



# UNIVERSITÀ DI PARMA

## ARCHIVIO DELLA RICERCA

University of Parma Research Repository

Efficient and reliable strategy for identifying muon sites based on the double adiabatic approximation

This is the peer reviewed version of the following article:

*Original*

Efficient and reliable strategy for identifying muon sites based on the double adiabatic approximation / Bonfa', Pietro; Sartori, F.; DE RENZI, Roberto. - In: JOURNAL OF PHYSICAL CHEMISTRY. C. - ISSN 1932-7447. - 119:8(2015), pp. 4278-4285. [10.1021/jp5125876]

*Availability:*

This version is available at: 11381/2817561 since: 2021-11-08T15:29:55Z

*Publisher:*

American Chemical Society

*Published*

DOI:10.1021/jp5125876

*Terms of use:*

Anyone can freely access the full text of works made available as "Open Access". Works made available

*Publisher copyright*

note finali coverpage

(Article begins on next page)

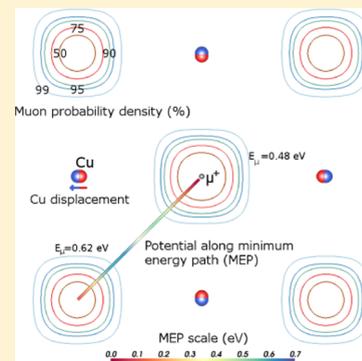
15 August 2025

# Efficient and Reliable Strategy for Identifying Muon Sites Based on the Double Adiabatic Approximation

P. Bonfà, F. Sartori, and R. De Renzi\*

Dipartimento di Fisica e Scienze della Terra, Parco Area delle Scienze 7/A, I-43124 Parma, Italy

**ABSTRACT:** We revise the simple and yet powerful approach of the Double Adiabatic Approximation (DAA) to study positive muon embedding sites in condensed matter. This method introduces a tractable and reasonably accurate description of the quantum nature of the muon in Density Functional Theory (DFT) simulations aiming at identifying muon sites. Moreover, this approach overcomes the limitations of the harmonic approximation in terms of both computational efforts and accuracy. Notably, it also improves treatment of muon diffusion. We use the DAA and Nudged Elastic Band calculations to determine the muon sites and the activation energies between equivalent sites in MnSi and copper. In metallic Cu, the proposed phonon-assisted mechanism for the low-temperature muon diffusion in the lattice is confirmed.



## INTRODUCTION

Muon spin rotation and relaxation ( $\mu$ SR) spectroscopy is an experimental technique that provides the time evolution of the muon spin polarization by exploiting the anisotropic emission of the decay positron.

The main field of application of  $\mu$ SR is material science, but it is also adopted in chemistry for studying molecular dynamics and radical kinetics.<sup>1–3</sup> Both  $\mu^-$ SR and  $\mu^+$ SR exist, but, since  $\mu^-$  undergoes nuclear capture and the surviving  $\mu^-$  fall into atomic orbitals extremely close to the nuclei,  $\mu^+$ SR is more commonly used to investigate condensed matter.

$\mu$ SR experiments provide a measure of the microscopic field distribution at the interstitial site(s) where the  $\mu^+$  stop inside the sample. A seemingly embarrassing point is that these sites are usually unknown to the experimenter and the additional lack of knowledge on the perturbation generated locally by the positive muon probably represent the most common criticisms of the experimental technique. Even though in a large variety of cases ignoring the muon position does not represent a limitation, having access to information on interstitial sites and on muon-induced perturbations might be crucial to evaluate electronic properties such as long-range magnetic orders or localized magnetic moments.

Predicting the position of interstitial muon sites is not a trivial task. During the final stages of thermalization in the sample the scattering between the muon and the atoms of the compound leads to a kinetic energy degradation from hundreds to tenths of electronvolts. Nonetheless, the identification of diamagnetic muon sites with approaches based on the Density Functional Theory (DFT) is emerging as a new and valuable strategy to routinely assist  $\mu$ SR experiments interpretation. After the pioneering work of Van de Walle et al., in recent years, this method, which provides information on the electronic and crystalline perturbations introduced by the

muon, has been validated in many experimental cases with great success.<sup>4–13</sup>

There are two main difficulties in the DFT approach. One is inherited from the mean-field description which cannot always correctly describe some classes of materials, like strongly correlated electrons systems or even some semiconductors mistaken for metals. This problem can be alleviated with the many ad hoc corrections that have been developed so far.<sup>14–18</sup> The second problem arises from the omission of the quantum nature of the nuclei. In standard DFT simulations, the nuclei are treated with the usual Born–Oppenheimer (BO) approximation in order to solve two separate Schrödinger equations for the nuclei and for the electrons. The BO approximation represents one of the major drawbacks in the description of the muon/sample interactions since the muon enters as a (light) proton in the Kohn–Sham Hamiltonian, which is self-consistently solved only for the electrons. When modeling the effect of the impurity, one usually finds many metastable configurations that turn out to be unstable when the kinetic energy of the muon is taken into account.

Motivated by the study of muon vibrational energies or proton coupled transfer reactions, many approaches to go beyond the BO scheme have been developed.<sup>19–29</sup> However, since our aim is to provide a supporting tool for  $\mu$ SR data analysis (as it is already the case for many other spectroscopic techniques), these methods are found to be prohibitively demanding of storage and computer time. For this reason the quantum nature of the muon, which is of course relevant given its small mass, is introduced a posteriori.<sup>8,30</sup>

**Received:** December 17, 2014

**Revised:** January 30, 2015

78 A method already used in this context is the linear response  
79 approach to study the vibrational modes of the muon impurity  
80 in the hosting material.<sup>8,31</sup> This strategy has the advantage of  
81 treating the muon and the nuclei on the same footing and uses  
82 the usual BO separation for the electrons. This is reasonable in  
83 view of the small ratio between the proton mass and the muon  
84 mass. However, it is known that, even for the protons, the  
85 harmonic approximation can break down.<sup>32</sup> Of course, this is  
86 usually the case also for the muon. For this reason we recovered  
87 a different approach based on the Double Adiabatic  
88 Approximation (DAA) which has already been used for both  
89 the proton and the muon to study their ground state  
90 energy.<sup>23,30</sup> While its applicability is limited to materials having  
91 heavy nuclei, starting from magnesium the ratio  $m_{\text{Mg}}/m_{\mu} \sim 214$   
92 exceeds  $m_{\mu}/m_e$ , making the electronic BO separation the main  
93 source of approximation. Moreover, as discussed below, this  
94 approach has the additional advantage of providing a rough but  
95 cost-effective analysis of the diffusion mechanisms which can  
96 take place after muon's thermalization.<sup>33–38</sup>

97 The article is divided as follows. In the next section we briefly  
98 summarize our DFT approach to identify muon sites and report  
99 the DAA equations for clarity. Then we present two examples  
100 which illustrate the advantages of using the DAA method for  
101 studying the ground state energy of the muon.

