. However, the delta distribution of Eq. 2.24 is never detected in real materials since the local magnetic field is usually broadened by the presence of vacancies, self-interstitials, magnetic impurities, dislocations or domain walls. A more realistic approach is to consider a Gaussian distribution for the internal magnetic fields in the i-th direction

$$f(B_i) = \frac{\gamma_{\mu}}{\sqrt{2\pi\Delta}} \exp\left(-\frac{\gamma_{\mu}^2 (B_i - \bar{B}_i)^2}{2\Delta^2}\right)$$
(2.26)

where i = x, y, z identify the three field components. Let the local field at the muon site be the sum of two components with angular independent distributions given by Eq. 2.24 and Eq. 2.26 and assume for the latter  $\bar{B}_i$  equal zero. The integration over angular variables gives the distribution [29]

$$f(|\mathbf{B}|) = \frac{1}{(2\pi)^{3/2} \Delta \bar{B} |\mathbf{B}|} \exp\left(-\frac{\bar{B}^2 + B^2}{2\Delta^2}\right) \sinh\left(\frac{\bar{B}|\mathbf{B}|}{\Delta^2}\right) \qquad (2.27)$$

which is known as Koptev-Tarasov distribution. From Eq. 2.23, for  $\bar{B} \gg \Delta$ , one has

$$G(t) = \frac{1}{3} + \frac{2}{3}\cos(\gamma_{\mu}\bar{B}t)\exp\left(-\frac{\gamma_{\mu}^{2}\Delta^{2}t^{2}}{2}\right)$$
(2.28)

which evidence a damping of the oscillating component which originates from the de-phasing of the muon spins due to the presence of a distribution of local fields. This is the typical signal found in static magnetically ordered samples, characterised by disorder or impurities.

Considering the Gaussian distributions of Eq. 2.26 with  $\bar{B}_{x,y,z} = 0$  for all the three directions, integration of Eq. 2.21 gives

$$G(t) = \frac{1}{3} + \frac{2}{3}(1 - \gamma_{\mu}^{2}\Delta^{2}t^{2})\exp\left(-\frac{\gamma_{\mu}^{2}\Delta^{2}t^{2}}{2}\right).$$
 (2.29)

Eq. 2.29 is known as static Kubo-Toyabe relaxation function (Fig. 2.8b) and describes the  $\mu$ SR signal of randomly oriented classical dipoles. This is the case, for example, of nuclear magnetic dipoles but potentially also static magnetic disorder of electronic origin.

Finally, if a magnetic field is applied along the *i*-th direction parallel to the muon spin (LF configuration),  $\bar{B}_i \neq 0$  and the integral of Eq. 2.22 yields [37]:

#### 2. A short introduction to $\mu$ SR



Figure 2.8.: In (a) a sketch depicting randomly oriented local moments in a lattice. The resulting distribution of fields projected onto an axis is showed on the left. In (b) the Kubo-Toyabe relaxation function for several values of  $\Delta$  is plotted.

$$G(t) = 1 - \frac{2\Delta^2}{\bar{B}_i^2} \left[ 1 - \cos(\gamma_\mu \bar{B}t) \exp\left(-\frac{\gamma_\mu^2 \Delta^2 t^2}{2}\right) \right] + o(\frac{\Delta^3}{\bar{B}_i^3}) \quad (2.30)$$

If  $\bar{B}_i \gg \Delta$ , the polarisation of the muon is fixed and the spin will be aligned along the *i*-direction.

Up to now we have only considered static local fields on the timescales investigated (which depend on  $\gamma_{\mu}$ ). When dynamical fluctuations of internal field sets in, they introduce an additional relaxation processes which is independent from magnetic disorder.

There are two possible reasons why a magnetic system could appear dynamic in  $\mu$ SR signals. Either fluctuations of the local field are

present or the muon is dynamic, i.e. it diffuses in a static spin system. A solution for a dynamical modulation of local magnetic field, resulting either from the muon hopping from site to site or from the internal fields instantly changing as a consequence phase shifts, can be accounted for within the strong collision Markovian approximation [37].

For slow hopping rate in a local moment environment described by a Gaussian field distribution, the asymptotic form of static Kubo-Toyabe distribution (Eq. 2.29) is modified and may be evaluated approximately as

$$G(t) \sim \frac{1}{3} \exp\left(-\frac{2}{3}\nu t\right) \tag{2.31}$$

where the fluctuation frequency  $\nu$  is the inverse of the hopping correlation time ( $\tau_c = \nu^{-1}$ ). Eq. 2.31 shows the signature of dynamic contributions to the asymmetry, i.e the loss of the 1/3 tail. Indeed in the case of slow dynamics the asymptote progressively reduces from  $^{1/3}$ to 0 as a function of  $\nu$ . In the fast fluctuation limit, the depolarisation has the form

$$G(t) \sim \exp(-\lambda t)$$
. (2.32)

with  $\lambda = 2(\gamma_{\mu}\Delta)^{2}\tau_{c}$ . This is the so called "motional narrowing limit" in which the depolarisation of the asymmetry signal is inhibited by the fast hopping rate. In the intermediate fluctuation rate, G(t) is

$$G(t) = \exp\left[-2\frac{\gamma_{\mu}^{2}\Delta^{2}}{\nu^{2}}\left(\exp(-\nu t) - 1 + \nu t\right)\right]$$
(2.33)

This is the so called "Abragam relaxation function" [38, 39].

## 2.6. Quantum description of the dipolar interaction

All of the above results are based on a semi-classical description of the electromagnetic interaction taking place between the muon spin and the localised moments in a sample. Celio and Meier were the first to consider the dipolar interaction between the muon and the nuclei in a pure quantum-mechanical fashion in the context of  $\mu$ SR [40]. They



Figure 2.9.: The time evolution  $G_p(t)$  of the normalised asymmetry for an axial F- $\mu$ -F site with  $\omega_d = 0.16$  MHz in a powdered sample.

showed that the difference between a Kubo-Toyabe function, which is expected from classical arguments, and a quantum description of the same interaction produces small differences that can be observed within the  $\mu$ SR time window. However, a marked departure from the classically expected trend was first observed in LiF [41]. Indeed in fluorides, because of the high nuclear moment of F nuclei (<sup>19</sup>F has spin I = 1/2 and ~ 100% natural abundance) and of the high electronegativity of this element, the interaction, commonly referred as F- $\mu$ -F<sup>†</sup>, is more pronounced. Here we briefly revise the analysis proposed in the article by Brewer and co-workers for LiF.

An entangled quantum state develops between the muon and the surrounding nuclei and the system may be described with the following Hamiltonian

$$\mathcal{H} = \sum_{i>j} \frac{\mu_0 \gamma_i \gamma_j}{4\pi r^3} \left[ \mathbf{S}_i \cdot \mathbf{S}_j - 3(\mathbf{S}_i \cdot \hat{\mathbf{r}}) (\mathbf{S}_j \cdot \hat{\mathbf{r}}) \right], \qquad (2.34)$$

where **r** is the vector between spins  $S_i$  and  $S_j$  of either the fluorine nuclei or the muon, which have gyromagnetic ratios  $\gamma_i$  and  $\gamma_j$ . The muon depolarisation is given by:

<sup>&</sup>lt;sup>†</sup>We mention that "F-Mu-F" is probably a more appropriate label for this "molecule-in-a-crystal" [18] structure. Indeed, Mu identifies both the  $\mu^+$  particle and the electronic orbital forming the bonds with the F nuclei. However, we prefer to stick with the original and widely used notation.

#### 2.6. Quantum description of the dipolar interaction

$$G_{\zeta}(t) = \frac{1}{N} \sum_{m,n} e^{i(\omega_m - \omega_n)t} |\langle m | \sigma_{\zeta} | n \rangle|^2$$
(2.35)

where N is the Hilbert space dimension,  $|m\rangle$  and  $|n\rangle$  are eigenstates of  $\mathcal{H}$  and  $\hbar\omega_{m,n}$  are the corresponding eigenvalues,  $\sigma_{\zeta}$  is the Pauli spin matrix corresponding to the quantization direction and h is the Planck constant. In a powdered sample with cubic symmetry, the observed signal is the result of the weighted average over all directions, i.e.

$$\overline{|\langle m|\sigma_{\zeta}|n\rangle|^{2}} = \frac{1}{3} \left( |\langle m|\sigma_{z}|n\rangle|^{2} + |\langle m|\sigma_{y}|n\rangle|^{2} + |\langle m|\sigma_{x}|n\rangle|^{2} \right)$$

$$(2.36)$$

Since the dipolar interaction is inversely proportional to the cube of the inter-nuclear distance, one usually consider only up to next neighbouring atoms in order to make the calculation of the muon polarisation computationally inexpensive within a negligible loss of accuracy. Moreover, the coupling between F nuclear spins may be often disregarded with a limited loss of accuracy even if its inclusion does not lead to an increase of the computational load.

For an axially symmetric  $F-\mu$ -F complex, as in the case for LiF which is discussed in Chapter 5.2, when considering only two nearest neighbouring F atoms, the analytic solution of Eq. 2.34 for a powder averaged depolarisation is:

$$G_{p}(t) = \frac{1}{6} \left( 3 + \cos\sqrt{3}\omega_{d}t + (1 - \frac{1}{\sqrt{3}})\cos\frac{3 - \sqrt{3}}{2}\omega_{d}t + (1 + \frac{1}{\sqrt{3}})\cos\frac{3 + \sqrt{3}}{2}\omega_{d}t \right)$$
(2.37)

where  $\omega_d = \mu_0 \gamma_F \gamma_\mu h/(2r^3)$ . This characteristic signal (shown in Fig. 2.9) allowed to identify the muon site in LiF and other flurides [41, 42].

## 2.7. Identification of muon sites

In  $\mu$ SR experiments, the location of the muon site is, *a priori*, unknown. A few experimental and computational approaches allow the identification of muon sites in condensed matter systems. Here we shortly revise the strategies discussed so far in literature.

### 2.7.1. Experimental approaches

From the experimental side, three strategies for identifying muon sites have mainly been used:

**Study of the dipolar tensor in a transverse field experiment.** This approach provides information on the symmetry of the occupied muon site(s) through the study of the muon Knight-shift. It requires single crystal compounds and a large transverse applied field. Moreover the sample should have a well defined shape in order to simplify the dependence of the demagnetisation component of the local field at the muon site on the angle of application of the transverse field. The symmetry of the precession pattern allows to identify the symmetry of the site and the calculation of the dipolar field together with the determination of the hyperfine field enable the comparison between the muon site predictions and the experiment. For additional details and some examples see Ref. [29, 43, 44].

Analysis of the relaxation functions. This approach is particularly useful in materials containing nuclei with large nuclear moments (eg. F, H). Oscillations in the asymmetry which are due to the interaction between the muon spin and the nuclear moments are usually observed. The precession frequencies can be evaluated by considering the quantum dipolar interaction between the spin of the muon and those of the neighbouring nuclei as shown in the previous section. Since the position of the nuclei is known (even though some distortions may occur) the identification of the muon position is usually straightforward (see for example Ref. [45–50]). Unfortunately the distance between the muon and the nuclei must be small enough to allow the acquisition of the muon spin precession in the  $\mu$ SR time window. For example, the interaction between the muon and a fluorine nuclear moment in a F- $\mu$  bond 1.5 Å long produces an oscillating signal with frequencies of the order of 0.1 MHz which barely fit the  $\mu$ SR resolution.

Analysis of the electric field gradient through muon level crossing resonance ( $\mu$ LCR). ( $\mu$ LCR) is a form of cross relaxation involving the muon spin and nuclear energy levels suggested by Abragam [51]. The key idea is that by varying the applied longitudinal field, the non-interacting muon and nuclear spin energies may become degenerate. These degeneracies are removed in the presence of a small interaction and the degenerate states become mixed. The resonance is detected as a dip in the muon relaxation rate as a function of the applied field. As for the previous cases, LCR experiments can be used together with numerical simulations to identify the local geometry of the muon site.

#### 2.7.2. Theoretical approaches

Simulations aiming at identifying muon sopping sites with quantum mechanical approaches have been around since the very beginning of  $\mu$ SR experiments. To the best of our knowledge, the first theoretical investigation on muon perturbations in matter is Ref. [52] which dates back in 1975. From then on, a large number of authors adopted DFT or HF simulation techniques to identify muon sites and investigate muon perturbations from first principles.

In early studies, semiconductors and transition metal elements attracted most of the attention [13, 53–59]. However, paramagnetic muon sites (i.e. muonium sites) were mainly considered.

Shortly after, copper oxides insulators were the subject of intense studies due to due to the discovery of high temperature superconductivity [60–62]. Also in this case both density functional and HF approaches were often used. Finite clusters with a relatively large number of atoms were constructed in order to accurately reproduce the material under study avoiding the introduction Periodic Boundary Conditions (PBC) which can become computationally expensive when considering the effect of interstitial impurities (see Sec. 3.4).

From then on, on one hand, the muon regarded as a light isotope of the hydrogen took both experimental and computational attention [18, 20, 59]. On the other hand more sophisticated strategies were developed to take into account the large ground state energy of the muon, the most successful probably being Feynman path integral approaches to molecular dynamics [63].

During the last ten years, the exponential growth of the available computational power marked a rebirth of the DFT approach to the identification of the muon sites. As of today, DFT simulations can provide accurate descriptions of materials of interest for the solid state research and are used both for studying the unperturbed electronic ground state and the perturbed electronic configuration which results from the interstitial  $\mu^+$  [16–18, 20, 23]. In this thesis, these aspects are discussed in detail.

# A short introduction to DFT

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The fundamental power of DFT resides in the idea of disregarding the many-body wave function of an interacting-particle system and instead extract the observables with functionals of the particle density, which is a scalar function of only space and time. The earliest tractable approach using density functionals is the Thomas-Fermi method, which however had several failings, the most notable being the inability to bind atoms to form molecules. Later on, Hohenberg and Kohn (HK) [64] and Kohn and Sham (KS) [65] showed that it is possible to introduce a mapping of the many-body problem to a non-interacting one-particle problem. The mapping is formally exact but, in practice, one must rely on approximations. Despite that, the available approximations have had a tremendous success and make the theory extremely powerful for ground state total energy estimations. More recently, the time-dependent analogue of the HK theorems, known as Time-Dependent Density Functional Theory (TDDFT), was formally introduced by Runge and Gross [66] to treat the dynamics of many-body systems in the presence of time-dependent potentials. These scientific advances made DFT an extremely powerful computational method in quantum physics, used for modelling both ground-state and excitation properties of solids in a variety of scientific applications. A brief introduction to DFT is required for the discussion of the muon site problem. In summarising the key points I took inspiration from Ref. [67–69].

## 3.1. The Hohenberg-Kohn theorems

Hohenberg, Kohn and Sham formulated their famous theorems in 1964 [64] and 1965 [65]. They turned out to be a milestone in the development of density functional formalism since they provide the formal justification to use the electron density as the basic variable in determining the quantum properties of a system of interacting particles.

#### 3.1.1. One to one mapping

The first HK theorem states that, given the non degenerate groundstate of the external potential  $V_{ext}(\mathbf{r})$  with particle density  $n_0(\mathbf{r})$ , it is possible to unambiguously recover to the external potential from  $n_0(\mathbf{r})$ . In other words, there exists a one-to-one mapping between the external potential  $V_{ext}(\mathbf{r})$  and the particle density  $n_0(\mathbf{r})$  if the ground state is non-degenerate.

The proof uses the Rayleigh-Ritz principle and is given by *reductio* ad absurdum. Let  $|1\rangle$  and  $|2\rangle$  be the ground state wave functions of the external potentials  $\hat{V}_1$  and  $\hat{V}_2$  with  $\hat{V}_1 \neq \hat{V}_2 + \alpha$ . Suppose that  $n_0^{(1)}(\mathbf{r}) = n_0^{(2)}(\mathbf{r}) = \langle 1 | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | 1 \rangle = \langle 2 | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | 2 \rangle$  is the ground state density for both external potentials, which we identify as  $V_1$  and  $V_2$  for simplicity. One has:

$$E_1 = \langle 1|\hat{T} + \hat{V}_{int} + \hat{V}_1|1\rangle < \langle 2|\hat{T} + \hat{V}_{int} + \hat{V}_1|2\rangle$$
(3.1)

where  $\hat{T}$  and  $\hat{V}_{int}$  are the kinetic and interaction terms for the particle in the system. The right-hand term of Eq. 3.1 can be recast as follows:

$$\langle 2|\hat{T} + \hat{V}_{int} + \hat{V}_{1}|2 \rangle = \langle 2|\hat{T} + \hat{V}_{int} + \hat{V}_{2}|2 \rangle + \langle 2|\hat{V}_{1} - \hat{V}_{2}|2 \rangle$$
  
=  $E_{2} + \int n_{0}(\mathbf{r}) \left[\hat{V}_{1}(\mathbf{r}) - \hat{V}_{2}(\mathbf{r})\right] d^{3}r$ 

and we obtain

$$E_1 < E_2 + \int n_0(\mathbf{r}) \left[ \hat{V}_1(\mathbf{r}) - \hat{V}_2(\mathbf{r}) \right] d^3r$$
 (3.2)

We can now exchange 1 for 2 in the above inequality obtaining:

$$E_2 < E_1 + \int n_0(\mathbf{r}) \left[ \hat{V}_2(\mathbf{r}) - \hat{V}_1(\mathbf{r}) \right] d^3r$$
 (3.3)

Eq. 3.2 and Eq. 3.3 are obviously incompatible with the requirement  $n_0^{(1)}(\mathbf{r}) = n_0^{(2)}(\mathbf{r})$ . Thus we conclude that for  $\hat{V}_1^{(ext)} \neq \hat{V}_2^{(ext)}$  it must be  $n_0^{(1)}(\mathbf{r}) \neq n_0^{(2)}(\mathbf{r})$ .

#### 3.1.2. Variational principle

The second theorem of HK states that, for any choice of  $\hat{V}_{ext}$ , a universal functional of the density E[n] provides the ground state energy for the ground-state density  $n_0(\mathbf{r})$  that minimises the functional. Here we will follow the proof of Levy Lieb (LL) based on the constrained search approach.<sup>†</sup> Roughly speaking, the idea is to divide the minimisation in two steps. We start considering the infinite many body wave functions  $\Psi_{n_0}$  sharing the same density  $n_0(\mathbf{r})$  of the true many

 $<sup>^{\</sup>dagger}$ The LL approach has the valuable advantage of dealing with N-representability rather than V representability. This is discussed in the next section.

body ground state  $\Psi_0$ . The minimum-energy principle for the ground state gives

$$\langle \Psi_{n_0} | \hat{H} | \Psi_{n_0} \rangle \ge \langle \Psi_0 | \hat{H} | \Psi_0 \rangle .$$
(3.4)

This implies

$$E = \langle \Psi_{n_0} | \hat{T} | \Psi_{n_0} \rangle + \langle \Psi_{n_0} | \hat{V}_{int} | \Psi_{n_0} \rangle + \int d^3 r \ V_{ext}(\mathbf{r}) n_0(\mathbf{r})$$
(3.5)

$$E_0 = \langle \Psi_0 | \hat{T} | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}_{int} | \Psi_0 \rangle + \int d^3 r \ V_{ext}(\mathbf{r}) n_0(\mathbf{r})$$
(3.6)

$$E \ge E_0 \tag{3.7}$$

that corresponds to

$$\langle \Psi_{n_0} | \hat{T} + \hat{V}_{int} | \Psi_{n_0} \rangle \ge \langle \Psi_0 | \hat{T} + \hat{V}_{int} | \Psi_0 \rangle \tag{3.8}$$

From the above equation, one can define the functional of the density as

$$E_{LL}[n] = F_{LL}[n] + \int d^3r \ n(\mathbf{r}) V_{ext}(\mathbf{r})$$
(3.9)

where  $F_{LL}$  is a universal functional of n defined as

$$F_{LL}[n(\mathbf{r})] = \min_{|\Psi\rangle \to n(\mathbf{r})} \left\langle \Psi | \hat{F} | \Psi \right\rangle \quad , \tag{3.10}$$

with  $\hat{F}$  being

$$\hat{F} = \hat{T} + \hat{V}_{int} \quad . \tag{3.11}$$

The functional  $E_{LL}$  is manifestly a functional of the density and the ground state  $E_0$  is found by minimisation with respect to  $n(\mathbf{r})$ .

This completes the proof of HK theorems.

#### 3.1.3. V-representability and N-representability

Two fundamental questions, which are extremely important for practical implementations of DFT, remain unanswered in the above theorems. Firstly, whether it is possible to represent any density in terms of the ground-state density of a potential  $V_{ext}(\mathbf{r})$ . Secondly, whether all densities can be written in terms of an antisymmetric N-body wave function. The two question have been labelled V-representability and N-representability.

It has been shown [70] that any function  $\rho(\mathbf{r})$  satisfying

$$\rho(\mathbf{r}) \ge 0 \tag{3.12}$$

$$\int \rho(\mathbf{r}) \, d^3 r = N \tag{3.13}$$

$$\int |\nabla \rho(\mathbf{r})^{1/2}|^2 d^3 r < \infty \tag{3.14}$$

can be written in terms of some  $\phi(\mathbf{r}_1, \ldots, \mathbf{r}(n))$ , so any (reasonable) density is N-representable. However, for V-representability no general solution exists. For this reason, the constrained search formulation of Levy and Lieb discussed above was preferred over the proof given by HK which deals with V-representability.

#### 3.1.4. Kohn Sham iterative scheme

HK theorems do not provide a practical strategy to deal with a quantum many body problem. The second HK theorem is simply an existence theorem, which tells absolutely nothing about the actual dependence of the kinetic part and the particle-particle interaction part on the particle density. Indeed these are serious challenges for practical applications. The Thomas–Fermi theory provides approximations for both the kinetic and particle-particle terms, but they are not accurate enough, especially in what regards the kinetic energy part. Although advances have been made [71], there is still no (accurate) way to extract the kinetic energy of the system without reverting to an orbital description.

Moreover, even if the functional of the electron density providing the total energy were known, there is no straightforward way to analyse the properties of a material from its particle density. For example, it is not immediate to distinguish an insulating ground state from a metallic ground state by only considering the electronic density.

KS derived a set of coupled differential equations which provide the exact ground state density  $n_0(\mathbf{r})$  of the interacting system with the introduction of an auxiliary non interacting particle problem. The

method is based on an *ansatz*: the pure-state non-interacting V-representability of the interacting electrons density. In other words, we suppose that the exact ground state density can be reproduced by an auxiliary system of non-interacting particles (subject to a different external potential). There is no proof of this *ansatz* for real systems and its validity is assumed.

In what follows, we will specialise the results discussed up to now for general densities to the case of electrons in solids and focus the attention on the electron system which obeys the following non-relativistic Hamiltonian:

$$\hat{H}_{\rm el} = \hat{T}_e + \hat{V}_{en} + \hat{U}_{ee} + \hat{V}_{nn} , \qquad (3.15)$$

where<sup>†</sup>

$$\begin{split} T_e &= -\sum_i^{n_e} \frac{\hbar^2}{2m} \nabla_i^2 ,\\ V_{en} &= -\sum_i^{n_e} \sum_j^{n_N} \frac{Z_j e^2}{|\mathbf{R}_j - \mathbf{r}_i|} ,\\ U_{ee} &= \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} . \end{split}$$

where  $\mathbf{r}$  and  $\mathbf{R}$  are electronic and nuclear coordinates respectively.

In Eq. 3.15 we have removed the nuclear kinetic energy with the usual Born Oppenheimer (BO) approximation and the Coulomb interaction between nuclei enters just as the constant contribution  $V_{nn}$ .

The Hamiltonian of Eq. 3.15 can be recast, dropping the constant contribution  $V_{nn}$ , as follows:

$$H(n) = T(n) + U(n) + V(n) = T_s + U_H(n) + E_{xc} + V(n)$$
 (3.16)

where, on the left-hand side, U(n) includes internal potentials (terms arising from electron-electron interactions, the particles for which we are solving the Schrödinger equation) and V is the "external potential" (everything that stems from the interaction between the electrons and

 $<sup>^{\</sup>dagger}\textsc{Starting}$  from the next equation we drop the hat symbol for operators in this section.

other particles or fields). On the right-hand side, the kinetic term is split into the non interacting part,  $T_s$ , and the interacting part,  $T_c = T - T_s$  which enters  $E_{xc}$  as  $E_{xc} = T_c + (U - U_H)$ .  $U_H$  is the usual Hartree term which can be expressed as a function of the density as

$$U_H[n] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} .$$
 (3.17)

Aiming at introducing the auxiliary system of non-interacting particles, we evaluate the terms in Eq. 3.16 for an antisimmetrized product wave function  $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n)$  of single particle wave function  $\phi(\mathbf{r})$ . A functional of the density for the kinetic energy term,  $T_s[n]$ , is easily obtained as the sum of the kinetic energy of the single particle wave functions and is

$$T_{s}[\{\phi_{i}[n]\}] = -\frac{\hbar^{2}}{2m} \sum_{i}^{N} \int d^{3}r \,\phi_{i}^{*}(\mathbf{r}) \nabla^{2} \phi_{i}(\mathbf{r}) \quad .$$
(3.18)

 $E_{xc}$  is the sum of two contributions, the exchange energy  $E_x$  due to the Pauli principle and the correlation energy  $E_c$ . For the exchange part, in terms of single particle wave functions, the functional of the density is

$$E_x[\{\phi_i[n]\}] = -\frac{q^2}{2} \sum_{jk} \int d^3r \int d^3r' \, \frac{\phi_j^*(\mathbf{r})\phi_k^*(\mathbf{r})'\phi_j'(\mathbf{r})\phi_k(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.19)$$

which is known as the Fock term. The orbital description of the exchange contribution can be used to improve the accuracy of the description of  $E_{xc}$  which is not known in closed form (see for example Ref. [72, 73]). Indeed, a functional description of the correlation energy  $E_c$  is still unknown, either in terms of orbitals or densities.

The brightness of the KS approach is that, by explicit separation of the independent particle contribution from the kinetic term and the Hartree term, one can reasonably estimate the remaining terms with approximate functionals of the density.

To evaluate the ground state energy of the system of interacting electrons we proceed minimising the right-hand side of Eq. 3.16 with respect to the variation  $\delta n$ .

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The minimisation is formally obtained as

$$0 = \frac{\delta H[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V[n]}{\delta n(\mathbf{r})} + \frac{\delta U_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$
(3.20)

$$=\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}).$$
(3.21)

The term  $\frac{\delta U_H}{\delta n}$  yields the Hartree potential

$$v_H(\mathbf{r}) = e^2 \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(3.22)

and the term  $\frac{\delta E_{xc}}{\delta n}$  has been labelled  $v_{xc}$  in the right hand side of Eq. 3.21.

The minimisation of Eq. 3.21 is equivalent to the minimisation

$$0 = \frac{\delta E_s[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V_s[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}), \qquad (3.23)$$

which represent the total energy of a non-interacting particle system subject to the potential  $v_s(\mathbf{r})$ 

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) . \qquad (3.24)$$

Consequently, one can calculate the density of the interacting (manybody) problem, by solving the Schrödinger equation of a non-interacting electron system experiencing the effective potential  $v_s(\mathbf{r})$ . However, since the non-interacting kinetic energy functional of Eq. 3.18 is known only as an orbital functional and  $v_{xc}$  can be written only in terms of the electron density, one cannot directly minimise Eq. (3.16) with respect to n. For this reason, during the minimisation, both the orbital and the density representation will be needed.

The Schrödinger equation of the non-interacting auxiliary system is

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r})\right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) . \qquad (3.25)$$

In the exact DFT, Eq. 3.25 provides a product wave function that has exactly the same electron density  $n(\mathbf{r})$  of the interacting particle



Figure 3.1.: Flowchart describing the iterative solution of the KS equations.

system, i.e.

$$n(\mathbf{r}) = \langle \Psi_0 | n | \Psi_0 \rangle \equiv n_s(\mathbf{r}) = \sum_i^N f_i |\phi_i(\mathbf{r})|^2, \qquad (3.26)$$

where  $f_i$  is the occupation of the *i*'th orbital and  $\Psi_0$  is the true manybody wave function.

Since both  $v_H$  and  $v_{xc}$  depend on n, which is constructed from the orbitals  $\phi_i$ , which in turn are obtained from the solution of Eq. 3.24 and Eq. 3.25, the KS equations are a set of nonlinear integro-differential partial differential equations for the one-particle wave functions. The usual way of solving such problems is to start with an initial guess for  $n(\mathbf{r})$ , calculate the corresponding  $v_s(\mathbf{r})$ , and then solve the differential equation Eq. 3.25 for the  $\phi_i$ . From the latter one calculates a new density, using Eq. 3.26, and starts again. The iterative method is repeated until convergence is reached. A flowchart showing the algorithmic procedure is depicted in Fig. 3.1. Different convergence criteria (such as convergence of the total energy, of the density or of some other observables) and various convergence-accelerating algorithms [74–76] are commonly used.

