Ab initio studies of magnetism in the organic radical *p*-NPNN

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Abstract. We present the first *ab initio* calculations of the internal magnetic field of a molecular magnet using a modified Ewald method. We apply this to both the β-phase and γ-phase forms of the organic radical *para*-nitrophenyl nitronyl nitroxide (*p*-NPNN). The β-phase is known to exhibit molecular ferromagnetism, whilst the γ-phase is antiferromagnetic. These results are of particular relevance to the interpretation of muon spin-rotation (μ^+SR) experiments, where the muon acts as a local probe of the internal magnetic field. As further guidance to the interpretation of such experiments, we also calculate the isotropic hyperfine constant for implanted muons.

1. Introduction

Recently, there has been considerable interest in the discovery of magnetic ordering in a class of purely organic compounds, based on the nitronyl nitroxide radical. These materials may display a wide variety of magnetic behaviours, including paramagnetism, antiferromagnetism and ferromagnetism, with different compounds having 1D chains, 2D planes and 3D bulk ordering. The first such compound to be discovered was the orthorhombic β-phase of *para*-nitrophenyl nitronyl nitroxide (*p*-NPNN) [1], which has a Curie temperature (T_c) of 0.6 K and is a molecular ferromagnet. A second crystal phase, the triclinic γ-phase, was also discovered to have a magnetic ordering transition at 0.65 K [2]. The γ-phase was initially believed to be ferromagnetic but was later shown to be antiferromagnetic [3]. The interpretation of the experiments on the γ-phase was quite contentious at first, until it was realized that the γ-phase was thermodynamically unstable with respect to the β-phase even at low temperatures [3].

The magnetic ordering has been probed by a variety of experimental techniques, including heat capacity and AC susceptibility measurements [1, 2], neutron diffraction [4], electron paramagnetic resonance [5] and muon spin-rotation and relaxation (μ^+SR) experiments [6–8]. It is the μ^+SR experiments that provide the most direct probe of the magnetic order at such low temperatures, as the muon precession frequency is directly proportional to the local magnetic field at the muon site.

In a zero-field μ^+SR experiment, a beam of fully spin-polarized positive muons (μ^+) is implanted into the material. In these materials, the muons will lose energy and eventually capture electrons to form muonium (Mu = $\mu^+ e^-$) [9]. The muonium spin will then precess in the local magnetic field until the muon decays (lifetime ~ 2.2 μs) into a positron which

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can then be detected outside the sample. Muonium behaves chemically like a pseudo-isotope of hydrogen, and will readily bond to the organic radical, and this determines the actual site taken up by the muon at low temperatures. Each p-NPNN molecule contains a single unpaired spin, and this will couple to the Mu to form either a spin singlet ($S = 0$) or a spin triplet ($S = 1$). In general, any spin-triplet states formed are not experimentally detectable, as the resulting hyperfine field at the muon produces a precession frequency that is too high, and so μ^+SR experiments tend to be interpreted in terms of singlet states alone. For details about the theory and applications of μ^+SR see the review by Cox [9]. In simple ferromagnets, the muon often occupies a single high-symmetry site and the interpretation of the data is therefore relatively straightforward [10].

However, for these molecular materials, there are some problems in the interpretation of the μ^+SR data because of the large number of possible muon sites, which is due to the relatively complex molecular crystal structure. In this paper, we seek to address this issue by first calculating the possible muon sites by a sequence of *ab initio* spin-polarized total energy calculations of the binding of Mu to p-NPNN, and then calculating the local magnetic field at the energetically preferred sites from the molecular spin density. We consider both singlet and triplet states with a variety of possible spin-ordering directions, for both the β-phase and the γ-phase of p-NPNN. These predictions are therefore directly comparable to the experimental measurements. As a further guide to the interpretation of experimental results, we also calculate the isotropic hyperfine constant at each triplet site. Recent μ^+SR experiments [8] have suggested that as well as singlet states, there may also be a triplet state formed, the existence of which could be identified by a non-zero isotropic hyperfine constant.