## 102 ■ MUON SITE IDENTIFICATION WITH DFT

103 The main idea, introduced by many works so far,<sup>6–9,11,13</sup> is to  
104 consider the positive diamagnetic muon as a hydrogenoid  
105 impurity in the system under study. The relaxed positions for  
106 the charged impurity are then identified by sampling the  
107 interstitial space with a grid of points in the unit cell and  
108 minimizing the forces in the system for each of the starting  
109 positions. This kind of simulations are usually performed with  
110 periodic boundary conditions, therefore supercells are con-  
111 structed to limit the contribution arising from the interaction of  
112 the impurity with its periodic replica. It has been found that a  
113 neutral supercell approach provides the best results for metals,  
114 while a charged supercell with a corresponding compensating  
115 background is a better approximation for insulators.<sup>6–8,10</sup> This  
116 is understood by considering that in metals the charged particle  
117 is effectively screened by conduction electrons and the neutral  
118 supercell approach is therefore a better description of the real  
119 system.

120 During the above minimization procedure, many local  
121 minima are occasionally encountered. We label them  
122 “candidate muon sites”. Usually not all candidate sites are  
123 muon sites. This is due to the quantum nature of the muon  
124 which is neglected in the relaxation steps. This problem is not  
125 so relevant when studying hydrogen intercalation since small  
126 energy barriers are sufficient to trap hydrogen impurities.  
127 However, the ground state energy of the muon can be up to an  
128 order of magnitude larger than that of the proton, thus making  
129 many interstitial positions unstable. To discriminate between  
130 binding and nonbinding sites, the ground state energy of the  
131 muon must be evaluated.

132 Incidentally, we remark that the quantum description of the  
133 muon also provides relevant information on phenomena such  
134 as muon diffusion or hyperfine couplings.<sup>5,8</sup>

## 135 ■ DOUBLE ADIABATIC APPROXIMATION

136 As already discussed, a quantum description of the muon can  
137 be introduced by studying its vibrational modes. However,

apart from accuracy problems, the number of irreducible modes  
that have to be analyzed grows with the number of basis  
elements within the simulation cell. Since treating the muon as  
an impurity requires a supercell approach, this method often  
becomes extraordinarily demanding even for the most powerful  
supercomputers.

Here we propose instead to introduce a double adiabatic  
approximation to separate the degrees of freedom of the muon  
from those of the electrons and of the nuclei. This is a rather  
crude approximation in some cases, but it has at least three  
valuable advantages. First, it allows to take into account the  
potential felt by the muon beyond the harmonic approximation.  
Second, this method can provide ground state energies for  
unrelaxed structures. This is especially useful when studying  
diffusion processes as will be discussed later. Finally, this  
approach provides information on the muon wave function  
with a reasonable amount of computational effort.

We now briefly recall the DAA equations for a single muon  
in the sample. The total Hamiltonian of the system is

$$\mathcal{H}_{\text{tot}} = -\frac{\hbar^2}{2m_{\mu}}\nabla_{\mu}^2 - \sum_{j=1}^{N_N} \frac{\hbar^2}{2M_j}\nabla_{N_j}^2 + \mathcal{H}_e \quad (1)$$

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

$$\mathcal{H}_{\text{tot}}|\Psi\rangle = E|\Psi\rangle \quad (3)$$

where index  $j$  runs over the  $N_N$  nuclei having the set of position  
operators  $\mathbf{R}$  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  $m_e$   
and  $V(\mathbf{r}_e, \mathbf{r}_{\mu}, \mathbf{R})$  includes all the interactions between the  
electrons, the nuclei and the muon. If we approximate the total  
wave function  $|\Psi\rangle$  with the product wave function  $|\psi_e\rangle|\phi_{\mu}\rangle|\chi_N\rangle$ ,  
the position operators of the muon and of the nuclei enter only  
as parameters in the eigenvalue problem for the electrons  
 $\mathcal{H}_e\psi_e(\mathbf{r}_e; \mathbf{r}_{\mu}, \mathbf{R}) = \epsilon(\mathbf{r}_{\mu}, \mathbf{R})\psi_e(\mathbf{r}_e; \mathbf{r}_{\mu}, \mathbf{R})$  that is solved with the  
Kohn–Sham 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:.

$$\left(-\frac{\hbar^2}{2m_{\mu}}\nabla_{\mu}^2 + \epsilon(\mathbf{r}_{\mu}, \mathbf{R})\right)\phi_{\mu}(\mathbf{r}_{\mu}; \mathbf{R}) = E_{\mu}(\mathbf{R})\phi_{\mu}(\mathbf{r}_{\mu}; \mathbf{R}) \quad (4)$$

Let  $E_{\mu}^{(i)}$  be the  $i$ -th eigenvalue of eq 4, in the following we will  
refer to  $E_i = E_{\mu}^{(i)}(\mathbf{R}) - \min_{\mathbf{r}_{\mu}}[\epsilon(\mathbf{r}_{\mu}, \mathbf{R})]$  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 a points cloud formed by 5 to 10 hundred points.  
The favorable convergence against the supercell sizes (usually  
less than 100 atoms are required) and the constantly increasing  
computational power available on computer clusters make this  
method effective for many materials.

## 189 ■ EXPLORATION ALGORITHM

190 Cutting the computational costs needed to acquire the  
191 potential felt by the muon is of utmost importance. To this  
192 aim it is necessary to optimize the sampling process used to  
193 construct the points cloud on which the interpolation is  
194 performed. Acquiring all points in a cubic grid would probably  
195 result in a too expensive computational procedure. Moreover,  
196 only a small subset of the points acquired with this strategy  
197 could eventually be used to interpolate the potential of eq 4  
198 since interstitial positions close to the nuclei have rapidly  
199 increasing total energies  $\epsilon$ . Finally, as discussed in the next  
200 sections, the potential felt by the muon is usually far from being  
201 harmonic, thus, making the sampling over a sphere of  
202 increasing radius similarly inefficient.

203 A simple exploration algorithm was designed to perform an  
204 efficient sampling of the a priori unknown potential felt by the  
205 muon. The exploration is controlled by three parameters: a  
206 cutoff energy  $\epsilon_C$ , a grid separation length  $\delta$ , and a “search  
207 horizon”  $\Delta$ . The first parameter is used to specify the highest  
208 energy that should be explored. The second parameter governs  
209 the interspacing between explored points in a cubic grid. The  
210 third parameter controls the maximum distance between two  
211 consecutively examined points during the exploration process.  
212 This last parameter is essential for two reasons. First and  
213 especially in magnetic materials, the previously calculated  
214 electron density must be used to converge to the correct  
215 ground state and avoid other local minima in the total energy  
216 landscape which reproduce, for example, different magnetic  
217 configurations. This can be done only if the impurity is not too  
218 far from the position where the previous self-consistency was  
219 obtained. Second, reuse of electron densities speeds up the  
220 calculation significantly.

