Journal of Physics: Conference Series

**PAPER • OPEN ACCESS**

# The interaction between a positive muon and multiple quadrupolar nuclei

To cite this article: Nathan P Bentley and Stephen J Blundell 2023 *J. Phys.: Conf. Ser.* **2462** 012043

Journal of Physics: Conference Series **2462** (2023) 012043 doi:10.1088/1742-6596/2462/1/012043

# The interaction between a positive muon and multiple quadrupolar nuclei

**Nathan P Bentley and Stephen J Blundell**

Department of Physics, Clarendon Laboratory, Oxford University, Parks Road, Oxford OX1 3PU, United Kingdom

E-mail: `stephen.blundell@physics.ox.ac.uk`

**Abstract.** A positively charged muon implanted in copper sits at an octahedral interstitial site and experiences a magnetic dipolar coupling with six nearest-neighbour quadrupolar $I = 3/2$ copper nuclei. The resulting avoided level crossing resonance observed as a function of magnetic field provides a means of studying these interactions and understanding the effect of the electric-field gradient due to the muon acting on the quadrupolar nuclei. The effect is usually modelled by considering the interaction between the positive muon and a single copper nucleus, but the other five copper nuclei are equally important. By solving the problem in the full $2(2I + 1)^6 = 8192$-dimensional Hilbert space, we demonstrate the effect of these additional interactions.

## 1. Introduction

The average polarization measured in a muon-spin rotation ($\mu$SR) experiment increases with applied longitudinal field (repolarization [1, 2, 3]), but in the case of an avoided level crossing (ALC) in the energy levels, flip-flop transitions cause it to dip below 1 [4]. This feature in $P_z^\mu(B)$ is referred to as an avoided level crossing (ALC) resonance and such resonances contain information about the properties of the systems in which they are observed. The shape of the resonance reveals information about the local environment of the muon and the presence of molecular dynamics or spin dynamics [5]. ALC resonances occur in a variety of systems [6, 7, 8, 9, 10, 11, 12], but a paradigmatic case is given by the coupling of a muon to Cu nuclei in metallic copper [13, 14, 15]. The Cu nucleus has a spin of $I = \frac{3}{2}$ , so possesses a quadrupole moment. (69% of the nuclei are $^{63}$Cu and 31% are $^{65}$Cu, but both isotopes are spin-3/2 with a very similar magnetic moment.) The electric field gradient produced by the muon interacts with this quadrupole moment, leading to a quadrupolar term in the Hamiltonian. This paper considers the modelling of these resonances that goes beyond the simple treatment of coupling the muon to a single Cu nucleus, and includes the effect of the coupling to six identical Cu nuclei that comprise the octahedral environment around the muon [see Fig. 1(a)].

## 2. Theory

We model the muon coupled to six nearest-neighbour Cu spins, appropriate for the octahedral site. It is known that the muon produces only a very small distortion in the local environment

Journal of Physics: Conference Series **2462** (2023) 012043 doi:10.1088/1742-6596/2462/1/012043