#### 3.1.5. Exchange and correlation approximations

While DFT is, in principle, exact, in practice one has to rely on approximations since a functional providing the exact exchange and correlation energy is not known. However, the available approximations have had a tremendous success in various applications.

We prefer to avoid entering into the details of the several approximations introduced to evaluate the exchange and correlation term, but instead we stress that the exchange and correlation potential can be accurately evaluated even with the rather intuitive approach proposed by KS in their milestone paper which is based on the parametrization of the exchange and correlation energy of the electron gas. From then on, the study of exchange and correlation functionals became a very active field of research constantly improving the accuracy of DFT prediction for a wide class of materials.

The most widely used approximation for  $v_{xc}$  assumes that the exchange and correlation contribution to the total energy of a slowly varying density can be approximated with a contribution taken from the homogeneous electron gas scaled locally with the density. The exchange energy of a homogeneous electron gas with density n is known analytically and it is

$$\epsilon_x(n) = rac{-3e^2}{4} \left(rac{3}{\pi}
ight)^{1/3} n^{4/3}$$

On the other hand, the correlation energy density  $\epsilon_c$  for the homogeneous electron gas is not known analytically. However, it can be accurately estimated with Monte-Carlo approaches and subsequently parametrized [77]. This allows to obtain the exchange and correlation energy  $E_{xc}$  from  $\epsilon_{xc}(n) = \epsilon_x + \epsilon_c$  and one has:

$$E_{xc}(n) \simeq \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d^3r$$
 (3.27)

$$v_{xc}^{\text{LDA}}(\mathbf{r}) = \frac{\delta E^{\text{LDA}}}{\delta n(\mathbf{r})} = \epsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r})\frac{\partial \epsilon_{xc}(n(\mathbf{r}))}{\partial n(\mathbf{r})}$$
(3.28)

where  $\epsilon_{xc}(n)$  is the exchange-correlation energy density per electron as a function of the uniform electron gas density n. This approximation is known as Local Density Approximation (LDA). Experience has demonstrated that LDA works well also for systems that are characterised by strongly varying densities, i.e. non-metals. This unexpected success can be partially explained by the fact that the LDA satisfies important sum-rules due to a systematic error cancellation in the evaluation of the exchange and the correlation contributions [78].

A more accurate approximation can be obtained by including also a dependency on the density gradient.

$$E_{xc}(n) \simeq \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) d^3r \qquad (3.29)$$

$$v_{xc}^{\text{GGA}} = \epsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r}) \frac{\partial \epsilon_{xc}(n(\mathbf{r}))}{\partial n(\mathbf{r})} + \nabla \left( n(\mathbf{r}) \frac{\partial \epsilon_{xc}(n(\mathbf{r}))}{\partial \nabla n(\mathbf{r})} \right) \quad (3.30)$$

is the general form of the Generalized Gradient Approximation (GGA) [79–82]. Although GGA does not provide a consistent generalized improvement over LDA for all systems, it improves the binding energy and the bond lengths in many materials. For this reason, in this work the GGA was mainly used.

#### 3.1.6. Reciprocal space sampling

Bloch's theorem states that, for a periodic potential invariant under lattice translation vectors  $R_m = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3 \ (m \in \mathbb{Z})$ , the eigenfunctions of the Hamiltonian can be written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \tag{3.31}$$

where  $u_{\mathbf{k}}(\mathbf{r})$  has the same periodicity of the potential, i.e.

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{R} + \mathbf{r}) \tag{3.32}$$

and

$$u_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{R}+\mathbf{r})e^{-\mathbf{i}\mathbf{G}\cdot\mathbf{r}}$$
(3.33)

which stems from the fact that plane wave functions are periodic functions of the reciprocal lattice vector  $\mathbf{G} = l_1 \mathbf{b}_1 + l_2 \mathbf{b}_2 + l_3 \mathbf{b}_3$  (with  $\mathbf{a}_i \cdot \mathbf{b}_i = 2\pi \delta_{ij}$ ).

This has the valuable advantage of allowing to define the eigenstates only within the reciprocal unit cell, i.e., all  $\mathbf{k} + \mathbf{G}$  states with  $\mathbf{G} \neq 0$  are not needed and it is sufficient to know the energy dispersions only within the first Brillouin zone.

In periodic system, properties like the electron density or the total energy requires the integration of some quantities over the Brillouin zone.

Usually a finite number of k-points are used and the integration is performed as a finite sum

$$u(\mathbf{r}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} F(\mathbf{k}) d\mathbf{k} = \sum_j w_j F(\mathbf{k}_j)$$
(3.34)

where  $\Omega$  is the cell volume and the  $w_j$  are weighting factors. The set of "special" k-points that provide the best sampling of the Brillouin zone was discussed by Monkhorst and Pack (MP) in Ref. [83]. The k-points are distributed uniformly in reciprocal space as

$$\mathbf{k}_j = x_{1j}\mathbf{b}_1 + x_{2j}\mathbf{b}_2 + x_{3j}\mathbf{b}_3 \tag{3.35}$$

where  $x_{ij} = \frac{l_i}{n_j}$ ,  $j = 1, \ldots, n_j$ ,  $l_i$  are lengths of reciprocal lattice basis vectors, and  $n_j$  is an integer determining the number of special points in the set. If we are dealing with a supercell and the reciprocal space is therefore shrank and filled with folded single particle electronic bands, we can restrict the sum in Eq. 3.34 to just one point. In this case, the best choice, which depend on the reciprocal lattice symmetry, has been discussed by Baldereschi [84]. The choice of the point relies on two considerations: firstly, the first mean value theorem for integration states that, given  $G : [a, b] \to R$  a continuous function, a point x for which the integrand equals the integral exists, i.e.

$$\int_{a}^{b} G(t) dt = G(x)(b-a).$$
(3.36)

with  $x \in (a, b)$ . The second consideration regards the use of symmetry to find such a point approximately. The mean value points for simple cubic, face centred cubic and body centred cubic are  $\frac{\pi}{a}(0.5, 0.5, 0.5)$ ,  $\frac{2\pi}{a}(0.6223, 0.2953, 0.5), \frac{2\pi}{a}(0.1666, 0.1666, 0.5)$ .

Similarly, the point group symmetry of the lattice can substantially reduce the number of points over which the sum in Eq. 3.34 is performed. This allows one to write the sums as

$$f(\mathbf{r}) = \sum_{j=1}^{P(n_j)} w_j F(\mathbf{k}_j)$$
(3.37)

where  $P(n_j)$  is the symmetry-dependent number of points in the irreducible wedge of the Brillouin zone. The introduction of symmetry modify the weights of the points which are now determined by the ratio of the order of the point group to that of the group of the wavevector  $\mathbf{k}_j$  under consideration.

Finally we mention that, in large supercell, sampling the reciprocal space by considering only the  $\Gamma$  point ( $\mathbf{k} = 0$ ) leads to a substantial speed-up of the calculation since eigenfunctions become real-valued.

## 3.2. Ionic contribution to the total energy

Within the BO approximation, the KS Hamiltonian provide a means for obtaining the total energy of the electron system. However, the true ground state energy also include an ionic contribution, i.e.

$$E_{tot} = E_{el} + E_{ion}(\{\mathbf{R}\}) \tag{3.38}$$

where  $E_{ion}(\{\mathbf{R}\})$  is the contribution arising from the ion-ion interaction and  $E_{el}$  is the total energy of the electrons moving in the coulomb field of the ions.

The Schrödinger equation for the nuclei in the BO approximation is

$$H = T_N + V_{ext} + V_{NN} \tag{3.39}$$

where  $T_N = -\sum_i^{N_n} \frac{\hbar^2 \nabla^2}{2M_i}$  is the nuclear kinetic energy,  $V_{NN}$  is the nuclear interaction term and  $V_{ext}$  is an external potential acting on the nuclei. The kinetic term in Eq. 3.39 gives rise to collective nuclear motions which are commonly referred to as phonon modes. To analyse vibrational modes, the potential acting on nuclei must be evaluated. The Hellman-Feynman theorem provides a clever way to do so by allowing the evaluation of the forces acting on the nuclei as

$$F_{I} = -\frac{\partial E(\{\mathbf{R}\})}{\partial \mathbf{R}_{I}} = -\langle \Phi_{\{\mathbf{R}\}} | \frac{\partial H_{\{\mathbf{R}\}}}{\partial \mathbf{R}_{I}} | \Phi_{\{\mathbf{R}\}} \rangle$$
(3.40)

where  $\Phi_{\{\mathbf{R}\}}$  is the ground-state wave function of the KS Hamiltonian. This result is of extreme importance since it allows to obtain forces (and therefore the potential in the harmonic approximation) from ground state calculations. It also provides an efficient way to perform structural relaxations in geometry optimisation simulations.

In the BO scheme we can provide an approximate result for the ground state energy by varying the nuclear configuration  $\{\mathbf{R}\}\$  and constructing the BO potential energy surface for the nuclei. The vibrational contribution to the total energy is commonly computed in two ways. One is the direct approach, also known as frozen phonon method, in which the ground state energy and the forces of the system subject to a particular distortion are calculated from first principles. This approach has the advantage of allowing the evaluation of nonlinear effects. The second method is known as the *linear response* approach and uses the Density Functional Perturbation Theory (DFPT) to obtain, together with the ground state density  $n(\mathbf{r})$ , the linear response of the electron density to a distortion of the nuclear geometry, i.e.  $\partial n(\mathbf{r})/\partial R_I$ . This last method is usually more efficient and can be used to study vibrational excitations at any wavevector while the frozen phonon method is limited by the size of the supercell that is required to represent the distortion introduced by a given vibrational mode.

## 3.3. Basis sets

As already discussed, in order to solve numerically the KS iterative scheme, an orbital description of the density is needed and therefore a basis set must be defined. The general definition of the basis expansion is

$$\psi(\mathbf{r}) = \sum_{i} c_i \phi_i(\mathbf{r}) \tag{3.41}$$

and the basis functions  $\phi_i$  may or may not form a complete basis. Many different sets have been developed as of today. Here we will briefly introduce the basic concepts behind the two approaches used in this thesis: Plane Wave (PW) and Linearized Augmented Plane Waves (LAPW).

#### 3.3.1. Plane Waves

The PW expansion of a wave function  $\psi_i$  in a periodic system can be written as:

$$\phi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}f_i(\mathbf{r}) \tag{3.42}$$

where **k** is defined in the first Brillouin zone of the system and  $f_i$  takes the form

$$f_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$
(3.43)

with **G** being reciprocal lattice vectors. The basis set for a given wavevector **k** is therefore discrete but infinite. In order to use the basis in a computational implementation of the KS iteration, some approximations are needed. Firstly, a cutoff energy  $\frac{|\mathbf{k}+\mathbf{G}|^2}{2} \leq E_c$  is used to restrict to a sphere in reciprocal space the size of the sum over **G** in Eq. 3.43. In PW based DFT implementations, the cutoff energy is the only parameter that controls the accuracy of the basis set. This represents a substantial advantage over other basis sets which often require many parameters to control the basis expansion and in some cases, no systematic scheme for convergence is available (i.e. a variational principle is not available). The second approximation consists of removing the core region of the Coulomb potential which would require a prohibitively large number of plane waves to reach convergence. This is discussed in the next section.

#### **Pseudopotentials**

Pseudopotentials are always used in conjunction with the PW basis to remove the 1/r behaviour of the Coulomb potential which otherwise would make the use of this basis functions prohibitive. The need for pseudopotentials is nicely shown by Fig. 3.2 where the rapid oscillations which maintain the orthogonality between the core and valence electron states are depicted. The description of such rapid oscillations would require a large cutoff energy and is usually useless since in many cases one is interested in the description of atomic bonding which only requires an accurate description of the region where valence electrons overlap.



Figure 3.2.: Schematic illustration of the pseudopotential concept. For  $r > r_c$  the pseudo wave function,  $\tilde{\phi}$ , and the local part of the pseudopotential,  $V_{loc}$ , are equal to the all electron functions.

The concept of pseudization was introduced to overcome all these problems. Moreover for heavier atoms in which relativistic effects are important, and so the Dirac equation is required, the valence electrons can be treated non-relativistically. Therefore removal of the core electrons also allows to maintain the non-relativistic approach.

Pseudopotentials remove localised core states by modifying the charge state of the nucleus. This will lead to a modified valence wave function  $\tilde{\psi}$  that replaces the true valence eigenfunction  $\psi$  and is characterized by a smoothed form between the nucleus and some cut-off radius  $r_c$ . Beyond this radius,  $\tilde{\psi}$  is identical to the full all-electron wave function  $\psi$ .

In what follow we will consider only *ab initio* pseudopotential which are a class of pseudopotentials that are obtained from the inverse solution of the KS Schrödinger equation. Consider the Schrödinger equation for the *l* component of the radial part of the atomic orbital  $\phi_l(r)$ 

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Ze}{r} + V_H(r) + V_{xc}(r) - E_l\right]\phi_l(r) = 0 \quad (3.44)$$

where  $\phi = r\psi$  and  $V_H(r)$  and  $V_{xc}(r)$  were introduced in Eq. 3.21. To remove the core divergence we have to replace the  $-\frac{Ze}{r}$  term with an attractive  $V_{ps}$  which provide a different eigenfunction but the same eigenvalue. The problem can be formally written as

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{ps} + V_H(r) + V_{xc}(r) - E_l\right]\tilde{\phi}_l(r) = 0 \quad (3.45)$$

Usually one defines the form of the pseudo wave function  $\tilde{\psi}$  and the cutoff radius. Then  $V_{ps}$ , which is assumed to have the form

$$V_{ps} = V_{loc} + \sum_{lm} B_l |\chi_{lm}\rangle \langle \chi_{lm}|$$
(3.46)

where orbitals  $\chi_{lm}$  vanish outside the core region and are obtained from the solution of

$$\chi_{lm}(r) = \left\{ E_l - \left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{loc} + V_H(r) + V_{xc}(r) \right] \right\} \tilde{\psi}$$
(3.47)

where

$$B_l = \frac{1}{\langle \chi_{lm} | \tilde{\psi} \rangle} \tag{3.48}$$

It is clear from the above equation that we still have some freedom in the form of  $V_{loc}$ . This is used to fulfil two requirements that the pseudopotential should provide: softness and transferability. The former concept is a measure of the number of planewaves that are needed to describe the smooth wave function. The transferability is the accuracy that the pseudopotential provides for smooth wave functions different from the one for which it was generated. Accuracy and good transferability are obtained, at the expense of softness, by introducing norm conserving pseudopotentials [85]. These are defined by the condition: r

$$\int_{0}^{r_{c}} r^{2} dr |\psi(r)|^{2} = \int_{0}^{r_{c}} r^{2} dr |\tilde{\psi}(r)|^{2}$$
(3.49)

together with the requirement that, for a given atomic configuration, the pseudopotential provides the exact eigenvalues of the all electron potential. This constraints fix the form of  $V_{loc}$  and therefore also  $V_{ps}$ .

However, norm-conservation requires exceedingly high cutoff energies for the first row elements and for transition metals. To solve this issue, Vanderbilt introduced the concept of ultrasoft pseudopotentials. The key idea is to relieve the norm-conserving condition for the smooth wave functions but guarantee the correct evaluation of the core charge. This is achieved by introducing a generalised eigenvalue problem of the form

$$\hat{H}|\tilde{\psi}_l\rangle = \varepsilon_i \hat{S}|\tilde{\psi}_l\rangle \tag{3.50}$$

$$\langle \tilde{\psi}_l | \hat{S} | \tilde{\psi}_{l'} \rangle = \delta_{ll'} \tag{3.51}$$

where the requirement for charge conservation is included in the operator  $\hat{S}$ . For more details on this method, the reader is referred to the original article Ref. [86].

Finally, shortly after the introduction of ultrasoft pseudopotentials, Blöchl proposed the Projector Augmented Wave (PAW) method [87]. Somehow resembling the APW method discussed in the next chapter, in the PAW method the core part of the smooth wave function is reconstructed by means of a linear transformation acting on  $\tilde{\phi}$ . This is obtained by defining a set of projector operators. The projection operators allow to describe the rapidly varying core wave function with linear combination of smooth wavefaunction like, for example, polynomials or Bessel functions.

We conclude this section by mentioning that the plane wave basis set offers a number of advantages, including the simplicity of the basis functions and, as a consequence, of matrix elements evaluation, the parallel efficiency and the easily tuning accuracy. Moreover, the adoption of plane-wave basis set provides simple expression for forces and stress tensor calculations and enables the full relaxation of the structure to minimize the forces in the system efficiently and accurately.

#### 3.3.2. Linearized Augmented Plane waves

The LAPW basis introduces a different approach to treat the core states. Rather then encapsulating their effect in a pseudopotential, the core states are included in the basis set. Therefore, since the LAPW basis does not require any shape approximation to the effective one-electron potential  $v_s$ , it is usually referred to as a Full Potential (FP) method.

The basis is constructed by dividing the unit cell in non overlapping spheres centred at the atomic sites, called muffin-tin (MT), and interstitial regions (I). While the potential is almost spherically symmetric in the muffin-tin region, it will be fairly flat in the interstitial. For this reason, in the latter space, plane waves are used to describe the non-interacting wave function. In the interstitial space, plane waves are augmented by the introduction of localised orbitals of the form

$$u_l(r, E)Y_l^m(\theta, \phi) \tag{3.52}$$

where  $Y_l^m(\mathbf{r})$  is the spherical harmonic function of angular momentum quantum numbers l and m,  $\mathbf{r}$  is defined with respect to the centre of each MT sphere and the angles  $\theta, \phi$  specify the direction of  $\mathbf{r}$  in spherical coordinates. The  $u_l$  function is the solution of the radial Schrödinger equation. In order to introduce LAPW we first discuss the Augmented Plane Waves (APW) basis functions [88, 89]. These are constructed from the two wave functions used in the solution of the Schrödinger equation discussed above:

$$\phi_i = \begin{cases} V^{-1/2} e^{i\mathbf{k}\mathbf{r}} & \mathbf{I} \\ \sum_{lm} a^i_{lm} u_l(r, E) Y^m_l(\theta, \phi) & \mathrm{MT} \end{cases}$$
(3.53)

The coefficients  $a^i$  are fixed by imposing the matching between the plane waves and the localised states at the MT boundary  $r_{\rm MT}$ .

Each augmenting function  $u_l(r, E)$  represent the exact muffin-tin potential eigenstate of eigenenergy E. Therefore, any eigenstate of different eigenenergy will be poorly described by the augmentation

#### 3. A short introduction to DFT

function. Thus, in order to keep a manageable basis set size, the basis functions must be re-evaluated for each new energy E examined. This makes the APW basis functions energy dependent and extremely computationally expensive.

To solve this issue, O. K. Andersen [90] introduced the Linearized APW basis. The fundamental idea is to substitute the augmentation function in the MT region with an expression providing enough flexibility to represent the eigenstates in a region around E. This is obtained with the basis containing the following augmentation function:

$$\phi_i = \begin{cases} V^{-1/2} e^{i\mathbf{k}\mathbf{r}} & \mathbf{I} \\ \sum_{lm} \left[ a_{lm}^i u_l(r, E) + b_{lm}^i \dot{u}_l(r, E) \right] Y_l^m(\theta, \phi) & \mathrm{MT} \end{cases}$$
(3.54)

where  $\dot{u}_l(r, E)$  is the energy derivative of  $u_l$  taken at the same energy E.

The coefficients a and b are now obtained by matching in both value and slope the augmentation function to the plane wave at  $r_{MT}$ . This new augmentation function resembles a first order Taylor expansion in which the a and b coefficients provide enough flexibility to describe the neighbouring energies of E thus removing the energy dependence of the basis set. The cost of doing this is the loss of the optimal shape inside the muffin-tin spheres. Moreover a larger secular matrix with respect to the APW case must be considered. However the LAPW method provides a great improvement over the APW method, since it removes the energy dependence of the APW basis.

In general, the LAPW basis is used in conjunction with other basis functions in order to take into account semicore states or core orbitals. Among the many possible approaches, we mention the APW+"lo" approach [91, 92] and the LAPW+LO approach [93], which are used respectively in the Elk and Wien2K codes [94, 95].

The convergence of this basis set is controlled by many parameters. These include the plane wave expansion for the interstitial space, the size of muffin tin radii, the description of core and semicore states. For the plane wave expansion the dimension of the basis is defined by the adimensional number  $\min(R_{MT}) \times \max(|\mathbf{G} + \mathbf{k}|)$ . The above adimensional quantity is preferred over the dimensional value  $\max(|\mathbf{G} + \mathbf{k}|)$  because it includes a reference to the border of the smallest muffin tin sphere which is the most problematic point for the plane wave expansion. The more we increase the muffin tin radius, the smaller the plane wave basis set must be to achieve the same accuracy in the description of the interstitial space. Small radii will require a large plane wave basis set. Big radii will reduce the dimension of the plane wave set but also produce unconverged results since the atomic function are not suited to describe the wave function in the region far from the nucleus.

## 3.4. DFT for muon site identification

The methodology used for the identification of muon sites with DFT inherits most of the knowledge developed for first principles analysis of impurities and defects. For this reason, a short overview on the details of alloys and impurities simulation is given below. Afterwards, these results are specialised to the muon case and the peculiarities of the interstitial site identification problem are discussed.

#### 3.4.1. Alloys, impurities and defects

In this section we briefly review some aspects of the analysis of disorder in solids studied with theoretical approaches. Many of the concepts developed in this field provide the theoretical background for the analysis of muon sites from first principles.

There are two popular ways to calculate the effects of defect or impurities from first principles: one is the Korringa-Kohn-Rostocker (KKR) approach (in its Green Function formulation  $^{\dagger}$ ) and the other is DFT calculations on supercells. In the former method, the electron problem is tackled as a multiple-scattering problem between electrons and nuclei. The Schrödinger equation is transformed into an equivalent integral equation and the problem is transformed into the evaluation of a multiple scattering model.

The solution of a single atomic site embedded in a free electron environment is first evaluated. In addition, one considers the scat-

<sup>&</sup>lt;sup>†</sup>For a recent review see for example Ref. [96]

tering of an incoming electronic wave by the single site potential. This will produce an outgoing wave characterised by a phase shift. The scattering process can be equivalently expressed as a single-site scattering t-matrix and, instead of using eigenfunctions and eigenvalues, the single-particle Green function is used to solve the scattering problem. The system's Green function is obtained by requiring that the incoming and outgoing wave function at each (possibly different) atomic site must be identical.

One of the most important outcomes of the KKR method is the possibility to treat impurities and alloys in the coherent potential approximation which yields superior results with respect to the virtual crystal approximation in which the alloy is replaced by an averaged crystal potential. We finally mention that one of the advantages of this method is represented by the limited computational effort that is required to compute large quantum mechanical problems (up to thousand of atoms). Moreover effective parallelization strategies can be introduced.

In the supercell method, a direct calculation on a supercell, which becomes the new unit cell of the system once the impurity/dislocation is introduced, is performed and the effect of disorder is subsequently considered. The disadvantage of the supercell method is that, for a point-defect in a three-dimensional system, a three-dimensional periodic array of defects is actually simulated. Despite that, PBC enable fast and accurate calculations for the estimation of impurity energetics, structural parameters, vibrational modes and other physical characteristics. Indeed the great advantage of supercell calculations is that the Bloch theorem is maintained and therefore the results discussed in the previous sections, with special reference to the plane wave basis, can be applied directly.

The disadvantage is that supercells are computationally demanding and the periodicity introduces spurious interactions between the defects or impurities and dispersion of the defect/impurity-induced electronic states. These must be carefully considered in preliminary convergence tests against the supercell size.

A typical consequence of the presence of point defects, which is especially relevant for the charged ones, is the introduction of elastic stress in the host lattice. In real systems, this is relieved by ionic displacements, i.e., lattice relaxation. However, when dealing with supercells, the ionic relaxations around the defect are limited by the supercell size. The presence of periodic replica imply that the relaxation pattern is truncated midway between the defect and its nearest replica. An argument often used in supercell calculations is that the ion displacements should vanish near the borders of the supercell. However, this does not necessarily guarantee that the long-range ionic relaxations are correctly described, as the supercell symmetry may fix the positions of the ions at the border of the supercell. For this reason, the forces and the displacements of all ions in the supercell should be inspected.

Another, more difficult problem arises with charged defects. In order to avoid the divergence of the electrostatic energy, a commonly adopted solution is to introduce a neutralizing background charge, often in the form of a uniform "jellium", which enables the evaluation of electrostatic (Coulomb) energies. The well known problem with this approach is that there are no general predictions of the convergence of the Coulomb energy against the supercell size [69]. Many possibilities have been proposed to estimate and correct the influence of the neutralizing charge on the total energy (and derived quantities) convergence [97–100]. We do not enter into the details here but just remark once more the importance of checking convergence against supercell size especially in charged impurities calculations.

Finally, it is important to note that defect and impurity calculations should be carried out using the lattice constant optimised for the bulk unit cell or, alternatively, experimental lattice constants. This is crucial in order to avoid spurious elastic interactions between the defects or impurities of the supercell and that of the periodic replica. Otherwise the calculation results would refer to a system containing an ordered array of highly concentrated defects/impurities.

#### 3.4.2. The muon as a charged impurity

The identification of the muon site with DFT takes advantage of the knowledge developed over the years for charged defects and impurities. Being leptons, muons are identical to electrons except for the finite lifetime of  $\sim 2.2 \ \mu$ s and for their mass being around 200 times the

electron mass. However, from the standpoint of  $\mu$ SR and electronic structure calculations, the muon looks rather like a light isotope of the proton, with spin 1/2 and a magnetic moment.

As already discussed in the introduction, the final stage of the muon's deceleration process in matter takes place by electrostatic interactions with the sample and, passing from kinetic energies of tens to fractions of eV, the muon travels up to 1  $\mu m$  before coming to rest in an interstitial site [32]. Thus the most simple approach to obtain physical intuition for the final muon site is to inspect the electrostatic potential for the muon in the hosting system. The electrostatic potential felt by the positive muon is defined as

$$V_{\mu}(\mathbf{r}) = -e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + \sum_{i} \frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_i|} , \qquad (3.55)$$

where  $\mathbf{r}$  and  $\mathbf{R}$  are electronic and nuclear coordinates respectively and i runs over the nuclei.

Quite surprisingly, the (absolute or relative) minima of the unperturbed bulk electrostatic potential are close to the muon sites in a variety of metallic materials. To check the stability of the various sites, at first we solved the Schrödinger equation for the muon in electrostatic potential of Eq. 3.55 or in an approximated form in the vicinity of each minimum. This provides the eigenstates' energies  $E^{(i)}_{\mu}$ that are reported according to

$$E_i^{(j)} = E_\mu^{(i)}(\mathbf{R}) - \min_{\mathbf{r}_\mu} [V_\mu^{(j)}(\mathbf{r}_\mu)]$$
(3.56)

where i enumerates the eigenvalues (i = 0 being the ground state) and j, if present, identifies the approximated potential for which the Schrödinger equation was solved.

The analysis of the Ground State Energy (GSE) of the muon in the electrostatic potential usually reveals that many local minima are unstable, i.e. the muon can overtake the barrier towards interstitial positions with lower energy. In the rest of this thesis we label possible muon sites the minima that remain disconnected when the GSE of the muon is evaluated in the unperturbed  $V_{\mu}$  potential of Eq. 3.55.

The remarkable accuracy provided by this simple strategy in several materials can be understood by considering the central role played by conduction electron in the screening of the charged particle. If the screening is effective, it guaranties a small modification of the charge densities forming the chemical bonds in the system. However, there is no rigorous account for this effect even in metals and no reason that the minima of  $V_{\mu}(\mathbf{r})$  will provide the correct muon sites in semiconductors or insulators.

In view of this fact, a different approach, based on DFT supercell calculations, has been considered. The simulation of the positively charged muon is achieved by introducing an interstitial hydrogen, i.e. a classical positive point charge, and checking the convergence of the electronic perturbation it provides against the supercell size. Indeed, as already mentioned, it is important to avoid the spurious contributions from the replica introduced by PBC. An estimation of the accuracy of the simulation can be obtained by considering the parameters already discussed in the previous section: the tensile stress introduced in the supercell by the impurity, the range of the force field, the variation of total energy differences and bond lengths for supercells of increasing dimension, the width of impurity bands in the system and possibly also the changes in the band structure of the material (for example, doping effects)<sup>†</sup>.