221 The algorithmic procedure begins with the definition of the  
222 starting point for the exploration (labeled  $i$ ) and the evaluation  
223 of its total energy  $\epsilon_i$ . Let  $n(i)$  be the number of neighboring  
224 points of point  $i$  in a cubic grid for which the total energy has  
225 not been calculated yet (in the implementation used in this  
226 article we considered only the nearest neighbors: left, right, up,  
227 down, front, back). From the initial point, the iteration  
228 proceeds as follows:

- 229 • The total energies of the neighboring points  $n(i)$  of the  
230 current point  $i$  are inspected.
- 231 • The number of unexplored neighbors  $n(i)$  for all  
232 explored points  $i$  is updated.
- 233 • Among the already explored points  $j$ , those with  $n(j) > 0$   
234 form the set of the candidate positions for the next move.  
235 The point  $j$  having the lowest energy  $\epsilon_j$  and having  
236 distance  $d(i,j) < \Delta$  is chosen as the next point for the  
237 exploration.
- 238 • The current position is set to position  $j$  and the algorithm  
239 is iterated.

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

242 For  $\Delta = \infty$  (infinite “search horizon”) all points with  $\epsilon < \epsilon_C$   
243 will be explored. This is no longer true when we limit the  
244 maximum distance between consecutively explored points since  
245 the algorithm can remain trapped in dead-end paths. To avoid  
246 this situation we can imagine to label visited points with three  
247 different colors: red, explored points whose energy exceeds the  
248 cutoff energy,  $\epsilon > \epsilon_C$ ; yellow, explored points having  $\epsilon < \epsilon_C$  and  
249 at least one neighbor unexplored; green, explored points  
250 without unexplored neighbors.

When a dead-end point is reached, there are two possible  
scenarios: either none of the explored points is yellow or there  
is at least one yellow point. In the first case, the exploration is  
finished, otherwise, we move from point  $k$ , where the system is  
trapped, to the nearest yellow point,  $l$ . If reuse of electron  
density is required, the path that minimizes the distance  $d(k,l)$   
obtained for example with the algorithm by Klein and co-  
workers,<sup>39</sup> can be used in order to reduce the additional  
computational cost of traversing already explored points.

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.<sup>40–42</sup>

In what follows we will refer to the above algorithm as  
Potential Exploration Algorithm (PEA).

## ■ COMPUTATIONAL DETAILS

The DFT simulations were performed with the QUANTUM  
ESPRESSO suite of codes.<sup>43</sup> The PEA code is built on top of  
the routines of PW.X.

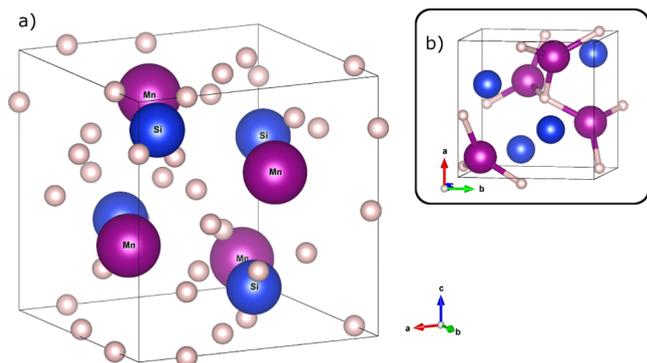
In all the calculations shown hereafter, we used the GBRV  
pseudopotential library and the generalized gradient approx-  
imation (GGA) as parametrized by Perdew–Burke–Ernzerhof  
(PBE) to describe the exchange–correlation potential.<sup>44,45</sup> The  
self-consistency threshold for electronic optimization 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 has been used for structural  
optimization.

To locate the saddle points and optimize the transition path  
between equivalent muon sites, we performed Nudged Elastic  
Band (NEB) calculations.<sup>46,47</sup> 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 saddle point 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.

## ■ MANGANESE SILICIDE

The muon site in ferromagnetic MnSi has been thoroughly  
studied in a recent experiment by Amato and co-workers.<sup>48</sup> A  
single muon site is identified with high accuracy using  
transverse field  $\mu$ SR measurements of the dipolar tensor in  
the paramagnetic state. For this reason, MnSi represents an  
ideal test-case for our computational scheme.

The candidate muon sites were identified by performing  
structural relaxations on a 64 atoms MnSi supercell plus the  
muon impurity. We used a cutoff of 60 and 400 Ry for plane  
waves expansion and for the charge density respectively and a  
 $2 \times 2 \times 2$  Monkhorst–Pack (MP) grid for reciprocal space  
sampling.<sup>49</sup> Spin polarization was included in all simulations.  
With these parameters the total energy was converged to 15  
meV. Four starting points were selected to sample the  
interstitial space in the unit cell. Their positions together  
with the symmetry replica are shown in Figure 1. We find three  
candidate muon sites which are reported in Table 1.

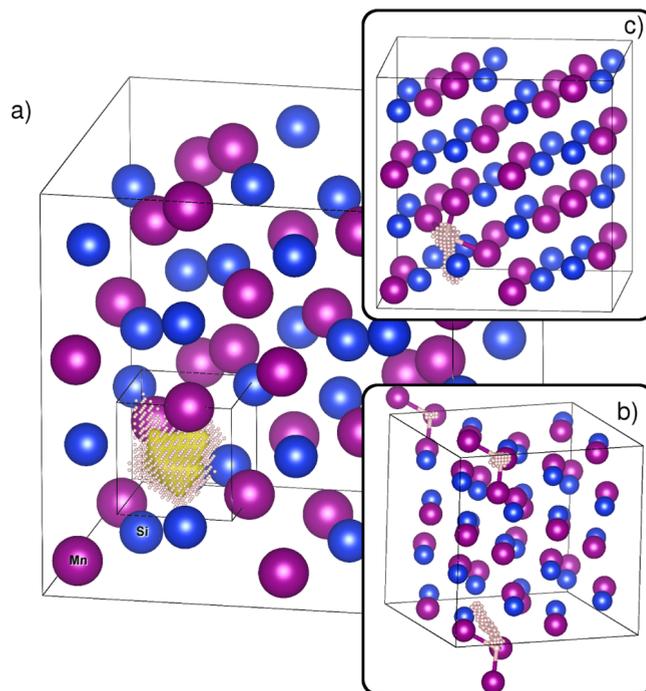


**Figure 1.** (a) Interstitial points (together with the symmetry replica) used as starting positions for the identification of the candidate muon sites. (b) Stable site found in MnSi (some equivalent sites outside the unit cell are shown to help the comparison with Figure 2b,c).