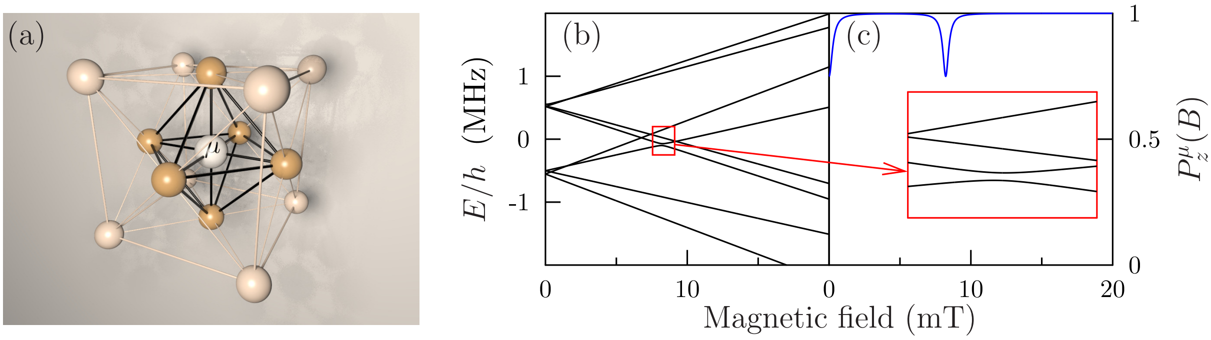


**Figure 1.** (a) The muon sits at an octahedral interstitial site in the face-centred cubic lattice of Cu. The six nearest-neighbours of Cu are shown in the darker copper colour. (b) The energy levels for a muon coupled to a single Cu nuclear spin. (c) The corresponding ALC resonance, with the inset showing a magnified portion of the avoided crossing.

[13], probably due to screening effects [16]. The Hamiltonian is given by

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\rm Z}^{\mu} + \sum_{i=1}^{N} \hat{\mathcal{H}}_{\rm Z}^{i} + \hat{\mathcal{H}}_{\rm dip}^{\mu,i} + \hat{\mathcal{H}}_{\rm Q}^{i}, \tag{1}$$

where the sum over $i$ includes all $N = 6$ Cu spins, $\hat{\mathcal{H}}_{\rm Z}$ is a Zeeman term ($\hat{\mathcal{H}}_{\rm Z}^{\mu}$ for the muon and $\hat{\mathcal{H}}_{\rm Z}^{i}$ for each of the six Cu spins), and $\hat{\mathcal{H}}_{\rm dip}^{\mu,i}$ is the dipolar interaction between the muon spin $\boldsymbol{S}$ and the $i$th Cu spin $\boldsymbol{I}^i$ which is given by

$$\hat{\mathcal{H}}_{\rm dip}^{\mu,i} = \hbar\omega_{\rm D}\left[\boldsymbol{S}\cdot\boldsymbol{I}^i - 3(\boldsymbol{n}^i\cdot\boldsymbol{S})(\boldsymbol{n}^i\cdot\boldsymbol{I}^i)\right], \tag{2}$$

where $\boldsymbol{n}^i$ is the unit vector separating the muon and the $i$th Cu spin and the dipolar frequency $\omega_{\rm D}$ is given by $\omega_{\rm D} = \mu_0\hbar\gamma_\mu\gamma_{\rm Cu}/4\pi r^3$, where $r$ is the separation between the muon and the Cu spins. We neglect the dipolar interaction between Cu spins since this is an order of magnitude lower than that between a Cu spin and the muon. The quadrupolar term $\hat{\mathcal{H}}_{\rm Q}^{i}$ for the $i$th Cu spin is given by

$$\hat{\mathcal{H}}_{\rm Q}^{i} = \hbar\omega_{\rm Q}\left[(\boldsymbol{n}^i\cdot\boldsymbol{I}^i)^2 - \frac{I(I+1)}{3}\right], \tag{3}$$

where the quadrupolar frequency $\omega_{\rm Q}$ is given by $\omega_{\rm Q} = 3e^2qQ/4\hbar I(2I-1)$, where $Q$ is the quadrupole moment and $eq$ is the magnitude of the electric-field gradient. The quadrupole moment in Cu is negative, and so the $\pm\frac{3}{2}$ levels are lowered in energy and the $\pm\frac{1}{2}$ levels are raised in energy. The direction $\boldsymbol{n}^i$ of the electric field gradient due to the muon is different for each of the Cu nuclei and is directed towards the muon from each Cu site.