It was found that a neutral supercell approach provides the best results for metals while a charged supercell with a corresponding compensating background is a better approximation for insulators [16, 18, 19, 101, 102]. This difference can be understood again by considering that in metals the charged particle is effectively screened by conduction electrons. Considering a neutral supercell is therefore a better description of the real system. On the other hand, in insulators, the correct description of the muon sites is obtained by removing an electron from the system and adding a compensating jelium charge to provide supercell charge neutrality and avoid Coulomb energy divergence. In the rest of this thesis we will refer to the addition of a hydrogen atom inside the host material (with the possible removal of an electron) as the simulation of the  $\mu$  particle in the embedding

<sup>&</sup>lt;sup>†</sup>To compare the bulk band structure with the one obtained from a supercell calculation, a procedure to unfold the supercell band structure is required. Within the QUANTUM ESPRESSO suite of codes this can be done with the tool of Appendix D.2

system.

Starting from a grid of possible interstitial positions, the effect of the muon embedding is inspected. The grid is usually selected by requiring that initial muon positions are far enough from the atoms in the system (usually more than 1 Å) and sample the whole interstitial space in the unit cell. By considering the point group symmetry of the system, the number of interstitial positions that are needed to sample the whole interstitial volume can be significantly reduced. We mention that, in some cases, owing to the simplicity and the limited size of the unit cells of the various materials, a slightly different approach was used. Instead of constructing a grid of interstitial points, random position inside the unit cell are selected by hand and a graphic method is used to check whether the interstitial positions explore the whole interstitial space.

For each of the starting points, electron density rearrangements and lattice distortions are obtained by letting the atoms' position relax towards a configuration which minimises the forces in the system. A convergence threshold for both the total energy differences between the relaxation steps and total forces must be reached. Many (local) minima of the total energy hyper-surface are identified by the above procedure. We label them candidate muon sites. Usually not all candidate sites are stable muon sites. This is due to the quantum nature of the muon which is neglected in the relaxation step. This problem is not so relevant when studying hydrogen intercalation since small energy barriers are sufficient to trap hydrogen impurities. However, the GSE of the muon can be up to an order of magnitude larger than that of the proton  $(m_p/m_\mu \sim 9)$ , thus making many interstitial position unstable. To discriminate between binding and non-binding sites, the ground state energy of the muon must be carefully evaluated. Many approaches to go beyond the BO scheme have been developed [103–108]. However, since our aim is to provide a supporting tool for  $\mu$ SR data analysis, these methods are found to be prohibitively demanding of storage and computer time when materials of real interest for condensed matter research are considered. For this reason the quantum nature of the muon, which is of course relevant given its small mass, is introduced a posteriori [18, 109]. During the development of the work presented in this thesis, two approaches have been considered. One is the study of the vibrational modes of the impurity as discussed in Ref. [18]. This method has the advantage of treating the nuclei and the muon on the same footing. However the calculation of phonon modes can become computationally expensive in supercell simulations. Moreover, usually the light mass of the muon makes the muon wave function quite extended, hence the harmonic approximations not sufficiently accurate. Therefore, we opted for a different scheme following the lines of the Double Adiabatic Approximation (DAA) which was developed in Ref. [18, 110]. This scheme is presented in the next section.

#### 3.4.3. Double Adiabatic Approximation

The muon is roughly ten times lighter than the proton, thus, a proper account of its larger GSE when confined or bound is very important. In this section we briefly recall the formal equations for the DAA used in chapters 6 and 7 to evaluate the quantum ground state of the muon. This procedure has already been introduced in literature [109] to study the quantum effects of muonium in silicon and germanium. The total Hamiltonian of a system which describes a host lattice formed by nuclei and electrons and a single muon is:

$$\mathcal{H}_{\text{tot}} = \mathcal{H}_N + \mathcal{H}_\mu + \mathcal{H}_e \tag{3.57}$$

$$\mathcal{H}_{\mu} = -\frac{\hbar^2}{2m_{\mu}}\nabla^2_{\mu} \tag{3.58}$$

$$\mathcal{H}_{N} = -\sum_{j=1}^{N_{N}} \frac{\hbar^{2}}{2M_{j}} \nabla_{N_{j}}^{2}$$
(3.59)

$$\mathcal{H}_e = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla_i^2 + V(\mathbf{r}_e, \mathbf{r}_\mu, \mathbf{R})$$
(3.60)

$$\mathcal{H}_{\text{tot}}|\Psi\rangle = E|\Psi\rangle \tag{3.61}$$

where index j runs over the  $N_N$  nuclei having the set of position operators **R** and masses  $M_j$ ,  $\mathbf{r}_{\mu}$  and  $m_{\mu}$  are the position operator and the mass of the muon and the index i runs over the  $N_e$  electrons having the set of coordinate operators  $\mathbf{r}_e$  and mass  $m_e$ . If we approximate the total wave function  $|\Psi\rangle$  with the product wave function  $|\psi_e\rangle|\phi_{\mu}\rangle|\chi_N\rangle$ ,
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the position operators of the muon and of the nuclei enter only as parameters in the Hamiltonian for the electrons  $\mathcal{H}_e \psi_e(\mathbf{r_e}; \mathbf{r}_\mu, \mathbf{R}) = \varepsilon(\mathbf{r}_\mu, \mathbf{R}) \psi_e(\mathbf{r_e}; \mathbf{r}_\mu, \mathbf{R})$  that is solved with the KS iterative scheme. By solving the Schrödinger equation of the electrons for the positions  $\{\mathbf{r}_\mu\}$ we can construct the potential entering the Schrödinger equation of the muon

$$\left(-\frac{\hbar^2}{2m_{\mu}}\nabla^2_{\mu} + \varepsilon(\mathbf{r}_{\mu}, \mathbf{R})\right)\phi_{\mu}(\mathbf{r}_{\mu}; \mathbf{R}) = E_{\mu}(\mathbf{R})\phi_{\mu}(\mathbf{r}_{\mu}; \mathbf{R}) , \qquad (3.62)$$

where, for a nuclear lattice with coordinates  $\mathbf{R}$ ,  $V_{\mu}(\mathbf{r}_{\mu}) = \varepsilon(\mathbf{r}_{\mu}, \mathbf{R})$ . Let  $E_{\mu}^{(i)}$  be the *i*-th eigenvalue of Eq. 3.62, in the following we will refer to

$$E_{i} = E_{\mu}^{(i)}(\mathbf{R}) - \min_{\mathbf{r}_{\mu}}[V_{\mu}(\mathbf{r}_{\mu})]$$
(3.63)

as the *i*-th energy of the *i*-th muon eigenfunction (i = 0 being the ground state).

At a first sight it may seem that this approach is rather impractical since it requires the execution of a large number of self consistent loops. However the intermediate mass of the muon greatly reduces the number of points to be acquired. Indeed the ground state energy of the muon is usually slightly less than 1 eV. This makes the calculation feasible since it is possible to obtain a good accuracy up to a couple of eV by interpolating from 5 to 10 hundred points in a points cloud. The favourable convergence against the supercell sizes (usually less than 100 atoms are needed) and the constantly increasing computational power available on computer clusters make this method effective for many materials of interest in condensed matter research.

The computational scheme developed to evaluate  $V_{\mu}$  is discussed in details in Appendix B. The method, which involves the sampling of the potential on a grid of points which form a points cloud that is subsequently interpolated, is referred to as Double Born Oppenheimer (DBO) in the next chapters.

### **Iron Pnictides**

studying the unperturbed system

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In this chapter we present an elementary method for identifying muon sites based on the inspection of the minima of the unperturbed electrostatic potential of the material under study. This is the simplest and quickest approach that can be used to have a rough estimation of possible muon sites. As discussed hereafter, a surprisingly good description of the  $\mu$  embedding positions is obtained for many metallic materials with this approach. However, it was shown that the minima of the electrostatic potential do not match the muon sites in insulators where the muon usually occupy low-symmetry positions (see for example chapters 6 and 7). Moreover, also in metallic compounds, muon sites can be quite far from the minima of the unperturbed electrostatic potential due to the perturbation introduce by the muon on the valence electrons forming the chemical bonds in the system.

Summarising, to date there is no clear strategy to distinguish between the cases in which the muon site is accurately provided by the unperturbed electrostatic potential and those where this approach is doomed to fail. For this reason we refer to the positions provided by this method as *possible muon sites*. In this chapter, *possible muon*  sites are validated by comparison with the experiment. In the next sections we show that Iron Pnictides Superconductors (IPSCs) represent a fortunate case that is worth reporting since the simple strategy presented here offer a quick and computationally inexpensive way to help locating muon sites.

#### 4.1. Introduction

The discovery of IPSCs represented a breakthrough in condensed matter research and boosted the interest for the analysis of the mechanism governing the formation of the Cooper pairs in high  $T_c$  superconductors. These materials, as the cuprates superconductors, are characterised by a phase diagram showing neighbouring or even overlapping magnetic and superconducting states as a function of the charge doping. This evidence renewed the debate on the relation between superconductivity and magnetic fluctuations in high temperature superconductors.  $\mu$ SR is one of the best technique to probe the crossover between magnetic and superconducting phases due to its effectiveness in acquiring the small local fields generated either by nanoscopically coexisting magnetic orders or external fields penetrating in the vortex phase of a superconductor. Indeed a  $\mu$ SR experiment provided one of the first electronic phase diagrams of LaFeAs $O_{1-x}F_x$ , the first compound showing high temperature superconductivity discovered by Prof. Hosono's group [111–113].

For what concerns the description of the muon sites in the IPSCs, to the best of our knowledge, an initial estimation was obtained with a modified Thomas-Fermi approach for LaFeAsO and FeSe [114–116]. The crude description offered by the Thomas-Fermi functionals is sufficient to correctly identify the two muon sites present in the two materials. We confirmed these results with FP DFT simulations. Moreover, we identified muon sites in LaCoPO and unveiled the origin of an unexpectedly large effect of pressure on the local field at the muon site in this material.

#### 4.2. LaFeAsO

LaFeAsO is one of the parent compounds of the IPSCs. It belongs to the 1111 family, a class of materials of the type REFeAsO (RE=Rare earth element). In this family, superconductivity is achieved by both hole and electron doping in the spacing REO layer or at the iron site. Differently from other families of the IPSCs, in REFeAsO the coexistence of superconductivity and magnetic order may or may not be observed depending on both the element providing the charge doping and on the rare earth element forming the spacing layer [117–119]. The coexistence of the magnetic and the superconducting state on a nanoscopic scale has important implication on the description of the Cooper pair condensate. Therefore, this aspect has been extensively studied during the last six years.

The identification of the muon sites in this class of materials allowed a direct comparison with other compounds, other techniques used to detect the magnetic order and a deeper understanding of the magnetic properties of the system. Moreover, the presence of two muon sites provides a route to simultaneously analyse both the long-range order of the Fe plane and of the rare earth atoms. This was nicely shown by Mäter and coworkers in Ref. [115].

As already discussed in Sec. 3.4.2, the crystallographic sites where muon stop after thermalization processes may be identified, to a first extent, by calculating the ground state electron density of the unperturbed material under investigation and subsequently obtaining the electrostatic potential with Eq. 3.55. In what follows we will describe the identification of the *possible muon sites* in LaFeAsO and the degree of agreement that was obtained with the this crude approximation.

The electrostatic potential was obtained with a FP-DFT approach as implemented in the Wien2K package. The other details of the calculation are given in Sec. A.1.

 $V_{\mu}(\mathbf{r})$  is shown in Fig. 4.1 where three local minima labelled A, B and C can be identified. Two of them are close to the LaO layer one in the 2c position, the other is in the 4f position. A third minimum is just above the FeAs plane, again in the Wyckoff position 2c.

To understand whether the minima A, B and C are stable sites, a simple approach was used: the potential around each minimum



Figure 4.1.: Isosurfaces of the electrostatic potential of unperturbed LaFeAsO for  $V(\mathbf{r}) = V_0^{(i)} + E_0^{(i)}$  (see text). The three minima are labeled A, B and C. [Plotted with XCRYSDEN, Ref. [120], reprinted with permission from Ref. [121]]



Figure 4.2.: The long-range AFM order of the Fe ions that develops below  $T_N \sim 140$  K. The paramagnetic unit cell is also depicted. The muon resideds in the positions obtained by glide reflection of As and La sites, but at different height from the Fe or O planes respectively. was modelled with an anisotropic harmonic well and the GSE for the harmonic oscillator in each site  $E_0^{(i)}$ , with i=A,B or C, was considered. The results are reported in Tab 4.1 and pictorially shown in Fig. 4.1 where isosurfaces for  $V(\mathbf{r}) = V_0^{(i)} + E_0^{(i)}$  were drown  $(V_0^{(i)})$  being the energy of the *i*-th minimum).

Assuming that in each minimum the muon can overtake any barrier lower or equal to  $E_0^{(i)}$ , we see that minima A and B are disconnected, while in C an interconnected network is formed since the migration barrier is lower than  $E_0^{(C)}$ . Therefore, minimum C is unstable and we are led to conclude that, while the muon potential has three nonequivalent minima, only *possible muon sites* A and B are surrounded by barriers high enough to guarantee muon confinement. These two sites correspond roughly to those identified in Ref. [115].

**Table 4.1.:** Possible muon sites: cell coordinates x, y, z, potential V (eV) referred to the minimum, GSE  $E_0$ , first excited level  $E_1$  (eV), and local dipolar field, assuming a value of the Fe moment  $m_{\rm Fe} = 0.68 \, \mu_B$  (see text).

site	x	y	z	$V - V_{\rm A}$	$E_0$	$E_1$	$B^d_\mu (\mathrm{mT})$
$\mu_{ m A}$	0.75	0.75	0.572	0	0.63	0.29	165
$\mu_{ m B}$	0.25	0.25	0.137	0.55	0.51	0.09	29
$\mu_{ m C}$	0.5	0.0	0.703	0.94	0.54	0.25	-

In agreement with the above findings, two oscillating signals are observed. The two local fields at the muon sites  $B_1 = 0.165(5)$  T and  $B_2 = 0.019(1)$  T were extracted from  $\mu$ SR data for  $T \rightarrow 0$  K.

A very good estimate of  $B_1$  is obtained by considering only the dipole field contribution and, within this approximation,  $\mu$ SR yields a direct measurement of the moment on iron atoms. By assuming that the internal fields at the muon site originates from the Fe magnetic moments  $m_{\rm Fe}$ , in the known [122] AFM structure (see Fig. 4.2), and that  $B_1$  originates in site A (see Ref. [121]), the value  $m_{\rm Fe} = 0.68(2)$  $\mu_B$  along the (110) direction is obtained. We note that this value is in very close agreement with neutron scattering (Ref. [123]),  $m_{\rm Fe} =$  $0.63(1)\mu_{\rm B}$ , and NMR (Ref. [124]),  $m_{\rm Fe} = 0.58(9)$   $\mu_{\rm B}$  results.



Figure 4.3.: Isopotential surfaces  $V(\mathbf{r})$  for minima in A and B calculated at the respective  $V^{(A,B)}(\mathbf{r}) = V_0^{(A,B)} + E_0^{(A,B)}$ . The disjointed inner surfaces (red) refer to A minima, while the interconnected sheets (yellow) to the B minima. [Plotted with VESTA, Ref. [125], reprinted with permission from Ref. [126]]

By the same token, site B cannot be the main muon site since it would require an unacceptably large value of the Fe moment (3.6  $\mu_{\rm B}$ ) to reproduce  $B_1(T = 0)$ . The field reported in Tab. 4.1 for site B, with 0.68  $\mu_{\rm B}$  on Fe, agrees within a factor 1.6 with  $B_2(T = 0)$ .

#### 4.3. FeTe

Iron tellurium (FeTe) and iron selenium (FeSe) are two parent compounds of the 11 family of IPSCs. These materials reach a low superconducting critical temperatures when a small excess of Fe is present, but also by other chemical doping or by applying pressure [127–130]. The superconducting temperature can be raised up to ~ 40 K by tuning the anion height from the Fe plane with externally applied pressure [131]. However, they recently attracted much interest since they constitute the first example of iron based superconductors with  $T_C$  higher than liquid nitrogen temperature when synthesized as single layer film [132]. Moreover, these materials are the simplest realisation of Fe-based superconductors and also have comparably low toxicity with respect to the other families. This makes the 11 class of IP-SCs one of the best candidates for applications among the Fe-based

Site	Position	$z_{\mu}$ WFC	$V_0 - V_0^{(A)}$ (eV)	$E_0 (eV)$
A	(1/4, 1/4, 0.245)	0.27	0	0.36
(B)	(3/4, 1/4, 0.500)	0.50	0.9	0.39

**Table 4.2.:** Results obtained from the analysis of the electrostatic potential. The reported positions correspond to the minima of the potential  $V(\mathbf{r})$  (Eq. 3.55). The respective Wyckoff positions are A 2c and B 2b.  $E_0$  is the GSE of the muon in the approximated potential (see text) and WFC is the maximum probability point of the muon's wave function.

superconductors.

In order to characterise the ground state AFM order of  $Fe_{1+x}Te_{1+x}$ we studied single crystals of these compounds by means of  $\mu$ SR and magnetometry measurements. We focus once more on the muon site assignment task that allowed us to estimate the value of the local moment on the Fe atoms. In order to determine possible muon sites in FeTe, the same approach discussed for LaFeAsO was used. Two inequivalent minima were found, whose positions are shown in Fig. 4.3a, and their coordinates are reported in Tab. 4.2. The absolute minimum (A) replicates the one determined in Ref. [116] for FeSe, while the secondary minimum (B) coincides with the centre of the tetrahedron formed by Te atoms. The latter site turned out to be unstable against the GSE of the muon which was accounted for by modelling the potential minimum with an anisotropic harmonic well  $V(r) = \frac{1}{2}m_{\mu}(\omega_x^2 x^2 + \omega_u^2 y^2 + \omega_z^2 z^2)$  and evaluating the GSE  $E_0^{(j)}$  (j =A,B) of the implanted muon. The resulting isosurfaces for  $V(\mathbf{r}) = V_0^{(A,B)} + E_0^{(A,B)}$  are presented in Fig. 4.3b. While A minima remain on disconnected isosurfaces,  $V^{(B)}(\mathbf{r})$  forms an interconnected network that rules out the presence of muon bound states in positions B. Hence, interstitials of type A represent the only possible muon site in the FeTe crystal.

Note that the electrostatic potential has an anharmonic component along the c direction. Therefore, the equilibrium position of the muons may not correspond to the potential minimum. Indeed, considering the anharmonicity, we find that the correct value for the site A is

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(1/4, 1/4, 0.27), as obtained from the maximum probability point of the ground-state wave function. If we neglect the Fermi contact contribution [115], by considering the ordered configuration of Fe magnetic moments (each carrying 2.54  $\mu_{\rm B}$ , as from neutron powder diffraction on Fe<sub>1+y</sub>Te polycrystalline samples) [133], the dipolar contribution  $\vec{B}_{\rm dip}$  is the only non-vanishing term in Eq. 2.17. The expected value of the local field at the muon implantation site is ~ 238 mT. This last result is in good agreement with 197 ± 11 mT, the value obtained from ZF- $\mu$ SR data [126]. The residual discrepancy can be attributed to small inaccuracies in the determination of the muon position or to a possible contribution arising from the Fermi-contact term, that was neglected until now.

#### 4.4. LaCoPO

The interest for LaCoPO, a Ferromagnetic (FM) metallic compound isostructural to LaFeAsO, stems from mainly two issues, both connected to the superconducting phenomenon. One is related to the raise and subsequent suppression of superconductivity when Co is progressively substituted to Fe and to the influence of the different magnetic order of the Co parent compound [134, 135]. A second aspect is the role of rare earth atoms and their non trivial effect on both the magnetic and the superconducting properties [117]. These two points are probably linked and relevant insights can be obtained with the P/As isovalent substitution for the pnictide element which is known to introduce a strong chemical pressure pushing the R ions much closer to the itinerant layers. Incidentally we also mention that the efficiency of chemical substitutions of the TM element in providing chemical doping has been largely debated in literature [136–139].

In order to evidence how crucial is the role of the chemical pressure on the magnetic properties of LaCoPO, muon spin spectroscopy and magnetometry measurements under pressure were performed. A few results summarising the magnetic properties as a function of pressure are shown in Fig. 4.4. The full discussion of the experimental data can be found in Ref. [101]. As it is evident from the insets of Fig. 4.4, LaCoPO is a ferromagnet with a magnetic moment arising from the



Figure 4.4.: Experimental results obtained with ZF- $\mu$ SR and magnetometry measurements. In the main panel, the local field at the muon site as a function of the applied pressure is shown. In the upper inset, the magnetization as a function of the applied field at T = 5 K for various applied pressures is reported (the linear paramagnetic term due to the  $Pr^{3+}$  ions was subtracted). It is observed that all the curves collapse on the same trend. In the lower inset, the Curie temperatures for various applied pressures are presented. For further details on the data analysis see Ref. [101].

Co d orbitals of  $m_{\rm Co} \sim 0.3 \mu_{\rm B}$  and a Curie temperature  $T_{\rm C}$  varying between 33 K and 39 K as a function of the applied pressure.

We now focus only on the sudden jump of the local field at the muon site which is detected in  $\mu$ SR measurements for  $P \sim 7$  kbar. As it is evident from the upper inset of Fig. 4.4, magnetization measurements show that pressures up to 10 kbar do not change the size of  $m_{\rm Co}$ significantly. This is a clear indication that the jump in the local field at the muon site must be associated with a variation of the coupling parameters which govern the interaction between the muon and the Co moment. Moreover, the sharp jump is not reflected in the pressure dependence of  $T_{\rm C}$  (lower inset of Fig. 4.4) that steadily increases in a linear fashion across the whole experimental pressure range.

As discussed in section 2.5, in a ferromagnet the local field at the muon site may be due to three main contributions: the field of the distant point dipoles, the demagnetizing field and the transferred or contact hyperfine field. In order to understand the origin of the drastic reduction observed for  $B_{\mu}$  we have investigated the behaviour of the quantities related to the contributions entering Eq. 2.17. The precession frequency of the muon spin around the local field depend on the value of the Co ordered magnetic moment,  $m_{\rm Co}$ , on the structural and magnetic order transitions and on the electronic spin polarization at the muon site. All these factors may vary as a function of pressure.

To examine whether structural or magnetic phase transitions could be responsible for the sudden jump of the local field at the muon site, we studied the ground state properties of LaCoPO with DFT. Energy-volume curves were obtained from the PW-based calculations by constant volume energy minimisation. The optimised unit cell volume at ambient pressure for LaCoPO is 133.21 Å<sup>3</sup> with lattice parameters a = 3.966 Å and c = 8.468 Å. In accordance with previous findings [140], the DFT calculations reproduce the experimental structural parameters with errors ~ 1%.

No anomalies in the energy-volume curves are observed within the explored pressure range. At the same time, the FM-ordered configuration is found to be the ground state for pressure values up to 100 kbar in agreement with experimental results [140]. The results then suggest that both the crystal structure and the FM ground state are stable against the increase of pressure in LaCoPO at least in the investigated pressure range.

The value of the magnetic moment from our calculation,  $m_{\rm Co} = 0.57 \ \mu_{\rm B}$ , is in agreement with previous DFT reports [140]. This value is slightly higher than the experimental estimate  $m_{\rm Co} \simeq 0.3 \ \mu_{\rm B}$ . A disagreement of this entity is not uncommon for DFT but, whereas the precise absolute value may not be very accurate, its relative pressure variation may still be significant. We find that the value of  $m_{\rm Co}$ is substantially unchanged for P < 40 kbar while, for higher pressures, the magnetic moment on Co atoms linearly decreases reaching  $0.55 \ \mu_{\rm B}$  for P = 100 kbar. Therefore, these results do not explain the experimental observations.

In analogy with the case of LaFeAsO, we studied the muon localisation by analysing the minima of the electrostatic potential of the bulk material. Three inequivalent minima are computed for LaCoPO. Minimum A (B) is located within the LaO (CoP) tri-layers while minimum C is aligned with O and Co in between the different tri-layers, as shown in Fig. 4.5b. The barrier between minima C and B is found to be too small to bind the muon. Therefore we identify two *possible muon sites* in this material.

Remarkably, we note that the electrostatic interaction favours site A unlike what is found in RECoAsO and REFeAsO where the interstitial site close to the transition metal plane is favoured [121, 141]. More detailed information about the crystallographic positions of the two possible muon sites and their evolution upon increasing pressure is reported in Tab. 4.3 and in Fig. 4.5. The local magnetic fields at the possible muon sites  $\mathbf{B}_{dip}$  arising from the dipolar contribution of  $m_{\rm Co} = 0.3 \ \mu_{\rm B}$  magnetic moments were also computed and reported in Tab. 4.3 (assuming an undistorted lattice).

The electrostatic potential of the unperturbed material is shown in Fig. 4.5 for P=0 and P=30 kbar. As a function of pressure, the potential is only slightly modified. Minima B and C, in particular, increase their energy with respect to site A while the eigenstates' energies of both sites (obtained from the solution of Schrödinger equation for the muon in the potential  $V_{\rm r}$  from Eq. 3.55) do not change significantly. This allows us to conclude that those sites remain practically unchanged upon increasing pressure. In conclusion, no evidence for sudden changes of interstitial site may be derived from DFT calculations. From the experimental side, no sign of occupancy of different sites is present in all measurements. No sign of structural transitions upon increasing pressure were evidenced by DFT computations, therefore, a complete redistribution of the site occupation between the two inequivalent sites A and B is highly unlikely.



Figure 4.5.: Isosurfaces of the electrostatic potential of LaCoPO for ambient pressure (upper) and P = 30 kbar (lower). For each pressure, the energies corresponding to the three eigenvalues i=1,2,3 having probability maximum in minima A, B, and C respectively are shown, i.e.,  $V(\mathbf{r}) = E_0$ for a) and d);  $V(\mathbf{r}) = E_1$  for b) and e);  $V(\mathbf{r}) = E_2$  for c) and f). [Plotted with VESTA, Ref. [125], reprinted with permission from Ref. [101]]

-	Wyckoli position	x (a), $y$ (a), $z$ (c)	$B_{\mathrm{dip}}^{\mathrm{recom}}$ (G)	$B_{dip}^{r}$ (G)	V <sub>0</sub> <sup>°</sup> (ev)	$E_i$ (eV)
	Ambient	pressure ( $\Delta_{AB} = \Delta_B$	c = 1.42  eV, 1	$\Delta_{ m AC} = 1.06~{ m eV}$	(,	
A	2c	1/4 $1/4$ $0.875$	330	170	0	0.45
В	2c	$^{1/4}$ $^{1/4}$ 0.42	1100	550	0.27	0.63
C)	4f	3/4 $1/4$ $0.30$	I	I	0.56	1.13
	P = 30	0 kbar ( $\Delta_{AB} = \Delta_{BC}$ =	= 1.36 eV, $\Delta_{\rm A}$	$_{\rm C} = 1.08 {\rm eV})$		
A	2c	1/4 $1/4$ $0.875$	330	170	0	0.45
В	2c	1/4 $1/4$ $0.42$	1100	550	0.37	0.73
<i>C</i> )	4f	$^{3/4}$ $^{1/4}$ 0.30	I	ı	0.62	1.22

Table 4.	<b>3.:</b> Crystallographic positions of the <i>possible muon sites</i> A, B and of the minimum C (reported for the sake of completeness) at two different values of pressure. The absolute values of the local magnetic field at A, B and C arising only from the $\mathbf{B}_{dip}$ contribution in Eq. 2.17 are reported for two different FM configurations of $m_{Co}$ . The value of $B_L$ is 170 G. The values of the minima of
	potential energy for the three sites are denoted by $V_0^{(i)}$ while $E_i$ are the eigenvalues corresponding to the eigenstates of a muon with probability maximum in the three potential dip. The values for
	the energy barriers between different sites are denoted as $\Delta_{i,i'}$ . All the energy values $(V_0^{(i)}, E_i)$
	and $\Delta_{i,i'}$ ) are conventionally referred to $V_0^{(A)}$ .