2. Method

The *ab initio* total energy calculations have been performed using the projector augmented-wave (PAW) method [11] implementation of density functional theory, with the local spin-density (LSD) approximation. This combination of the PAW method and LSD has been demonstrated before to be capable of accurate calculation of the muon binding sites in a simple organic magnet [12]. As the PAW method is an all-electron method, it is also suited to the calculation of the isotropic hyperfine constant as was demonstrated recently [13, 14].

The muonium binding sites were evaluated by a series of total energy minimizations using the PAW method with damped dynamics, allowing full structural relaxation of the p-NPNN molecule in the presence of the muonium atom. These initial calculations were performed on a single molecule with periodic boundary conditions in a $20 \times 30 \times 15$ au box at zero temperature. The box size was chosen to be sufficiently big that there would be no interactions with image molecules. It is expected that the details of the muonium binding site will be determined by the local molecular environment and not by the crystal structure. These results may then be readily transferred to any given crystal structure. The weakness of the intermolecular magnetic interactions in these materials can be seen by the very low ordering temperatures, typically 0.6 K, and hence are neglected in the following calculations.

The electronic wavefunctions were expanded in plane waves up to an energy cut-off of 25 Ryd, with effective-electron-mass preconditioning above 2 Ryd [16]. Such a reasonably low cut-off was possible because of the use of a non-norm-conserving projector set for the oxygen atoms. The use of a norm-conserving projector for oxygen would have necessitated a cut-off of at least 40 Ryd, which would have been much more expensive in terms of computer resources.
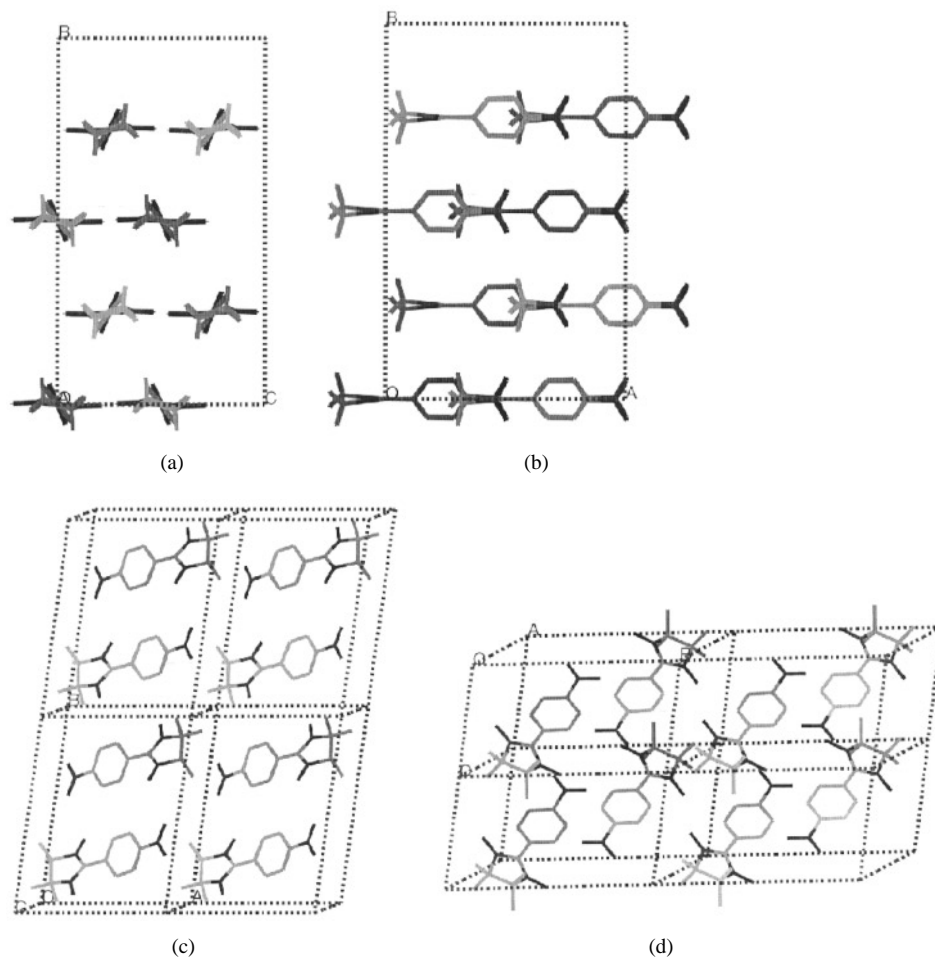
Figure 1. The crystal structure of the β-phase of p-NPNN (a) viewed along the [001] axis and (b) viewed along the [100] axis. The crystal structure of the γ-phase of p-NPNN (c) viewed along a direction close to the [001] axis and (d) viewed along a direction close to the [100] axis.

