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RAL-94-034 Science and Engineering Research Council

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## Muon Sites and Electronic Structure

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March 1994

# MUON SITES AND ELECTRONIC STRUCTURE

Steve Cox

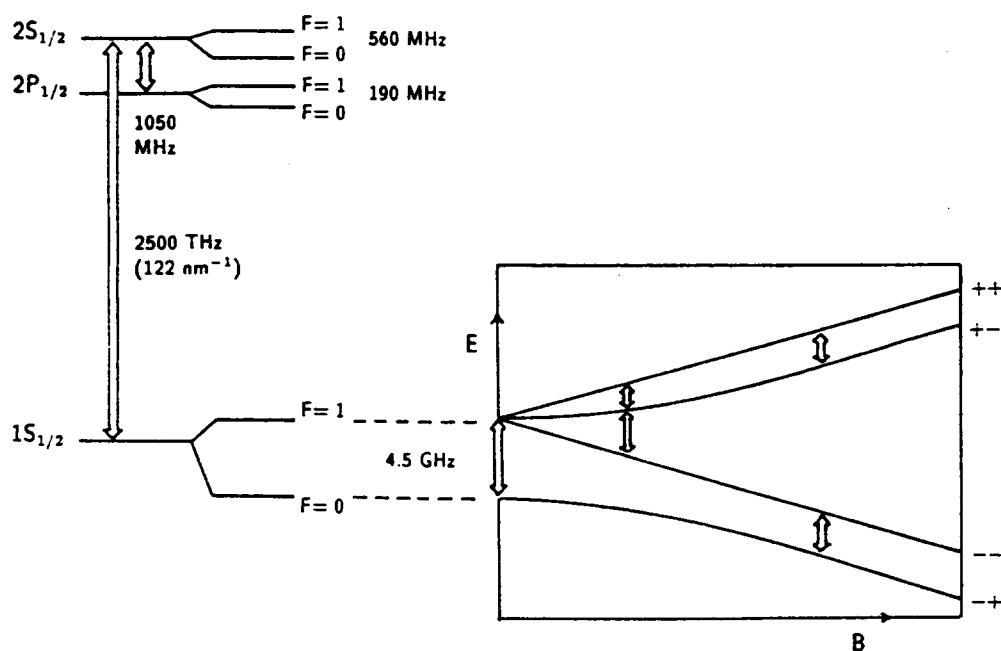
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*Lecture given at the International Summer School on  $\mu$ SR Spectroscopy,  
Maui, Hawaii, 31 May - 4 June, 1993.*

This Lecture concerns the sites adopted by positive muons implanted in different materials. It examines how the nature of the material determines the muons' environment, as relevant to  $\mu$ SR studies. The terms *muon state* or *muonium state* are often used (these are not to be confused with the spin states). The guiding principle is that muons, like protons, cannot remain as the free particles once thermalized in matter, whether in gases, liquids or solids. They seek to lower their energy by association with electrons, in inert materials by the formation of muonium – the bound state with a single electron – and in more reactive hosts by becoming intimately incorporated into the structure of the lattices or molecules. Physicists refer to this as *localisation* and *local electronic structure*; chemists refer to it simply as bonding. Analogies with the chemical behaviour of protons or atomic hydrogen are invaluable, provided proper account is taken of the larger zero-point energy of the muon when confined or bound. The relevant properties of atomic muonium are given, followed by a description of how these are modified in various hosts, dielectric, semiconducting, molecular and metallic. The various possibilities are well illustrated by the muonium states observed in the different allotropes of carbon.

## 1. MUONIUM

Atomic muonium is formed in a variety of of inert materials, gases, liquids and solids. That is, the initially energetic incoming muon picks up an electron at some stage during



*Energy levels for vacuum-state muonium.*

the course of its thermalization [1]. The closest approximation to the free-atom state is achieved for muonium formed in rare gases at low pressure, or formed in thin foil or fine powder production targets and ejected into a vacuum space beyond. This serves for the determination of the fundamental spectroscopic parameters [2].