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However, all of the above considerations do not take into account the perturbation effect that the muon induces on its neighbourhood. We studied the effect of the muon on the chemical bonds of the neighbouring atoms. In considering the electrostatic potential we are implicitly assuming that the dielectric screening is so efficient that the positive muon does not cause a significant lattice distortion. However, here we are dealing with a material that is a poor metal, and so it is important to get an estimate of the lattice distortion effect. Since we need to get just an estimate, this time we ignore the effect of muon's GSE. We model the isolated impurity within the supercell approach discussed in Sec. 3.4 by building a 64 atoms supercell from our bulk structure calculations. For the hydrogen impurity we chose possible muon site A as the initial interstitial position. The final optimised position for the impurity provides the *candidate muon site* and represents the refined position for the previously determined *possible muon site*. We found that the refined muon position is in agreement with the one obtained by analysing the electrostatic potential minima. Fully relaxed structures at ambient pressure, at P = 15 kbar and at P = 30 kbar show that both the muon position inside the cell and the distance between muon and P ions varies by less than 0.04 Å. The phosphorus ion close to the muon is pushed closer to the Co plane by  $\sim 0.06$  Å and its four neighbouring Co atoms increase their magnetic moment to 0.6  $\mu_{\rm B}$ . However, once more, no appreciable modification of the crystal structure and of the magnetic properties of the whole system (crystal and muon) which could in principle justify the drop of the internal field observed around  $P \sim 7$  kbar could be computed as a function of pressure. Even the increase of the nearest neighbours magnetic moments  $\mu_{\rm Co}$  has little effect since  $B_{\mu}$  in a ferromagnet is slowly converging and local moments count less than in an antiferromagnet.

To the aim of studying possible changes of the spin density at the muon site we computed band structures to evaluate the conduction electron contribution to the hyperfine field as a function of pressure. At  $P \sim 38$  kbar, an unoccupied electron band shifts across the Fermi energy (as shown in Fig. 4.6) creating a large cylindrical Fermi surface owing to the flat dispersionless trend along  $\Gamma$ -Z. The modification of the band structure as a result of applied pressure strongly suggests that the variation of the local field with pressure is due to



Figure 4.6.: Upper panels: energy bands of LaCoPO at ambient and at 100 kbar ( $E_F = 0$ ). Black(red) colour refer to majority (minority) spin bands. Lower panel: difference between the energy at  $\Gamma$  and the Fermi energy  $E_F$  for the band crossing the Fermi energy. Inset: energy band dispersion for selected pressure values.

a change in the hyperfine contact field  $\mathbf{B}_{\text{cont}}(\mathbf{r}_{\mu})$  which stems from the Fermi surface rearrangement. It should also be remarked that, according to Tab. 4.3, for the in-plane orientation of the spins one has  $\mathbf{B}_{\text{dip}}(\mathbf{r}_{\mu}(A)) \simeq -\mathbf{B}_{L}$  and the muon in site A is therefore mostly sensitive to  $\mathbf{B}_{\text{cont}}(\mathbf{r}_{\mu})$ .

#### 4.5. Discussion

In this chapter we have shown a simple method for the identification of muon sites, namely the inspection of the minima of the unperturbed electrostatic potential. This approach is found to be surprisingly accurate for IPSCs as demonstrated by dipolar field calculations and the supercell approach used for LaCoPO. Moreover, from the solution of the Schrödinger equation for the muon in the electrostatic potential, the correct number of muon sites is obtained for LaFeAsO. However, the same does not hold true for LaCoPO: we found experimental evidence of just one populated muon site, but, according to our simulation, there should be two muon sites, in close analogy with the case of LaFeAsO. In principle, the difference could arise from a different population of the muon sites in the two compounds and, since muon site population depends on kinetic considerations that are outside the scope of our models, we have no way to support this hypothesis.

In conclusion, we remark that the successful outcomes obtained for IPSCs are rather fortuitous since they are based on crude and not well justified assumptions. On one hand, by solving the Schrödinger equation for the muon in the electrostatic potential we assume that ions are infinite mass particles and electrons are frozen in their unperturbed configuration. While the former approximation can be reasonable the latter is obviously never observed in real materials. On the other hand, it is well known that the electron density at the interstitial site is significantly modified by the charged impurity (among the many, see for example Ref. [142–144]). In view of these considerations, the somehow unexpected high accuracy of the "electrostatic potential" approach still remains a puzzle.

It's worth noting that an accurate analysis of the unperturbed electronic structure of the compound under study can provide valuable additional information to the experimenter. LaCoPO represent one of these cases since the details of the electronic structure turned out to be responsible for the change in the coupling parameters between the muon spin and conduction electrons.

# 5

### Fluorides a more rigorous method

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In the previous section we discussed a simple approach for the identification of muon sites. Even though that procedure was found to be sufficiently accurate for some IPSC compounds, here we show that in wide band gap fluorides the same approach badly fails. This is possibly due to the absence of conduction electron screening that contribute to the inhibition of hydrogen bond formation between the electron cloud surrounding the  $\mu$  and other valence electrons. Indeed bond formation is more frequent in insulators, where the positive muon interact with the most electronegative atomic species present in the host material. For this reason, the final interstitial location can be different from the position of the minimum of the electrostatic potential. One is therefore forced to include the muon inside the DFT description of the material under investigation.

Wide band gap fluorides constitute an ideal class of materials to study muon site localization in insulators. This is because the dipolar interaction between the muon spin and the F nuclear moment leads to a fingerprint in the asymmetry signal which usually uniquely identifies the muon lattice site(s). This is the case, for example, for the results by Brewer and co-workers published in Ref. [41]. Using the approach



Figure 5.1.: The asymmetry signal in various fluorides compounds. The solid lines are fit to the axial F- $\mu$ -F depolarisation function of Eq. 2.37. Reprinted with permission from Ref. [41]. Copyright (1986) by the American Physical Society.

discussed in Sec. 2.6 for an axially symmetric  $F-\mu$ -F bond, they could correctly reproduce the experimental signal observed in several fluorides compounds. Their experimental data are shown, together with the expected depolarisation signal, in Fig. 5.1. The use of the simplified model containing only the F nuclei is justified by the rapid decay characteristic of the dipolar interaction and by the peculiar site occupied by the muon in these materials. Indeed, as discussed later, the muon distorts its local neighbourhood by forming a hydrogen bond with two F nuclei which are attracted by the charged impurity. The analysis based on the quantum mechanical description of the dipolar interaction (see Sec. 2.6) allowed to identify the muon site and the displacements introduced by the muon on the two F nuclei forming the bond.

The results obtained by Brewer and co-workers allow an immediate and reliable comparison of the simulation data with the experiment. Moreover, non magnetic fluorides are accurately described by the DFT



Figure 5.2.: Electrostatic potential for a muon in LiF. The isosurface for  $V(\mathbf{r}) = E_0 + V_0$  ( $V_0$  being the absolute minimum) is shown in c). The points A, B and C are the three *candidate muon sites* found with the structural relaxation. [Plotted with XCRYSDEN, Ref. [120], reprinted with permission from Ref. [102]]

approach and several materials belonging to this class have been thoroughly characterised experimentally at the end of the last century.

Before continuing, we mention that when publishing this work we had not enough computing power to carefully study the muon GSE in the DAA approximation discussed in Sec. 3.4.3. Hence the conclusions of this chapter are still partially based on the comparison with the experiment.

#### 5.1. The supercell approach

As already discussed in Sec. 3.4.2, in this chapter the muon is represented by the hydrogen pseudo potential in the PAW formalism [87]. A supercell is built up reproducing several bulk structure unit cells in order to limit the interactions between the impurity and its periodic replica. In Sec. 3.4 we mentioned that the accuracy of supercell approach is limited by the size of the simulation. For neutral light impurities  $2 \times 2 \times 2$  supercells are generally large enough. However, since we deal with charged impurities (muon interstitial), we made a convergence test using the SIESTA code [145]. Comparing the structure and the total energy of  $2 \times 2 \times 2$  and  $3 \times 3 \times 3$  supercells we estimate the numerical error on the energy and on the optimised distances to be  $\sim 5~{\rm meV}$  and  $\sim 0.02$  Å respectively.

#### 5.2. LiF

LiF has the NaCl crystal structure, with a four formula unit conventional cubic cell, containing eight cubic cages with vertexes at four Li and four F atoms. As shown in Fig. 5.2 the minima of the electrostatic potential in LiF are located approximately at the centre of each cage. There are two symmetry inequivalent minima inside each cage. Their position roughly correspond to the position of the candidate muon sites B and C discussed later. In Fig. 5.2(b) the minimum close to B is at the very centre of the cage and is surrounded by four equivalent minima (close to label C) each displaced along the direction towards a neighbouring F atom. The isosurface of these minima becomes connected for  $E \ge V_0 + 75$  meV ( $V_0$  absolute minimum of  $V(\mathbf{r})$ ), forming a tetrahedron shaped structure. All of these positions are incompatible with the experimental muon site which is known from literature [41] and was obtained with the strategy presented in Sec. 2.6 and 2.7.

From the solution of the Schrödinger equation for the muon in the bulk electrostatic potential, the GSE  $E_0 = 500$  meV is obtained for LiF. Fig. 5.2(c) shows that the isosurface  $V(\mathbf{r}) = V_0 + E_0$  forms a connected network across the crystal suggesting a delocalized muon state even at T=0 K. The experimental position, labelled A in Fig. 5.2(b), is at the boundary of the isosurface. As it is evident from Fig. 5.2(b), from the analysis of the electrostatic potential one would mistakenly predict the existence of muon sites close to the centre of the cubic cage. Moreover, the known experimental position is not even in a (relative) minimum of the electrostatic potential and, from the analysis of the GSE, a delocalized muon wavefuction is obtained, in complete disagreement with the experimental evidence of a static muon site.

It's only by taking into account the  $\mu$ -sample interaction within the DFT simulation that a correct prediction is obtained. Indeed by allowing nuclei to relax in the minimum energy configuration we obtain large nuclear displacements from the periodic bulk for all of the sites considered in this chapter. Starting from random interstitial sites

		LiF		YF <sub>3</sub>		
	A	B	C	A	В	C
F- $\mu$ distance [Å]	1.15	1.56	1.01	1.144	1.134	1.144
$\varepsilon_i - \varepsilon_A [\text{eV}]$	0	0.89	0.54	0	-0.64	0.36

**Table 5.1.:** Results for the structural optimisation with  $\mu$  in the interstitial positions A, B and C (see text and Fig. 5.4). Site A is always the experimental/predicted site. F- $\mu$  is the distance between the  $\mu^+$  and its nearest neighbour F atom(s),  $\varepsilon_i - \varepsilon_A$  is the difference between DFT ground state energies of the relaxed structures.

three *candidate muon sites* were obtained and are labelled A, B and C in Fig. 5.2. In particular, a strong modification of the crystal structure is found when the muon is added to the interstitial position A. While F nuclei are attracted by the charged impurity, Li atoms are repelled. The distance between the muon and its neighbouring F nuclei is 1.15 Å in excellent agreement with the experimental data [41]. Also next neighbouring F atoms are affected by the muon and are subject to a displacement of 0.04 Å. The relaxed atomic positions correctly describe the formation of a F- $\mu$  bonding. The relaxed structure for the *candidate muon site* B shows a similar behaviour: the distance between the muon and its neighbouring F atoms reduces from 1.76 Å to 1.56 Å. We note anyway, that the F- $\mu$  distance in this case is too large to reproduce the experimental fast decay of the  $\mu$ SR signal. Candidate muon site C constitutes a local minimum for the structural relaxation and the hydrogenoid impurity remains trapped there. However, given its small binding energy, it is reasonably expected that an analysis of the GSE of the muon would make the site unstable. The muon would therefore get out of the local minimum and reach site A. This behaviour is moreover energetically favoured if we look at the total energies for the  $\mu$ -sample system given by our DFT simulations. The total energy for site A, B and C are reported in Tab. 5.1. The inclusion of structural relaxation effects allows to recover the agreement with the experimental findings: site A has a total energy which is 0.89 eV lower with respect to site B and is thus confirmed to be the muon stopping site in LiF. The formation of the  $F-\mu$ -F complex has



Figure 5.3.: Expected muon asymmetry spectra for the three *candidate muon sites* and relaxed atomic coordinates in powdered LiF. Sites are labelled according to Fig. 5.2. Dipolar calculations include all the neighbouring atoms giving rise to couplings larger than one tenth of the maximum coupling constant (see Eq. 2.34, the number of F atoms considered depends on the muon interstitial site). Position A gives the best agreement with the measured data of Ref. [41].

important consequences on  $\mu$  delocalization in LiF. Indeed the lattice relaxation breaks the lattice periodicity, while the formation of a bond with F enhances the  $\mu$  localisation hindering its diffusion across the material in agreement with the experimental evidence.

The results of our calculations are further confirmed by comparison with experimental data. The expected depolarisations for *candidate muon sites A*, *B* and *C* are shown in Fig. 5.3. As already mentioned in the introduction, the muon polarisation for the three inequivalent sites are very different and this allows us to discard sites *B* and *C*. Only site *A* is compatible with the observed asymmetry spectra, while the other two locations for the muon give significantly worse fits (*C*) and non physical values for the local modification of the bonds length and distances between  $\mu$  and F nuclei (*B*). Fitting the experimental results with  $\mathbf{r}_{\mu-\mathbf{F}}$  as a free parameter in Eq. 2.34, we find that the distorted crystal structure obtained from DFT calculations reproduces



Figure 5.4.: Candidate muon sites in YF<sub>3</sub> (left and center) and LiF (right). The label A identifies the expected site in both compounds. Isosurfaces for  $V(\mathbf{r}) = E_0 + V_0$  are shown in dark yellow for YF<sub>3</sub>. The electrostatic potential sections in YF<sub>3</sub> and LiF allow a direct comparison the GSEs of the muon obtained from the solution of the Schrödinger equation in the electrostatic potential of the two compounds. Unrelaxed lattice structures are shown for the sake of clarity. [Plotted with VESTA, Ref. [125], reprinted with permission from Ref. [102]]

the experimental F-F distance [41] with  $\sim 1\%$  precision.

#### 5.3. YF<sub>3</sub>

DFT calculations in LiF find the known muon site, the same that was identified in the original experimental work. The  $YF_3$  case is more complicated and DFT provides the insight.

The Coulomb potential for the unperturbed bulk crystal shows only one minimum corresponding to the *possible muon site* with fractional coordinates (1/2, 1/2, 0) (with reference to the crystalline structure shown in Fig. 5.4) that yields a depolarisation which cannot capture the experimental asymmetry time spectra. Moreover the experimental depolarisation signal is only roughly captured by the *axial*  $F-\mu$ -F model (Eq. 2.37) as shown in Fig. 5.5.<sup>†</sup>

 $<sup>^{\</sup>dagger}$ It is noted that authors of Ref. [42] show a better fit to Eq. 2.37 of the data

#### 5. Fluorides: a more rigorous method

Therefore in  $YF_3$  the uncertainty in the muon site assignment can be removed only with the help of DFT calculations.

Following the same procedure detailed before, we relax the structure with the muon in asymmetric interstitial positions. Six candidate muon sites were found after structural relaxations starting from random interstitial positions. The three most energetically favourable inequivalent sites (shown in Fig. 5.4) are all close to the minimum of the unperturbed electrostatic potential. They are all characterised by a slightly distorted F- $\mu$ -F bond with the muon shifted perpendicular to the F-F axis forming, for sites A and C, an angle of ~ 144° between the two bonds. For site B the angle changes to ~ 160° (in Fig. 5.4 the unrelaxed structures are shown for the sake of clarity). The three remaining sites will not be considered since they have higher ground state energies and produce depolarisation functions that are incompatible with the experimental results.

The depolarisations arising from the relaxed structures of sites A, B and C are compared in Fig. 5.6. The relaxed energies with the relevant parameters obtained from the DFT structural relaxation, are reported in Tab. 5.1.

In order to identify the muon site, all the above results must be considered. Indeed, after the structural relaxation, site B, which has the lowest energy, does not provide a correct description of the depolarisation function (Fig. 5.7). Instead a good description of the experimental data is obtained when considering the expected depolarisation from site A, as shown in Fig. 5.5. This led us to conclude that the F- $\mu$ -F complex in site A is the maximally populated muon site in YF<sub>3</sub>. A complete understanding of the physical motivation underlying the preferential occupation of site A is still missing. It is reasonable to consider either an inaccuracy due to the limited size of the supercell or the possible role of reaction kinetics, which are neglected in the

with respect to the one in Fig. 5.5. The difference originates from the assumption of distinct relaxation rates for the constant and the oscillating parts of Eq. 2.37. In this work we compute the expected asymmetry spectra with more atoms then just the first neighbouring F nuclei and we also add F-F interactions. As a consequence, the nuclear component of the relaxation rate (for the relevant time interval of the asymmetry spectra) is included in the  $G_{F\mu F}$  term of Eq. 5.1 and only one phenomenological relaxation rate, of electronic origin, is introduced in Eq. 5.1.



Figure 5.5.: Fit of YF<sub>3</sub> data from Ref. [42] with the conventional F- $\mu$ -F model (Eq. 2.37) and with the depolarisation calculated for the DFT predicted site in the fully relaxed structure. The parameters of the fit are detailed in the text and reported in Tab. 5.2.

identification of the stable sites with the structural relaxation. Indeed non-adiabatic and/or kinetic effects may be responsible for the stability and the selection of different interstitial sites.

The experimental data were fitted according to the equation:

$$A(t) = A_0 \left[ p_1 G_{F\mu F}(t, \delta \omega) \exp\left(-(\lambda_{F\mu F} t)^{\beta}\right) + (1 - p_1) \exp\left(-(\sigma t)^2\right) \right] + A_{calbg}$$

$$(5.1)$$

where  $A_0$  is the total asymmetry arising from the sample (and the sample holder),  $p_1$  measures the fraction of muons reaching the F- $\mu$ -F site,  $1 - p_1$  and  $\sigma$  account for a phenomenological depolarisation present in many  $\mu$ SR measurements of fluorides (see for example Fig. 5.1 and Ref. [41]) and  $A_{calbg}$  is added in order to compensate for the background and for the unknown calibration of the detectors.  $G_{F\mu F}$  is obtained by solving Eq. 2.34 with the lattice structure obtained from DFT calculations and  $\delta\omega$  is a parameter that accounts for small discrepancies between F- $\mu$  calculated and experimental distances.

The parameters obtained from the best fits shown in Figs. 5.5 and 5.7 are reported in Tab. 5.2. We finally add that site C is also com-



Figure 5.6.: Expected asymmetry spectra for optimised muon sites and atomic coordinates in powdered  $YF_3$ . Sites are labelled as in Fig. 5.4. Calculations include all the neighbouring atoms giving rise to couplings higher than one tenth of the maximum coupling constant (see Eq. 2.34). Position A gives the best agreement with the measured data.

patible with the experimental data and therefore we cannot rule out the possibility of a partial occupation of this site.

#### 5.4. Discussion

In this chapter we showed that a supercell approach for the analysis of the effect of the  $\mu$  impurity allows to get the refined atomic structure and *candidate muon sites*. The procedure was tested in LiF, where we showed that the bulk electrostatic potential fails to correctly predict the actual  $\mu^+$  site. Instead, upon structural refinement we were able to reproduce the formation of the F- $\mu$ -F complex and its structural details (F- $\mu^+$  distance). These results are also confirmed by a similar computational work on this and other fluorides compounds [18]. We then extended our investigation on YF<sub>3</sub> where the presence of several candidate interstitial site makes impossible the identification of the  $\mu$ position from experimental knowledge alone. Comparing the experimental data with the refined structure obtained by DFT investigation

	Conv. $F-\mu$ -F	Site $A$	Site $B$
$A_0$	0.202(1)	0.184(1)	0.188(1)
$p_1$	0.77(1)	0.76(1)	0.75(1)
$A_{calbg}$	-0.028(1)	-0.012(1)	-0.014(1)
$\lambda_{F\mu F}$	$0.18(1) \ \mu s^{-1}$	0.19(1)	0.15(1)
$\beta$	1.27(6)	1.45(1)	1.23(1)
$r_{F-\mu}$	$1.23(1) { m ~\AA}$	$1.17(1) { m \ \AA}$	1.22(1) Å
$\sigma$	$0.73(1) \ \mu s^{-1}$	$0.97(1) \ \mu s^{-1}$	$1.00(2) \ \mu s^{-1}$
$\chi^2_r$	4.7	2.3	4.1

**Table 5.2.:** Parameters for Eq. 5.1 obtained from the best-fit to the data of Fig. 5.5. In the first column the results obtained with  $G_{F\mu F}$  defined in Eq. 2.37 (already obtained by the authors of Ref. [42]) are reported. In the second and third columns  $G_{F\mu F}$  is calculated from DFT results (see text).  $r_{F-\mu}$  is the distance between the muon and the first neighbouring F atom(s) for a given  $\mu$  site. Small discrepancies between the experimental and calculated  $r_{F-\mu}$  (that may possibly arise from the non-vanishing GSE neglected in Eq. 2.34) are accounted by the  $\delta \omega$  parameter (see text). The final F- $\mu$  distance is obtained by conveniently scaling all the distances between the  $\mu$  and the atoms included in the sum of Eq. 2.34. All the scaling factors are smaller than 5%.

we were able to predict the correct location and shape for the F- $\mu$ -F complex in YF<sub>3</sub>. An open problem of the above implementation is the lack of a systematic investigation of the  $\mu$  GSE when chemical bonds with the valence electrons of the host system are formed. Indeed, during the relaxation process many local minima in the total energy hyper-surface are encountered both in YF<sub>3</sub> and LiF (see for example Fig. 5.2) and it is reasonably expected that not all of them constitute trapping muon sites. In this preliminary work we relied on the best fit of the experimental asymmetry to identify the site, since DFT stand alone criteria were still not sufficient. However, an accurate determination of the ground state energy of the muon can, in principle, alleviate the problem and provide a way to distinguish between trapping and non trapping muon sites from first principles.



Figure 5.7.: Fit of YF<sub>3</sub> data from Ref. [42] with the conventional F- $\mu$ -F model (Eq. 2.37) and with the depolarisation calculated from DFT results obtained for site A and B.

This is considered in the next section where the DFT approach is extended with the DAA for the analysis of muon sites' stability.

# 6

## MnSi and Cu

#### Contents

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In this chapter we complete the *ab initio* approach for the identification of muon sites by taking into account the GSE of the muon within the DFT formalism. Indeed, in all the cases already presented, the muon's GSE was always calculated by considering the unperturbed electrostatic potential of the material under investigation. Instead, in this and in the following chapter we use a supercell approach for the simulation of the impurity and the DAA to evaluate the GSE of the muon. MnSi and Cu are two interesting compounds for testing this approach. The former material was thoroughly studied with Knight shift experiments that allowed to identify the muon site with high accuracy [44]. In FCC copper, the muon diffuses through the material with an activation energy of about 80 meV [146]. This makes the material an ideal test case to benchmark the accuracy of the DAA approach.

#### 6.1. MnSi

MnSi represents an interesting realisation of a magnetic system with lack of inversion symmetry. This last property guaranties the presence of a spin-orbit Dzyaloshinsky-Moriya interaction which has attracted



Figure 6.1.: a) Angular dependence of the four frequencies originating from the dipolar contribution to the local field at the muon site. b) The Fourier transform of the asymmetry for one of the point in a). In both images, the lines are best fit to the model reported in Ref. [44].

a lot of interest in the fields of multiferroic interactions and non-trivial magnetic structures. Indeed, below 29.5 K, the material develops a homochiral spin spiral order with a wavelenght of 18 nm. This magnetic ground state is found to be extremely sensitive to applied fields and pressure [147, 148]. Among the many characteristics of the magnetic phase of MnSi, the emergence of a skyrmion lattice has been identified near the magnetic ordering temperature [149]. Skyrmions are topologically protected field configurations that are stabilised by an external magnetic field. The skyrmionic phase con be naïvely regarded as the magnetic equivalent of the flux lattice in superconductors. As for the flux lattice, the skyrmionic lattice can be tuned by varying the applied magnetic field. However, it has been shown that individual skyrmions can be manipulated with spin-polarised currents from a scanning tunnelling microscope [150]. This makes the materials showing a skyrmionic phase important candidates for spintronic applications devoted to information-storage.

During the characterisation of MnSi with  $\mu$ SR experiments, a controversy regarding the muon stopping site and the existence of magnetic polarons was raised [151]. To lift the controversy, the muon site was independently studied with transverse field experiments and with *ab initio* methods [44]. Here we will only describe the latter method



Figure 6.2.: The possible muon site as identified from the minima of the electrostatic potential. The red isosurfaces of the electrostatic potential identify four symmetry equivalent positions for the muon site. The isosurface energy is set to  $V = E_0/2 + V_0$  with  $V_0$  absolute minimum of the electrostatic potential and  $E_0$  obtained from the solution of the Schrödinger equation for the muon in the potential of Eq. 3.55. [Plotted with XCRYSDEN, Ref. [120]]

and the results obtained. However, for the sake of completeness, experimental data showing the angular dependence of the dipolar field that allowed to identify the muon site in the 4a Wyckoff position with fractional coordinates (0.532, 0.532, 0.532) are reported in Fig. 6.1.

To verify if the simple method used for IPSCs yields the correct result also for MnSi, we analysed the minima of the electrostatic potential obtained from the ground state electronic density of the unperturbed material. There are four equivalent minima in the unit cell, as shown in Fig. 6.2, which correspond to the 4a Wyckoff position with fractional coordinates (0.523, 0.523, 0.523). Notably, this coarse estimation nicely agrees with the experimentally evaluated embedding site.

We then performed full structural relaxation for the muon in the material with the supercell DFT approach and stable muon sites were then determined with the DAA approximation.

Candidate sites	Position	$\varepsilon^{(i)} - \varepsilon^{(A)} $ (eV)	$E_0 (eV)$
А	(0.542,  0.542,  0.542)	0	0.6
В	(0.607, 0.477, 0.220)	0.86	-
$\mathbf{C}$	$(0.329 \ 0.329, \ 0.329)$	1.12	-

**Table 6.1.:** Candidate muon sites obtained with structural relaxations in a 64 atom supercell.  $\varepsilon^{(i)}$  are the total energies of the relaxed structures,  $E_0$  is the ground state energy of the muon (see Eq. 3.62). The Mn and Si positions are assumed at (0.1381, 0.1381, 0.1381) and (0.8462, 0.8462, 0.8462) respectively in the cubic unit cell. The experimentally identified muon site is in fractional coordinates (0.532, 0.532), 0.532). The mismatch between the two results is less than  $5 \times 10^{-2}$  Å.

The *candidate muon sites* were identified by performing structural relaxations on a 64 atoms MnSi supercell plus the muon impurity. Four starting points were selected to sample the interstitial space in the unit cell. Their positions together with the symmetry replica are shown in Fig. 6.3. We find three *candidate muon sites* which are reported in Table 6.1.

To verify if the *candidate muon sites* are binding sites we used the DAA approximation introduced in Sec. 3.4.3. A trade off between speed and accuracy is needed to efficiently perform the DBO simulations and extract the potential to solve the Schrödinger equation of the muon. For this reason, we report some details on the parameters used in first principles calculations for MnSi and discuss briefly the accuracy that is obtained. Indeed, for sake of speed, in the DBO simulations we slightly reduced the accuracy of the calculation by lowering to 50 and 250 Ry the kinetic energy and charge expansions and sampling the Brillouin zone using only the Baldereschi point [84]. This guaranties a convergence of the total energy of  $\sim 0.5 \text{ meV/atom}$ . While the total energy convergence may seem poor, we checked the accuracy of the differences between the relaxed and the displaced position energies by performing calculations with higher cutoff and a  $2 \times 2 \times 2$ MP sampling grid for reciprocal space. These tests were done for the first 20 points of the DBO calculation and for other random points.



Figure 6.3.: In a) the interstitial points (together with the symmetry replica) used as starting positions for the identification of the *candidate muon sites*. In b) the stable site found in MnSi (some equivalent sites outside the unit cell are shown to help the comparison with Fig 6.4b and 6.4c).

The worst case discrepancy was 4 meV with an average value of 1.5 meV. The cutoff for the potential exploration in the DBO calculation was set to  $E_C = 1.2$  eV and the spacing  $\delta = 0.15875$  Å for the cubic grid was used. The maximum step length between consecutive moves was set to  $3\sqrt{3}\delta$ .

For sites B and C the barrier towards site A is slightly less than 0.25 eV. Indeed during the exploration process the barrier between candidate sites B (C) and A is reached and the algorithm finally reaches site A. In both cases it is found that the barrier separating B and C from site A is too small to bind the muon.

On site A the potential is interpolated over a 827 points cloud and the Schrödinger equation is solved in a 2.54 Å edge cubic box with both Dirichlet and PBC. From the solution of the Schrödinger equation we obtain a ground state energy  $E_0 = 0.6$  eV. This is small enough to guarantee the stability of the muon site A since the potential is still well confining even at 1 eV (see also Fig. 6.4).

From these results we can conclude that only one muon site is present in MnSi. This is in agreement with the experimental results and the position obtained with the supercell approach differs from the experimental results by less than 0.05 Å [44].



Figure 6.4.: The main panel a) shows the potential felt by the muon in the DAA approximation and the points cloud used for the interpolation. The isosurface is at 0.8 eV. In b) and c) the small dots identify some of the points acquired with the exploration algorithm described in the text starting from sites B and C which are found to be local minima and non-trapping sites. In both cases site A (see Table 6.1) is reached.