**Table 1. Candidate Muon Sites Obtained with Structural Relaxations in a 64 + 1 Atoms Supercell<sup>a</sup>**

candidate sites	position	$\epsilon^{(i)} - \epsilon^{(A)}$ (eV)	$E_0^{(i)}$ (eV)
A	(0.542, 0.542, 0.542)	0	0.6
B	(0.607, 0.477, 0.220)	0.86	
C	(0.329 0.329, 0.329)	1.12	

<sup>a</sup> $\epsilon^{(i)}$  is the total energy of the relaxed structure,  $E_0^{(i)}$  is the ground state energy of the muon (see eq 4). The Mn and Si positions in the unperturbed cubic lattice are assumed at (0.1381, 0.1381, 0.1381) and (0.8462, 0.8462, 0.8462), respectively. The experimentally identified muon site is in fractional coordinates (0.532, 0.532, 0.532).



**Figure 2.** 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. (b, c) 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 nontrapping sites. In both cases, site A (see Table 1) is reached.

310 We checked if candidate muon sites are binding sites with the  
 311 DAA approximation. For the sake of speed, in the PEA  
 312 simulations we slightly reduced the accuracy of the calculation  
 313 by lowering to 50 and 250 Ry the kinetic energy and charge  
 314 expansions and sampling the Brillouin zone using only the  
 315 Baldereschi point.<sup>50</sup> This guarantees a convergence of the total  
 316 energy of  $\sim 0.5$  meV/atom. While the total energy convergence  
 317 may seem poor, we checked the accuracy of the differences  
 318 between the relaxed and the displaced positions energies by  
 319 performing calculations with higher cutoff and a  $2 \times 2 \times 2$  MP  
 320 sampling grid for reciprocal space. These tests were done for  
 321 the first 20 points of the PEA calculation and for other random  
 322 points. The worst case discrepancy was 4 meV with an average  
 323 value of 1.5 meV. The spacing  $\delta = 0.15875$  Å was used for the  
 324 cubic grid and the maximum step length between consecutive  
 325 moves was set to  $3\sqrt{3}\delta$ .

326 Sites B and C are local minima in  $V(r_\mu)$  and the barrier  
 327 toward site A, which in both cases is lower than 0.15 eV, is too  
 328 small to bind the muon.

329 Starting from site A, 827 points provide an accurate sampling  
 330 of the potential up to 1.13 eV. The points cloud shown in  
 331 Figure 2a is used for the interpolation and the Schrödinger  
 332 equation for the muon is solved in a  $2.54$  Å edge cubic box with  
 333 both Dirichlet and periodic boundary conditions. From the  
 334 solution of the Schrödinger equation we obtain a ground state  
 335 energy  $E_0 = 0.6$  eV (independently of the interpolation method  
 336 and the boundary conditions used). The probability density of  
 337 the ground state wave function (not shown) is well localized  
 338 and, by considering the concept of turning point volume,<sup>6</sup> the  
 339 same conclusion can be drawn from Figure 2a, where even the  
 340 isosurface for  $V_\mu = 0.8$  eV is found to be confined inside the  
 341 points cloud acquired during the simulation.

It should be noted that  $E_0^{(A)}$  is smaller than what it is reported  
 342 by Amato et al.<sup>48</sup> This is because in our previous paper we  
 343 provided preliminary results obtained by solving the  
 344 Schrödinger equation for the muon in the unperturbed  
 345 electrostatic potential. The disagreement between the two  
 346 approaches is not surprising since in the latter case the  
 347 electrons are frozen in the unperturbed ground state density.  
 348

From these results we can conclude that only one muon site  
 349 is present in MnSi. This is in agreement with the experimental  
 350 outcomes and the position obtained from the simulation differs  
 351 from the experimental estimation by less than 0.05 Å.<sup>48</sup> 352

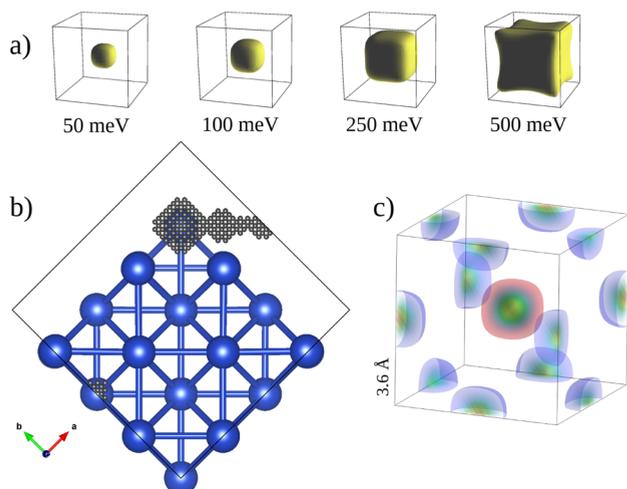
## ■ COPPER

353 Face-centered cubic copper represents an interesting test case  
 354 since it is known that the muon diffuses through the material  
 355 with a correlation time  $\tau_c$  which, in the temperature range from  
 356 100 to 300 K, follows an exponential law and ranges from  $\tau_c^{-1}$   
 357  $\sim 0.1$  to  $10 \mu\text{s}^{-1}$ .<sup>35</sup> The diffusion mechanism was thoroughly  
 358 studied with both experimental and theoretical ap-  
 359 proaches.<sup>36,51–54</sup> In one of the last experiments performed on  
 360 highly pure FCC copper samples, the high temperature data  
 361 could be fitted with both a classical thermal activated law, that  
 362 is,  $\tau_c^{-1} \propto \exp(-E_A/k_B T)$  ( $E_A$  activation energy to overjump the  
 363 barrier) and a phonon-mediated tunneling model that takes  
 364 into account the small polaron theory.<sup>55,56</sup> In the latter case, a  
 365 temperature-dependent prefactor multiplies the exponential  
 366 law.<sup>51,57</sup> Above 300 K, a few experimental data points seem to  
 367 completely miss the 90–300 K and Schilling et al.<sup>51</sup> and  
 368 Teichler<sup>57,58</sup> suggested that, at high temperature, an additional  
 369 diffusion mechanism should take place. 370

Here we checked if the DAA approach is sufficiently accurate  
 371 to allow the description of the diffusion mechanism(s). The 372

373 identification of the muon site followed the standard procedure  
 374 described above. A cubic supercell with 32 Cu atoms and the  
 375 muon was considered. Two candidate positions in the  
 376 octahedral (O) and the tetrahedral (T) cavity sites were  
 377 correctly identified with the structural relaxations. In the T and  
 378 O sites, the nearest neighboring Cu atoms are outward  
 379 displaced from the muon by 5.9 and 2.3%, respectively. The  
 380 latter value is slightly smaller than what is experimentally  
 381 observed, but it is in agreement with previous calculations.<sup>52,59</sup>  
 382 The same result is also obtained with a 109 atom cell, thus,  
 383 confirming the convergence against the supercell size.