## 1.1 Hyperfine interaction

We focus attention on the electronic ground state, described by a 1s hydrogenic wavefunction. The electron spin  $S$  and muon spin  $I$  are coupled by an interaction of the form  $A\mathbf{I}\cdot\mathbf{S}$ , variously known as the hyperfine, Fermi or contact interaction. It results from the magnetic interaction between muon and electron which has the property – for a spherical or s-state electronic distribution – that it sums to zero except where the electronic wavefunction actually overlaps the nucleus [3]. This is the origin of the name “contact” term and it implies that the *hyperfine constant*,  $A$ , is a measure of the electron density at the nucleus:  $A \propto |\psi(0)|^2$ . The hyperfine constant is usually expressed in units of frequency. For the vacuum-state atoms the value for muonium is greater than that for protium by the ratio (to within about 1%) of the magnetic moments of muon and proton. This implies essentially the same electron density at the nuclei, confirming the notion of muonium as a pseudo-isotope of hydrogen and serving as a starting point for examining the changes which arise on incorporation into materials.

## 2. MUONIUM IN DIELECTRICS.

### 2.1 The Breit-Rabi diagram

The energy level scheme for ground state muonium in an applied magnetic field is shown framed in the above figure. It is known as the *Breit-Rabi diagram*, originally conceived for atomic hydrogen (*i.e.* protium). Characteristic frequencies corresponding to the transitions between the various states appear in the muon spin rotation or resonance spectra, with intensities reflecting the field-dependent selection rules. The hyperfine constant may be deduced from these frequencies, either from the sum of the two frequencies in the high-field spectrum or, less precisely, from the difference of the two frequencies in low field (the so-called *triplet muonium* spectrum) [3]. The hyperfine constant appears in the energy level diagram as the zero-field splitting between the singlet and triplet spin states and can be measured directly in null field in exceptional cases.

### 2.2 Influence of the medium

In inert and non-conducting solid media, muonium can exist in a form which closely resembles the atomic state, but which is located or *trapped* in the interstitial spaces of the lattice. In some alkali fluorides its hyperfine constant is slightly higher than the vacuum-state value, as though the electronic wavefunction were compressed, increasing its amplitude at the muon. More commonly, the hyperfine constant is lower – in the semiconductors considerably lower – than in the free atom. This implies some *dilation* of the electronic wave function, *i.e.* its delocalisation onto the neighbouring atoms. The wavefunction of the unpaired electron must be expressed as a linear combination of atomic orbitals (LCAO):

$$\psi = \alpha_s \psi_s + \alpha_p \psi_p + \sum_i \alpha_i \psi_i. \quad (1)$$

Here  $\psi_s$  and  $\psi_p$  are s and p wavefunctions centred on the muon (it is unlikely that energy states higher than 1s, 2s and 2p ever contribute significantly) and the  $\psi_i$  are valence wavefunctions centred on other (host lattice) atoms.

The hyperfine interaction for such a state will in general no longer be isotropic. An axial tensor usually provides an adequate description, which can be written either in terms of its principal values or as a sum of isotropic and traceless anisotropic terms:

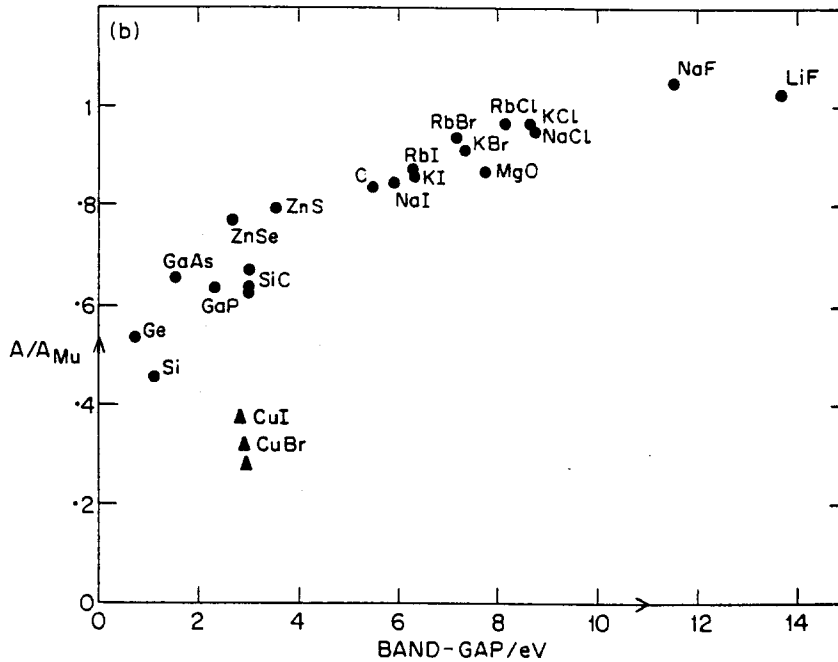
$$A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y) = (A_{iso} + 2B) I_z S_z + (A_{iso} - B) (I_x S_x + I_y S_y) \quad (2)$$