Once the most stable sites had been identified, the three most stable sites (all singlets) and a representative triplet site were then considered in more detail. For each crystal phase, the spin density over the full unit cell was calculated. This was generated by superposition of the spin density of a single p-PYNN molecule in the respective unit cell, using the appropriate symmetry operations. This spin density, together with the spin density for a single p-PYNN molecule with a muonium atom at the appropriate site, was then used to calculate the internal magnetic field at that muon site, using a modified Ewald sum (see appendix 1). We therefore assumed that the effect of muonium bonding to a given molecule is local to that molecule, and that there is perfect intermolecular order. These assumptions seem reasonable and result in considerable computational cost saving, as the unit cells are large and contain many atoms. The beta phase has an orthorhombic unit cell, $a = 12.347$ Å, $b = 19.350$ Å, $c = 10.960$ Å with $Z = 8$, whilst the gamma phase has a triclinic unit cell, with $a = 9.193$ Å, $b = 12.105$ Å, $c = 6.471$ Å, $\alpha = 97.35°$, $\beta = 104.44°$ and $\gamma = 82.22°$, and $Z = 2$. The crystal structures are shown in figure 1.
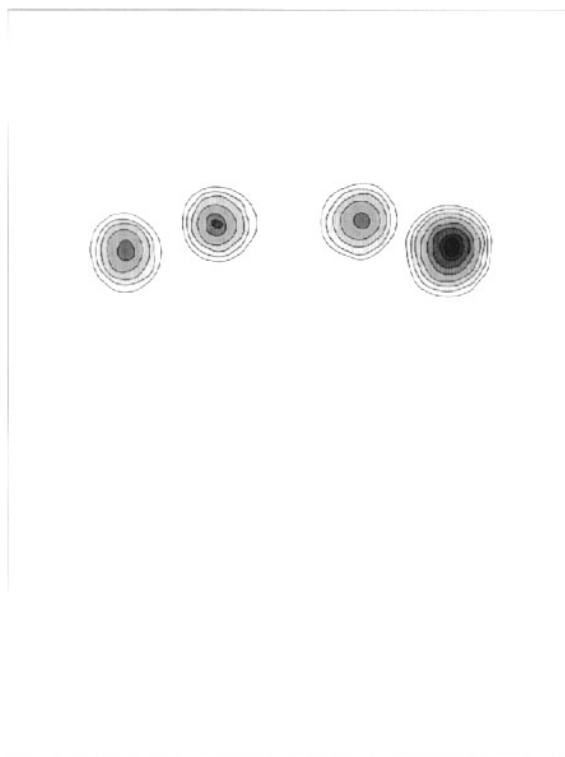
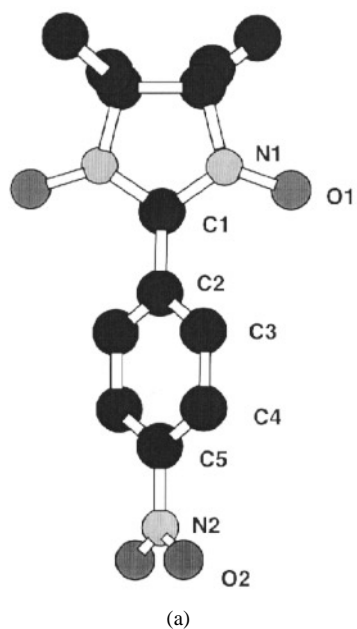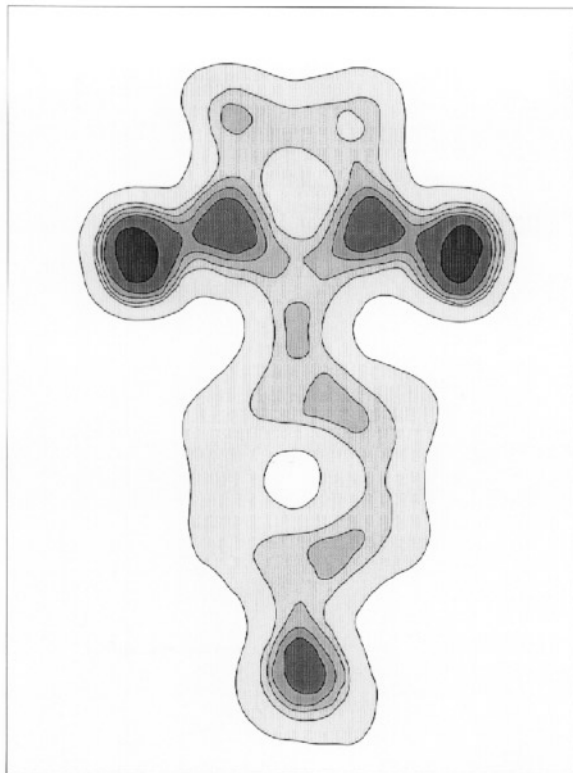(a)