384 We collected the points needed to interpolate  $V_\mu$  with PEA  
 385 calculations performed with cutoffs of 50 and 250 Ry for the  
 386 plane wave and the charge density expansion respectively and a  
 387  $3 \times 3 \times 3$  MP grid for reciprocal space integration. The same  
 388 spacing  $\delta$  used for MnSi was adopted. Starting from the T site,  
 389 the barrier toward O sites is just 0.3 eV and no localized states  
 390 at the T site were found. The first 800 points acquired starting  
 391 from the O site are shown in Figure 3b. As it is evident from



**Figure 3.** (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. (b) First 800 points acquired during the exploration with the PEA. Copper atoms are in blue, while all the positions occupied by the muon are in gray. The route toward the neighboring octahedral site passing through the tetrahedral site is clearly visible. Copper atoms do not appear at all the cell boundaries because of the small distortion introduced by the muon (see text). (c) Probability densities for the ground state and the degenerate excited states are depicted with a color map and the 95% probability densities are shown with red (central) and blue (corners) isosurfaces, respectively.

392 the figure, during the exploration process the PEA reached the  
 393 saddle point between the O and the T site, explored the T site  
 394 and then moved to the equivalent O minimum of the  
 395 neighboring cell.

396 In conclusion, the O site is clearly the global minimum of  $V_\mu$   
 397 and we can deduce that the muon hops among O sites only.<sup>52</sup>

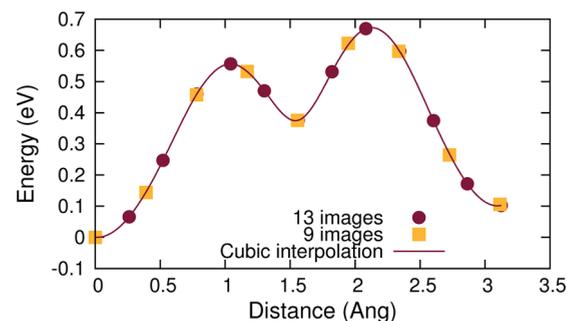
398 To check if the mechanism responsible for the muon  
 399 diffusion is the classical overbarrier hopping or a phonon-  
 400 assisted quantum tunneling, the energy barrier between the O  
 401 sites and the eigenstates for a muon in the distorted O site and  
 402 in the neighboring sites must be evaluated.

403 By imposing the 48 point group symmetry operations on the  
 404 acquired points, a 9301 points cloud was obtained and used to

interpolate the potential of the distorted O site and of the 12  
 neighboring equivalent sites, providing an accurate description  
 of the potential up to 1.5 eV. We then solved the Schrödinger  
 equation for the muon in the potential  $V_\mu$  which is obtained by  
 interpolation of the data points with radial basis functions (with  
 $r$ ,  $r^3$ , and  $r^2 \times \log(r)$  as basis functions) and trilinear  
 interpolation with periodic boundary conditions.

We found a ground state with  $E_0 \sim 0.48$  eV and degenerate  
 excited states at  $E_1 = 0.62$  eV (the results from the various  
 interpolation schemes differ by about 10 meV). As shown in  
 Figure 3c, the two energies correspond to a muon completely  
 localized in the distorted O site and in the neighboring O sites,  
 respectively. No states localized only in the T site were found  
 for energies up to 1 eV.

To evaluate the overbarrier activation energy, the minimum  
 energy path between equivalent O sites was calculated with  
 NEB simulations. The results, obtained using the same  
 parameters for reciprocal space integration and convergence  
 criteria as for the PEA calculations, are shown in Figure 4. The



**Figure 4.** Minimum energy path between equivalent octahedral muon sites obtained with 13 and 9 images NEB simulations. The solid line, obtained from the cubic interpolation of the 13 images NEB results, is used to estimate the value of the saddle points' energy. The difference between the initial and the final energy is due to the distortion introduced by the muon in its starting site.

curve is asymmetric due to the distortion introduced by the  
 muon in the starting O site. The best path toward the  
 neighboring O site passes through the T site. The saddle point  
 energy between the O and the T site is at  $E_{OT} = 0.56$  eV, while  
 the one between two neighboring O sites is at about  $E_{OO} = 0.66$   
 eV above the energy of the starting muon site. The same  
 information can be directly extracted from the interpolated  
 potential. The estimation of  $E_{OT}$  and  $E_{OO}$  extracted from the  
 interpolated potential agrees to within 5 meV with the one  
 obtained with the NEB approach. The path between O sites  
 passing through a Cu–Cu bond has a much higher saddle point  
 energy (about 1.6 eV).

The energy difference  $E_{OO} - E_1 \sim 40$  meV indicates that the  
 phonon-assisted quantum tunneling dominates over the  
 classical hopping at low temperature, that is, 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.<sup>51</sup> The value  
 found with the DAA is about 1.7 times larger, but this is  
 probably an overestimation due to the adiabatic approximation.

## 446 ■ DISCUSSION AND CONCLUSION

447 The main message of this paper is that an accurate analysis of  
448 the ground state energy of the muon (possibly beyond the  
449 harmonic approximation) allows to evaluate the stability of the  
450 numerous candidate muon sites that are provided by the  
451 structural relaxations. This can strikingly improve the predictive  
452 power of DFT simulations in providing muon embedding sites.  
453 In this paper we discussed an efficient and yet sufficiently  
454 accurate method to obtain a quantum description of the muon.  
455 The PEA machinery provides a reliable way to distinguish  
456 between trapping and nontrapping muon sites (which are  
457 routinely obtained during the structural relaxations) with a  
458 computationally tractable description of the ground state  
459 energy of the muon. Moreover, differently from methods  
460 based on the analysis of the vibrational modes of the  $\mu^+$   
461 impurity, this approach can provide eigenfunctions and energies  
462 for a muon in an unrelaxed neighborhood, thus allowing the  
463 analysis of quantum tunneling mechanisms. The estimation of  
464 the muon wave function can also produce accurate ab initio  
465 evaluations of many observables (e.g., contact and transferred  
466 hyperfine couplings).<sup>8,30</sup> While the applicability of the DAA is  
467 limited to the compounds having heavy nuclei, even the mass  
468 ratio  $m_\mu/m_C$  is smaller than 1%.

469 The accuracy and the limits of the BO approximation have  
470 been extensively discussed in literature.<sup>60–62</sup> An encouraging  
471 result for the muon case in this context has been provided by  
472 Takahashi and Takatsuka who considered the accuracy of the  
473 BO approximation for the  $pp\mu^-$  molecule ( $p$  stands for proton)  
474 and found a deviation smaller than 5% from the non-BO  
475 vibronic energies calculated with semiclassical methods.<sup>63</sup>  
476 It should also be noted that for both MnSi and Cu the  
477 potential felt by the muon is far from being harmonic nor it is  
478 possible to fully describe it with small an-harmonic corrections  
479 as evidenced in Figure 2a and Figure 3a. This is the case for  
480 almost all the compound that we examined so far.