$$= A_{iso} \mathbf{I} \cdot \mathbf{S} + B \{2I_z S_z - (I_x S_x + I_y S_y)\} \quad (3)$$

The isotropic term is the *contact interaction* and is a measure of the muonium s-wave character. Its value as a proportion of the free muonium hyperfine constant,

$$\alpha_s^2 = A_{iso}/A_{Mu} = \frac{1}{3}(A_{\parallel} + 2A_{\perp})/A_{Mu}, \quad (4)$$

is referred to as the *spin-density* on the muon. Values for a number of materials are reported in the figure.



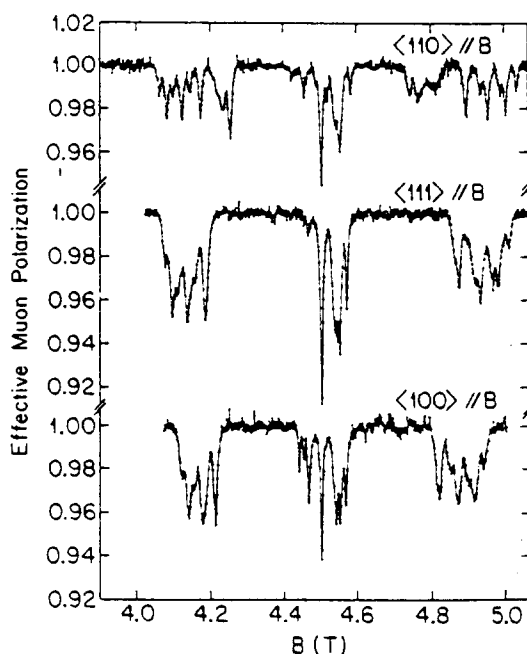
*Hyperfine constant for interstitial muonium in semiconductors and dielectrics [4].*

In the above data, there is in fact no anisotropy: for these muonium states  $A_{\parallel} = A_{\perp} = A_{iso}$  (see Section 3.1). This implies that the p-wave contribution is negligible, or that

the neighbouring atoms are disposed about the muon with cubic symmetry, or that the muonium is diffusing rapidly in the lattice. Diffusion results in a modulation of the interaction with neighbouring spins and may be studied *via* muon spin relaxation [5, 6]. In the group-IV elemental semiconductors, spin density on the muon falls as low as 50% of the free atom value.<sup>1</sup>

### 2.3 Level crossing resonance

Provided the muonium is static in the lattice, or nearly so, spin density on the surrounding atoms (represented by the square of each coefficient  $\alpha_i$  in equation (1)) can be measured by a double resonance technique. The figure shows such a *level crossing resonance* spectrum for one of the cuprous halides, from which the muonium site may be assigned to the centre of the interstitial cage defined by four  $\text{Cu}^+$  nearest neighbours [7]<sup>2</sup>



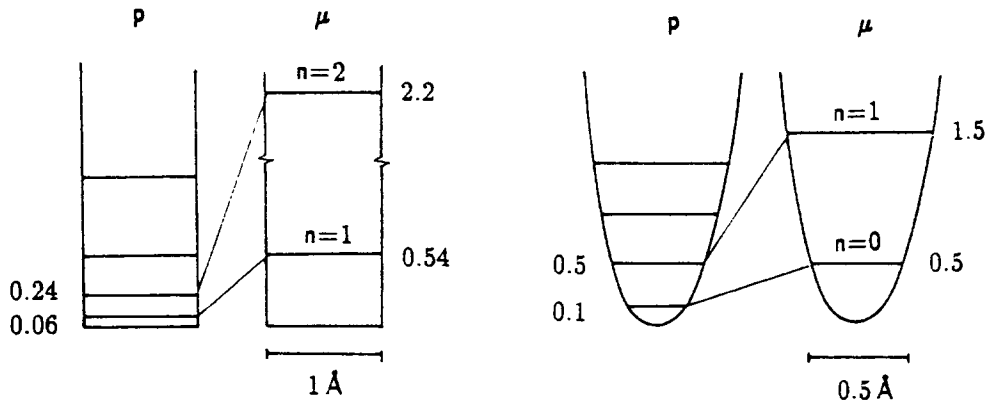
*LCR spectrum for interstitial muonium in CuCl [9].*