#### 6.2. Copper

Face centred cubic copper represents an interesting test case since it is known that the muon diffuses through the material [152]. The muon site and the diffusion mechanism have been thoroughly studied both with experimental and theoretical approaches [146, 153–156]. Camani *et al.* [154] and Hartmann [157] showed that considering the quadrupolar interaction between the copper nuclei and the electric field gradient generated by the muon it is possible to describe the value of the asymmetry depolarization rate  $\sigma$  obtained for the various crystal orientations as a function of the applied field. The study of the field dependence of the depolarization  $\sigma$  in single-crystal compounds allowed to identify the muon site. Indeed they concluded that muons occupy the octahedral interstitial sites in the temperature region be-



Figure 6.5.: Experimental correlation time  $\tau_c$  for various orientations of Cu FCC crystals. The broken lines correspond to a fit of the Arrhenius law, the full curves are fits to the Teichler model (see text). Circles and squares points were acquired in 200 G and 4500 G applied fields respectively. Reprinted with permission from J. Phys. F: Met. Phys. 12 875 (1982) [146]

tween 20 and 80 K and that a 5% dilatation of the copper lattice around the muon was necessary to reproduce the experimental value of  $\sigma$ .

In one of the last experiment performed on highly pure FCC copper samples, the high temperature data were analysed with both a classical thermal activated law, i.e.  $\tau_c^{-1} \propto \exp(-E_A/k_BT)$  ( $E_A$  activation energy to over-jump the barrier) and a phonon assisted quantum diffusion model that takes into account the small polaron theory of Ref. [158, 159] by Teichler. The latter differs from the Arrhenius law by a temperature dependent prefactor [146, 160]. The experimental data together with the two possible fits are shown in Fig. 6.5 and a simplified representation of the two diffusion processes is sketched in


Figure 6.6.: Schematic description of the two possible diffusion mechanisms for the muon in FCC copper.  $E_0$  and  $E_1$  are the energies for a muon in the distorted and in the neighbouring O sites respectively.  $E_{ph}$  is the energy of the phonon contribution that makes  $E_0 + E_{ph} = E_1$  possibly resulting in a quantum tunnelling between the two sites.  $E_A$ is the activation energy for the classical over the barrier hopping.

Fig. 6.6. Both authors of Ref. [146, 160, 161] also proposed that, at high temperature, the activation of an additional diffusion mechanism could justify the presence of some experimental points that completely miss the 90-300 K trend for T > 300 K.

We performed DBO and Nudged Elastic Band (NEB) [162, 163] calculations to extract the activation energies for both the classical and the phonon assisted diffusion mechanisms. The DBO and NEB calculations were performed with cutoffs of 50 Ry and 250 Ry for plane wave expansion and for the charge density respectively and a  $3 \times 3 \times 3$  MP grid was used. A cubic supercell with 32 Cu atoms and the muon was considered. Two candidate position in the octahedral (O) and the tetrahedral (T) cavity sites were identified with the structural relaxations, in agreement with previous results. The nearest neighbours Cu atoms are outward displaced away from the muon in the O site by 2.3%<sup>†</sup>, slightly less than what is obtained from the experiment but in agreement with previous calculations [154, 164].

DBO calculations starting from the T site showed that the barrier towards O sites is just 0.2 eV, definitively to small to bind the muon and indeed, as detailed below, no localised states at the T site were found. In order to construct  $V_{\mu}$  for the O site with the DBO strategy,

<sup>&</sup>lt;sup>†</sup>To check the convergence of this result against the supercell size we performed the same relaxation calculation with a 109 atoms supercell and obtained the same value for the Cu displacement.



Figure 6.7.: In a) four isosurfaces for the interpolated potential felt by the muon in the octahedral site. Notice that at nuclear "phonon-like" energies the potential almost retains its spherical shape. On the other hand, at muon vibration energies, the potential is far from being harmonic. In b) the points acquired during the dense grid DBO exploration. The route towards the neighbouring octahedral site passing through the tetrahedral site is clearly visible. Copper atoms are in blue while all the positions occupied by the muon are in grey. Copper atoms do not appear at all the cell boundaries because of the small distortion introduced by the muon. In c) the probability density for the ground state and the degenerate excited state are depicted with a colour map and the 95% probability densities are shown with red and blue isosurfaces respectively.



Figure 6.8.: The minimum energy path between equivalent octahedral muon sites. The curve is asymmetric due to the distortion introduced by the muon in its starting site.

the same parameters used for MnSi were adopted. The first 800 points acquired during the simulation are shown in Fig. 6.7b.

In this case it was not possible to reach the cutoff energy of 1.2 eV. Indeed, as it is evident from Fig. 6.7b, during the exploration process the DBO algorithm reached the saddle point between the O and the T site, explored the T site and then moved to the equivalent O minimum of the neighbouring cell.

The O site is clearly the global minimum of  $V_{\mu}$  and we can conclude that the muon hops among O sites only [154].

To check if the mechanism responsible for the muon diffusion is the classical over-barrier hopping or a phonon assisted tunnelling the ground state energy of the muon in both the distorted O site and the neighbouring sites must be evaluated.

To this aim we acquired more points above the saddle point between the distorted O sites and one of the nearest neighbouring O site and reconstructed the potential by imposing the 48 point group symmetry operations. From this procedure we obtained an accurate description of the potential up to 1.5 eV. We then solved the Schrödinger equation for the muon with PBC in the potential  $V_{\mu}$  obtained by interpolation of the data points with radial basis functions (with  $r, r^3$  and  $r^2 * \log(r)$ as basis functions) and trilinear interpolation (see Sec. B).<sup>†</sup>

<sup>&</sup>lt;sup>†</sup>PBCs probably represent another relevant approximation since the potential

We find a GSE  $E_0 \sim 0.48$  eV and an excited state at  $E_1 \sim 0.62$  eV (the results from the various interpolation schemes differ by about 10 meV). As shown in Fig. 6.7c the two energies correspond to a muon in the distorted O site and in the neighbouring O sites. No states localised only in the T site were found for energies up to 1 eV.

To understand if the phonon assisted mechanism dominates over the over-barrier hopping a detailed description of the energy barrier is required. To identify the minimum energy path between equivalent O sites we performed NEB calculations. The results are shown in Fig. 6.8. The curve is asymmetric due to the distortion introduced by the muon in the starting O site. The best path towards the neighbouring O site is through the T site. The saddle point between the O and the T site is at  $E_{\rm ST} = 0.56$  eV, while the one between two neighbouring O sites, which represents the classical activation energy  $E_A$ , is at about  $E_{\rm SO}=0.66$  eV above the energy of the starting muon site. The path between O sites passing through a Cu-Cu bond has a much higher saddle point (about 1.6 eV).

The energy difference  $E_{SO} - E_1 = 40$  meV indicates that the phonon assisted quantum tunnelling dominates over the classical hopping at low temperature, i.e. in the 80-300 K range. However, the classical diffusion mechanism should take place at slightly higher temperatures. Indeed, Schilling and co-workers found a better agreement of the experimental data with the phonon assisted small polaron diffusion theory and extracted an activation energy of about 80 meV [146]. The value found with the DAA is about 1.7 times larger, but this is probably an overestimation due to the adiabatic approximation.

### 6.3. Discussion

The DAA approach provides a reliable way to distinguish between trapping and non-trapping muon sites (which are routinely obtained in calculations aiming at identifying muon sites) with a computationally tractable method to introduce the quantum description of the

in the polaron site is replicated in the neighbouring cells. However, the distance between the next-nearest-neighbouring site (about 3.6 Å ) is large enough to guarantee a small dependence of the results on the inaccurate periodic images.

muon. A detailed description of the muon wave function can also produce accurate *ab initio* evaluations of many observables (e.g. contact and transferred hyperfine couplings). While its applicability is limited to the compounds having heavy nuclei, even the mass ratio  $m_{\mu}/m_{\rm C}$ is smaller than 1%. In this context it's also worth citing the work by Takahashi and Takatsuka who considered the accuracy of the BO approximation for the  $pp\mu^-$  molecule (*p* stands for proton) and found a deviation smaller than 5% from the non-BO vibronic energies calculated with semi-classical methods [165]. It should also be noted that for both MnSi and Cu the potential felt by the muon is far from being harmonic nor it's possible to fully describe it with small an-harmonic corrections as evidenced in Fig. 6.4a and Fig. 6.7a. This is the case for almost all the compound that we examined so far.



#### Contents

7.1.	Introduction
7.2.	Electrostatic potential
7.3.	Muon site estimation
7.4.	Ground state energy
7.5.	Discussion

In this section we discuss one of the main advantages that stems from the knowledge of muon sites' interstitial position, namely the possibility of identifying the magnetic moment and, in some cases, also the long-range magnetic order of crystalline solids. Indeed, this was done in T'-La<sub>2</sub>CuO<sub>4</sub>, a parent compound of the high temperature cuprates superconductors characterised by the presence of multiple magnetic transitions as a function of the temperature. Its magnetic characterisation has been conducted, up to now, only with  $\mu$ SR and NMR since neutron scattering measurements are problematic because of the small magnetic moments in the system (which make the magnetic scattering from the sample too weak) and of the presence on inelastic H scattering (which originates from a minority phase of hexagonal H<sub>3</sub>LaO<sub>3</sub>). The accurate prediction of the muon site provided by DFT allowed, together with symmetry constrains, to extract from the  $\mu$ SR measurements the long-range magnetic order of the sample.



Figure 7.1.: The T' and T crystalline structures of La<sub>2</sub>CuO<sub>4</sub>. The La, Cu, and O atoms are represented by the large, medium and small sized balls, respectively. [Plotted with VESTA, Ref. [125]]

## 7.1. Introduction

La<sub>2</sub>CuO<sub>4</sub> can be synthesised in both the T and in the T' lattice structure. The main difference between the two structures is the presence/absence of apical oxygen as shown in Fig. 7.1. T'-La<sub>2</sub>CuO<sub>4</sub> represents the true parent compound of electron doped cuprates. Indeed, starting from La<sub>2</sub>CuO<sub>4</sub>, which is usually grown in the stable T-structure, the substitution of La by Sr and Ce yields hole and electron doping [166–168], but the two charge states crystallize in different structures, namely the T and T'-structure, respectively.

Recently  $La_2CuO_4$  was stabilised in the metastable T' structure by a low-temperature synthesis method [169]. Being the true parent compound of electron-doped cuprates, the material attracted much interest, especially with regards to the study of its magnetic properties. As a side note, we mention that T'-La<sub>2</sub>CuO<sub>4</sub> is of great interest also in the field of low dimensional quantum magnetism and candidates itself as one of the best experimental model systems in this context. The material has been thoroughly characterised with synchrotron powder diffraction, neutron scattering, bulk  $\mu$ SR, and NMR measurements. A body-centred-tetragonal structure (BCT) was identified and a series of magnetic transitions as a function of temperature were evidenced by NMR and  $\mu$ SR measurements [170].

The true ground state of bulk T'-La<sub>2</sub>CuO<sub>4</sub> is still debated. Two independent groups obtained the T' structure with different chemical routes but the two realisations differ significantly. While the compound obtained with the method discussed above is an AFM insulator, T' La<sub>1.8</sub>Y<sub>0.2</sub>CuO<sub>4</sub> obtained with molecular beam epitaxy in thin films is a metal and superconduct at low temperature [171].

From the theoretical point of view, DFT with the GGA for the exchange and correlation potential provides a metallic ground state with vanishing magnetic moment on the Cu atoms. By including on-site Hubbard corrections the local moment on Cu atoms increases and a gap opens in the density of states. The details of the electronic band structure are discussed in Appendix A.7. A more refined study based on DFT+Dynamical Mean Field Theory (DMFT) calculations obtained a metallic ground state at the verge of a metal-to-insulator transition [172].

As discussed in the appendix, we considered both the insulating and the metallic ground state and obtained the same muon site. Indeed, even if a Fermi surface exists, the material can be regarded as a bad metal as shown in Ref. [172] and in Fig. A.3. The results reported in this section were obtained considering the insulating and AFM ground state.

#### 7.2. Electrostatic potential

As already discussed for MnSi, to verify if the *possible muon sites* obtained from the unperturbed electrostatic potential yield a correct prediction, we evaluated the bulk electrostatic potential with a FP-DFT approach [94]. The electrostatic potential (Eq. 3.55) isosurfaces for unperturbed T'-La<sub>2</sub>CuO<sub>4</sub> are shown in Fig. 7.2 for  $V(\mathbf{r}) = 0.5$  and 1.1 eV above the potential absolute minimum, respectively in panel a and b. The potential has symmetry equivalent absolute minima close



Figure 7.2.: Electrostatic potential isosurfaces for V=0.5 eV in a) and 1.1 eV in b) (the absolute minimum is set to 0 eV). The symmetry equivalent minima form a tetrahedra around the O atoms as shown in c). [Plotted with VESTA, Ref. [125]]

to the oxygen atoms in the LaO planes shown in Fig. 7.2c. There are also narrow relative minima between the O atoms of different planes at  $V(\mathbf{r}) \sim 0.7$  eV and close to the O atoms in the CuO plane at  $V(\mathbf{r}) \sim 0.9$  eV. This is expected considering the high electronegativity of the oxygen atoms.

None of the above points is found to be the correct muon site. Indeed, by considering only the dipolar contribution for the local field at the muon site, they all yield values for the magnetic moment on the Cu atoms that are inconsistent with the results obtained from NMR measurements (for additional details see Ref. [173]).



Figure 7.3.: Schematic representation of the final interstitial *candidate* muon sites labelled A, B and C. [Plotted with VESTA, Ref. [125]]

#### 7.3. Muon site estimation

Starting from random interstitial positions, we relax the muon's position and the surrounding crystal lattice with the method discussed in Sec. 3.4.2. Three symmetry inequivalent *candidate muon sites*, labelled A, B and C, were identified and are shown in Fig. 7.3. For sake of clarity, in the figure we sketch the final interstitial sites in the  $\sqrt{2} \times \sqrt{2} \times 1$  rather than showing the whole relaxed supercells. A description of the perturbation introduced by the muon on the lattice structure is reported in Table 7.1 and it is also displayed, for site A, in Fig. 7.4c. In the same table we show the difference between the total energies of the three sites and the occupation and polarisation obtained from the projection of the electronic density on a s orbital surrounding the muon.<sup>†</sup>

The three *candidate muon sites* are all characterised by the for-

<sup>&</sup>lt;sup>†</sup>The occupation and the polarisation reported in Tab 7.1 are referred to the s orbital of hydrogen.

Site	$\varepsilon^{\rm tot} - \varepsilon^{\rm tot}_A [{\rm eV}]$	$d(O,\mu)$	d(O,O)	$\mu$ s-orbital occ.	pol.
A	0	1.03	2.56	0.6	0
B	0.10	1.02	2.65	0.65	0
C	0.44	1.00	2.70	0.67	0.0006

Table 7.1.: Total energy differences and structural details for the three candidate muon sites. The total energy differences are listed with respect to site A in the second column. The distances, indicated as d(1,2) with 1 and 2 being either the oxygen nucleus or the muon, refer to the first neighbouring O atoms for the muon in the various sites. The last two columns describe the electronic occupation and the spin polarization of a spherically symmetric s-orbital at the muons' sites.

mation of bonds between the muon and an oxygen atom. The total energies for the three configurations are different and it is noted that, the smaller the  $\mu$ -Cu distance is, the higher is the energy of the configuration. We also point out that a muon in site A negligibly modify the Cu magnetic moments. On the other hand, for a  $\mu$  in site B, the magnetic moment of the neighbouring Cu atom slightly decreases. The exchange integral mediated by O atoms in the Cu-O plane is drastically perturbed by a muon in site C, leading to a reduction of the neighbouring Cu magnetic moment of about 40% of its original value. Finally, we stress that we cannot draw a clear connection between the occupation of the *candidate muon sites* and the total energies of the final positions obtained from the DFT calculations, mainly because the occupation probability depends on kinetic considerations. However, we mention that site A is close to the energetically favourable diffusion path as suggested by the electrostatic potential isosurface of Fig. 7.2b.

The experimental results show that only one site is present and the local fields at the  $\mu$  position are only compatible with position A, irrespective of the Cu long-range magnetic order.



Figure 7.4.: In a) and b) the probability density for the muon in site A is depicted. The coloured shadows are a pictorial view of the muon's probability density distribution with a linear scale of opacity and colours from blue to red. In c) the muon site A and the lattice distortions are shown.[Plotted with MAYAVI and XCRYSDEN, Refs. [120, 174]]

### 7.4. Ground state energy

Using the DAA presented in Sec. 3.4.3, we acquired the potential felt by the muon in A. This was done by performing small displacements from the muon's relaxed position. To achieve a sufficiently accurate energy profile, we performed displacements up to  $\sim 1.7$  Å with the smallest step being 4 pm. We interpolated the potential on 597 irregularly distributed points cloud obtaining an accurate description of  $V_{\mu}$  up to  $\sim 1.3$  eV.

From the solution of the Schrödinger equation for the muon in the interpolated potential, a GSE of 0.8 eV is obtained. The probability density for the ground state wave function is shown in Fig. 7.4. These results confirm that site A is a trapping site since the ground state energy is smaller than the potential barriers. The oval shape of the probability density in the xy plane (Fig. 7.4a) is due to the anharmonicity of the potential while the elliptic shape in the yz plane is a consequence of the neighbouring La atoms. Two remarks are in order.

#### 7. T'-La<sub>2</sub>CuO<sub>4</sub>: field glasses for $\mu SR$

First, the large area explored by the muon<sup>†</sup> is a well known consequence of its light mass compared to the proton. In principle, the  $\mu$ wave function can be used to determine the contact hyperfine field at the muon site. However, the electronic spin polarisation at site Atends to 0 and is barely above the numerical error of the DFT simulation thus making the *ab initio* estimation of  $B_{\rm cont}$  unreliable. Second, quite notably the most probable position for the muon is shifted from the potential minimum by ~ 0.07 Å along the oxygen-oxygen bond direction and is located 1.10 Å away from the closest oxygen in the LaO plane. This shows that the anharmonicity of the potential produces relevant effects also in the determination of the interstitial site's position.

#### 7.5. Discussion

 $T'-La_2CuO_4$  represents a peculiar case in which an accurate analysis of  $\mu$ SR data supported by the DFT outcomes on the position occupied by the muon in the sample and symmetry considerations on the magnetic orders compatible with the crystal structure provide conclusive information on the long-range magnetic structure [170]. Indeed, the knowledge of the muon site allows to unambiguously identify the non-collinear magnetic structure of the low temperature phase of T'- $La_2CuO_4$ . The reader is referred to the doctoral thesis by G. Pascua (Ref. [173]) for the description of the  $\mu$ SR and NMR experimental results and for a detailed discussion of the symmetry allowed magnetic orders in T'-La<sub>2</sub>CuO<sub>4</sub>. There are four possible inequivalent magnetic structures (labelled Col I, NCol I, Col II, NCol II in Fig. 7.5) for the Cu atoms in this compound. All of them give the same magnetic field at the La nuclei for a given value of the magnetic moment of the Cu atoms,  $m_{Cu}$ . Therefore <sup>139</sup>La NMR provides, irrespective of the long-range magnetic order, the value of the magnetic moment on Cu atoms. On the other hand, owing to the non-symmetrical interstitial position occupied by the muon, it is possible to distinguish between the various long-range magnetic orders with  $\mu$ SR measurements. This

 $<sup>^{\</sup>dagger}\text{With}$  90% probability, the muon resides within a sphere of radius 0.56 Å centred at the maximum probability point.



Figure 7.5.: Possible local fields distributions for the four symmetry allowed (non-)collinear magnetic structures (shown with different colours) and the two magnetic domains (shown with the same colour) of the tetragonal T'-La<sub>2</sub>CuO<sub>4</sub> lattice. The green line is the Fourier transform of the zero-field asymmetry data. Taken from Ref. [173]

is shown in Fig. 7.5 where the four different magnetic structures produce 8 local fields as a consequence of the twin domains. In general, the two domains give rise to different local magnetic fields at the muon site, except for one configuration. Since only one frequency is observed in the Fourier transform of the asymmetry, one can identify the long-range magnetic order from  $\mu$ SR data and, at the same time, extract the spin polarisation of the *d* orbitals of the Cu atoms. The value  $m_{\rm Cu} = 0.33 \ \mu_{\rm B}$  obtained with  $\mu$ SR data is in nice quantitative agreement with the value obtained from the <sup>139</sup>La NMR. We have therefore determined the low temperature magnetic structure of T'-La<sub>2</sub>CuO<sub>4</sub> with the sole use of local probes.

# Conclusions

The aim of the work presented in this thesis is to provide a solid ground for the identification of muon sites with *ab initio* methods. This is clearly beyond the possibilities of a single research but, from the developments discussed here and by many research groups across the world, DFT simulations seem to be a promising method to fulfil this task.

Our steps towards the identification of a reliable strategy based on DFT *ab initio* approaches have been detailed with many examples. We started from the most naïve way of identifying muon sites, i.e. the inspection of the minima of the unperturbed electrostatic potential. In IPSCs and in MnSi this simple strategy is found to be surprisingly accurate. Having the possibility of identifying the muon sites with the sole knowledge of the electronic properties of the unperturbed material would be a great advantage since it would save a huge amount of computational power. However it was soon realised that, in many cases, the electron density modification introduced by the charged impurity had to be included in the simulation. Unfortunately, to the best of our knowledge there is no sharp way to distinguish between the cases in which we expect the electrostatic potential approach to be reliable and those where the charge density rearrangement will lead to substantial differences. The unexpected high accuracy obtained for IPSCs and MnSi is not justified on theoretical grounds but is surprising. For this reason it will deserve more attention in future studies.

To overcome the limitations of the unperturbed electrostatic approach, we opted for the inclusion of the muon as a charged hy-

#### 8. Conclusions

drogenoid impurity in the system. DFT have been intensively used over the years to study impurities in semiconductors and the vast knowledge developed in this context served as a background for the specific case of the identification of muon sites in solids. We first inspected YF<sub>3</sub> and LiF, two compounds which have been accurately characterised experimentally. DFT results correctly identified the muon site and confirmed the well known experimental knowledge that the interstitial  $\mu$  alter not only the charge distribution of the material but also distort the crystal structure in its neighbourhood.

The central role of the ground state energy of the muon in the site assignment procedure was considered in all the cases presented. The electrostatic potential was initially used. This allowed an inexpensive but inaccurate estimation of the GSE of the muon in some cases. However a refined strategy for all the materials where the charge density is strongly perturbed by the charged impurity had to be introduced. This is especially needed since, as it was shown, many minima are usually encountered in the total energy profile explored during the structural relaxation, but most of them are too narrow to bind the light impurity.

The inclusion of a quantum description of the muon in the DFT simulation can be computationally expensive. Having dropped the possibility of solving the Schrödinger equation for the muon in the unperturbed electrostatic potential, we considered many different approaches to approximate the quantum interaction between the  $\mu$  and the hosting system. This subject has been extensively discussed in literature and a variety of different methods have been proposed. However, most of them had to be discarded owing to the extreme computational cost they require. We identified two possible strategies: the use of density functional perturbation theory for studying the vibrational modes of the muon in the harmonic approximation and the DAA. We opted for the latter, since, even if it is not always applicable, it provides the best trade off between computational costs and accuracy.

We showed that a detailed analysis of the GSE of the muon is crucial for a correct determination of the muon site. For example, in MnSi, two relative minima are found to be unstable when the GSE is taken into account. Moreover, the DAA provides access to both ground state and excited energy levels for the muon in the system. Compared to the harmonic approximation approach, this represents an additional advantage which allowed, for example, the estimation of the activation energy for the phonon assisted quantum tunnelling of the muon in FCC Copper.

Finally, we discussed the interesting case of T'-La<sub>2</sub>CuO<sub>4</sub>, the true parent compound of electron doped cuprates, which shows a noncollinear AFM ground state at low temperature. T'-La<sub>2</sub>CuO<sub>4</sub> is one of the many materials in which neutron scattering measurements, the technique of election for long-range magnetic structure identification, cannot be used. Indeed, to date, the small magnetic moment of Cu atoms and the presence of H contamination have prevented the identification of the long-range magnetic order with neutron spectroscopy. The  $T \rightarrow 0$  K magnetic order was instead established by combining accurate experimental  $\mu$ SR measurements and the knowledge of the muon site obtained with the DFT approach.

To conclude, we propose DFT in the DAA approximation as an efficient method to predict muon sites. Even though some of the approximations introduced either by DFT or the DAA can be drastic, this approach has the notable advantage of being simple, efficient and sufficiently accurate for a large set of materials. These are essential requirements to offer a DFT based support tool for  $\mu$ SR data analysis that can really boost the technique potentialities.

# Technical details of the simulations

#### A.1. LaFeAsO

The details of the DFT simulations are reported in Ref. [121]. We used the Wien2K package to perform DFT with a FP basis. The LDA as parameterized by Perdew and Wang and Hubbard corrections (LSDA + U) as implemented in the all-electron LAPW code Wien2K [95] were adopted. In all the simulations, the magnetic order was taken into account in the collinear LSDA formalism. The muffin-tin radii for La, Fe, As, and O are chosen equal to 2.3, 2.2, 2.0, and 1.9 Bohr, respectively.  $R_{\min}^{MT} \times \max(|\mathbf{k}|) = 7 (R_{\min}^{MT}$  is the smallest muffin-tin radius in the unit cell and  $\max(|\mathbf{k}|)$  the largest wave number of the basis set) is used for the plane-wave cutoff. Magnetic fields at the muon site were calculated with dipole sums performed in real space with a Lorentz sphere radius of 120 Å.

## A.2. FeTe

The details of the calculation are reported in Ref. [126]. We considered an ideal stoichiometric FeTe crystal within the DFT formalism with GGA [79] for the exchange and correlation potential. We adopted the FP LAPW method, as implemented in the Elk code [94]. In particular, we considered a bicollinear magnetic order on a  $2a \times a \times c$  cell with P4/nmm symmetry [133]. The experimental atomic positions and lattice constant are used.  $R_{\min}^{MT} \times |\mathbf{G} + \mathbf{k}|_{\max} = 8$  is chosen for the



Figure A.1.: Comparison of the band structure of LaCoPO obtained with the PW basis (black lines) and the FP-LAPW (red lines) basis. The Fermi energy is set to 0 eV. In the vicinity of the Fermi energy, the band structures overlap almost perfectly.

expansion of the wave functions in the interstitial region. The reciprocal space was sampled with a  $8 \times 8 \times 6$  MP grid and the convergence threshold is set to 0.1 mHa for the total energy and to  $0.1 \times 10^{-5}$  Ha for the root mean square value of the changes in  $v_s$  (see Eq. 3.24). The resulting magnetic moment per iron atom was 2.24  $\mu_{\rm B}$ , in reasonable agreement with 2.54  $\mu_{\rm B}$ , the experimental value obtained via neutron powder diffraction [133].

## A.3. LaCoPO

The details of the calculation are reported in Ref. [101]. We used both the PW and the FP-LAPW methods as implemented in the VASP [175, 176] and Elk [94] packages. The Perdew Burke Ernzerhof (PBE) functional was used in order to evaluate the exchange-correlation potential [79]. As for the PW approach, the electron density was described by the PAW pseudopotentials method [87]. Electronic convergence was set up at  $10^{-6}$  eV and the sampling of the Brillouin zone was performed with the MP scheme [83] on a  $8 \times 8 \times 4$  grid.



Figure A.2.: Comparison of the band structure of LiF obtained with the LCAO basis (red lines) and the FP-LAPW (black lines) basis. Below the Fermi energy, arbitrarily set within the gap, the band structures nicely match.

A plane-wave cutoff of 600 eV and a Gaussian smearing of 0.02 eV was used throughout. FP-LAPW calculations were carried out using a basis set with  $R_{\min}^{\text{MT}} \times |\mathbf{G} + \mathbf{k}|_{\max} = 7.5$ , and  $l_{\max} = 8$  for the angular momentum expansion in the MTs (for both the wave functions and the potential). The reciprocal space was sampled with the same grid used in the PW approach. The results obtained with the two computational methods are in close agreement. The convergence criteria for forces minimization was set to  $5 \times 10^{-3} \text{ eV/Å}$  and  $10^{-5} \text{ eV}$  was used as threshold for self-consistent electronic cycles. Since in Sec. 4.4 we deal with subtle modifications of the energy dispersions at the Fermi level as a function of pressure, the accuracy of the pseudopotential approach was checked by comparing the band structures obtained with the PW and the FP basis. The two single particle band structures nicely match in the vicinity of the Fermi energy as shown in Fig. A.1 confirming the validity of the plane wave approach.