The density matrix of the system at $t = 0$ is written as $\rho = \frac{1}{M}(1+\sigma_z^\mu)\otimes\left(\bigotimes_{i=1}^{6}\mathbb{1}^i\right)$, meaning that the muon is initially in a pure state (polarized along $z$) and the Cu nuclear spins are in mixed states (with $\mathbb{1}^i$ being a $4\times 4$ unit matrix for the $i$th Cu spin). A completely mixed state is justified because the splitting of the energy levels of the system in the regime of interest is $\approx$ 1MHz, corresponding to a temperature of $\approx$ 0.05mK, so the nuclear spin system before muon implantation will be in the infinite temperature limit. Here the Hilbert space dimensionality $M = 2(2I+1)^6 = 8192$. The time-evolved muon polarization after implantation is then $P_z^\mu = \frac{1}{M}{\rm Tr}\left[{\rm e}^{-{\rm i}\mathcal{H}t}\sigma_z^\mu{\rm e}^{{\rm i}\mathcal{H}t}\sigma_z^\mu\right]$, which simplifies to

$$P_z^\mu = \frac{1}{M}\left[\sum_n |\langle n|\,\sigma_z^\mu\,|n\rangle|^2 + 2\sum_{n<m}|\langle n|\,\sigma_z^\mu\,|m\rangle|^2\cos(\omega_{mn}t)\right], \tag{4}$$

in which the sums are over the $M$ energy eigenstates of the system and $\omega_{nm} = \omega_n - \omega_m$. The oscillating term is typically high frequency and is mainly averaged out in experiment, and so one can focus on the first term. (However, since the frequencies will be of the order of the dipolar coupling, in an integral counting experiment such oscillating terms will be multiplied by the intrinsic muon decay and could, in principle, contribute to the resulting signal, reducing the peak amplitude of the resonances and increasing their broadening. Since we wish to focus purely on the effect of multiple dipolar couplings, we neglect this effect in our treatment.)

In the high-field limit, the $z$-components of the muon and nuclear spins are good quantum numbers, and so $P_z^\mu = 1$, unless the eigenstates mix, which they do when levels cross. In that case, "flip-flop" terms of the form $S_+I_-^i + S_-I_+^i$ in the Hamiltonian can cause an ALC resonance, and thus require a level crossing between levels of the form $|\uparrow, n_i\rangle$ and $|\downarrow, n_i + 1\rangle$, i.e. between states in which a flip-flop between the muon and a Cu nuclear spin is possible (here we are only labelling the $i$th Cu nuclear spin, since the other Cu nuclear spins are the same for the two states). If the states in the levels don't take this form then they are not mixed by relevant "flip-flop" terms, so the level crossing isn't avoided and no resonance is produced.

The computational modelling has been carried out utilising the QuTiP python package [17]. This provides functionality for handling spins as quantum objects using python classes, so one has access to a range of functions that allow for the easy calculation of relevant quantities, such as the matrix elements of the muon spin operator. Our approach uses exact diagonalisation of the Hamiltonian, before calculating the matrix elements of $\sigma_z^\mu$ that contribute to the polarization, and avoids the Trotter formula approximation that has been used in previous approaches [15, 18]. The method of exact diagonalisation of finite quantum spin systems (as used recently in studying the muon coupled to arrays of fluorine nuclei [19]) possesses the key advantage that it allows extraction of all the energy eigenvalues of the system, which isn't the case for the method utilising the Trotter formula, so we are able to observe the relationship between the energy levels of the system and the resulting ALC resonances.