### 2.4 Zero point energy

In contrast to the free-atom case, where the spin density at the nucleus is the same for all isotopes, the spin density on the muon for muonium in each of the above materials is somewhat less than that on the proton for the equivalent states of interstitial hydrogen. This can be understood in terms of the greater zero-point energy of the lighter isotope, when confined in an interstitial cavity. The text-book cases of square wells and harmonic

<sup>1</sup>The broad correlation with band-gap can be justified in a *molecular orbital* description: the greater the disparity between the levels of the states to be mixed, the smaller is the degree of mixing (*i.e. the more the muonium retains its atomic character*).

<sup>2</sup>There are in fact two muonium states with slightly different hyperfine constants in CuCl. The LCR spectra show that the muonium site is the same for each, apparently one with and one without an associated local distortion of the lattice. This is a remarkable example of *metastability* in muonium dynamics.

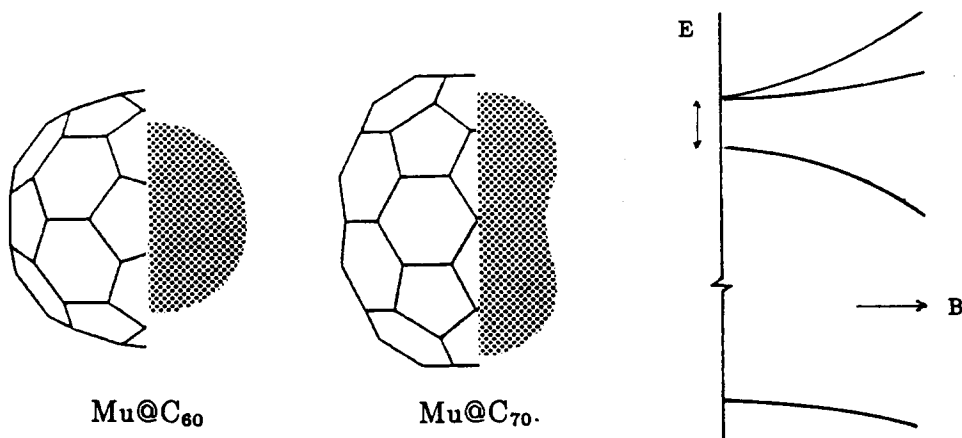


*Zero point and vibrational energy levels for confined protons and muons.*

oscillators are illustrated in the sketch, with representative values of zero-point energy. In most cases the harmonic potential is the closer approximation to the *potential energy surface* which governs the dynamics, and two observations can be made. Firstly, the uncertainty in the muon position (the spread of the *nuclear wavefunction*) is greater than for the proton. That is, the muon is on average closer to the neighbouring atoms. One can imagine that this forces a greater overlap of the muonium *electronic wavefunction*, reducing its amplitude at the muon. Hence the isotope effect in hyperfine constant. Secondly, since the mass ratio is close to 1/9, the muon zero point energy is about 3 times higher than that for the proton, in the harmonic approximation. This places its ground vibrational state about on a level with the first excited state for a proton. One can imagine the muon acting as a *hot proton* in its dynamical behaviour.