#### A.4. LiF and $YF_3$

All the details of the simulation are reported in Ref. [102]. The results presented in the thesis and in the above reference were obtained with the plane wave and pseudpotential approach as implemented in the QUANTUM ESPRESSO suite of codes [177]. The plane wave cutoff

was set to 60 Ry and a  $8 \times 8 \times 8$  MP grid was used to sample the reciprocal space when dealing with the conventional cubic cell (see Sec. 5.2). In  $2 \times 2 \times 2$  supercells, the reciprocal space grid was halved. The experimental lattice constants were used.

To check convergence against supercell sizes, we reverted to the linear combination of atomic orbitals (LCAO) based code SIESTA since we could not afford plane wave simulations' computational costs. The accuracy of the LCAO basis is confirmed by the comparison of the band structure obtained with a FP-LAPW approach (Ref. [94]) shown in Fig. A.2. From the structural relaxation, similar results were obtained with the  $2 \times 2 \times 2$  and the  $3 \times 3 \times 3$  supercell.

Since we are interested in the electrostatic potential generated by electrons and nuclei, our calculations may be affected by the pseudoization of the potential inside the atomic core region. For this reason, we double-checked our simulations by comparing the results we got for the perfect bulk system with the full-potential method implemented in the WIEN2K package [95]. We found that *possible muon sites* are not affected by the electrostatic potential's approximate description due to the pseudoization.

#### A.5. MnSi

To analyse the electronic structure of MnSi we use the FP-LAPW approach as implemented in the ELK code [94]. The GGA as formulated by PBE is used to approximate the exchange and correlation potential [79]. The cutoff for the plane wave expansion in the interstitial region is set to  $R_{\min}^{\text{MT}} \times |\mathbf{G} + \mathbf{k}|_{\max} = 9$ . The reciprocal space is sampled on a  $16 \times 16 \times 16$  MP grid [83]. The experimental atomic positions and lattice constant are used. A FM ground state is considered and the resulting magnetic moment on the Mn atoms is 1  $\mu_B$  to be compared to the experimental value of 0.41  $\mu_B$ . Indeed MnSi in a well known case in which the mean field approximation leads to an overestimation of the magnetic moments [178, 179]. For the supercell methods used to study the effect of the muon impurity, a plane wave basis was used. The simulations were performed with the QUANTUM ESPRESSO suite of codes [177]. We set a cutoff of 60 Ry and 400

Ry for plane waves expansion and for the charge density respectively. In the 64+1 atoms supercell, a  $2 \times 2 \times 2$  MP grid for reciprocal space sampling [83]. Spin polarisation was included in all simulations. With these parameters the total energy was converged to 15 meV.

#### A.6. Cu

The DFT simulations for FCC Cu were performed with the QUANTUM ESPRESSO suite of codes [177].

In all the calculations we used the GBRV pseudopotential library built using PBE for exchange and correlation [79, 180]. The selfconsistency threshold for electronic optimization was set to  $\leq 10^{-8}$ Ry. For relaxation calculations, in order to reach convergence, two conditions had to be met: less than  $10^{-3}$  Ry/Bohr for forces and total energy differences between relaxation steps smaller than  $10^{-4}$ Ry. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used for structural optimization. The reciprocal space in the supercell was sampled with a  $3 \times 3 \times 3$  MP grid in DBO simulations.

To identify the minimum energy paths between equivalent muon sites we performed NEB calculations. To comply with the DAA approximation we kept the atoms of the compound fixed in their relaxed positions in all the images of the NEB simulations. This gives an upper bound for the minimum transition energy between equivalent muon sites. In all NEB calculations the convergence threshold was set to 0.05 eV/Å for the forces normal to the path.

## A.7. T'-La $_2$ CuO $_4$

T'-La<sub>2</sub>CuO<sub>4</sub> crystallizes in a BCT structure with one formula unit per unit cell. In chapter 7, we considered the magnetic unit cell and other bigger supercells starting from the simple tetragonal structure which has two formula units per cell. In all our calculations we used the experimental cell parameters a = 4.0084 and c/a = 3.1281. Nonetheless we point out that the fully relaxed cell compare extremely well with the experimental one having parameters a = 4.0360 and c/a = 3.1481. Except for the supercell calculations where all the atomic positions are fully relaxed, also  $z_{La} = 0.35198$  is kept fixed. Relaxing the La position results in  $z_{La} = 0.3510$ , again in good agreement with the experimental data.

In all calculations, a PW basis set and ultrasoft pseudopotentials [86] as implemented in the QUANTUM ESPRESSO suite of codes [177] was used. We set a kinetic-energy cutoff of 65 Ry (300 Ry for the charge density) for supercells' relaxation calculations and of 75 Ry (400 Ry for the charge density) for the refinement of the relaxation calculations. The latter cutoff is also used for the analysis of the electronic band structures and the evaluation of the Cu magnetic moments. These cutoffs guaranties a self-consistent total energy of the system converged to within 0.8 mRy/atom in geometrical relaxations, and an improved convergence of  $3 \times 10^{-3}$  mRy/atom for refined calculations. The convergence criterion for relaxation calculations was set to 0.1 mRy for the total energy differences between the relaxation steps and to 0.008 Ry/Bohr for forces. The reciprocal space sampling was performed on a MP  $12 \times 12 \times 6$  grid for the magnetic unit cell  $(\sqrt{2} \times \sqrt{2} \times 1 \text{ cell obtained from the conventional simple tetragonal})$ cell). For supercell relaxation calculations and to sample the potential felt by the muon in the DAA, the gamma point or the Baldereschi point were used. The density of states were obtained with Methfessel-Paxton smearing [181] or the tetrahedron sampling method [182] on a uniform  $14 \times 14 \times 14$  k-points grid.

The electronic structure of T'-La<sub>2</sub>CuO<sub>4</sub> was studied with both GGA and GGA+U. For the exchange and correlation potential we used the parametrization introduced by PBE [79]. Within the GGA, the material is found to be a metal with a small density of states at the Fermi level. These results were published in literature together with DFT+DMFT calculations [172]. The latter approach provided a metallic ground state on the verge of an metal-to-insulator transition.

DFT+U simulations where performed in the simplified rotationally invariant scheme of Cococcioni and De Gironcoli [183]. The density of states as a function of U is shown in Fig. A.3. For U > 2 eV a gap opens and the material is described as an insulator. As expected from crystal field theory, the  $d_{x^2-y^2}$  orbital has the highest energy and is found to be partially occupied in the symmetrized atomic orbital projection scheme.



Figure A.3.: Total density of states as a function of the value of Hubburd U used in the simulations of T'-La<sub>2</sub>CuO<sub>4</sub>. The Fermi energy is conventionally set to 0 eV. The inset shows a zoom of the total density close to the Fermi energy.

In the supercell simulations discussed in Chpater 7, the insulating ground state is achieved with the use of a Cu pseudopotential that favours the  $3d^9$  configuration for Copper. This is a sort of an artefact to reproduce the onsite Hubburd corrected results and optimize the performances at the same time. Moreover, the introduction of the impurity often leads to problematic convergence of GGA+U simulations when the crystalline symmetry is broken and the projection on localised orbitals is impaired by the charge density redistribution close to the impurity. This is especially the case for muon sites close to the Cu-O plane. As for the GGA+U approach, with the above strategy a gap opens in the density of states and the structural properties estimated in this way matches very well the experimental values.

The muon site analyses were performed with both the insulating and the metallic ground states. Both gave similar results for the muon po-

#### A. Technical details of the simulations

sition of the populated site A. The O- $\mu$  distance in the metallic ground state simulations is found to be 1.02 Å (see Tab. 7.1 for comparison).

# B The DBO code

Cutting the computational costs needed to acquire the potential felt by the muon in the DAA is of utmost importance. To this aim it is necessary to optimise the sampling process used to construct the points cloud on which the interpolation is performed. Acquiring all points in a cubic grid would probably result in a too expensive computational procedure. Moreover that may eventually produce only a small set of points useful for the interpolation of the potential of Eq. 3.62 since interstitial positions close to the nuclei have rapidly increasing total energies. Finally, as shown in chapters 6 and 7, the potential felt by the muon is usually far from being harmonic, thus making the sampling over a sphere of increasing radius similarly inefficient.

A simple exploration algorithm was designed to perform an efficient sampling of the *a priori* unknown potential  $V_{\mu}$  of Eq. 3.62. The exploration is controlled by three parameters: a cutoff energy  $\epsilon_C$ , a grid separation length  $\delta$  and a "search horizon"  $\Delta$ . The first parameter is used to specify the highest energy that should be explored. The second parameter governs the inter-spacing between explored points in a cubic grid. The third parameter controls the maximum distance between two consecutively examined points during the exploration process. The latter parameter is essential for two reasons. Firstly and especially in magnetic materials, the previously calculated electron density must be used to converge to the correct ground state and avoid other local minima in the total energy landscape which reproduce, for example, different magnetic configurations. This can be done only if the impurity is not too far from the position where the previous self consistency was obtained. Secondly, reuse of electron

#### B. The DBO code

densities speeds up the calculation significantly.

The algorithmic procedure begins with the definition of the starting point for the exploration (labelled i) and the evaluation of its total energy  $\epsilon_i$ . Let n(i) be the number of neighbouring points of point i in a cubic grid<sup>†</sup> for which the total energy has not been calculated yet. From the initial point the iteration proceeds as follows:

- The total energies of the neighbouring points n(i) of the current point i are inspected.
- The number of unexplored neighbours n(i) for all explored points i is updated.
- Among the already explored points j, those with n(j) > 0 form the set of the candidate positions for the next move. The point j having the lowest energy  $\epsilon_j$  and having distance  $d(i, j) < \Delta$  is chosen as the next point for the exploration.
- The current position is set to position j and the algorithm is iterated.

The iteration stops when there are no points j fulfilling the conditions n(j) > 0,  $d(i, j) < \Delta$  and  $\epsilon_j < \epsilon_C$ .

For  $\Delta = \infty$  (infinite "search horizon") all points with  $\epsilon < \epsilon_C$  will be explored. This is no longer true when we limit the maximum distance between consecutively explored points since the algorithm can remain trapped in dead-end paths. To avoid this situation we can imagine to label visited points with three different colours:

- red) explored points whose energy exceeds the cut-off energy,  $\epsilon > \epsilon_C$ .
- yellow) explored points having  $\epsilon < \epsilon_C$  and at least one neighbour unexplored.
- green) explored points without unexplored neighbours.

<sup>&</sup>lt;sup>†</sup>In the implementation used in this thesis we used only the nearest neighbours (left, right, up, down, front, back).

When a dead-end point is reached there are two possible scenarios: none of the explored points is yellow, or there is at least one yellow point. In the first case the routine ends, otherwise we move from point k, where the system is trapped, to the nearest yellow point, l. In doing so, the path which minimise the distance d(k, l), obtained with the algorithms described in Ref. [184], is used in order to minimise the computational cost.

At the present stage, it is up to the user to check if the set of explored points can accurately interpolate the potential up to the threshold that is required for the subsequent analysis.

Starting from the points cloud  $\{\epsilon(\mathbf{r}_{\mu})\}\$ , the potential  $V_{\mu}$  is obtained by interpolation with radial basis function (RBF) interpolants and with the Quadratic Shepard method [185–187].

# Solving the Schrödinger equation

To evaluate the ground state energy of the muon, we solved the stationary Schrödinger equation  $(\hbar = m = 1)$ ,

$$H\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r}), \qquad i = 0, 1, 2, \dots$$
(C.1)

where

$$H = T + V(\mathbf{r}) = -\frac{1}{2}\Delta_{\mathbf{r}} + V(\mathbf{r}) . \qquad (C.2)$$

 $V(\mathbf{r})$  is the interpolated potential and  $\Delta$  is the Laplacian operator. An important property of the Hamiltonian H is that, being an Hermitian operator, its eigenvalues  $E_i$  are real valued and non-negative (by properly shifting the origin of the potential), and its corresponding real eigenfunctions  $\phi_i(x)$  can be chosen to form a real orthonormal basis of the underlying Hilbert space.

The 3D Schrödinger equation has been solved with both periodic and Dirichlet boundary conditions. For Dirichlet boundary conditions the eigenfunction  $\phi_i(x)$  are expanded on a spline basis with finite element approach. The method used in this thesis is discussed in detail in Ref. [188]. The expansion on B-splines is defined as

$$\Psi_i = \sum_{1}^{N} c_{il} \beta_l(\mathbf{r}) \tag{C.3}$$

where l runs over the N basis functions  $\beta_l = B_i^{(n)}(x) B_j^{(n)}(y) B_k^{(n)}(z)$ 

and B functions are

$$B_k^{(n)}(x) = A^{(n)}(x/h - k)$$
(C.4)

$$A^{(n)}(x) = \frac{x}{n} A^{(n-1)}(x) + \frac{n-x+1}{n} A^{(n-1)}(x-1) \quad \text{for} \quad x \in [0, n+1)$$
(C.5)

$$A^{(0)}(x) = 1$$
 for  $x \in [0, 1)$  (C.6)

where h is the spacing between the grid points in the finite elements approach.

The finite elements expansion gives a generalised eigenvalue problem whose matrix elements are

$$T_{ij} = \frac{1}{2} \int \nabla \beta_i(\mathbf{r}) \cdot \nabla \beta_j(\mathbf{r}) \, d^3r \tag{C.7}$$

$$S_{ij} = \int \beta_i(\mathbf{r}) \beta_j(\mathbf{r}) \ d^3r \tag{C.8}$$

$$V_{ij} = \int \beta_i(\mathbf{r}) V(\mathbf{r}) \beta_j(\mathbf{r}) \ d^3r \quad . \tag{C.9}$$

The advantage provided by the spline basis is that the kinetic T and the overlap S terms can be evaluated analytically. The problem is then solved with a sparse eigenvalue solver which provides the eigenvalues in a specified energy interval. In the implementation used for the calculations performed in this thesis, we adopted the FEAST algorithm [189].

The approach used to solve the Schrödinger equation with periodic boundary conditions is discussed in Ref. [190]. Shortly speaking, the solution of Eq. C.1 is obtained by reverting to the corresponding timedependent Schrödinger equation (rewritten in 1 dimension for the sake of simplicity)

$$i\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t), \qquad \psi(x,0) = \psi_0(x).$$
 (C.10)

By introducing the imaginary time  $t = -i\tau$  (Wick rotation), the formal solution is given by the evolution operator  $\mathcal{T} = \exp(-\tau H)$ . This can be used to obtain the eigenfunctions of Eq. C.1 because, in principle, for any initial wave function, under the action of  $\exp(-\tau H)$ , the imaginary time evolution converges asymptotically to the ground state solution for  $\tau \to \infty$ .

Indeed Eq. C.10 is transformed by the Wick rotation into the diffusion equation

$$-\frac{\partial}{\partial\tau}\psi(x,\tau) = H\psi(x,\tau) \tag{C.11}$$

where  $\psi(x,\tau) = e^{-\tau H} \psi(x,0)$ . By expanding  $\psi_0$  on the basis formed by the eigenfunctions of Eq. C.1,  $\phi_i$ ,

$$\psi_0(x) = \sum_i c_i \phi_i(x), \qquad c_i = \langle \phi_i(x) | \psi(x,0) \rangle, \qquad (C.12)$$

we obtain the time evolution, Eq. C.11, as

$$\psi(x,\tau) = e^{-\tau H} \psi(x,0) = \sum_{i} e^{-\tau E_i} c_i \phi_i(x).$$
(C.13)

Since for excited states Eq. C.13 decays more rapidly, for a sufficiently long imaginary time evolution we get  $\psi(x,\tau) \rightarrow e^{-\tau E_0} c_0 \phi_0$ . The speed of convergence depends on the separation between the ground state energy and excited state eigenvalues. If the ground state is degenerate, a linear combination of the ground state eigenfunctions will be obtained.

The operator  $\exp(-\tau H)$  cannot be calculated exactly an therefore it is usually expanded with the so-called Suzuki-Trotter formula [191]

$$\mathcal{T}(\tau) = \exp(-\tau H) = \exp(-\frac{1}{2}\tau V) \exp(-\tau T) \exp(-\frac{1}{2}\tau V) + \mathcal{O}(\epsilon^3)$$
(C.14)

which descends from the known property of self adjoint operators

$$e^{t(A+B)} = \lim_{(n \to \infty)} \left( e^{tA/n} e^{tB/n} \right)^n.$$
 (C.15)

However, from a computational point of view, in order to obtain a well converged result,  $\tau$  steps must be small, thus requiring many iterations to reach convergence. For this reason, fourth order factorizations of the evolution operator is used in Ref. [190] to improve the performance of the method.

#### C. Solving the Schrödinger equation

The ground state energy is easily calculated as  $E_0 = \langle \phi_0 | H | \phi_0 \rangle$ . By propagating in imaginary time multiple wave functions and guaranteeing their orthonormalization, for example with the Gram-Schmidt orthonormalization or diagonalizing the overlap matrix, it is also possible to obtain excited state eigenfunctions and eigenvalues.

# Codes

Part of the work presented in this thesis relies on computer codes that were developed on top of the QUANTUM ESPRESSO routines. In the spirit of open science these codes are made freely available to the community under GPL license.

# D.1. DBO

DBO is a tool to efficiently sample the potential for an impurity in a supercell simulation within the DAA. The potential is obtained by interpolation of the acquired points cloud and the Schrödinger equation for the impurity in the supercell is subsequently solved. The set of tools providing the exploration algorithm discussed in Appendix B, the interpolation of the points cloud (adapted from [192, 193]) and the solution of the Schrödinger equation (adapted and provided with permission from the authors of Ref. [188, 190]) will be published under GPL at the following internet address:

http://www.fis.unipr.it/~derenzi/dispense/pmwiki.php?n=MuSR. MuonSite as soon as the related article will be published.

# D.2. Unfold

This code performs supercell band structure unfolding. The tool can be used to identify the effect of localised impurities in plane wave supercell simulations. Inspecting the effect of the impurity in reciprocal space by comparing the band structure of the bulk and
## $D. \ Codes$

the perturbed electron densities gives information on effects such as doping, delocalised states, depth of the impurity energy levels. The code is provided under GPL at the following internet address: http://qe-forge.org/gf/project/unfold/.

## References

- S. J. Blundell. Spin-polarized muons in condensed matter physics. Contemporary Physics, 40(3):175-192, May 1999. ISSN 1366-5812. doi: 10.1080/ 001075199181521. URL http://dx.doi.org/ 10.1080/001075199181521.
- [2] E. L. Silva, A. G. Marinopoulos, R. C. Vilão, R. B. L. Vieira, H. V. Alberto, J. Piroto Duarte, and J. M. Gil. Hydrogen impurity in yttria: Ab initio and μSR perspectives. Physical Review B, 85: 165211, Apr 2012. doi: 10.1103/PhysRevB. 85.165211. URL http://link.aps.org/doi/10.1103/PhysRevB.85.165211.
- [3] SFJ Cox. Implanted muon studies in condensed matter science. Journal of Physics C: Solid State Physics, 20:3187, 1987. URL http://iopscience.iop.org/ 0022-3719/20/22/005.
- [4] M Camani, F. N. Gygax, W Rüegg, A. Schenck, and H. Schilling. Positive Muons in Copper: Detection of an Electric-Field Gradient at the Neighbor Cu Nuclei and Determination of the Site of Localization. *Physical Review Letters*, 39(13):836-839, September 1977. ISSN 0031-9007. doi: 10.1103/PhysRevLett.39.836. URL http:// link.aps.org/doi/10.1103/PhysRevLett.39.836.
- [5] R. De Renzi, G. Guidi, P. Podini, R. Tedeschi, C. Bucci, and S. F. J. Cox. Magnetic properties of MnF<sub>2</sub> and CoF<sub>2</sub> determined by implanted positive muons. I. Localization studies. *Physical Review B*, 30: 186-196, Jul 1984. doi: 10.1103/PhysRevB. 30.186. URL http://link.aps.org/doi/10. 1103/PhysRevB.30.186.
- [6] K.H. Chow, R.L. Lichti, R.F. Kiefl, S. Dunsiger, T.L. Estle, B. Hitti, R. Kadono, W.A. MacFarlane, J.W. Schneider, D. Schumann, and M. Shelley. Identification of neutral bond-centered muonium in n-type semiconductors by longitudinal muon-spin relaxation. *Physical Review B*, 50:8918-8921, Sep 1994. doi: 10.1103/PhysRevB.50.8918. URL http://link.aps.org/doi/10.1103/PhysRevB.50.8918.
- [7] J.H. Brewer, R.F. Kiefl, J.F. Carolan, P. Dosanjh, W.N. Hardy, S.R. Kreitzman, Q. Li, T.M. Riseman, P. Schleger, H. Zhou, et al. Site of the positive muon in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. *Hyperfine Interactions*, 63 (1):177-181, 1991.
- [8] R. F. Kiefl, M. Celio, T. L. Estle, S. R. Kreitzman, G. M. Luke, T. M. Riseman, and

E. J. Ansaldo. <sup>29</sup>Si Hyperfine Structure of Anomalous Muonium in Silicon: Proof of the Bond-Centered Model. *Physical Review Letters*, 60:224–226, Jan 1988. doi: 10.1103/PhysRevLett.60.224. URL http:// link.aps.org/doi/10.1103/PhysRevLett.60.224.

- F. Giustino. Materials Modelling Using Density Functional Theory: Properties and Predictions. Oxford University Press, 2014. ISBN 9780199662449.
- [10] M.A.L. Marques. Fundamentals of Time-Dependent Density Functional Theory. Lecture notes in physics. Springer, 2012. ISBN 9783642235184.
- [11] K. Petzinger and R. Munjal. Hyperfine field of positive muons in Ni. *Physical Review B*, 15:1560–1567, Feb 1977. doi: 10.1103/ PhysRevB.15.1560. URL http://link.aps. org/doi/10.1103/PhysRevB.15.1560.
- [12] S. Estreicher, A. Ray, J. Fry, and Dennis Marynick. Interstitial hydrogen in diamond: A detailed Hartree-Fock analysis. *Physical Review B*, 34:6071-6079, Nov 1986. doi: 10.1103/PhysRevB.34.6071. URL http: //link.aps.org/doi/10.1103/PhysRevB.34.6071.
- [13] P. Jena, Shashikala G. Das, and K. S. Singwi. Electric-field gradient at Cu nuclei due to an interstitial positive muon. *Physical Review Letters*, 40:264-266, Jan 1978. doi: 10.1103/PhysRevLett.40. 264. URL http://link.aps.org/doi/10.1103/ PhysRevLett.40.264.
- [14] Tom A. Claxton, Andrew Evans, and Martyn C. R. Symons. Self-consistent field cluster investigation of muonium-related paramagnetic centres in diamond. Journal of the Chemical Society, Faraday Transactions, 82:2031-2037, 1986. doi: 10.1039/ F29868202031. URL http://dx.doi.org/10. 1039/F29868202031.
- [15] Stefan Estreicher. Equilibrium sites and electronic structure of interstitial hydrogen in Si. Physical Review B, 36:9122-9128, Dec 1987. doi: 10.1103/PhysRevB.36. 9122. URL http://link.aps.org/doi/10.1103/ PhysRevB.36.9122.
- [16] R. Foronda, F. F. Lang, S. Möller, J. T. Lancaster, T. Boothroyd, A. L. Pratt, F. R. Giblin, S. D. Prabhakaran, and J. Blundell, S. Anisotropic Local Modification of Crystal Field Levels in Pr-Based Pyrochlores: A Muon-Induced Effect Modeled Using Density Functional Theory. *Physical Review Letters*, 114:017602, Jan 2015. doi: 10.1103/PhysRevLett.114. 017602. URL http://link.aps.org/doi/10. 1103/PhysRevLett.114.017602.

- [17] Stephen J. Blundell, Johannes S. Möller, Tom Lancaster, Peter J. Baker, Francis L. Pratt, Gonca Seber, and Paul M. Lahti. µSR study of magnetic order in the organic quasi-one-dimensional ferromagnet F4BImNN. Physical Review B, 88:064423, Aug 2013. doi: 10.1103/PhysRevB.88. 064423. URL http://link.aps.org/doi/10. 1103/PhysRevB.88.064423.
- [18] J. S. Möller, D. Ceresoli, T. Lancaster, N. Marzari, and S. J. Blundell. Quantum states of muons in fluorides. *Physi*cal Review B, 87:121108, Mar 2013. doi: 10.1103/PhysRevB.87.121108. URL http:// link.aps.org/doi/10.1103/PhysRevB.87.121108.
- [19] J S Möller, P Bonfà, D Ceresoli, F Bernardini, S J Blundell, T Lancaster, R De Renzi, N Marzari, I Watanabe, S Sulaiman, and M I Mohamed-Ibrahim. Playing quantum hide-and-seek with the muon: localizing muon stopping sites. *Physica Scripta*, 88(6): 068510, 2013. URL http://stacks.iop.org/ 1402-4896/88/i=6/a=068510.
- [20] R. C. Vilão, A. G. Marinopoulos, R. B. L. Vieira, A. Weidinger, H. V. Alberto, J. Piroto Duarte, J. M. Gil, J. S. Lord, and S. F. J. Cox. Hydrogen impurity in paratellurite α-TeO<sub>2</sub>: Muon-spin rotation and ab initio studies. *Physical Review B*, 84: 045201, Jul 2011. doi: 10.1103/PhysRevB. 84.045201. URL http://link.aps.org/doi/10. 1103/PhysRevB.84.045201.
- [21] S S Mohd-Tajudin, S N A Ahmad, D F Hasan-Baseri, E Suprayoga, N Adam, Rozlan A F, S Sulaiman, M I Mohamed-Ibrahim, and I Watanabe. An investigation of muon sites in YBa 2 Cu 3 O 6 by using Density Functional Theory. Journal of Physics: Conference Series, 551(1):012052, 2014. URL http://stacks.iop.org/1742-6596/ 551/i=1/a=012052.
- [22] Jun Sugiyama, Hiroshi Nozaki, Kazutoshi Miwa, Hiroyuki Yoshida, Masaaki Isobe, Krunoslav Prša, Alex Amato, Daniel Andreica, and Martin Månsson. Partially disordered spin structure in Ag<sub>2</sub>CrO<sub>2</sub> studied with μ<sup>+</sup>SR. Physical Review B, 88: 184417, Nov 2013. doi: 10.1103/PhysRevB. 88.184417. URL http://link.aps.org/doi/10. 1103/PhysRevB.88.184417.
- [23] Steven M. Disseler. Direct evidence for the all-in/all-out magnetic structure in the pyrochlore iridates from muon spin relaxation. *Physical Review B*, 89:140413, Apr 2014. doi: 10.1103/PhysRevB.89.140413. URL http:// link.aps.org/doi/10.1103/PhysRevB.89.140413.
- [24] B Adiperdana, E Suprayoga, N Adam, S S Mohd-Tajudin, A F Rozlan, S Sulaiman, M I Mohamed-Ibrahim, T Kawamata, T Adachi, I A Dharmawan, R E Siregar, Y Koike, and I Watanabe. An Effect of the Supercell Calculation on Muon

Positions and Local Deformations of Crystal Structure in La 2 CuO 4. Journal of Physics: Conference Series, 551(1):012051, 2014. URL http://stacks.iop.org/1742-6596/ 551/i=1/a=012051.

- [25] M I J Probert and A J Fisher. An ab initio study of muons in ethanal. Journal of Physics: Condensed Matter, 9(15):3241, 1997. URL http://stacks.iop.org/0953-8984/ 9/i=15/a=015.
- [26] Robert H Heffner and Kanetada Nagamine. Special issue on µSR: muon spin rotation, relaxation or resonance. Journal of Physics: Condensed Matter, 16(40), Sep 2004. ISSN 1361-648X. doi: 10.1088/0953-8984/16/ 40/e01. URL http://dx.doi.org/10.1088/ 0953-8984/16/40/e01.
- [27] P. Réotier and A. Yaouanc. Muon spin rotation and relaxation in magnetic materials. Journal of Physics: Condensed Matter, 9:9113, 1997. doi: 10.1088/0953-8984/ 9/43/002. URL http://iopscience.iop.org/ 0953-8984/9/43/002.
- [28] A Amato. Heavy-fermion systems studied by µSR technique. Reviews of Modern Physics, 69(1991), 1997. URL http://rmp. aps.org/abstract/RMP/v69/i4/p1119\_1.
- [29] A. Yaouanc and P.D. de Réotier. Muon Spin Rotation, Relaxation, and Resonance: Applications to Condensed Matter. International Series of Monographs on Physics. OUP Oxford, 2011. ISBN 9780199596478.
- [30] C. S. Wu. Experimental Test of Parity Conservation in Beta Decay. *Physical Review*, 105(4):1413-1415, February 1957. ISSN 0031-899X. doi: 10.1103/PhysRev. 105.1413. URL http://link.aps.org/doi/10. 1103/PhysRev.105.1413.
- [31] T. D. Lee and C. N. Yang. Question of Parity Conservation in Weak Interactions. *Physical Review*, 104:254-258, Oct 1956. doi: 10.1103/PhysRev.104.254. URL http: //link.aps.org/doi/10.1103/PhysRev.104.254.
- [32] Chappert J. and Grynszpan R.I. Muons and pions in materials research. North-Holland, 1984.
- [33] D. K. Brice. Effect of surface impurities on low-energy implanted-ion depth distributions. *Physical Review B*, 18:990-994, Aug 1978. doi: 10.1103/PhysRevB.18. 990. URL http://link.aps.org/doi/10.1103/ PhysRevB.18.990.
- [34] G. W. Ford and C. J. Mullin. Scattering of Polarized Dirac Particles on Electrons. *Physical Review*, 108:477-481, Oct 1957. doi: 10.1103/PhysRev.108.477. URL http: //link.aps.org/doi/10.1103/PhysRev.108.477.