## 3. Results

Considering a muon coupled to a single Cu nuclear spin, or to two Cu nuclear spins, results in particularly simple cases because all spins can be made collinear. (This will of course not be the case when considering the full octahedral environment.) Simulations with a single Cu nuclear spin are shown in Fig. 1(b), illustrating how the energy levels behave as a function of field. They are split into two groups in zero field with energy approximately $\pm|h\nu_\mathrm{Q}|$ (for $|I_z| = \frac{1}{2}$ and $\frac{3}{2}$) where $|\nu_\mathrm{Q}| = |\omega_\mathrm{Q}|/(2\pi) = 0.527$ MHz. The asymmetry rapidly repolarizes in fields above $\approx 1$ mT, as shown in Fig. 1(c), and above this the high field limit is achieved. The dipolar coupling is very small ($\nu_\mathrm{D} = 0.017$ MHz $\ll \nu_\mathrm{Q}$), but provides the flip-flop term connecting the level crossing between the $|\uparrow, \frac{1}{2}\rangle$ and $|\downarrow, \frac{3}{2}\rangle$ levels and this leads to the ALC resonance shown in Fig. 1(c). Since the splitting between the two groups of levels at $B = 0$ is approximately $2|h\nu_\mathrm{Q}|$, the avoided level crossing should occur at a field given by the ratio of $2|\nu_\mathrm{Q}|$ to the difference of the gyromagnetic ratios $\frac{\gamma_\mu}{2\pi} - \frac{\gamma_\mathrm{Cu}}{2\pi}$ so that $B_\mathrm{ALC} = 4\pi|\nu_\mathrm{Q}|/(\gamma_\mu - \gamma_\mathrm{Cu}) \approx 8.5$ mT. Including the presence of the dipolar coupling leads to a splitting of the energy levels within their quadrupolar "groups", breaking the degeneracy of the system in the zero field limit. The breaking of this degeneracy can be characterised by two types of behaviour. The first type of behaviour corresponds to cases in which either the eigenstates of the system remain unchanged or are mixed within a quadrupolar "group". This consists of the $|\uparrow, \frac{3}{2}\rangle$ and $|\downarrow, -\frac{3}{2}\rangle$ eigenstates in the lower group of levels, which remain unmixed and are both shifted by $-\frac{3}{2}\nu_D$ and the $|\uparrow, -\frac{1}{2}\rangle$ and $|\downarrow, \frac{1}{2}\rangle$ eigenstates in the upper group of levels, which are mixed into $\frac{1}{\sqrt{2}}(|\uparrow, -\frac{1}{2}\rangle - |\downarrow, \frac{1}{2}\rangle)$ and $\frac{1}{\sqrt{2}}(|\uparrow, -\frac{1}{2}\rangle + |\downarrow, \frac{1}{2}\rangle)$, forming a "singlet/triplet like" pair that are shifted by $-\frac{1}{2}\nu_D$ and $\frac{3}{2}\nu_D$ respectively. The second type of behaviour corresponds to a very weak mixing of eigenstates between the quadrupolar groups. The states which are mainly $|\downarrow, \frac{3}{2}\rangle$ and $|\uparrow, -\frac{3}{2}\rangle$ are both shifted by $1.487\nu_{\rm D}$; those which are mainly $|\uparrow, \frac{1}{2}\rangle$ and $|\downarrow, -\frac{1}{2}\rangle$ are both shifted by $-0.487\nu_{\rm D}$.