### 2.5 Non-spherical confinement

The sketch below illustrates topical examples of muonium confined in spherical and non-spherical cavities. These are muonium trapped *inside* the cages of the fullerene molecules – the *endohedral* states denoted  $\text{Mu@C}_{60}$  and  $\text{Mu@C}_{70}$ . The environment is spherically symmetric inside  $\text{C}_{60}$ ; the muonium hyperfine interaction is isotropic and close to the free atom value. But for  $\text{Mu@C}_{70}$ , it develops a p-wave contribution to



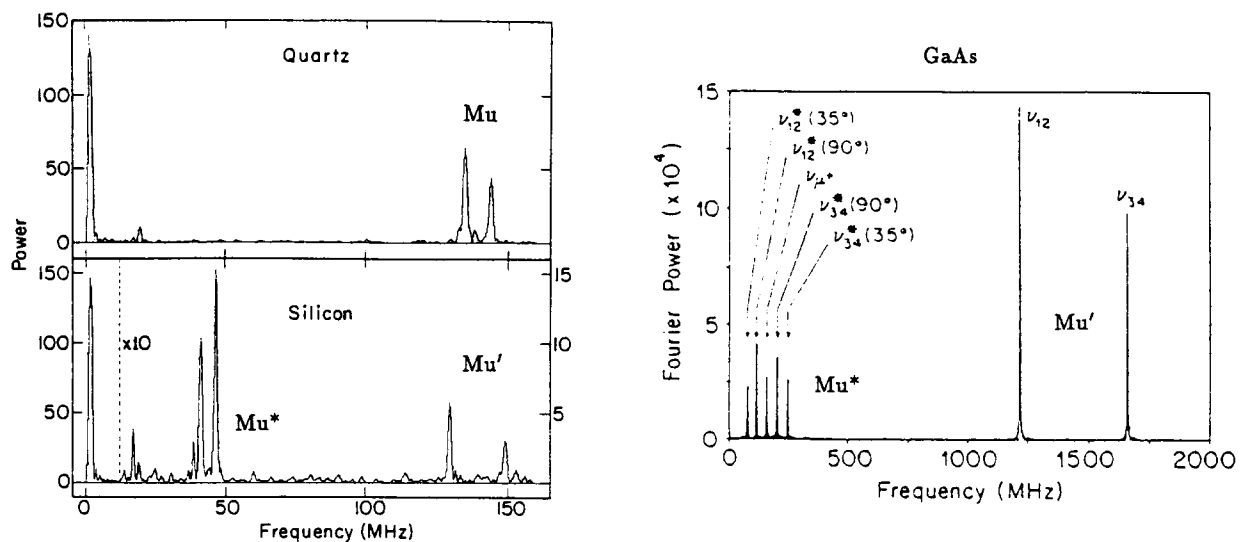
*Contours of electronic density for muonium inside  $\text{C}_{60}$  and  $\text{C}_{70}$  and the additional zero-field energy splitting for axial asymmetry.*

match the elongated cavity. The result is an additional zero-field splitting in the Breit-Rabi diagram (lifting the degeneracy of the triplet state) which manifests itself as a low-frequency oscillation in the zero-field spectrum [8]. The isotropic component is correspondingly reduced.

A small degree of anisotropy of the hyperfine tensor for muonium in quartz at low temperature, and also in ice, may also be described in these terms. Species where anisotropy results from spin density located on neighbouring atoms are introduced in the following sections.

### 3. MUONIUM IN SEMICONDUCTORS

Some classic spectra of the  $\mu$ SR literature are shown in the following figures. Spectra taken at the same low field in silica and silicon reveal a) the effect of the different hyperfine constant on the splitting of the two muonium lines and b) the existence of a group of lines in Si which is absent in  $\text{SiO}_2$ . The high field spectrum in gallium arsenide similarly reveals two distinct states of muonium.



*Fourier transform  $\mu$ SR spectra for  $\text{SiO}_2$ , Si [10] and GaAs [11].*

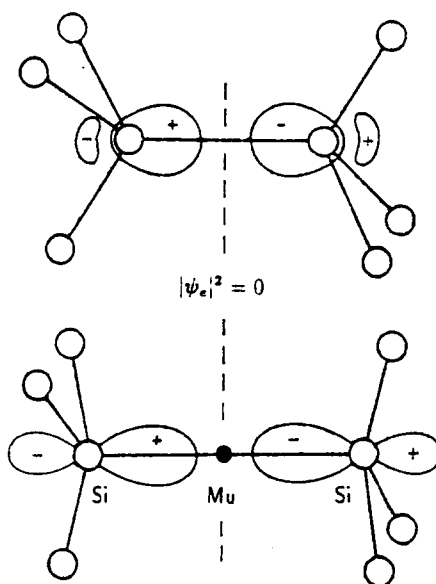
#### 3.1 Normal muonium, Mu'

In each case the pair of lines at the higher frequencies indicates an isotropic hyperfine interaction – these frequencies do not depend on the crystalline orientation in the magnetic field and are detectable equally well in polycrystalline samples. They correspond to the expected interstitial state, located at or near the large cage centres or *T-sites* in the tetrahedrally coordinated lattice. The term *normal muonium* is commonly used in the literature despite the low values of hyperfine constant in the semiconductors; in the following, the nomenclature Mu' is used to distinguish this from the free atom. It appears to be a mobile state, diffusing rapidly between the interstitial cages.