(b)

Figure 2. (a) A 'ball and stick' picture of a single molecule of *p*-NPNN with labels identifying the atomic sites referred to in the text. (b) A 2D section through the spin density of a single molecule of *p*-NPNN in the same orientation as (a), with the plane passing through O1–N1–C1. (c) The corresponding 2D section through the charge density of a single molecule of *p*-NPNN.

(c)

Figure 2. (Continued)

It should be noted that as these calculations are based upon local density functional theory for an isolated molecule, we only have the spin density at each site, and not the actual spin wavefunction. We must therefore choose a direction for the spin vector to point in, and use this direction with the spin density to form the magnetic dipole vector at each site. We were therefore able to consider a range of possible spin directions, corresponding to different directions of the internal magnetization vector. Experiments suggest that for the beta phase, the easy axis is [010] whilst for the gamma phase the antiferromagnetic ordering is along the [011] direction [3]. For convenience therefore we only considered possible spin directions along the principal crystal axes and main diagonals.

For computational convenience, the spin density was split into two contributions, corresponding to the local part centred on each atomic core, and the plane-wave part. This splitting is a natural consequence of the PAW methodology and enables substantial savings in computer resources to be made. This is because it is only necessary to sample the plane-wave part relatively coarsely (1.0 au grid) due to the truncation of the plane-wave expansions. However, the local part needs to be sampled at a finer resolution (0.2 au grid) as it varies rapidly in a small volume around each atomic core. Both of these contributions were treated independently in the above procedure and the final results combined.

It is also possible to calculate the isotropic part of the hyperfine constant (A) from the spin density at the muon. This can then be readily compared to the experimental value. Within the approximations that we have used, there will only be a non-zero value of A if

the spin wavefunction of the local molecule is not a singlet. Recent μ^+SR experiments [8] on the β-phase of p-NPNN have suggested a value of $A \sim 400 \pm 100$ MHz. (The uncertainty is quite large because this value was determined by the repolarization technique from longitudinal field measurements and not directly as in a transverse field experiment.) We have therefore also calculated a value for A for the triplet spin state at each muon site, but have not included effects of zero-point motion of the muonium. The effect of zero-point motion of muonium has previously been shown to be significant in the calculation of A [13–15] particularly if there is the possibility of bond rotation or hyperconjugation.

Table 1. Results from *ab initio* energy minimizations. Typical sampling errors in each quantity are given in the first row of the table. E_0 is the lowest-energy bound state of the p-NPNN plus muonium atom system, which is approximately 16.09 eV below the ground-state energy of an isolated p-NPNN molecule and muonium atom with the same simulation parameters.