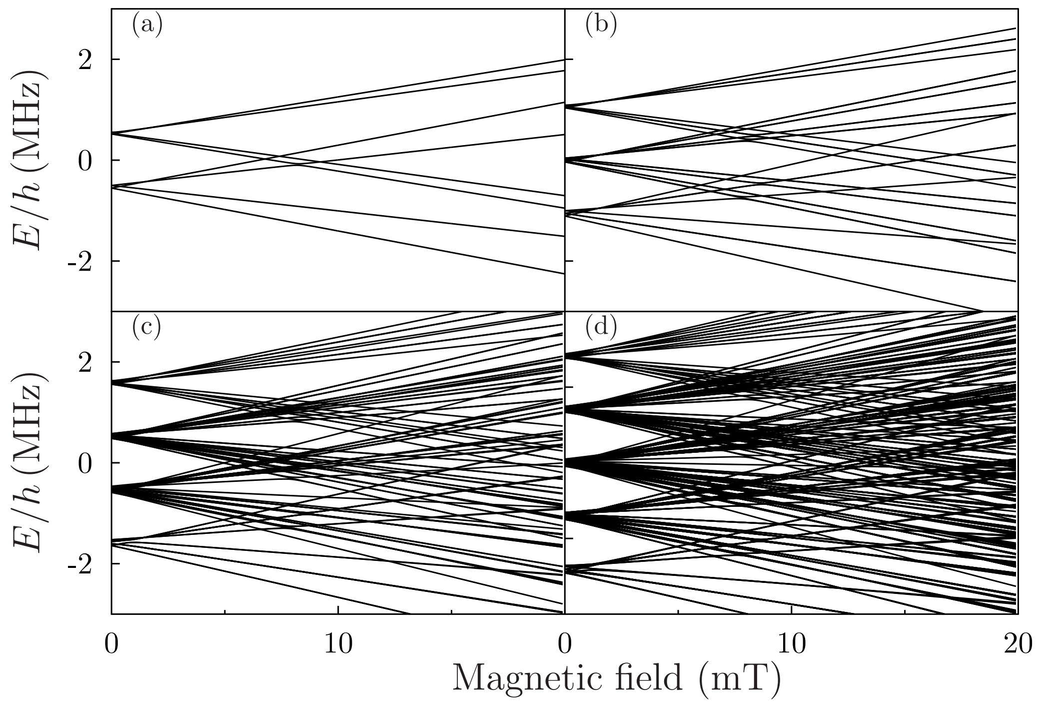


**Figure 2.** The energy levels for a muon coupled via the Hamiltonian in equation 1 to (a) a single Cu nucleus (8 levels), (b) two Cu nuclei (32 levels), (c) three Cu nuclei (128 levels), and (d) four Cu nuclei (512 levels).

We then considered modelling the system with an increasing number $N$ of Cu nuclear spins, each equidistant from the muon. With $N$ copper spins, the zero-field energy levels are mainly determined by the quadrupolar term (which gives an energy contribution of $\pm|h\nu_{\rm Q}|$ depending on whether $|I_z^i|$ equals $\frac{1}{2}$ or $\frac{3}{2}$, where $z$ labels the local quantization axis of the $i$th Cu moment). This implies that the $2\times 4^N$ energy levels are split into $N+1$ groups, which can be labelled $n=0$ (the lowest) to $n=N$ (the highest) with energy ranging from $E=-N|h\nu_{\rm Q}|$ to $E=N|h\nu_{\rm Q}|$ with spacing between levels equal to $2|h\nu_{\rm Q}|$ (so that $E_n=(-N+2n)|h\nu_{\rm Q}|$), with the degeneracy of the $n$th level being $2^{N+1}N!/[(N-n)!n!]$. This splitting is apparent in the energy level diagrams shown in Fig. 2 for $N=1$, $N=2$, $N=3$ and $N=4$. (We have also calculated the energy levels up to $N=6$, but the density of lines obscures the analogous plots.) Including the dipolar contribution results in splittings within each group in zero-field, and the flip-flop terms result in avoided level crossings. The presence of multiple Cu nuclear spins means that multiple avoided level crossings occur, as the condition for an avoidance is satisfied by multiple pairs of levels. This produces many ALC resonances that superpose to give a single broadened resonance. Larger $N$ implies that a greater number of avoided level crossings can occur over a wider range of field values, leading to a broadening and deepening of the resonance. This effect is apparent in Fig. 3 which shows the calculated $P_z^\mu(B)$ for different values of $N$.

It is instructive to consider the $N=2$ case and compare it to the $N=1$ case. As stated above, for $N=1$ a single resonance at $B=4\pi|\nu_{\rm Q}|/(\gamma_\mu-\gamma_{\rm Cu})=8.50$ mT results from transitions