### 3.2 Anomalous muonium, $Mu^*$

The lower frequencies are assigned to another state known variously as *anomalous muonium* or  $Mu^*$ . For this state, the hyperfine coupling is strongly anisotropic.<sup>3</sup> Careful single-crystal studies as a function of orientation determined the symmetry to be axial about the  $\{111\}$  directions and measured the principal components  $A_{\parallel}$  and  $A_{\perp}$  of the hyperfine tensor [13].<sup>4</sup>

A  $Mu^*$  state is observed in the group IV semiconductors Si and Ge, in diamond (which has the same crystal structure) and in a variety of tetrahedrally coordinated compound semiconductors. Despite detailed spectroscopic characterisation, its nature remained a longstanding puzzle. It was analysis of the tensor components in terms of the isotropic and dipolar components, as in equation (3), which eventually suggested the solution. The isotropic term, with coefficient  $A_{iso} = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$ , is extremely small in the elemental materials, indicating negligible electron density at the muon site. The anisotropy term in (3), with coefficient  $B = \frac{1}{3}(A_{\parallel} - A_{\perp})$ , has the form of a dipolar interaction; its magnitude for  $Mu^*$  suggests that the unpaired electron is nonetheless located close by. Some supporting chemical reasoning pointed to a muon site at the *centre* of a silicon-silicon, or gallium-arsenic bond, as appropriate, so that the muon is at (in Si) or close to (in GaAs) a *node* of the singly occupied orbital [14].



*Antibonding orbital for a Si-Si pair as the basis for a model of  $Mu^*$ .*

This assignment is now substantiated by double resonance or *level crossing resonance* experiments which measure how the spin density is partitioned over the neighbouring atoms [7, 15]. Theoretical modelling reveals that, with a suitable *relaxation*<sup>5</sup> of the

<sup>3</sup>The polycrystalline spectrum or *powder pattern* is too broad to be detected except at a certain *magic field* [12].

<sup>4</sup>The concepts of *effective fields* experienced by the muon provide a valuable means of manipulating the spin Hamiltonian [12].

<sup>5</sup>The term is used here to mean a local distortion; this is not to be confused with *spin-lattice relaxation* [16, 6, 18]!



surrounding lattice, the bond centre in fact provides a deeper potential well for hydrogen or muonium than does the cage centre. The energy required to produce this distortion must represent a barrier to conversion of  $\text{Mu}'$  to  $\text{Mu}^+$ , however. This would account for their coexistence in the low-temperature spectra, *i.e.* the *metastability* of  $\text{Mu}'$ .

### 3.3 Spin-polarization

In silicon, the small isotropic component of the hyperfine tensor is in fact negative, indicating a spin-polarization of bonding orbitals. The effect may be explained as follows. The unpaired electron has a wavefunction which is antisymmetric about the muon site, so the direct contact interaction is zero from this *singly occupied molecular orbital*. The two valence electrons forming the original Si-Si bond, on the other hand, have wavefunctions which are symmetric about the bond centre: their amplitudes are considerable at the muon site.<sup>6</sup> These electrons are spin-paired, so that their net contact interaction with the muon would also be zero if the spatial wavefunctions for the spin-up and spin-down electrons were identical. They are not quite identical, however. The presence of the unpaired electron is said to *polarize* the bonding orbitals. The net contact interaction is negative because the spin state with greater amplitude at the muon is opposed to that of the singly occupied orbital. Similar effects are found in molecular species (Section 4.3) and can contribute to hyperfine fields and *Knight shifts* in metals (Section 5.1).