- [35] H. Frauenfelder, E.M. Henley, and A. Garcia. Subatomic physics. Prentice-Hall, 1974. ISBN 0138590826.
- [36] NIST. CODATA values online. http://physics.nist.gov/constants, 2014.
- [37] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo. Zero-and low-field spin relaxation studied by positive muons. *Physical Review B*, 20:850-859, Aug 1979. doi: 10.1103/ PhysRevB.20.850. URL http://link.aps. org/doi/10.1103/PhysRevB.20.850.
- [38] Amit Keren. Generalization of the Abragam relaxation function to a longitudinal field. *Physical Review B*, 50:10039-10042, Oct 1994. doi: 10.1103/PhysRevB. 50.10039. URL http://link.aps.org/doi/10. 1103/PhysRevB.50.10039.
- [39] A. Abragam. The Principles of Nuclear Magnetism. International series of monographs on physics. Clarendon Press, 1961.
- [40] M. Celio and P. F. Meier. Spin relaxation of positive muons due to dipolar interactions. *Physical Review B*, 27:1908-1910, Feb 1983. doi: 10.1103/PhysRevB.27.1908. URL http: //link.aps.org/doi/10.1103/PhysRevB.27.1908.
- [41] J.H. Brewer, S.R. Kreitzman, D.R. Noakes, E.J. Ansaldo, D.R. Harshman, and R. Keitel. Observation of muon-fluorine" hydrogen bonding" in ionic crystals. *Physical Review B*, 33(11):7813–7816, 1986. URL http: //prb.aps.org/abstract/PRB/v33/i11/p7813\_1.
- [42] D. R. Noakes, E. J. Ansaldo, S. R. Kreitzman, and G. M. Luke. The FµF ion in solid fluorides. Journal of Physics and Chemistry of Solids, 54(7):785–792, 1993.
- [43] T. U. Ito, W. Higemoto, K. Ohishi, N. Nishida, R. H. Heffner, Y. Aoki, A. Amato, T. Onimaru, and H. S. Suzuki. Quantized Hyperfine Field at an Implanted μ<sup>+</sup> Site in PrPb<sub>3</sub>: Interplay between Localized f Electrons and an Interstitial Charged Particle. Physical Review Letters, 102:096403, Mar 2009. doi: 10.1103/PhysRevLett.102. 096403. URL http://link.aps.org/doi/10. 1103/PhysRevLett.102.096403.
- [44] A. Amato, P. Dalmas de Réotier, D. Andreica, A. Yaouanc, A. Suter, G. Lapertot, I. M. Pop, E. Morenzoni, P. Bonfa, F. Bernardini, and R. De Renzi. Understanding the μSR spectra of MnSi without magnetic polarons. *Physical Review B*, 89: 184425, May 2014. doi: 10.1103/PhysRevB. 89.184425. URL http://link.aps.org/doi/10. 1103/PhysRevB.89.184425.
- [45] T. Lancaster, S. J. Blundell, P. J. Baker, W. Hayes, S. R. Giblin, S. E. McLain, F. L. Pratt, Z. Salman, E. A. Jacobs, J. F. C.

Turner, and T. Barnes. Intrinsic magnetic order in  $\rm Cs_2AgF_4$  detected by muonspin relaxation. Physical Review B, 75: 220408, Jun 2007. doi: 10.1103/PhysRevB. 75.220408. URL http://link.aps.org/doi/10.1103/PhysRevB.75.220408.

- [46] Mauro Riccò, Daniele Pontiroli, Marcello Mazzani, Mohammad Choucair, John A. Stride, and Oleg V. Yazyev. Muons Probe Strong Hydrogen Interactions with Defective Graphene. Nano Letters, 11(11):4919– 4922, 2011. doi: 10.1021/nl202866q. URL http://dx.doi.org/10.1021/nl202866q. PMID: 21988328.
- [47] M Riccò, M Aramini, M Mazzani, D Pontiroli, M Gaboardi, and O V Yazyev. Muons probe magnetism and hydrogen interaction in graphene. *Physica Scripta*, 88(6):068508, 2013. URL http://stacks.iop.org/1402-4896/ 88/i=6/a=068508.
- [48] Anton Potocnik, Andrej Zorko, Denis Arcon, Evgenij Goreshnik, Boris Zemva, Robert Blinc, Pavel Cevc, Zvonko Trontelj, Zvonko Jaglicić, and James F. Scott. Muon spin relaxation in some multiferroic fluorides. *Physical Review B*, 81:214420, Jun 2010. doi: 10.1103/PhysRevB.81. 214420. URL http://link.aps.org/doi/10. 1103/PhysRevB.81.214420.
- [49] T Lancaster, F L Pratt, S J Blundell, I McKenzie, and H E Assender. Muon-fluorine entanglement in fluoropolymers. Journal of Physics: Condensed Matter, 21(34):346004, 2009. URL http://stacks. iop.org/0953-8984/21/i=34/a=346004.
- [50] T. Lancaster, S. J. Blundell, P. J. Baker, M. L. Brooks, W. Hayes, F. L. Pratt, J. L. Manson, M. M. Conner, and J. A. Schlueter. Muon-Fluorine Entangled States in Molecular Magnets. *Physical Review Letters*, 99:267601, Dec 2007. doi: 10.1103/ PhysRevLett.99.267601. URL http://link. aps.org/doi/10.1103/PhysRevLett.99.267601.
- [51] A. Abragam. Spectrométrie par croisements de niveaux en physique du muon. Comptes Rendus des Séances de l'Académie des Sciences Paris, Serie II, 299:95-100, 1984. URL http://visualiseur.bnf.fr/ark: /12148/bpt6k6139155c.
- [52] Meier P. F. Electron densities at charged impurities in metals. *Helvetica Physica Acta*, 48:227-241, 1975. doi: 10.5169/ seals-114673. URL http://retro.seals.ch/ digbib/view?pid=hpa-001:1975:48::838.
- [53] Chris G. Van de Walle. Structural identification of hydrogen and muonium centers in silicon: First-principles calculations of hyperfine parameters. *Physical Review Letters*, 64:669-672, Feb 1990. doi: 10.1103/ PhysRevLett.64.669. URL http://link.aps. org/doi/10.1103/PhysRevLett.64.669.

- [54] H. Katayama, K. Terakura, and J. Kanamori. Hyperfine field of positive muon in ferromagnetic nickel. Solid State Communications, 29(5):431 - 434, 1979. ISSN 0038-1098. doi: 10.1016/0038-1098(79)91210-9. URL http://www.sciencedirect.com/science/ article/pii/0038109879912109.
- [55] J. Rath, M. Manninen, P. Jena, and C.S. Wang. Effect of zero point motion on the hyperfine field at an interstitial positive muon site in ferromagnetic Ni. Solid State Communications, 31(12):1003 - 1007, 1979. ISSN 0038-1098. doi: 10.1016/0038-1098(79) 90019-X. URL http://www.sciencedirect. com/science/article/pii/003810987990019X.
- [56] N. Sahoo, K.C. Mishra, and T.P. Das. Hartree-fock cluster investigation of location and hyperfine properties of normal muonium in silicon-trend with respect to diamond. *Hyperfine Interactions*, 32(1-4): 601-606, 1986. ISSN 0304-3843. doi: 10. 1007/BF02394962. URL http://dx.doi.org/ 10.1007/BF02394962.
- [57] N. Sahoo, K. C. Mishra, and T. P. Das. Identification of anomalous muonium in semiconductors as a vacancy-associated center. *Physical Review Letters*, 55:1506– 1509, Sep 1985. doi: 10.1103/PhysRevLett. 55.1506. URL http://link.aps.org/doi/10. 1103/PhysRevLett.55.1506.
- [58] M. Manninen and P. Jena. Self-consistent calculation of hyperfine fields at impurity sites in ferromagnetic host. *Physical Re*view B, 22:2411-2419, Sep 1980. doi: 10. 1103/PhysRevB.22.2411. URL http://link. aps.org/doi/10.1103/PhysRevB.22.2411.
- [59] A Mainwood and A M Stoneham. Interstitial muons and hydrogen in diamond and silicon. Journal of Physics C: Solid State Physics, 17(14):2513, 1984. URL http:// stacks.iop.org/0022-3719/17/i=14/a=009.
- [60] ShukriB. Sulaiman, N. Sahoo, Sudha Srinivas, F. Hagelberg, T.P. Das, E. Torikai, and K. Nagamine. Location and associated hyperfine properties of μ<sup>+</sup> in la2cuo4. Hyperfine Interactions, 79(1-4):901-907, 1993. ISSN 0304-3843. doi: 10.1007/BF00567625. URL http://dx.doi.org/10.1007/BF00567625.
- [61] Shukri B. Sulaiman, Sudha Srinivas, N. Sahoo, F. Hagelberg, T. P. Das, E. Torikai, and K. Nagamine. Theory of the location and associated hyperfine properties of the positive muon in la<sub>2</sub>cuo<sub>4</sub>. *Physical Review B*, 49:9879-9884, Apr 1994. doi: 10.1103/PhysRevB.49.9879. URL http://link.aps.org/doi/10.1103/PhysRevB.49.9879.
- [62] H.U. Suter, E.P. Stoll, and P.F. Meier. Muon sites and hyperfine fields in La<sub>2</sub>CuO<sub>4</sub>. *Physica B: Condensed Matter*,

326(1-4):329 - 332, 2003. ISSN 0921-4526.doi: 10.1016/S0921-4526(02)01651-4. URL http://www.sciencedirect.com/science/ article/pii/S0921452602016514.

- [63] Rafael Ramírez and Carlos P. Herrero. Distinct quantum behavior of hydrogen and muonium in crystalline silicon. *Physical Review Letters*, 73:126-129, Jul 1994. doi: 10.1103/PhysRevLett.73.126. URL http:// link.aps.org/doi/10.1103/PhysRevLett.73.126.
- [64] P. Hohenberg and W. Kohn. Inhomogeneous Electron Gas. *Physical Review*, 136:B864-B871, Nov 1964. doi: 10.1103/PhysRev.136. B864. URL http://link.aps.org/doi/10.1103/ PhysRev.136.B864.
- [65] W. Kohn and L. J. Sham. Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review*, 140:A1133-A1138, Nov 1965. doi: 10.1103/PhysRev. 140.A1133. URL http://link.aps.org/doi/ 10.1103/PhysRev.140.A1133.
- [66] Erich Runge and E. K. U. Gross. Density-Functional Theory for Time-Dependent Systems. *Physical Review Letters*, 52:997– 1000, Mar 1984. doi: 10.1103/PhysRevLett. 52.997. URL http://link.aps.org/doi/10. 1103/PhysRevLett.52.997.
- [67] R.M. Martin. Electronic Structure: Basic Theory and Practical Methods. Cambridge University Press, 2004. ISBN 9780521782852.
- [68] G. Grosso and G.P. Parravicini. Solid State Physics. Elsevier Science, 2013. ISBN 9780123850317.
- [69] D.A. Drabold and S. Estreicher. Theory of Defects in Semiconductors. Topics in Applied Physics. Springer Berlin Heidelberg, 2010. ISBN 9783642070037.
- [70] T. L. Gilbert. Hohenberg-Kohn theorem for nonlocal external potentials. *Physical Review B*, 12:2111-2120, Sep 1975. doi: 10.1103/PhysRevB.12.2111. URL http:// link.aps.org/doi/10.1103/PhysRevB.12.2111.
- [71] Lin-Wang Wang and Michael P. Teter. Kinetic-energy functional of the electron density. *Physical Review B*, 45:13196-13220, Jun 1992. doi: 10.1103/PhysRevB. 45.13196. URL http://link.aps.org/doi/10. 1103/PhysRevB.45.13196.
- [72] Axel D. Becke. A new mixing of Hartree-Fock and local density-functional theories. *The Journal of Chemical Physics*, 98(2):1372, 1993. ISSN 0021-9606. doi: 10.1063/1.464304. URL http://dx.doi.org/ 10.1063/1.464304.

- [73] John P. Perdew, Matthias Ernzerhof, and Kieron Burke. Rationale for mixing exact exchange with density functional approximations. The Journal of Chemical Physics, 105(22):9982, 1996. ISSN 0021-9606. doi: 10.1063/1.472933. URL http://dx.doi.org/ 10.1063/1.472933.
- [74] D.R Bowler and M.J Gillan. An efficient and robust technique for achieving self consistency in electronic structure calculations. *Chemical Physics Letters*, 325(4):473 - 476, 2000. ISSN 0009-2614. doi: 10.1016/S0009-2614(00) 00750-8. URL http://www.sciencedirect.com/ science/article/pii/S0009261400007508.
- [75] Péter Pulay. Convergence acceleration of iterative sequences. the case of scf iteration . Chemical Physics Letters, 73(2):393 - 398, 1980. ISSN 0009-2614. doi: 10.1016/0009-2614(80)80396-4. URL http://www.sciencedirect.com/science/ article/pii/0009261460803964.
- [76] G P Srivastava. Broyden's method for self-consistent field convergence acceleration. Journal of Physics A: Mathematical and General, 17(6):L317, 1984. URL http: //stacks.iop.org/0305-4470/17/i=6/a=002.
- [77] D. M. Ceperley. Ground State of the Electron Gas by a Stochastic Method. *Physical Review Letters*, 45(7):566-569, Aug 1980.
  ISSN 0031-9007. doi: 10.1103/physrevlett.
  45.566. URL http://dx.doi.org/10.1103/ PhysRevLett.45.566.
- [78] R. O. Jones and O. Gunnarsson. The density functional formalism, its applications and prospects. *Reviews of Modern Physics*, 61:689-746, Jul 1989. doi: 10.1103/ RevModPhys.61.689. URL http://link.aps. org/doi/10.1103/RevModPhys.61.689.
- [79] John Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized Gradient Approximation Made Simple. *Physical Review Letters*, 77:3865–3868, Oct 1996. doi: 10.1103/ PhysRevLett.77.3865. URL http://link. aps.org/doi/10.1103/PhysRevLett.77.3865.
- [80] A. Becke. Density-functional exchangeenergy approximation with correct asymptotic behavior. *Physical Review A*, 38:3098-3100, Sep 1988. doi: 10.1103/PhysRevA.38. 3098. URL http://link.aps.org/doi/10.1103/ PhysRevA.38.3098.
- [81] John Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized Gradient Approximation Made Simple [Physical Review Letters 77, 3865 (1996)]. Physical Review Letters, 78:1396-1396, Feb 1997. doi: 10.1103/ PhysRevLett.78.1396. URL http://link. aps.org/doi/10.1103/PhysRevLett.78.1396.

- [82] John Perdew, J. Chevary, S. Vosko, Koblar Jackson, Mark Pederson, D. Singh, and Carlos Fiolhais. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Physical Review B*, 46:6671– 6687, Sep 1992. doi: 10.1103/PhysRevB.46. 6671. URL http://link.aps.org/doi/10.1103/ PhysRevB.46.6671.
- [83] Hendrik J. Monkhorst and James D. Pack. Special points for Brillouin-zone integrations. *Physical Review B*, 13:5188-5192, Jun 1976. doi: 10.1103/PhysRevB.13. 5188. URL http://link.aps.org/doi/10.1103/ PhysRevB.13.5188.
- [84] A. Baldereschi. Mean-value point in the brillouin zone. *Physical Review B*, 7:5212-5215, Jun 1973. doi: 10.1103/PhysRevB.7. 5212. URL http://link.aps.org/doi/10.1103/ PhysRevB.7.5212.
- [85] D. R. Hamann, M. Schlüter, and C. Chiang. Norm-Conserving Pseudopotentials. *Physical Review Letters*, 43:1494-1497, Nov 1979. doi: 10.1103/PhysRevLett.43. 1494. URL http://link.aps.org/doi/10.1103/ PhysRevLett.43.1494.
- [86] David Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B*, 41:7892-7895, Apr 1990. doi: 10.1103/PhysRevB.41. 7892. URL http://link.aps.org/doi/10.1103/ PhysRevB.41.7892.
- [87] P. E. Blöchl. Projector augmented-wave method. Physical Review B, 50:17953-17979, Dec 1994. doi: 10.1103/PhysRevB. 50.17953. URL http://link.aps.org/doi/10. 1103/PhysRevB.50.17953.
- [88] J. C. Slater. Wave Functions in a Periodic Potential. *Physical Review*, 51:846-851, May 1937. doi: 10.1103/PhysRev.51. 846. URL http://link.aps.org/doi/10.1103/ PhysRev.51.846.
- [89] J. C. Slater. A Simplification of the Hartree-Fock Method. *Physical Review*, 81:385-390, Feb 1951. doi: 10.1103/PhysRev.81. 385. URL http://link.aps.org/doi/10.1103/ PhysRev.81.385.
- [90] O. Krogh Andersen. Linear methods in band theory. *Physical Review B*, 12:3060-3083, Oct 1975. doi: 10.1103/PhysRevB.12. 3060. URL http://link.aps.org/doi/10.1103/ PhysRevB.12.3060.
- [91] David Singh. Ground-state properties of lanthanum: Treatment of extended-core states. *Physical Review B*, 43:6388-6392, Mar 1991. doi: 10.1103/PhysRevB.43. 6388. URL http://link.aps.org/doi/10.1103/ PhysRevB.43.6388.

- [92] E Sjöstedt, L Nordström, and D J Singh. An alternative way of linearizing the augmented plane-wave method. Solid State Communications, 114(1):15-20, 2000. ISSN 00381098. doi: 10.1016/S0038-1098(99) 00577-3. URL http://linkinghub.elsevier. com/retrieve/pii/S0038109899005773.
- [93] P. Blaha, D. J. Singh, P. I. Sorantin, and K. Schwarz. Electric-field-gradient calculations for systems with large extendedcore-state contributions. *Physical Review* B, 46:1321-1325, Jul 1992. doi: 10.1103/ PhysRevB.46.1321. URL http://link.aps. org/doi/10.1103/PhysRevB.46.1321.
- [94] Kay Dewhurst, Sangeeta Sharma, Lars Nordström, Francesco Cricchio, Fredrik Bultmark, Oscar Grånäs, Hardy Gross, Clas Persson, Claudia Ambrosch-Draxl, Christian Brouder, Rickard Armiento, Andrew Chizmeshya, Per Anderson, Igor Nekrasov, Frank Wagner, Fateh Kalarasse, Jürgen Spitaler, Stefano Pittalis, Nektarios Lathiotakis, Tobias Burnus, Stephan Sagmeister, Christian Meisenbichler, Sébastien Lebègue, Yigang Zhang, Fritz Körmann, Alexey Baranov, Anton Kozhevnikov, Shigeru Suehara, Frank Essenberger, Antonio Sanna, Tyrel McQueen, Tim Baldsiefen, Marty Blaber, Anton Filanovich, Torb-jörn Björkman, Martin Stankovski, Jerzy Goraus, Markus Meinert, Daniel Rohr, Vladimir Nazarov, Kevin Krieger, Pink Floyd, Arkardy Davydov, Florian Eich, Aldo Romero Castro, Koichi Kitahara, James Glasbrenner, Konrad Bussmann, Igor Mazin, Matthieu Verstraete, Elk, An all-electron full-potential linearised augmented-plane wave (FP-LAPW) code, http://www.wien2k.at.
- [95] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria), 2001. ISBN 3-9501031-1-2, http://www.wien2k.at.
- [96] H Ebert, D Ködderitzsch, and J Minár. Calculating condensed matter properties using the KKR-Green's function methodrecent developments and applications. *Reports on Progress in Physics*, 74(9):096501, 2011. URL http://stacks.iop.org/0034-4885/ 74/i=9/a=096501.
- [97] J Lento, J-L Mozos, and R M Nieminen. Charged point defects in semiconductors and the supercell approximation. Journal of Physics: Condensed Matter, 14(10):2637, 2002. URL http://stacks.iop.org/0953-8984/ 14/i=10/a=314.
- [98] G. Makov and M. C. Payne. Periodic boundary conditions in *ab initio* calculations. *Physical Review B*, 51:4014-4022, Feb 1995. doi: 10.1103/PhysRevB.51.4014. URL http: //link.aps.org/doi/10.1103/PhysRevB.51.4014.

- [99] M. R. Jarvis, I. D. White, R. W. Godby, and M. C. Payne. Supercell technique for totalenergy calculations of finite charged and polar systems. *Physical Review B*, 56:14972– 14978, Dec 1997. doi: 10.1103/PhysRevB. 56.14972. URL http://link.aps.org/doi/10. 1103/PhysRevB.56.14972.
- [100] M Leslie and N J Gillan. The energy and elastic dipole tensor of defects in ionic crystals calculated by the supercell method. *Journal of Physics C: Solid State Physics*, 18 (5):973, 1985. URL http://stacks.iop.org/ 0022-3719/18/i=5/a=005.
- [101] G. Prando, P. Bonfà, G. Profeta, R. Khasanov, F. Bernardini, M. Mazzani, E. M. Brüning, A. Pal, V. P. S. Awana, H.-J. Grafe, B. Büchner, R. De Renzi, P. Carretta, and S. Sanna. Common effect of chemical and external pressures on the magnetic properties of *RCoPO (R = La*, Pr). *Physical Review B*, 87:064401, Feb 2013. doi: 10.1103/PhysRevB.87.064401. URL http://link.aps.org/doi/10.1103/ PhysRevB.87.064401.
- [102] F. Bernardini, P. Bonfà, S. Massidda, and R. De Renzi. Ab initio strategy for muon site assignment in wide band gap fluorides. *Physical Review B*, 87:115148, Mar 2013. doi: 10.1103/PhysRevB.87. 115148. URL http://link.aps.org/doi/10. 1103/PhysRevB.87.115148.
- [103] Takashi Miyake, Tadashi Ogitsu, and Shinji Tsuneyuki. Quantum Distributions of Muonium and Hydrogen in Crystalline Silicon. *Physical Review Letters*, 81:1873-1876, Aug 1998. doi: 10.1103/PhysRevLett.81. 1873. URL http://link.aps.org/doi/10.1103/ PhysRevLett.81.1873.
- [104] R.M. Valladares, A.J. Fisher, and W. Hayes. Path-integral simulations of zero-point effects for implanted muons in benzene. *Chemical Physics Letters*, 242:1 - 6, 1995. ISSN 0009-2614. doi: 10.1016/0009-2614(95)00771-U. URL http://www.sciencedirect.com/science/ article/pii/000926149500771U.
- [105] a Kerridge, a H Harker, and a M Stoneham. Quantum behaviour of hydrogen and muonium in vacancy-containing complexes in diamond. Journal of Physics: Condensed Matter, 16(47):8743-8751, December 2004. ISSN 0953-8984. doi: 10. 1088/0953-8984/16/47/024. URL http:// stacks.iop.org/0953-8984/16/i47/a=024?key= crossref.ff?edb17ee9eb6a7c0c5f33f503c7160.
- [106] N. I. Gidopoulos and E. K. U. Gross. Electronic non-adiabatic states: towards a density functional theory beyond the Born-Oppenheimer approximation. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 372(2011):20130059-20130059, Feb

2014. ISSN 1471-2962. doi: 10.1098/rsta. 2013.0059. URL http://dx.doi.org/10.1098/ rsta.2013.0059.

- [107] Alexander V. Soudackov and Sharon Hammes-Schiffer. Removal of the double adiabatic approximation for protoncoupled electron transfer reactions in solution. Chemical Physics Letters, 299 (5):503 - 510, 1999. ISSN 0009-2614. doi: 10.1016/S0009-2614(98)01347-5. URL http://www.sciencedirect.com/science/ article/pii/S0009261498013475.
- [108] Simon P. Webb, Tzvetelin Iordanov, and Sharon Hammes-Schiffer. Multiconfigurational nuclear-electronic orbital approach: Incorporation of nuclear quantum effects in electronic structure calculations. The Journal of Chemical Physics, 117(9):4106-4118, 2002. doi: 10.1063/1.1494980. URL http://scitation.aip.org/content/aip/ journal/jcp/117/9/10.1063/1.1494980.
- [109] A. R. Porter, M. D. Towler, and R. J. Needs. Muonium as a hydrogen analogue in silicon and germanium: Quantum effects and hyperfine parameters. *Physical Review B*, 60:13534-13546, Nov 1999. doi: 10.1103/ PhysRevB.60.13534. URL http://link.aps. org/doi/10.1103/PhysRevB.60.13534.
- [110] Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso, and Paolo Giannozzi. Phonons and related crystal properties from density-functional perturbation theory. Reviews of Modern Physics, 73:515-562, Jul 2001. doi: 10.1103/RevModPhys.73. 515. URL http://link.aps.org/doi/10.1103/ RevModPhys.73.515.
- [111] Yoichi Kamihara, Takumi Watanabe, Masahiro Hirano, and Hideo Hosono. Iron-Based Layered Superconductor  $La[O_{1-x}F_x]FeAs$  (x = 0.05-0.12) with  $T_c$ = 26 K. Journal of the American Chemical Society, 130(11):3296-3297, Mar 2008. ISSN 1520-5126. doi: 10.1021/ja800073m. URL http://dx.doi.org/10.1021/ja800073m.
- [112] Hiroki Takahashi, Kazumi Igawa, Kazunobu Arii, Yoichi Kamihara, Masahiro Hirano, and Hideo Hosono. Superconductivity at 43 K in an iron-based layered compound LaO<sub>1-x</sub>F<sub>x</sub>FeAs. Nature, 453 (7193):376-378, Apr 2008. ISSN 1476-4687. doi: 10.1038/nature06972. URL http://dx.doi.org/10.1038/nature06972.
- [113] H. Luetkens, H.-H. Klauss, M. Kraken, F. J. Litterst, T. Dellmann, R. Klingeler, C. Hess, R. Khasanov, A. Amato, C. Baines, M. Kosmala, O. J. Schumann, M. Braden, J. Hamann-Borrero, N. Leps, A. Kondrat, G. Behr, J. Werner, and B. Büchner. The electronic phase diagram of the LaO<sub>1-x</sub>F<sub>x</sub>FeAs superconductor. Nat Mater, 8(4):305-309, Apr 2009. ISSN 1476-1122. doi: 10.1038/nmat2397. URL http: //dx.doi.org/10.1038/nmat2397.