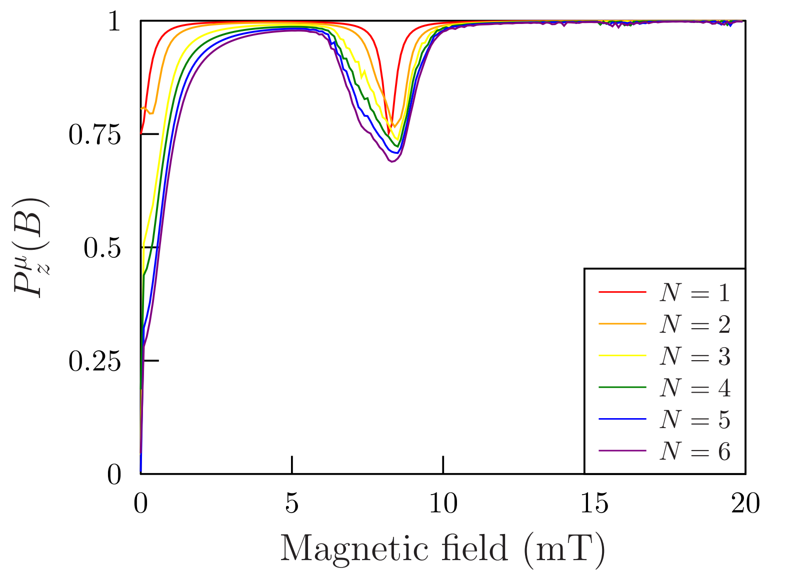


**Figure 3.** The calculated ALC resonances for different values of the number $N$ of Cu nuclei included in the model.

from $|\uparrow, \frac{1}{2}\rangle$ to $|\downarrow, \frac{3}{2}\rangle$. This mixes two of the eight states at the resonance, resulting in a drop in polarization of $\frac{1}{4}$, exactly as observed in Fig. 1 and Fig. 3. For $N = 2$, there are four avoided level crossings:

(i) $|\uparrow, \frac{3}{2}, \frac{1}{2}\rangle$ to $|\downarrow, \frac{3}{2}, \frac{3}{2}\rangle$, at $B \approx 2\pi(2|\nu_{\rm Q}| - 5\nu_{\rm D})/(\gamma_\mu - \gamma_{\rm Cu}) = 7.82$ mT.

(ii) $|\uparrow, -\frac{3}{2}, \frac{1}{2}\rangle$ to $|\downarrow, -\frac{3}{2}, \frac{3}{2}\rangle$, at $B \approx 2\pi(2|\nu_{\rm Q}| + \nu_{\rm D})/(\gamma_\mu - \gamma_{\rm Cu}) = 8.65$ mT.

(iii) $|\uparrow, \frac{1}{2}, \frac{1}{2}\rangle$ to $|\downarrow, \frac{1}{2}, \frac{3}{2}\rangle$, at $B \approx 2\pi(2|\nu_{\rm Q}| - 3\nu_{\rm D})/(\gamma_\mu - \gamma_{\rm Cu}) = 8.09$ mT.

(iv) $|\uparrow, -\frac{1}{2}, \frac{1}{2}\rangle$ to $|\downarrow, -\frac{1}{2}, \frac{3}{2}\rangle$, at $B \approx 2\pi(2|\nu_{\rm Q}| - \nu_{\rm D})/(\gamma_\mu - \gamma_{\rm Cu}) = 8.36$ mT.

Level crossings (ii) and (iv) result from the crossing of doubly degenerate levels (e.g. $|\uparrow, -\frac{3}{2}, \frac{1}{2}\rangle$ and $|\uparrow, \frac{1}{2}, -\frac{3}{2}\rangle$ are degenerate), so 4 levels mix at each of (ii) and (iv). In contrast, (i) and (iii) involve the crossing of a doubly degenerate level and a singly degenerate level, and only 2 states mix at each of these crossings. Accordingly, a total of 12 out of 32 states mix at the level crossing, but because they occur at slightly different magnetic fields, an otherwise sharp dip of 3/8 is instead blurred out into the resonance shown in Fig. 3. These results apply for the field along the Cu–$\mu$–Cu bond axis, but as the field is rotated away from this axis the resonances alter as shown in Fig. 4. In a polycrystalline sample, one would average over all of these orientations.