### 3.4 Diamagnetic states

The localized electronic states of the muonium defect centres have energy levels which lie deep in the energy gap between valence and conduction band states. In the neutral paramagnetic states the levels are *singly occupied*. Loss of the electron (ionization) or double occupation of the level (when the Fermi level lies higher) both lead to muon states which are said to be *diamagnetic*. Theoretical modelling suggests that, in Si,  $\text{Mu}^+$  is stable at the bond centre,  $\text{Mu}^- = \mu^+ e^- e^-$ , at the cage centre.

Diamagnetic muon states coexist with paramagnetic muonium in most dielectrics and semiconductors, in proportions which depend on the material and the temperature. In fluorides, for instance, a state analogous to the particularly stable  $(\text{F-H-F})^-$  ion is known (Section 4.2).

Pairing with other impurities can also lead to diamagnetic states; in semiconductors this would correspond to the *passivation* of dopants by hydrogen, a process which drastically alters electronic properties by removing electrically active levels from the gap.

A potentially important link with materials science,  $\mu\text{SR}$  studies of passivation, and of the interplay between charge state and location, promise to be fruitful in the future.

## 4. MUONIUM IN MOLECULAR MATERIALS

The very limited solubility of hydrogen in materials such as the crystalline semiconductors makes its detection by conventional spectroscopies difficult or impossible. In such cases, muonium has provided a unique substitute. More generally, proton and hydrogen chemistry is well documented and can be used as a guide to the states expected of muons and muonium.

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<sup>6</sup>In fact, their charge density makes this an attractive site for the  $\text{Mu}^+$  charge state, which is also stable at the bond centre.

## 4.1 Protonation of bases

Protons are known to “stick” to lone electron pairs such as commonly exist on oxygen or nitrogen, in the process known as *protonation*. Positive muons are expected to do likewise and add, for instance, to water:

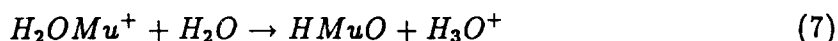


or to a nitrogen molecule:



(Note that the free particle is denoted here  $\mu^+$  and the chemically bound particle  $Mu^+$ .)

In the case of water, either the muon or one of the protons can then change its allegiance, with the net result that the charge migrates away to leave the muon substituted in a neutral molecule [1]:



## 4.2 Identification of diamagnetic states

The products of reactions such as (5–7), whether ionic or neutral, are all *closed shell*, *i.e.* *diamagnetic*. There is no unpaired electron in the vicinity of the muon, and therefore no hyperfine interaction. The same is true for the muonium states in semiconductors which are charged ( $Mu^-$  or  $Mu^+$ ) rather than neutral, or which are paired with other impurities or dopants. The muon spin rotation spectrum for such species shows a single line at a frequency close to the muon Larmor frequency appropriate to the applied field. There is in principle a small *chemical shift*, due to diamagnetic shielding currents in the molecule, but these have only been measured in a few favourable cases.<sup>7</sup>

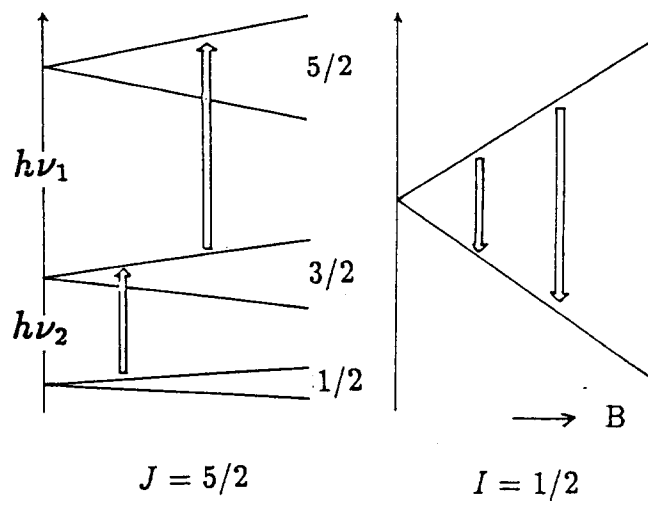
In crystalline materials, the site of diamagnetic states may often be determined from the orientation dependence of the transverse field  $\mu$ SR linewidth [19], and occasionally from the form of the zero-field relaxation function. The  $(F-Mu-F)^-$  ion, for instance, shows a particularly distinctive zero field relaxation.