481 To verify the accuracy of the DAA, we had to revert to the  
482 comparison with the experiment. In doing so, we chose two  
483 nontrivial examples that have been thoroughly characterized  
484 experimentally. In MnSi, we found that the ground state energy  
485 of the muon makes two candidate sites unstable leaving only  
486 one trapping muon site per unit cell. The final site is in nice  
487 quantitative agreement with the measured muon position,  
488 which differs by less than 0.05 Å. In FCC copper, an accurate  
489 evaluation of the ground state energy of the muon allowed to  
490 distinguish between classical and phonon-mediated tunneling  
491 diffusion, providing slightly overestimated values for the  
492 activation energies, but correctly identifying a lower activation  
493 energy for the phonon-mediated mechanism, in agreement with  
494 the experimental data.

495 Moreover, even though in literature correct estimations of  
496 the muon sites were drawn from the analysis of the electrostatic  
497 potential in metals, these must be regarded as fortunate cases  
498 since they are based on crude and not well-justified  
499 assumptions. On the other hand, it is always possible to  
500 estimate the accuracy of the DAA approach by comparing the  
501 kinetic energies of the species forming the compound under  
502 study.

503 As a side remark, we add that the PEA code can also be used  
504 for studying proton vibrational energies in those compounds  
505 where the harmonic approximation is not sufficiently accurate.  
506 We tested some textbook cases (hydrogen compounds HRB

and HI) and found that the DAA approach slightly improves 507  
the agreement with the experimental results. 508

We finally mention that the results shown in this article were 509  
obtained with a computational power ranging from 8 to 64 510  
cores operating at clock speeds between 2.2 and 3 GHz. These 511  
performances are nowadays becoming available also on 512  
standalone workstations. 513

The source codes used for the PEA calculations, which 514  
include the potential exploration tool and the 1D and 3D 515  
Schrödinger equation solvers,<sup>64,65</sup> are published on the web.<sup>66</sup> 516

## 517 ■ AUTHOR INFORMATION

## 518 Corresponding Author

\*E-mail: roberto.derenzi@unipr.it. 519

## 520 Notes

The authors declare no competing financial interest. 521

## 522 ■ ACKNOWLEDGMENTS

The authors thank computing resources provided by STFC's 523  
Scientific Computing Department and by Paul Scherrer 524  
Institute with the Merlin4 Cluster. We acknowledge financial 525  
support from PRIN Project 2012 × 3YFZ2. Special thanks are 526  
due to Johannes Möller, Franz Lang, Alex Amato, and Roberto 527  
Cammi for fruitful discussions. 528

## 529 ■ REFERENCES

- (1) Yaouanc, A.; Dalmas de Réotier, P. *Muon Spin Rotation, Relaxation, and Resonance: Applications to Condensed Matter*; International Series of Monographs on Physics; OUP: Oxford, 2011. 530–532
- (2) Clayden, N. J. Muons in Chemistry. *Phys. Scr.* **2013**, *88* (068507), 533–534
- (3) Percival, P. W.; Addison-Jones, B.; Brodovitch, J.-C.; Ji, F.; Horoyski, P. J.; Thewalt, M. L. W.; Anthony, T. R. <sup>13</sup>C Hyperfine Coupling Constants in  $\text{MuC}_{60}$ . *Chem. Phys. Lett.* **1995**, *245*, 90–94. 535–537
- (4) Van de Walle, C. G.; Denteneer, P. J. H.; Bar-Yam, Y.; Pantelides, S. S. Theory of Hydrogen Diffusion and Reactions in Crystalline Silicon. *Phys. Rev. B* **1989**, *39*, 10791–10808. 538–540
- (5) Van de Walle, C. G. Structural Identification of Hydrogen and Muonium Centers in Silicon: First-Principles Calculations of Hyperfine Parameters. *Phys. Rev. Lett.* **1990**, *64*, 669–672. 541–543
- (6) Bernardini, F.; Bonfà, P.; Massidda, S.; De Renzi, R. Ab Initio Strategy for Muon Site Assignment in Wide Band Gap Fluorides. *Phys. Rev. B* **2013**, *87* (115148), 1–7. 544–546
- (7) Möller, J. S.; Bonfà, P.; Ceresoli, D.; Bernardini, F.; Blundell, S. J.; Lancaster, T.; De Renzi, R.; Marzari, N.; Watanabe, I.; Sulaiman, S.; et al. Playing Quantum Hide-and-Seek With the Muon: Localizing Muon Stopping Sites. *Phys. Scr.* **2013**, *88* (068510), 1–7. 547–550
- (8) Möller, J. S.; Ceresoli, D.; Lancaster, T.; Marzari, N.; Blundell, S. J. Quantum States of Muons in Fluorides. *Phys. Rev. B* **2013**, *87* (121108), 1–5. 551–553
- (9) Blundell, S. J.; Möller, J. S.; Lancaster, T.; Baker, P. J.; Pratt, F. L.; Seber, G.; Lahti, P. M.  $\mu$ SR Study of Magnetic Order in the Organic Quasi-One-Dimensional Ferromagnet  $\text{F4BImNN}$ . *Phys. Rev. B* **2013**, *88* (064423), 1–6. 554–557
- (10) Prando, G.; Bonfà, P.; Profeta, G.; Khasanov, R.; Bernardini, F.; Mazzani, M.; Brüning, E. M.; Pal, A.; Awana, V. P. S.; Grafe, H.-J.; et al. Common Effect of Chemical and External Pressures on the Magnetic Properties of RCoPO (R = La, Pr). *Phys. Rev. B* **2013**, *87* (064401), 1–11. 558–562
- (11) Disseler, S. M. Direct Evidence for the All-In/All-Out Magnetic Structure in the Pyrochlore Iridates From Muon Spin Relaxation. *Phys. Rev. B* **2014**, *89* (140413), 1–5. 563–565
- (12) Mantz, Y. A.; Gemmen, R. S. Protonated Forms of Monoclinic Zirconia: A Theoretical Study. *J. Phys. Chem. C* **2010**, *114*, 8014–8025. 566–567
- (13) Foronda, F. R.; Lang, F.; Möller, J. S.; Lancaster, T.; Boothroyd, S. A. T.; Pratt, F. L.; Giblin, S. R.; Prabhakaran, D.; Blundell, S. J. 568–569