Simple analytical expressions for the positions of level crossings for higher values of $N$ are not available, even in the case in which the field aligns with one of the octahedral axes, since the different nuclear quantization axes complicate the analysis (for $N = 1$ and $N = 2$, the muon and Cu nuclei lie in a straight line and with the field applied along this line, the nuclear quantization axis and the field direction are identical; when we add the next spin, starting to build up the octahedral environment, we necessarily introduce an additional quantization axis).

Nevertheless, we can make some broad statements summarising the effect of increasing $N$ up to $N = 6$, the case observed in experiment. The position of the ALC resonance does not change with $N$, but always occurs close to $B_{\rm ALC}$ for the single Cu case because the dominant level crossing is due to a 'downward' travelling energy level with an 'upward' travelling level from adjacent branches. Nevertheless, there are some additional very small resonances that occur at higher fields when $N > 2$ (see Fig. 3) which arise from the crossing of levels from more distant

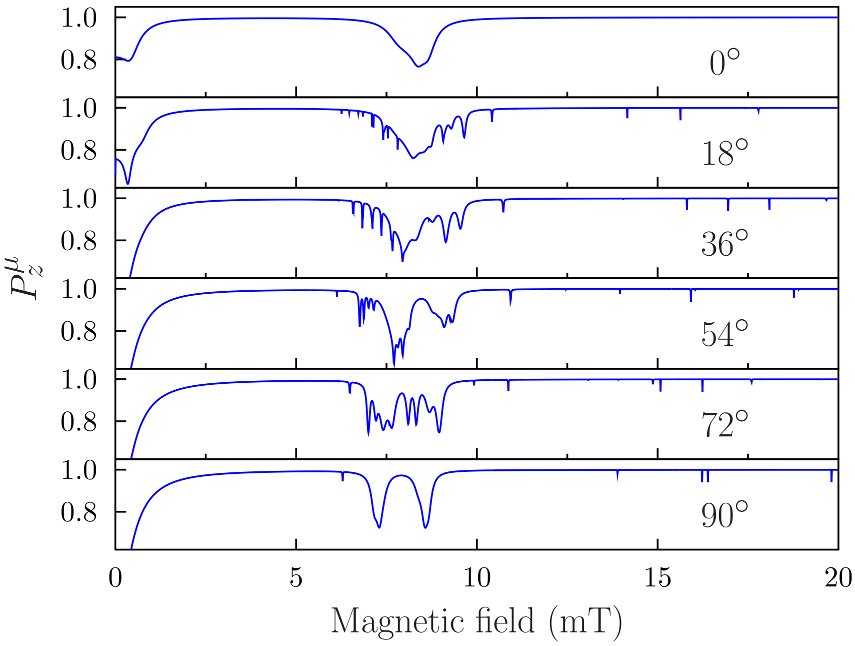


**Figure 4.** The calculated ALC resonances for $N = 2$ as a function of angle between the Cu–$\mu$–Cu bond and the magnetic field.

branches. Small variations around $B_{\mathrm{ALC}}$ in the field of the individual avoided level crossings that contribute to the main resonance occur due to three main effects. First, the zero-field splittings within a given quadrupolar "group" that are caused by the dipolar interaction are not the same in each of the groups for a given $N$, so the levels start from different places. Second, the slopes of the energy levels depend on the $I_z^i$ quantum numbers, which vary between the levels for a given $N$. Third, for $N > 2$ the vectors joining the additional Cu nuclei from the muon are no longer parallel to the field direction, and this results in some differences in the field dependences of the lines. The net result of these three effects is a broadening of the main ALC resonance as $N$ increases up to $N = 6$. The location and shape of the ALC resonance depends on just a few parameters: $\nu_{\mathrm{Q}}$, $\nu_{\mathrm{D}}$ and the local environment of the positive muon's implantation site. One can computationally simulate analogous systems with differences in these parameters in a similar fashion and then compare these results to experimental data. The calculation shown in Fig. 3 has been carried out for the case of a single crystal of Cu with the field oriented along one of the $\langle 100 \rangle$ axes. For the polycrystalline case, different orientations can be calculated and appropriately averaged, and this leads to additional broadening of the ALC resonance, as does the effect of the intrinsic muon decay resulting in an imperfect averaging out of the oscillations of the dipolar coupling in an integral counting experiment.