Site	Singlet energy (eV above E_0)	Triplet energy (eV above E_0)	Triplet isotropic hyperfine constant (MHz)
O1	0.179 ± 0.003	11.63 ± 0.03	198 ± 5
N1	0.552	0.972	176
C1	0.371	1.813	282
C3	0.847	0.908	827
C4	0	1.148	435
N2	0.232	1.524	17.5
O2	0.134	1.121	−8.3

3. Results and discussion

The structure of a single molecule of p-NPNN is shown in figure 2(a), with the labels referring to the possible binding sites of a muonium atom considered. The extra hydrogen atoms are not shown for clarity but were included in the calculations. The results of the *ab initio* energy minimizations of a single molecule of p-NPNN and a muonium atom are shown in table 1, for both spin-singlet and spin-triplet states. The corresponding isotropic hyperfine constant (A) is also included for the triplet states. From this table, it can be seen that all of the low-energy sites correspond to spin singlets. The lowest-energy state corresponds to the muonium atom bonding to the C4 carbon atom in the aromatic ring. The next two lowest-energy sites correspond to the muonium atom bonding to oxygen atoms, either in the nitronyl nitroxide group (O1), or at the NO_2 group (O2). All three of these sites are within 0.2 eV of each other, and were therefore considered in more detail. Previous calculations on simpler nitronyl nitroxide organic magnets such as p-PYNN [12] have found the singlet O1 site to be the lowest in energy. This is in line with chemical intuition, and so a similar lowest-energy site might also have been expected here.

The triplet sites were all considerably higher (at least 0.7 eV) in energy than these three sites. However, the calculated values of A for the first five triplet states seem reasonable as there is experimental evidence for a triplet site with a hyperfine constant $\sim$400 MHz, with the C4 site being the closest to this experimental value. It is interesting to note that this site corresponds to the triplet version of the lowest-energy singlet state.

The last two triplet states in the table seem to have a hyperfine constant that is an order of magnitude smaller than the experimental value and it might therefore seem that they should be discounted. However, at the O2 binding site there could be hyperconjugation arising from the N2 atom. Therefore if the zero-point motion of the muonium atom were

included (which might be of large amplitude given the amount of steric freedom associated with this position), there might be a considerable change in the expectation value of *A* from this instantaneous value [13, 14]. Therefore this site may not be ruled out by the experimental value of *A* once zero-point motion has been properly included. The triplet O2 site was therefore considered in the subsequent Ewald calculations.

A 2D section though the spin density for a single molecule is shown in figure 2(b), along with the corresponding charge density in figure 2(c). From this it can be seen that the spin density is concentrated around the nitronyl nitroxide group (primarily on the oxygen atoms), although there is a small negative contribution from the NO_2 group at the opposite end of the molecule which cannot be seen in this particular section. It can also be seen that the spin wavefunction has a considerable spatial extent, which reinforces the need for a proper *ab initio* treatment. Previous attempts to calculate the internal magnetic field in these systems have approximated the spin density by a localized magnetic dipole on the C1 atom and assumed this was also the position of the muonium atom [5, 8], or used an empirical fit to magnetization data to get 0.6 μ_B/molecule which was then used in a single-point-dipole calculation [4]. Both of these approaches are unsatisfactory in their treatment of the muonium binding site and the extended spin wavefunction.

Table 2. The internal magnetic field (G) at the muon site, for the β-phase, for a range of different easy-axis directions.

Site	[100]	[110]	[101]	[010]	[011]	[001]
O1 singlet	173	188	163	127	111	198
C4 singlet	129	353	273	368	384	320
O2 singlet	83	64	87	44	74	118
O2 triplet	118	66	121	63	87	84

Table 3. The internal magnetic field (G) at the muon site, for the γ-phase, for a range of different easy-axis directions.