- 570 Anisotropic Local Modification of Crystal Field Levels in Pr-Based  
571 Pyrochlores: A Muon-Induced Effect Modeled Using Density  
572 Functional Theory. *Phys. Rev. Lett.* **2015**, *114* (017602), 1–5.
- 573 (14) Levine, Z. H.; Allan, D. C. Linear Optical Response in Silicon  
574 and Germanium Including Self-Energy Effects. *Phys. Rev. Lett.* **1989**,  
575 *63*, 1719–1722.
- 576 (15) Gonze, X.; Lee, C. Dynamical Matrices, Born Effective Charges,  
577 Dielectric Permittivity Tensors, and Interatomic Force Constants  
578 From Density-Functional Perturbation Theory. *Phys. Rev. B* **1997**, *55*,  
579 10355–10368.
- 580 (16) Anisimov, V. I.; Zaanen, J.; Andersen, O. K. Band Theory and  
581 Mott Insulators: Hubbard U Instead of Stoner I. *Phys. Rev. B* **1991**, *44*,  
582 943–954.
- 583 (17) Petukhov, A. G.; Mazin, I. I.; Chioncel, L.; Lichtenstein, A. I.  
584 Correlated Metals and the LDA+U Method. *Phys. Rev. B* **2003**, *67*  
585 (153106), 1–4.
- 586 (18) Ortenzi, L.; Mazin, I. I.; Blaha, P.; Boeri, L. Accounting for Spin  
587 Fluctuations Beyond Local Spin Density Approximation in the Density  
588 Functional Theory. *Phys. Rev. B* **2012**, *86* (064437), 1–6.
- 589 (19) Miyake, T.; Ogitsu, T.; Tsuneyuki, S. Quantum Distributions of  
590 Muonium and Hydrogen in Crystalline Silicon. *Phys. Rev. Lett.* **1998**,  
591 *81*, 1873–1876.
- 592 (20) Valladares, R.; Fisher, A.; Hayes, W. Path-Integral Simulations of  
593 Zero-Point Effects for Implanted Muons in Benzene. *Chem. Phys. Lett.*  
594 **1995**, *242*, 1–6.
- 595 (21) Kerridge, A.; Harker, A. H.; Stoneham, A. M. Quantum  
596 Behaviour of Hydrogen and Muonium in Vacancy-Containing  
597 Complexes in Diamond. *J. Phys.: Condens. Matter* **2004**, *16*, 8743–  
598 8751.
- 599 (22) Gidopoulos, N. I.; Gross, E. K. U. Electronic Non-Adiabatic  
600 States: Towards a Density Functional Theory Beyond the Born-  
601 Oppenheimer Approximation. *Philos. Trans. R. Soc. A* **2014**, *372*  
602 (20130059), 1–9.
- 603 (23) Soudackov, A. V.; Hammes-Schiffer, S. Removal of the Double  
604 Adiabatic Approximation for Proton-Coupled Electron Transfer  
605 Reactions in Solution. *Chem. Phys. Lett.* **1999**, *299*, 503–510.
- 606 (24) Pak, M. V.; Hammes-Schiffer, S. Electron-Proton Correlation  
607 for Hydrogen Tunneling Systems. *Phys. Rev. Lett.* **2004**, *92* (103002),  
608 1–4.
- 609 (25) Webb, S. P.; Iordanov, T.; Hammes-Schiffer, S. Multiconfigura-  
610 tional Nuclear-Electronic Orbital Approach: Incorporation of Nuclear  
611 Quantum Effects in Electronic Structure Calculations. *J. Chem. Phys.*  
612 **2002**, *117*, 4106–4118.
- 613 (26) Tachikawa, M.; Mori, K.; Nakai, H.; Iguchi, K. An Extension of  
614 Ab Initio Molecular Orbital Theory to Nuclear Motion. *Chem. Phys.*  
615 *Lett.* **1998**, *290*, 437–442.
- 616 (27) Nakai, H. Nuclear Orbital Plus Molecular Orbital Theory:  
617 Simultaneous Determination of Nuclear and Electronic Wave  
618 Functions Without Born-Oppenheimer Approximation. *Int. J.*  
619 *Quantum Chem.* **2007**, *107*, 2849–2869.
- 620 (28) González, S. A.; Aguirre, N. F.; Reyes, A. Theoretical  
621 Investigation of Isotope Effects: The Any-Particle Molecular Orbital  
622 Code. *Int. J. Quantum Chem.* **2008**, *108*, 1742–1749.
- 623 (29) Posada, E.; Moncada, F.; Reyes, A. Negative Muon Chemistry:  
624 The Quantum Muon Effect and the Finite Nuclear Mass Effect. *J. Phys.*  
625 *Chem. A* **2014**, *118*, 9491–9499.
- 626 (30) Porter, A. R.; Towler, M. D.; Needs, R. J. Muonium as a  
627 Hydrogen Analogue in Silicon and Germanium: Quantum Effects and  
628 Hyperfine Parameters. *Phys. Rev. B* **1999**, *60*, 13534–13546.
- 629 (31) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P.  
630 Phonons and Related Crystal Properties From Density-Functional  
631 Perturbation Theory. *Rev. Mod. Phys.* **2001**, *73*, 515–562.
- 632 (32) Erba, A.; Casassa, S.; Dovesi, R.; Maschio, L.; Pisani, C. Periodic  
633 Density Functional Theory and Local-Mp2 Study of the Librational  
634 Modes of Ice XI. *J. Chem. Phys.* **2009**, *130* (074505), 1–9.
- 635 (33) Powell, A. S.; Lord, J. S.; Gregory, D. H.; Titman, J. J. Muon  
636 Spin Relaxation Studies of Lithium Nitridometallate Battery Materials:  
637 Muon Trapping and Lithium Ion Diffusion. *J. Phys. Chem. C* **2009**,  
638 *113*, 20758–20763.
- (34) Gil, J. M.; Mendes, P. J.; Ferreira, L. P.; Alberto, H. V.; Vilão, R. 639  
C.; Ayres de Campos, N.; Weidinger, A.; Tomm, Y.; Niedermayer, C.; 640  
Yakushev, M. V.; et al. Modeling Hydrogen in CuInSe<sub>2</sub> and CuInS<sub>2</sub> 641  
Solar Cell Materials Using Implanted Muons. *Phys. Rev. B* **1999**, *59*, 642  
1912–1916. 643
- (35) Kadono, R.; Imazato, J.; Matsuzaki, T.; Nishiyama, K.; 644  
Nagamine, K.; Yamazaki, T.; Richter, D.; Welter, J.-M. Quantum 645  
Diffusion of Positive Muons in Copper. *Phys. Rev. B* **1989**, *39*, 23–41. 646
- (36) Luke, G. M.; Brewer, J. H.; Kreitzman, S. R.; Noakes, D. R.; 647  
Celio, M.; Kadono, R.; Ansaldo, E. J. Muon Diffusion and Spin 648  
Dynamics in Copper. *Phys. Rev. B* **1991**, *43*, 3284–3297. 649
- (37) Storchak, V. G.; Prokofev, N. V. Quantum Diffusion of Muons 650  
and Muonium Atoms in Solids. *Rev. Mod. Phys.* **1998**, *70*, 929–978. 651
- (38) Kiefl, R. F.; Kadono, R.; Brewer, J. H.; Luke, G. M.; Yen, H. K.; 652  
Celio, M.; Ansaldo, E. J. Quantum Diffusion of Muonium in KCl. *Phys.* 653  
*Rev. Lett.* **1989**, *62*, 792–795. 654
- (39) Klein, P. N.; Rao, S.; Raucht, M.; Subramanian, S. Faster 655  
Shortest-Path Algorithms for Planar Graphs. STOC'94 ACM 656  
Symposium on Theory of Computing, Montreal, QC, Canada, May 657  
23–25, 1994, ACM: New York, 1994, 27–37. 658
- (40) Franke, R. Scattered Data Interpolation: Tests of Some 659  
Methods. *Math. Comp.* **1982**, *38*, 181–200. 660
- (41) Renka, R. J. Algorithm 661: QSHEP3D: Quadratic Shepard 661  
Method for Trivariate Interpolation of Scattered Data. *ACM Trans.* 662  
*Math. Softw.* **1988**, *14*, 151–152. 663
- (42) Burkardt, J. Home Page. <http://people.sc.fsu.edu/~jburkardt/> 664  
(accessed Jan. 26, 2015). 665
- (43) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; 666  
Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; 667  
et al. QUANTUM ESPRESSO: A Modular and Open-Source Software 668  
Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* 669  
**2009**, *21* (395502), 1–19. 670
- (44) Garrity, K. F.; Bennett, J. W.; Rabe, K. M.; Vanderbilt, D. 671  
Pseudopotentials for High-Throughput DFT Calculations. *Comput.* 672  
*Mater. Sci.* **2014**, *81*, 446–452. 673
- (45) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient 674  
Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. 675
- (46) Weinan, E.; Ren, W.; Vanden-Eijnden, E. String Method for the 676  
Study of Rare Events. *Phys. Rev. B* **2002**, *66* (052301), 1–4. 677
- (47) Henkelman, G.; Jónsson, H. A Dimer Method for Finding 678  
Saddle Points on High Dimensional Potential Surfaces Using Only 679  
First Derivatives. *J. Chem. Phys.* **1999**, *111*, 7010–7022. 680
- (48) Amato, A.; Dalmás de Réotier, P.; Andreica, D.; Yaouanc, A.; 681  
Suter, A.; Lapertot, G.; Pop, I. M.; Morenzoni, E.; Bonfà, P.; 682  
Bernardini, F.; et al. Understanding the  $\mu$ SR Spectra of MnSi Without 683  
Magnetic Polarons. *Phys. Rev. B* **2014**, *89* (184425), 1–10. 684
- (49) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone 685  
Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192. 686
- (50) Baldereschi, A. Mean-Value Point in the Brillouin Zone. *Phys.* 687  
*Rev. B* **1973**, *7*, 5212–5215. 688
- (51) Schilling, H.; Camani, M.; Gygax, F. N.; Rüegg, W.; Schenck, A. 689  
Depolarisation Studies of Positive Muons in Copper, Vanadium, 690  
Niobium And tantalum single crystals. *J. Phys. F* **1982**, *12*, 875–893. 691
- (52) Camani, M.; Gygax, F. N.; Rüegg, W.; Schenck, A.; Schilling, H. 692  
Positive Muons in Copper: Detection of an Electric-Field Gradient at 693  
the Neighbor Cu Nuclei and Determination of the Site of Localization. 694  
*Phys. Rev. Lett.* **1977**, *39*, 836–839. 695
- (53) Clawson, C. W.; Crowe, K. M.; Rosenblum, S. S.; Kohn, S. E.; 696  
Huang, C. Y.; Smith, J. L.; Brewer, J. H. Low-Temperature Mobility of 697  
Positive Muons in Copper. *Phys. Rev. Lett.* **1983**, *51*, 114–117. 698
- (54) Hartmann, O.; Norlin, L.; Yaouanc, A.; Le Hericy, J.; Karlsson, 699  
E.; Niinikoski, T. Low Temperature Studies of Muon Localization in 700  
Copper. *Hyperfine Interact.* **1981**, *8*, 533–537. 701
- (55) Flynn, C. P.; Stoneham, A. M. Quantum Theory of Diffusion 702  
With Application to Light Interstitials in Metals. *Phys. Rev. B* **1971**, *3*, 703  
2819. 704
- (56) Flynn, C. P.; Stoneham, A. M. Quantum Theory of Diffusion 705  
With Application to Light Interstitials in Metals. *Phys. Rev. B* **1970**, *1*, 706  
3966–3978. 707

