First-principles study of quantized muons in materials

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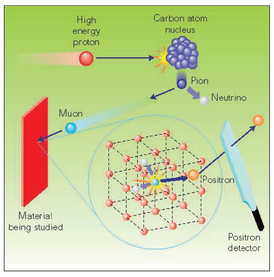
1. μSR technology and muon sites calculation

Muon Spin Rotation/Relaxation/Resonance (μSR) technique uses muons (positive muons) as probes to detect the magnetic (spin) structure and dynamics of matter at microscopic level. It is a unique complement to other methods such as Nuclear Magnetic Resonance (NMR) and neutron scattering. Its applications span a wide range of studies in physics, chemistry, and material science.



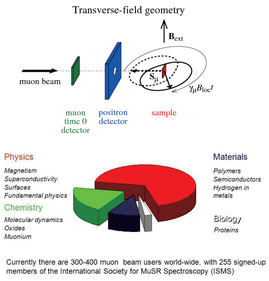


Fig 1: μSR technology.

In principle μSR can be sensitive to any nuclei-muon or electron-muon spin interactions within its scope. As a local probe, all further analysis depend on the information of the muon sites. Since the mass of the muon is ~206.77 of the electron, the Born-Oppenheimer approximation is generally used. The steps to find muon sites are:

1. Define the muon as a hydrogen nucleus, put it somewhere in the lattice.
2. Do the structure optimization calculation, find the stable muon site.
3. Change the initial muon sites sufficiently in the lattice, find the (several) lowest energy structures and corresponding muon sites (so-called candidate muon sites).

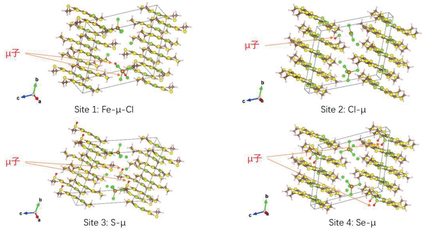


Fig 2: Four calculated candidate muon sites in STF-FeCl.

2. Quantum effects of the muon and TCDFT

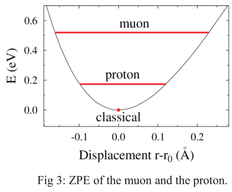


Fig 3: ZPE of the muon and the proton.

$M_\mu = 206.77\, M_e = 1/9\, M_p$

$M_\mu/M_e \approx M_{23Na}/M_\mu$

Muon is in an intermediate position between electrons and heavy nuclei.

Using harmonic model, the zero point energy (ZPE) of the muon is 3 times of the proton, which should not be ignored.

The basic idea is to quantize the muon at initial.

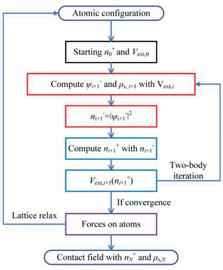


Fig. 4: TCDFT calculation loop.

Within the scheme of density functional theory (DFT):

$$\left[-\frac{1}{2}\nabla^2 + V_{ion}^- + V_H + V_{xc} + V_{coul}^- + V_{corr}^-\right]\psi^- = \varepsilon^-\psi^-$$

$$\left[-\frac{1}{2M}\nabla^2 + V_{ion}^+ + V_{coul}^+ + V_{corr}^+\right]\psi^+ = \varepsilon^+\psi^+$$

This is so-called two-component density functional theory (TCDFT). The one-body function of the muon and the muon should be solved simultaneously.

The key problem is how to describe the two-body correlation functional.

Based on the previous experience of the electrons or positrons functional, we attempt to parametrize the functional by simulating the homogeneous muon-electron gas system by quantum Monte Carlo (QMC).