Site	[100]	[110]	[101]	[010]	[011]	[001]
O1 singlet	329	327	428	283	344	340
C4 singlet	155	181	62	184	157	152
O2 singlet	262	254	210	247	236	39
O2 triplet	233	216	192	176	164	59

We therefore calculated the *ab initio* spin density across the full unit cell for both the β-phase and the γ-phase and then used the coordinates of the muon from the three lowest-energy singlet sites to calculate the local magnetic field at each site. This was done for six different spin directions, the results of which are shown in table 2 for the β-phase and table 3 for the γ-phase. The experimentally accepted value for the zero-temperature internal field at the muon site is 150 G for the β-phase [8] and is unknown for the γ-phase. It is also thought that the easy axis is [010] for the β-phase and [011] for the γ-phase [3]. It can be seen from these tables that changing the direction of the spin vector can make a large difference in the local magnetic field—particularly for the C4 and O2 sites. It can also be seen that the calculated local field for the O1 site in the β-phase for a spin direction of [010] is 127 G, which is remarkably close to the experimental value of 150 G. The corresponding local field at the C4 site is considerably higher than that seen experimentally, whilst at

the O2 site it is considerably lower. It would therefore seem likely that that O1 is the preferred bonding site for the muonium atom in these materials. If the ordering direction is indeed along [011] for the γ-phase, then we predict that the internal field seen in a μ^+SR experiment will be about 344 G.

To make a true comparison with experimental results, we ought to include the effects of demagnetization and polycrystallinity. Both of these effects will be strongly sample dependent. However, we can make a first approximation to the effects of polycrystallinity for the orthorhombic β-phase by averaging over the [100], [010] and [001] directions, which then gives the local field at the O1 site as being 166 G, which is in even better agreement with the experimental value. Similar calculations give 272 G for the C4 site and 82 G for the O2 site.

It may seem surprising that the C4 site in the β-phase has a considerably higher local magnetic field than either of the oxygen sites, as the net spin density is concentrated around the nitronyl nitroxide group (see figure 2(b)). However, in the spin singlet there is no contribution to the local magnetic field from the actual molecule that the muonium is bonded to, and so the dominant contributions arise from the nearest neighbouring molecules. It is the nitronyl nitroxide group on the neighbouring molecules that are closest to the C4 site and therefore cause the larger magnetic field there. In fact, it is the intermolecular overlap between the aromatic ring and the nitronyl nitroxide groups on neighbouring molecules that is believed to be the origin of the spin ordering in these materials. [1, 2]. For the γ-phase, the converse is true, because this phase is antiferromagnetic, with neighbouring molecules being anti-aligned.

4. Conclusions

In conclusion, we have performed the first *ab initio* calculations of the internal magnetic field of a molecular magnet. As a test system we have considered *p*-NPNN which is of interest as it is a wholly organic material, that can be either ferromagnetic (β-phase) or antiferromagnetic (γ-phase). The clearest indication of the magnetic ordering in this material comes from μ^+SR experiments, but the interpretation of the experimental results is difficult because of the many different possible binding sites of muonium in each molecule.

We therefore used the PAW *ab initio* method to calculate the most favourable binding sites for a muonium atom in the *p*-NPNN molecule, with both spin-singlet and spin-triplet states. We have used these sites with a modified Ewald sum to calculate the local magnetic field seen in a μ^+SR experiment, for both the β and γ crystal structures. We have also used the knowledge of the full electron wavefunction to calculate the isotropic hyperfine constant of muonium for the triplet states.

It seems likely from the local magnetic field values that the actual bonding site taken up is the O1 site with a singlet spin wavefunction, a conclusion which is backed up by chemical intuition and previous *ab initio* calculations on similar molecules. Other low-lying sites include the C4 and the O2 positions, but a muonium atom at these sites experiences quite different internal magnetic fields from those seen experimentally. The spin-singlet C4 site is found to be the lowest-energy site, but is probably shifted to slightly higher energies when the intermolecular overlap is taken into account. It is also possible that there is a distribution of occupied sites (for example O1, C4 and O2), which could average to give the experimental observations.