- 708 (57) Teichler, H. On the Theory of Muon Diffusion in Metals. *Phys.*  
709 *Lett. A* **1977**, *64*, 78–80.
- 710 (58) Teichler, H. On the Theory of Diffusion of Light Interstitials in  
711 Metals. *Hyperfine Interact.* **1979**, *6*, 251–254.
- 712 (59) Teichler, H. Microscopic Calculation of Lattice Distortions  
713 around  $\mu^+$  in Cu. *Phys. Lett. A* **1978**, *67*, 313–315.
- 714 (60) Hirata, S.; Miller, E. B.; Ohnishi, Y.-y.; Yagi, K. On the Validity  
715 of the BornOppenheimer Separation and the Accuracy of Diagonal  
716 Corrections in Anharmonic Molecular Vibrations. *J. Phys. Chem. A*  
717 **2009**, *113*, 12461–12469.
- 718 (61) Varandas, A.; Xu, Z. Singularities in the Hamiltonian at  
719 Electronic Degeneracies. *Chem. Phys.* **2000**, *259*, 173–179.
- 720 (62) Sutcliffe, B. T.; Woolley, R. G. Molecular Structure Calculations  
721 Without Clamping the Nuclei. *Phys. Chem. Chem. Phys.* **2005**, *7*,  
722 3664–3676.
- 723 (63) Takahashi, S.; Takatsuka, K. On the Validity Range of the Born-  
724 Oppenheimer Approximation: A Semiclassical Study for All-Particle  
725 Quantization of Three-Body Coulomb Systems. *J. Chem. Phys.* **2006**,  
726 *124* (144101), 1–14.
- 727 (64) Romanowski, Z. B-Spline Solver for One-Electron Schrödinger  
728 Equation. *Mol. Phys.* **2011**, *109*, 2679–2691.
- 729 (65) Janecek, S.; Krotscheck, E. A Fast and Simple Program for  
730 Solving Local Schrödinger Equations in Two and Three Dimensions.  
731 *Comput. Phys. Commun.* **2008**, *178*, 835–842.
- 732 (66) De Renzi, R. Home Page. [http://www.fis.unipr.it/home/  
733 roberto.derenzi/dispense/pmwiki.php?n=MUSR.MuonSite](http://www.fis.unipr.it/home/roberto.derenzi/dispense/pmwiki.php?n=MUSR.MuonSite) (accessed  
734 Jan. 26, 2015).