3. The way to find a good two-body functional

Local Spin Approximation (LDA):

The two-body correlation only depends on the density of the muon and the electrons. Simulate the homogeneous electron-muon gas system by QMC and parameterize the functional within LDA. What to simulate:

Correlation energy Ec:

$$E_{c,v} = E_v(N_e + N_\mu) - E_v(N_e) - E_v(N_\mu)$$

v stands for per volume

Pair correlation function (PCF) g:

$$\gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}') = N_\alpha(N_\beta - \delta_{\alpha\beta}) \cdot \frac{\int \Psi^*(\mathbf{r},\mathbf{r}',\mathbf{r}_3,...,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}',\mathbf{r}_3,...,\mathbf{r}_N)d\mathbf{r}_3...d\mathbf{r}_N}{\int \Psi^*(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)\Psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)d\mathbf{R}}$$

$$\gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}') = n_\alpha(\mathbf{r})n_\beta(\mathbf{r}')g_{\alpha\beta}(\mathbf{r},\mathbf{r}')$$

The observable contact magnetic field can thus be simulated:

$$B_{cont} = \int \frac{2\mu_0}{3}\mu_B\rho_S(\mathbf{r})g(0;\mathbf{r})\left|\psi_\mu(\mathbf{r})\right|^2 d^3\mathbf{r}$$

The results are 10% ~ 15% larger than experiments, but can be fixed by an empirical parameter α:

$$V_{corr}^-(n^+,n^-) = \begin{cases} V_1, & R \leqslant 10 \\ V_2 + (V_1 - V_2)e^{-\alpha\cdot(R-10)}, & R > 10 \end{cases}$$

α stands for the approaching speed from finite density to infinite density. α ~ 1.

Table I: calculation observable measurement vs experiment in some materials.

Material	Point-like muon①	Phonon-corrected②	This work	Experiment③
Fe-bcc	-1.25 T	-1.07 T	-1.076 T	-1.11 T
Co-hcp	-0.73 T	-0.68 T	-0.603 T	-0.58 T
Co-fcc	-0.79 T	-0.64 T	-0.614 T	-0.61 T
NaF	4389 MHz	4293 MHz	4513 MHz	4642 MHz
CaF_2	4610 MHz	4564 MHz	4469 MHz	4479 MHz
Diamond	4251 MHz	3597 MHz	4088 MHz	3711 MHz
Vacuum	4711 MHz		4455 MHz	4463 MHz

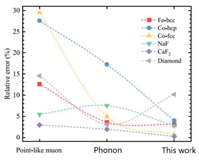


Fig 5: Relative error of Table I.

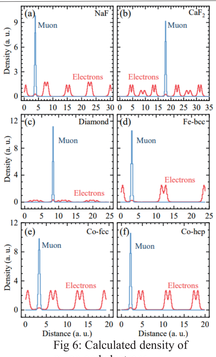


Fig 6: Calculated density of muon and electrons.

In fact, LDA is not a good enough approximation, because the interaction distance of muon-electron is short.

The simulation of one muon immersed in electrons gas, with an external potential to localize the muon, is more reasonable and close to the fact.

Further development of the functional is still ongoing…

4. Full-quantized muon in materials using QMC

The most essential way to consider the quantized muon is to introduce it into the many-body wave function directly:

$$\hat{H}[\psi(r_1,...r_N;R_\mu)] = E\psi(r_1,...r_N;R_\mu)$$

R_μ is the position of the muon. In QMC, if the trial one-particle orbits of the electrons and the muons are known, the many-body wave function can be solved directly.

Key problems:

1. **How to generate the orbits of the electrons.**

   Using DFT code with point-like muon.

2. **How to generate the orbits of the muon.**

   Convert the real space density of muon to plane-wave, then to blip.

3. **How to optimize the many-body wave function.**

   Slater-Jastrow-backflow (SJB) scheme, with variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC)

4. **How to simulate the observable measurement**

$$B_{cont} \sim [N_\uparrow \cdot g_\uparrow(0) - N_\downarrow \cdot g_\downarrow(0)]/V$$

At present, only a similar work for positron-in-material exists.

(Phys. Rev. Lett., 2022, 129: 166403)

We have successfully generated the many-body wave function of muon-in-material and estimated the observable hyperfine couplings, but the error bar is large and should be further improved (due to the offset of the average value). Some results:

Molecular acetone: 26±54 MHz (Experiment: 6 MHz, point-like muon: 31 MHz)

Molecular benzene: 466 ± 62 MHz (Experiment: 514 MHz, point-like muon: 483 MHz)