## 4. Conclusion

The computational modelling of a positive muon implanted in copper allows for the study of the effect of multiple quadrupolar nuclei on the energy levels of the system and the resulting ALC resonance. At zero field with $N$ Cu nuclei, the $2^{2N+1}$ energy levels split into $N + 1$ groups due to quadrupolar terms, where the $n$th group has a degeneracy of $2^{N+1}N!/[(N-n)!n!]$. Further splitting occurs due to the dipolar interaction, where the presence of flip flop terms mixes states of well defined $I_z^i$. Multiple Cu nuclei lead to both a broadening and deepening of the ALC

Journal of Physics: Conference Series **2462** (2023) 012043 doi:10.1088/1742-6596/2462/1/012043

resonance that forms, but its location (given by $B_{\mathrm{ALC}}$) remains unchanged. The lineshape of the ALC resonance is due to the distribution of the avoided level crossings in the energy levels in the system, which is influenced by the effect of zero field energy shifts and the set $\{I_z^i\}$ of quantum numbers of the quadrupolar nuclei.

**Acknowledgments**
We thank EPSRC (UK) for financial support, and J. M. Wilkinson for assistance with the supercomputer calculations.

## References

[1] Ferrell R A and Chaos F 1957 *Phys. Rev.* **107** 1322
[2] Orear J, Harris G and Bierman E 1957 *Phys. Rev.* **107** 322
[3] Pratt F L 1997 *Phil. Mag. Lett.* **75** 371
[4] Abragam A 1984 *C. R. Acad. Sei. Paris* **229** 85
[5] Graf M J, Lago J, Lascialfari A, Amato A, Baines C, Giblin S R, Lord J S, Tkachuk A M, Barbara B 2007 *Phys. Rev. Lett.* **99** 267203
[6] Heming M, Roduner E, Patterson B D, Odermatt W, Schneider J, Baumeler H, Keller H, Savic I 1986 *Chem. Phys. Lett.* **128** 100
[7] Kreitzman S R 1986 *Hyp. Int.* **31** 13
[8] Kiefl R F 1986 *Hyp. Int.* **32** 707
[9] Cox S F J 1992 *Z. Naturforsch. A* **47** 371
[10] Pratt F L, Pattenden P A, Blundell S J, Chow K H, Jestädt T, Hayes W, Kato R, Tamura M, Sawa H and Kashimura Y 1997 *Synth. Met.* **85** 1747
[11] Berlie A, Pratt F L, Huddart B M, Lancaster T and Cottrell S P 2022 *J. Phys. Chem. C* **126** 7529
[12] Blundell S J, De Renzi R, Lancaster T and Pratt F L (Eds) 2022 *Muon Spectroscopy* (Oxford: Oxford University Press)
[13] Camani M, Gygax F N, Ruegg W, Schenck A, and Schilling H 1977 *Phys. Rev. Lett.* **39** 836
[14] Kreitzman S R, Brewer J H, Harshman D R, Keitel R, Williams D L, Crowe K M and Ansaldo E J 1986 *Phys. Rev. Lett.* **56** 181
[15] Luke G M, Brewer J H, Kreitzman S R, Noakes D R, Celio M, Kadono R, Ansaldo E J 1991 *Phys. Rev. B* **43** 3284
[16] Bonfá P, Sartori F and De Renzi R 2015 *J. Phys. Chem. C* **119** 4278
[17] Johansson J R, Nation P D, Nori F 2013 *Comp. Phys. Comm.* **184** 1234
[18] Celio M 1986 *Hyp. Int.* **31** 41
[19] Wilkinson J M and Blundell S J 2020 *Phys. Rev. Lett.* **125** 087201