There is experimental evidence for a small fraction of occupied spin-triplet states. We find that these states are much higher in energy than the singlet states (at least 0.7 eV) which explains why they are rare. However, our calculated hyperfine constants are in line

with experimental observations, which therefore suggests that either the C4 site is the most likely triplet site, or else there is again some distribution of occupied triplet states which average to give the experimental result.

Acknowledgments

Appendix A. The modified Ewald sum for magnetic fields

The original Ewald sum [17, 18] was a technique developed to sum the Coulombic interaction energies at an ion in an ionic crystal due to all of the other ions. Such a sum is only conditionally convergent, due to the long range of the Coulomb force and the alternating sign of the contribution from successive shells going radially out from the summation point. In the Ewald method, each point charge in the original distribution is surrounded by a Gaussian charge distribution of equal magnitude and opposite sign:

$$\rho_i(r) = \frac{z_i \kappa^3 e^{-\kappa^2 r^2}}{\pi^{3/2}}$$

where κ determines the width of the distribution and r is measured from the centre of the distribution. This extra distribution effectively screens the ionic interaction and makes it short ranged, so it can now be summed in real space. The cancelling distribution may be conveniently summed in reciprocal space, and the result Fourier transformed back to real space and combined with the real-space sum (with the cancellation of the self-interaction term) to give the final result. With a judicious choice of κ, the real-space sum can be made convergent within a single unit cell, and the reciprocal-space sum can be simultaneously made to converge readily within a modest number of k-vectors. This basic technique may be adapted to the summation of electric or magnetic dipole energies as well [19–21]. Other developments of the technique have included analysis of the effect of boundary conditions, such as whether at the surface the system is terminated by a vacuum or some other medium [21], and the effectiveness of non-Gaussian distributions of the cancellation charge [22, 23].

For this problem, we are interested in the magnetic field at a single site due to the effect of a distribution of point magnetic dipoles (from the *ab initio* spin density of each molecule evaluated on a discrete mesh) in the unit cell, summed over the entire sample. This is actually simpler than the energy of interaction as it requires only a single and not a double sum over the dipole coordinates, but instead it requires a vector and not a scalar sum. The appropriate formula for this modified Ewald sum is then

$$B_{\text{Ewald}}(r) = B_{\text{real}}(r) + B_{\text{reciprocal}}(r) - B_{\text{self}}(r) + B_{\text{surface}}(r) \tag{A1}$$

where

$$B_{\text{real}}(r_i) = -\frac{\mu_0}{4\pi} \sum_j (m(r_j) B(|r_{ij} + n|) - (m(r_j) \cdot r_{ij}) r_{ij} C(|r_{ij} + n|)) \tag{A2}$$

$$B(r) = \frac{\text{erfc}(\kappa r)}{r^3} + \left(\frac{2\kappa}{\sqrt{\pi}} \frac{\exp(-\kappa^2 r^2)}{r^2} \right) \tag{A3}$$

$$C(r) = \frac{3 \, \text{erfc}(\kappa r)}{r^5} + \left(\frac{2\kappa}{\sqrt{\pi}} \frac{\exp(-\kappa^2 r^2)}{r^2} \right) \left(2\kappa^2 + \frac{3}{r^2} \right) \tag{A4}$$

$$B_{\text{reciprocal}}(\boldsymbol{r}_i) = -\frac{\mu_0}{4\pi} \sum_j \sum_{k \neq 0} \frac{1}{\pi V} \boldsymbol{k}(\boldsymbol{m}(\boldsymbol{r}_{ij}) \cdot \boldsymbol{k}) \left(\frac{4\pi^2 \exp(-|\boldsymbol{k}|^2/4\kappa^2)}{|\boldsymbol{k}|^2} \right) \cos(\boldsymbol{r}_{ij} \cdot \boldsymbol{k}) \quad \text{(A5)}$$

$$B_{\text{self}}(\boldsymbol{r}_i) = -\frac{\mu_0}{4\pi} \frac{2\kappa^3}{3\sqrt{\pi}} \boldsymbol{m}(\boldsymbol{r}_i) \tag{A6}$$