- [114] I. M. Reznik, F. G. Vagizov, and R. Troć. Chemical bonding in the UFe1-xNixAl alloys. *Physical Review B*, 51:3013-3020, Feb 1995. doi: 10.1103/PhysRevB.51. 3013. URL http://link.aps.org/doi/10.1103/ PhysRevB.51.3013.
- [115] H. Maeter, H. Luetkens, Yu. Y.G. Pashkevich, a. Kwadrin, R. Khasanov, a. Amato, AA Gusev, KV Lamonova, D. DA Chervinskii, R. Klingeler, Others, C. Hess, G. Behr, B. Büchner, and H.-H. Klauss. Interplay of rare earth and iron magnetism in RFeAsO (R= La, Ce, Pr, and Sm): Muon-spin relaxation study and symmetry analysis. *Physical Review B*, 80(9): 094524, September 2009. ISSN 1098-0121. doi: 10.1103/PhysRevB.80.094524. URL http://link.aps.org/doi/10.1103/PhysRevB. 80.094524http://prb.aps.org/abstract/PRB/ v80/19/e094524.
- [116] M. Bendele, A. Ichsanow, Yu. Pashkevich, L. Keller, Th. Strässle, A. Gusev, E. Pomjakushina, K. Conder, R. Khasanov, and H. Keller. Coexistence of superconductivity and magnetism in FeSe<sub>1-x</sub> under pressure. *Physical Review B*, 85:064517, Feb 2012. doi: 10.1103/PhysRevB.85.064517. URL http:// link.aps.org/doi/10.1103/PhysRevB.85.064517.
- [117] S. Sanna, P. Carretta, R. De Renzi, G. Prando, P. Bonfà, M. Mazzani, G. Lamura, T. Shiroka, Y. Kobayashi, and M. Sato. Onset of magnetism in optimally electron-doped  $LFe_{1-x}Ru_xAsO_{1-y}F_y$ (L = La, Nd, or Sm) superconductors around  $x = \frac{1}{4}$ . *Physical Review B*, 87:134518, Apr 2013. doi: 10.1103/PhysRevB.87.134518. URL http://link.aps.org/doi/10.1103/PhysRevB. 87.134518.
- [118] G Lamura, T Shiroka, P Bonfà, S Sanna, R De Renzi, F Caglieris, M R Cimberle, S Iimura, H Hosono, and M Putti. Crossover between magnetism and superconductivity in LaFeAsO with low H-doping level. Journal of Physics: Condensed Matter, 26(29): 295701, 2014. URL http://stacks.iop.org/ 0953-8984/26/i=29/a=295701.
- [119] A. J. Drew, Ch. Niedermayer, P. J. Baker, F. L. Pratt, S. J. Blundell, T. Lancaster, R. H. Liu, G. Wu, X. H. Chen, I. Watanabe, and et al. Coexistence of static magnetism and superconductivity in SmFeAsO<sub>1-x</sub>F<sub>x</sub> as revealed by muon spin rotation. *Nature Materials*, 8(4):310-314, Feb 2009. ISSN 1476-4660. doi: 10.1038/nmat2396. URL http://dx.doi.org/10.1038/nmat2396.
- [120] Anton Kokalj. Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale. *Computational Materials Science*, 28(2): 155 - 168, 2003. ISSN 0927-0256. doi: 10.1016/S0927-0256(03)00104-6. URL http://www.sciencedirect.com/science/

article/pii/S0927025603001046. Proceedings of the Symposium on Software Development for Process and Materials Design.

- [121] Roberto De Renzi, Pietro Bonfà, Marcello Mazzani, Samuele Sanna, Giacomo Prando, Pietro Carretta, Rustem Khasanov, Alex Amato, Hubertus Luetkens, Markus Bendele, Fabio Bernardini, Sandro Massidda, Andrea Palenzona, Matteo Tropeano, and Maurizio Vignolo. Effect of external pressure on the magnetic properties of LnFeAsO (Ln = La, Ce, Pr, Sm). Superconductor Science and Technology, 25 (8):084009, August 2012. ISSN 0953-2048. doi: 10.1088/0953-2048/25/8/ 084009. URL http://stacks.iop.org/ 0953-2048/25/i=8/a=084009?key=crossref. 421bc970dc0148f190e220672ab4ebf6.
- [122] M D Lumsden and A D Christianson. Magnetism in Fe-based superconductors. Journal of Physics: Condensed Matter, 22(20): 203203, 2010. URL http://stacks.iop.org/ 0953-8984/22/i=20/a=203203.
- [123] N. Qureshi, Y. Drees, J. Werner, S. Wurmehl, C. Hess, R. Klingeler, B. Büchner, M. T. Fernández-Díaz, and M. Braden. Crystal and magnetic structure of the oxypnictide superconductor LaFeAsO<sub>1-x</sub>F<sub>x</sub>: A neutron-diffraction study. *Physical Review B*, 82:184521, Nov 2010. doi: 10.1103/PhysRevB.82.184521. URL http://link.aps.org/doi/10.1103/ PhysRevB.82.184521.
- [124] H-J Grafe, G Lang, F Hammerath, D Paar, K Manthey, K Koch, H Rosner, N J Curro, G Behr, J Werner, N Leps, R Klingeler, H-H Klauss, F J Litterst, and B Büchner. Electronic properties of  $LaO_{1-x}$  $F_x$  FeAs in the normal state probed by NMR/NQR. New Journal of Physics, 11(3): 035002, 2009. URL http://stacks.iop.org/ 1367-2630/11/i=3/a=035002.
- [125] Koichi Momma and Fujio Izumi. VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data. Journal of Applied Crystallography, 44(6): 1272-1276, Dec 2011. doi: 10.1107/ S0021889811038970. URL http://dx.doi. org/10.1107/S0021889811038970.
- [126] G Lamura, T Shiroka, P Bonfà, S Sanna, F Bernardini, R De Renzi, R Viennois, E Giannini, A Piriou, N Emery, M R Cimberle, and M Putti. A magnetic glassy phase in Fe<sub>1+y</sub>Se<sub>x</sub>Te<sub>1-x</sub> single crystals. Journal of Physics: Condensed Matter, 25(15): 156004, 2013. URL http://stacks.iop.org/ 0953-8984/25/i=15/a=156004.
- [127] Yoshikazu Mizuguchi, Fumiaki Tomioka, Shunsuke Tsuda, Takahide Yamaguchi, and Yoshihiko Takano. Substitution Effects on FeSe Superconductor. Journal of the Physical Society of Japan, 78(7):074712, 2009.

doi: 10.1143/JPSJ.78.074712. URL http: //dx.doi.org/10.1143/JPSJ.78.074712.

- [128] Yoshikazu Mizuguchi and Yoshihiko Takano. Review of Fe Chalcogenides as the Simplest Fe-Based Superconductor. Journal of the Physical Society of Japan, 79(10):102001, 2010. doi: 10.1143/JPSJ.79.102001. URL http://dx.doi.org/10.1143/JPSJ.79.102001.
- [129] Yoshikazu Mizuguchi, Fumiaki Tomioka, Shunsuke Tsuda, Takahide Yamaguchi, and Yoshihiko Takano. Superconductivity in Ssubstituted FeTe. Applied Physics Letters, 94 (1):012503, 2009. doi: 10.1063/1.3058720. URL http://scitation.aip.org/content/aip/ journal/apl/94/1/10.1063/1.3058720.
- [130] Y. Han, W. Li, L. Cao, X. Wang, B. Xu, B. Zhao, Y. Guo, and J. Yang. Superconductivity in Iron Telluride Thin Films under Tensile Stress. *Physical Review Letters*, 104:017003, Jan 2010. doi: 10.1103/ PhysRevLett.104.017003. URL http://link. aps.org/doi/10.1103/PhysRevLett.104.017003.
- [131] H. Okabe, N. Takeshita, K. Horigane, T. Muranaka, and J. Akimitsu. Pressureinduced high-T<sub>c</sub> superconducting phase in FeSe: Correlation between anion height and T<sub>c</sub>. Physical Review B, 81:205119, May 2010. doi: 10.1103/PhysRevB.81. 205119. URL http://link.aps.org/doi/10. 1103/PhysRevB.81.205119.
- [132] Jian-Feng Ge, Zhi-Long Liu, Canhua Liu, Chun-Lei Gao, Dong Qian, Qi-Kun Xue, Ying Liu, and Jin-Feng Jia. Superconductivity above 100 K in single-layer FeSe films on doped SrTiO<sub>3</sub>. Nature Materials, Nov 2014. ISSN 1476-4660. doi: 10.1038/ nmat4153. URL http://dx.doi.org/10.1038/ nmat4153.
- [133] A. Martinelli, A. Palenzona, M. Tropeano, C. Ferdeghini, M. Putti, M. R. Cimberle, T. D. Nguyen, M. Affronte, and C. Ritter. From antiferromagnetism to superconductivity in Fe<sub>1+y</sub> Te<sub>1-x</sub>Se<sub>x</sub> (0 ≤ x ≤ 0.20): Neutron powder diffraction analysis. *Physical Review B*, 81:094115, Mar 2010. doi: 10.1103/PhysRevB.81.094115. URL http:// link.aps.org/doi/10.1103/PhysRevB.81.094115.
- [134] Athena Sefat, Ashfia Huq, Michael McGuire, Rongying Jin, Brian Sales, David Mandrus, Lachlan Cranswick, Peter Stephens, and Kevin Stone. Superconductivity in LaFe<sub>1-x</sub>Co<sub>x</sub>AsO. *Physical Review B*, 78:104505, Sep 2008. doi: 10.1103/PhysRevB.78.104505. URL http:// link.aps.org/doi/10.1103/PhysRevB.78.104505.
- [135] Athena Sefat, Rongying Jin, Michael McGuire, Brian Sales, David Singh, and David Mandrus. Superconductivity at 22 K in Co-Doped BaFe2As2 Crystals. *Physical Review Letters*, 101:117004, Sep

2008. doi: 10.1103/PhysRevLett.101. 117004. URL http://link.aps.org/doi/10. 1103/PhysRevLett.101.117004.

- [136] H. Wadati, I. Elfimov, and G. Sawatzky. Where Are the Extra d Electrons in Transition-Metal-Substituted Iron Pnictides? Physical Review Letters, 105:157004, Oct 2010. doi: 10.1103/PhysRevLett.105.157004. URL http://link.aps.org/doi/10.1103/ PhysRevLett.105.157004.
- [137] Tom Berlijn, Chia-Hui Lin, William Garber, and Wei Ku. Do Transition-Metal Substitutions Dope Carriers in Iron-Based Superconductors? *Physical Review Letters*, 108:207003, May 2012. doi: 10.1103/ PhysRevLett.108.207003. URL http://link. aps.org/doi/10.1103/PhysRevLett.108.207003.
- [138] E. Bittar, C. Adriano, T. Garitezi, P. Rosa, L. Mendon ca Ferreira, F. Garcia, G. de M. Azevedo, P. Pagliuso, and E. Granado. Co-Substitution Effects on the Fe Valence in the BaFe<sub>2</sub>As<sub>2</sub> Superconducting Compound: A Study of Hard X-Ray Absorption Spectroscopy. *Physical Review Letters*, 107:267402, Dec 2011. doi: 10.1103/ PhysRevLett.107.267402. URL http://link. aps.org/doi/10.1103/PhysRevLett.107.267402.
- [139] M. Merz, F. Eilers, Th. Wolf, P. Nagel, H. v. Löhneysen, and S. Schuppler. Electronic structure of single-crystalline  $Sr(Fe_{1-x}Co_x)_2As_2$  probed by x-ray absorption spectroscopy: Evidence for effectively isovalent substitution of Fe<sup>2+</sup> by Co<sup>2+</sup>. *Physical Review B*, 86:104503, Sep 2012. doi: 10.1103/PhysRevB.86. 104503. URL http://link.aps.org/doi/10. 1103/PhysRevB.86.104503.
- [140] Hiroshi Yanagi, Ryuto Kawamura, Toshio Kamiya, Yoichi Kamihara, Masahiro Hirano, Tetsuya Nakamura, Hitoshi Osawa, and Hideo Hosono. Itinerant ferromagnetism in the layered crystals LaCoOX (X = P, As). *Physical Review B*, 77:224431, Jun 2008. doi: 10.1103/PhysRevB.77.224431. URL http://link.aps.org/doi/10.1103/PhysRevB.77.224431.
- [141] Jun Sugiyama, Martin Månsson, Oren Ofer, Kazuya Kamazawa, Masashi Harada, Daniel Andreica, Alex Amato, Jess H. Brewer, Eduardo J. Ansaldo, Hiroto Ohta, Chishiro Michioka, and Kazuyoshi Yoshimura. Successive magnetic transitions and static magnetic order in RCoAsO (R = La, Ce, Pr, Nd, Sm, Gd) confirmed by muon-spin rotation and relaxation. *Physical Review B*, 84:184421, Nov 2011. doi: 10.1103/PhysRevB.84.184421. URL http://link.aps.org/doi/10.1103/PhysRevB. 84.184421.

- [142] Hung T. Dang, Emanuel Gull, and Andrew J. Millis. Theory of charged impurities in correlated electron materials: Application to muon spectroscopy of high-T<sub>c</sub> superconductors. *Physical Review B*, 81: 235124, Jun 2010. doi: 10.1103/PhysRevB. 81.235124. URL http://link.aps.org/doi/10. 1103/PhysRevB.81.235124.
- [143] P. Jena, K. S. Singwi, and R. M. Nieminen. Self-consistent screening of a positive muon in a spin-polarized electron gas. *Physical Review B*, 17:301-307, Jan 1978. doi: 10.1103/PhysRevB.17.301. URL http: //link.aps.org/doi/10.1103/PhysRevB.17.301.
- [144] S. Estreicher and P. F. Meier. Energy profiles for light impurities in simple metals. *Physical Review B*, 27:642-658, Jan 1983. doi: 10.1103/PhysRevB.27.642. URL http: //link.aps.org/doi/10.1103/PhysRevB.27.642.
- [145] José M Soler, Emilio Artacho, Julian D Gale, Alberto García, Javier Junquera, Pablo Ordejón, and Daniel Sánchez-Portal. The SIESTA method for ab initio order-N materials simulation. Journal of Physics: Condensed Matter, 14(11):2745, 2002. URL http://stacks.iop.org/0953-8984/ 14/i=11/a=302.
- [146] H Schilling, M Camani, F N Gygax, W Ruegg, and A Schenck. Depolarisation studies of positive muons in copper, vanadium, niobium and tantalum single crystals. Journal of Physics F: Metal Physics, 12 (5):875, 1982. URL http://stacks.iop.org/ 0305-4608/12/i=5/a=007.
- [147] J.D. Thompson, Z. Fisk, and G.G. Lonzarich. Perspective on heavy-electron and kondo-lattice systems from high pressure studies. *Physica B: Condensed Matter*, 161(1-3):317–323, Jan 1990. ISSN 0921-4526. doi: 10.1016/0921-4526(89) 90155-5. URL http://dx.doi.org/10.1016/ 0921-4526(89)90155-5.
- [148] Yoshikazu Ishikawa and Masatoshi Arai. Magnetic phase diagram of mnsi near critical temperature studied by neutron small angle scattering. J. Phys. Soc. Jpn., 53(8): 2726-2733, Ang 1984. ISSN 1347-4073. doi: 10.1143/JpSJ.53.2726. URL http://dx.doi. org/10.1143/JPSJ.53.2726.
- [149] S. Muhlbauer, B. Binz, F. Jonietz, C. Pfleiderer, A. Rosch, A. Neubauer, R. Georgii, and P. Boni. Skyrmion lattice in a chiral magnet. *Science*, 323(5916):915-919, Feb 2009. ISSN 1095-9203. doi: 10.1126/science. 1166767. URL http://dx.doi.org/10.1126/ science.1166767.
- [150] N. Romming, C. Hanneken, M. Menzel, J. E. Bickel, B. Wolter, K. von Bergmann, A. Kubetzka, and R. Wiesendanger. Writing and deleting single magnetic skyrmions. *Science*, 341(6146):

636-639, Aug 2013. ISSN 1095-9203. doi: 10.1126/science.1240573. URL http://dx. doi.org/10.1126/science.1240573.

- [151] Vyacheslav G. Storchak, Jess H. Brewer, Roger L. Lichti, Thomas A. Lograsso, and Deborah L. Schlagel. Electron localization into spin-polaron state in MnSi. *Physical Review B*, 83:140404, Apr 2011. doi: 10.1103/PhysRevB.83.140404. URL http:// link.aps.org/doi/10.1103/PhysRevB.83.140404.
- [152] R. Kadono, J. Imazato, T. Matsuzaki, K. Nishiyama, K. Nagamine, T. Yamazaki, D. Richter, and J.-M. Welter. Quantum diffusion of positive muons in copper. *Physical Review B*, 39:23–41, Jan 1989. doi: 10.1103/PhysRevB.39.23. URL http://link. aps.org/doi/10.1103/PhysRevB.39.23.
- [153] G. M. Luke, J. H. Brewer, S. R. Kreitzman, D. R. Noakes, M. Celio, R. Kadono, and E. J. Ansaldo. Muon diffusion and spin dynamics in copper. *Physical Review B*, 43:3284–3297, Feb 1991. doi: 10.1103/ PhysRevB.43.3284. URL http://link.aps. org/doi/10.1103/PhysRevB.43.3284.
- [154] M. Camani, F. N. Gygax, W. Rüegg, A. Schenck, and H. Schilling. Positive Muons in Copper: Detection of an Electric-Field Gradient at the Neighbor Cu Nuclei and Determination of the Site of Localization. *Physical Review Letters*, 39:836–839, Sep 1977. doi: 10.1103/PhysRevLett.39. 836. URL http://link.aps.org/doi/10.1103/ PhysRevLett.39.836.
- [155] C. W. Clawson, K. M. Crowe, S. S. Rosenblum, S. E. Kohn, C. Y. Huang, J. L. Smith, and J. H. Brewer. Low-Temperature Mobility of Positive Muons in Copper. *Physical Review Letters*, 51:114-117, Jul 1983. doi: 10.1103/PhysRevLett.51.114. URL http:// link.aps.org/doi/10.1103/PhysRevLett.51.114.
- [156] O. Hartmann, L.O. Norlin, A. Yaouanc, J. Le Hericy, E. Karlsson, and T.O. Niinikoski. Low temperature studies of muon localization in copper. *Hyperfine Interac*tions, 8(4-6):533-537, 1981. ISSN 0304-3843. doi: 10.1007/BF01037523. URL http: //dx.doi.org/10.1007/BF01037523.
- [157] O. Hartmann. Quadrupole influence on the dipolar-field width for a single interstitial in a metal crystal. *Physical Review Letters*, 39:832-835, Sep 1977. doi: 10.1103/ PhysRevLett.39.832. URL http://link.aps. org/doi/10.1103/PhysRevLett.39.832.
- [158] C. P. Flynn and A. M. Stoneham. Quantum Theory of Diffusion with Application to Light Interstitials in Metals. *Physical Review B*, 3:2819-2819, Apr 1971. doi: 10. 1103/PhysRevB.3.2819. URL http://link. aps.org/doi/10.1103/PhysRevB.3.2819.

- [159] C. P. Flynn and A. M. Stoneham. Quantum Theory of Diffusion with Application to Light Interstitials in Metals. *Physical Review B*, 1:3966-3978, May 1970. doi: 10. 1103/PhysRevB.1.3966. URL http://link. aps.org/doi/10.1103/PhysRevB.1.3966.
- [160] H. Teichler. On the theory of muon diffusion in metals. *Physics Letters* A, 64(1):78 - 80, 1977. ISSN 0375-9601. doi: 10.1016/0375-9601(77)90533-3. URL http://www.sciencedirect.com/science/ article/pii/0375960177905333.
- [161] H. Teichler. On the theory of diffusion of light interstitials in metals. Hyperfine Interactions, 6(1-4):251-254, 1979. ISSN 0304-3843. doi: 10.1007/BF01028802. URL http: //dx.doi.org/10.1007/BF01028802.
- [162] Graeme Henkelman and Hannes Jónsson. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. The Journal of Chemical Physics, 113(22):9978-9985, 2000. doi: 10.1063/1.1323224. URL http://scitation.aip.org/content/aip/ journal/jcp/113/22/10.1063/1.1323224.
- [163] Graeme Henkelman, Blas P. Uberuaga, and Hannes Jónsson. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. The Journal of Chemical Physics, 113(22): 9901-9904, 2000. doi: 10.1063/1.1329672. URL http://scitation.aip.org/content/aip/ journal/jcp/113/22/10.1063/1.1329672.
- [164] H. Teichler. Microscopic calculation of lattice distortions around  $\mu^+$  in Cu. *Physics Letters A*, 67(4):313 – 315, 1978. ISSN 0375-9601. doi: 10.1016/0375-9601(78) 90315-8. URL http://www.sciencedirect.com/ science/article/pii/0375960178903158.
- [165] Satoshi Takahashi and Kazuo Takatsuka. On the validity range of the Born-Oppenheimer approximation: A semiclassical study for all-particle quantization of three-body Coulomb systems. The Journal of Chemical Physics, 124(14): 144101, 2006. doi: 10.1063/1.2173997. URL http://scitation.aip.org/content/aip/ journal/jcp/124/14/10.1063/1.2173997.
- [166] Y. Tokura, H. Takagi, and S. Uchida. A superconducting copper oxide compound with electrons as the charge carriers. Nature, 337 (6205):345-347, Jan 1989. doi: 10.1038/ 337345a0. URL http://dx.doi.org/10.1038/ 337345a0.
- [167] L. Alff, Y. Krockenberger, B. Welter, M. Schonecke, R. Gross, D. Manske, and M. Naito. A hidden pseudogap under the 'dome' of superconductivity in electrondoped high-temperature superconductors. *Nature*, 422(6933):698-701, Apr 2003. ISSN 0028-0836. URL http://dx.doi.org/10.1038/ nature01488.

- [168] S-W. Cheong, G. Aeppli, T. Mason, H. Mook, S. Hayden, P. Canfield, Z. Fisk, K. Clausen, and J. Martinez. Incommensurate magnetic fluctuations in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>. *Physical Review Letters*, 67:1791-1794, Sep 1991. doi: 10.1103/ PhysRevLett.67.1791. URL http://link. aps.org/doi/10.1103/PhysRevLett.67.1791.
- [169] R Hord, G Pascua, K Hofmann, G Cordier, J Kurian, H Luetkens, V Pomjakushin, M Reehuis, B Albert, and L Alff. Oxygen stoichiometry of low-temperature synthesized metastable T'-La<sub>2</sub>CuO<sub>4</sub>. Superconductor Science and Technology, 26(10): 105026, 2013. URL http://stacks.iop.org/ 0953-2048/26/i=10/a=105026.
- [170] R. Hord, H. Luetkens, G. Pascua, A. Buckow, K. Hofmann, Y. Krockenberger, J. Kurian, H. Maeter, H.-H. Klauss, V. Pomjakushin, A. Suter, B. Albert, and L. Alff. Enhanced two-dimensional behavior of metastable T'-La<sub>2</sub>CuO<sub>4</sub>, the parent compound of electron-doped cuprate superconductors. *Physical Review B*, 82:180508, Nov 2010. doi: 10.1103/PhysRevB.82.180508. URL http://link.aps.org/doi/10.1103/ PhysRevB.82.180508.
- [171] K. M. Kojima, Y. Krockenberger, I. Yamauchi, M. Miyazaki, M. Hiraishi, A. Koda, R. Kadono, R. Kumai, H. Yamamoto, A. Ikeda, and M. Naito. Bulk superconductivity in undoped T'-La<sub>1.9</sub>Y<sub>0.1</sub>CuO<sub>4</sub> probed by muon spin rotation. *Physical Review B*, 89:180508, May 2014. doi: 10.1103/ PhysRevB.89.180508. URL http://link.aps. org/doi/10.1103/PhysRevB.89.180508.
- [172] Hena Das and Tanusri Saha-Dasgupta. Electronic structure of La<sub>2</sub>CuO<sub>4</sub> in the T and T' crystal structures using dynamical mean field theory. *Physical Review B*, 79: 134522, Apr 2009. doi: 10.1103/PhysRevB. 79.134522. URL http://link.aps.org/doi/10. 1103/PhysRevB.79.134522.
- [173] Gwendolyne Banasan Pascua. Structural and Magnetic Properties of the Insulating T'-RE<sub>2</sub>CuO<sub>4</sub> Parent Compounds of Electron-Doped Superconductors. PhD thesis, Physik-Institut der Universität Zürich, 2014.
- [174] P. Ramachandran and G. Varoquaux. Mayavi: 3D Visualization of Scientific Data. Computing in Science & Engineering, 13(2): 40-51, 2011. ISSN 1521-9615.
- [175] G. Kresse and J. Furthmuller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Material Science*, 6:15, 1996.
- [176] G. Kresse and J. Furthmüller. Efficient iterative schemes for *ab initio* totalenergy calculations using a plane-wave basis set. *Physical Review B*, 54:11169– 11186, Oct 1996. doi: 10.1103/PhysRevB.

54.11169. URL http://link.aps.org/doi/10. 1103/PhysRevB.54.11169.

- [177] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sclauzero, Ari P Seitsonen, Alexander Smogunov, Paolo Umari, and QUANTUM Renata M Wentzcovitch. ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter, 21(39):395502 (19pp), 2009. URL http://www.quantum-espresso.org.
- [178] T. Jeong and W. Pickett. Implications of the B20 crystal structure for the magnetoelectronic structure of MnSi. *Physical Review B*, 70:075114, Aug 2004. doi: 10.1103/ PhysRevB.70.075114. URL http://link.aps. org/doi/10.1103/PhysRevB.70.075114.
- [179] R.D. Collyer and D.A. Browne. Correlations and the Magnetic Moment of MnSi. Physica B: Condensed Matter, 403 (5-9):1420 - 1422, 2008. ISSN 0921-4526. doi: 10.1016/j.physb.2007.10.301. URL http://www.sciencedirect.com/science/ article/pii/S0921452607011726. Proceedings of the International Conference on Strongly Correlated Electron Systems.
- [180] Kevin F. Garrity, Joseph W. Bennett, Karin M. Rabe, and David Vanderbilt. Pseudopotentials for high-throughput {DFT} calculations. Computational Materials Science, 81(0):446 - 452, 2014. ISSN 0927-0256. doi: 10.1016/j.commatsci.2013. 08.053. URL http://www.sciencedirect.com/ science/article/pii/S0927025613005077.
- [181] M. Methfessel and A. T. Paxton. Highprecision sampling for Brillouin-zone integration in metals. *Physical Review B*, 40:3616-3621, Aug 1989. doi: 10.1103/ PhysRevB.40.3616. URL http://link.aps. org/doi/10.1103/PhysRevB.40.3616.
- [182] Peter E. Blöchl, O. Jepsen, and O. K. Andersen. Improved tetrahedron method for Brillouin-zone integrations. *Physical Review B*, 49:16223-16233, Jun 1994. doi: 10.1103/PhysRevB.49.16223. URL http:// link.aps.org/doi/10.1103/PhysRevB.49.16223.
- [183] Matteo Cococcioni and Stefano de Gironcoli. Linear response approach to the calculation of the effective interaction parameters in the LDA + U method. *Physical Re*view B, 71:035105, Jan 2005. doi: 10.1103/

PhysRevB.71.035105. URL http://link.aps. org/doi/10.1103/PhysRevB.71.035105.

- [184] Philip N. Klein, Satish Rao, Monika Raucht, and Sairam Subramanian. Faster shortest-path algorithms for planar graphs. In ACM Symposium on Theory of Computing, pages 27-37, 1994. doi: 10.1145/195058. 195092.
- [185] Richard Franke. Scattered Data Interpolation: Tests of Some Method. Mathematics of Computation, 38(157):pp. 181-200, 1982. ISSN 00255718. URL http://www.jstor.org/ stable/2007474.
- [186] Robert J. Renka. Algorithm 661: QSHEP3D: Quadratic Shepard Method for Trivariate Interpolation of Scattered Data. ACM Trans. Math. Softw., 14 (2):151-152, June 1988. ISSN 0098-3500. doi: 10.1145/45054.214374. URL http://doi.acm.org/10.1145/45054.214374.
- [187] John Burkardt. source code of the fortran implementation of the interpolation algorithms can be found at http://people.sc. fsu.edu/~jburkardt/, June 2014. URL http: //people.sc.fsu.edu/~jburkardt/.
- [188] Zbigniew Romanowski. B-spline solver for one-electron Schrödinger equation. Molecular Physics, 109(22):2679-2691, 2011. doi: 10.1080/00268976.2011.631055. URL http: //dx.doi.org/10.1080/00268976.2011.631055.
- [189] Lukas Krämer, Edoardo Di Napoli, Martin Galgon, Bruno Lang, and Paolo Bientinesi.

Dissecting the {FEAST} algorithm for generalized eigenproblems. Journal of Computational and Applied Mathematics, 244(0):1-9, 2013. ISSN 0377-0427. doi: 10.1016/j.cam. 2012.11.014. URL http://www.sciencedirect. com/science/article/pii/S0377042712005079.

- [190] S. Janecek and E. Krotscheck. A fast and simple program for solving local Schrodinger equations in two and three dimensions. Computer Physics Communications, 178(11):835 - 842, 2008. ISSN 0010-4655. doi: 10.1016/j.cpc.2008.01. 035. URL http://www.sciencedirect.com/ science/article/pii/S0010465508000453.
- [191] Masuo Suzuki. Generalized Trotter's formula and systematic approximants of exponential operators and inner derivations with applications to many-body problems. Commun.Math. Phys., 51(2):183-190, Jun 1976. ISSN 1432-0916. doi: 10.1007/bf01609348. URL http://dx.doi.org/10.1007/bF01609348.
- [192] John Burkardt. rbf\_interp\_nd, a library which defines and evaluates radial basis function (RBF) interpolants to multidimensional data., . URL http://people.sc.fsu. edu/~jburkardt/.
- [193] John Burkardt. toms661, a library which takes scattered data in 3D and creates an interpolating function F(X,Y,Z), called qshep3d. This is a version of ACM TOMS algorithm 661, by Robert Renka., URL http://people.sc.fsu.edu/-jburkardt/.