$$B_{\text{surface}}(\boldsymbol{r}_i) = -\frac{\mu_0}{4\pi} \sum_j \frac{4\pi}{V} \boldsymbol{m}(\boldsymbol{r}_j) \tag{A7}$$

where $\boldsymbol{m}(\boldsymbol{r}_i)$ is the magnetic dipole moment due to the spin density at $\boldsymbol{r}_i$, $\boldsymbol{n}$ is a real-space lattice vector, $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, κ is the inverse width of the Gaussian cancelling distribution in real space, V is the volume of the unit cell, and erfc is the complementary error function. It is necessary to choose appropriate values for κ and for the maximum number of plane waves to include in the reciprocal-space sum. It was found that choosing $\kappa = 0.5$ au^{-1} and truncating the plane-wave sum at 5 Hartree gave reliable convergence of the result.
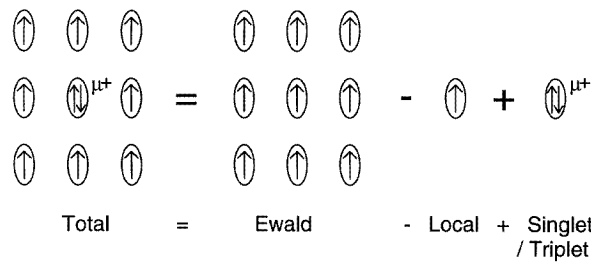

Figure A1. A schematic diagram of the modified Ewald method, showing how the local magnetic field at the muon site is built up from calculations of the perfect crystal with periodic boundary conditions, and also the local effect of a single molecule. The ellipses represent a single molecule of *p*-NPNN with the arrows indicating the net spin, and the single muon is shown as μ^+.

This modified Ewald sum then gives the magnetic field at a site due to the sum of all of the field contributions from the magnetic dipoles in the unit cell, repeated throughout the entire sample. However, this is not quite the item of interest. If we were to consider the muonium atom as a single impurity atom in an otherwise perfect *p*-NPNN crystal, then it can be seen that we need to modify this approach to include the effect of this single defect. In particular, if the muonium atom binds to a given *p*-NPNN molecule to form a spin singlet, then there will be no contribution to the magnetic field at the muon from the molecule that has been bonded to, and there will only be contributions from the other molecules in the unit cell, and from the surrounding crystal of perfect unit cells. Similarly, if the muonium bonds in a spin triplet, then there will be an extra contribution to the sums from the bonded molecule, which will be quite different to that of all of the other molecules (which are spin doublets). We therefore need a method for calculating the field from a single local molecule and then need to combine this with the results from the Ewald sum. The field due to a local distribution of magnetic dipoles is taken to be

$$B_{\text{local}}(\boldsymbol{r}_i) = -\frac{\mu_0}{4\pi} \sum_{r_j} \left(\frac{\boldsymbol{m}(\boldsymbol{r}_j) - 3\hat{\boldsymbol{r}}_{ij}(\boldsymbol{m}(\boldsymbol{r}_j) \cdot \hat{\boldsymbol{r}}_{ij})}{r_{ij}^3} \right) \tag{A8}$$

and so the resultant expression for the magnetic field at the muon site in a spin singlet is

$$B_{\text{total}}(\boldsymbol{r}_\mu) = B_{\text{Ewald}}(\boldsymbol{r}_\mu) - B_{\text{local}}(\boldsymbol{r}_\mu) \tag{A9}$$

and for a spin triplet it is

$$B_{\text{total}}(\boldsymbol{r}_\mu) = B_{\text{Ewald}}(\boldsymbol{r}_\mu) - B_{\text{local}}(\boldsymbol{r}_\mu) + B_{\text{triplet}}(\boldsymbol{r}_\mu) \tag{A10}$$

where B_{Ewald} is the result for the Ewald sum for the perfect p-NPNN crystal at the muon site $\boldsymbol{r}_\mu$, B_{local} is the field at the muon site due to a single molecule of p-NPNN and B_{triplet} is the field at the muon site due to a single molecule of p-NPNN bonded to the muonium atom forming a spin triplet. This is shown pictorially in figure A1.

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