Otherwise, there may be no signature in the  $\mu$ SR spectra of diamagnetic muon states which readily allows their chemical identity to be established. When the muon is located immediately adjacent to a *quadrupolar* nucleus ( $J > 1/2$ ), however, muon level crossing resonance can provide such a signature. Level crossing resonance (LCR) experiments use a longitudinal field to tune the muon Zeeman energy to match the combined Zeeman and quadrupolar energy on the neighbouring nucleus; the muons then lose polarization by *flip-flop* transitions or cross-relaxation with their neighbours.

The technique requires solid samples, but not necessarily single-crystals, since LCR spectra are only weakly dependent on orientation. The spectra provide a measurement of the quadrupole energy splittings which are characteristic of the molecular species, in the same manner as for interstitial muons in metals [7, 15, 16]. Addition to oxygen and nitrogen as in reactions (5–7) has been demonstrated in this way, and the method applied to characterise muon sites in the oxide superconductors. The spectra below are

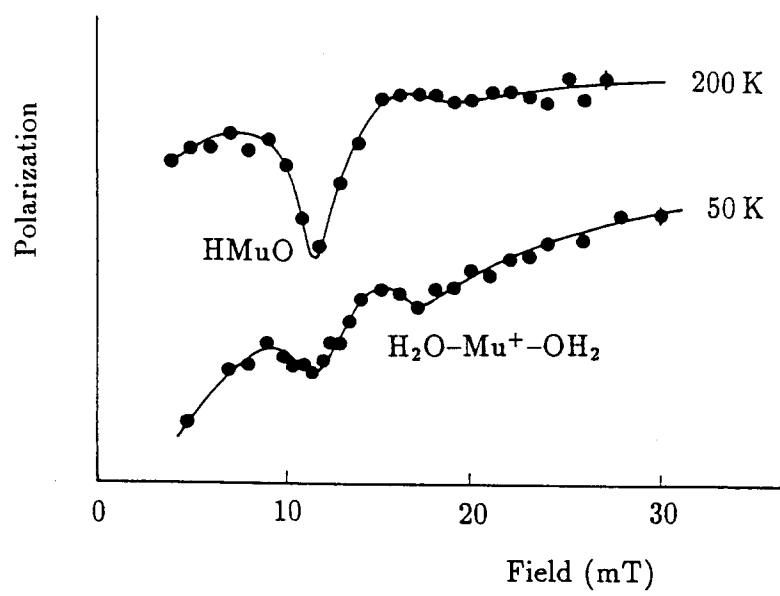
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<sup>7</sup>RF resonance at high fields offers the best promise for chemical shift measurements but the muon lifetime, as well as the RF power necessary, set limits on resolution.



Resonant cross relaxation between a muon ( $I = \frac{1}{2}$ ) and a nucleus with  $J = \frac{5}{2}$ , e.g.  $^{17}\text{O}$ .

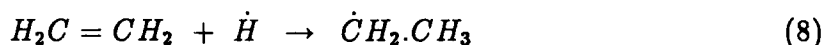
for ice, with resonances assigned to the substituted molecules HMuO and to the ionic intermediary, thought to be muons trapped at a defect in the hydrogen bond network.



LCR spectra for ice, enriched with  $\text{H}_2\ ^{17}\text{O}$  [17].

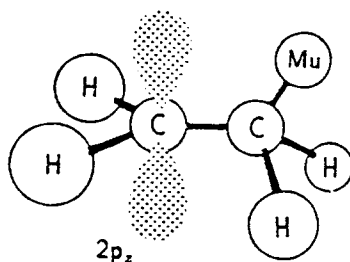
### 4.3. ORGANIC RADICALS

A chemical reaction which is well known for atomic hydrogen is addition at multiple bonds in *unsaturated* organic compounds. Addition to the carbon-carbon double bond of ethylene, for instance, forms the *ethyl radical*, which is known to ESR spectroscopy:



In this notation the dot is used to emphasize the existence of the unpaired electron spin, the term *radical* or *free radical* being used to denote open-shell or paramagnetic molecules.<sup>8</sup>

Muonium does likewise, forming the *muonic* or *muonium-substituted ethyl radical*.<sup>9</sup> This is the net result of implanting positive muons in ethylene, liquid or gas.



*Structure of the muonium-substituted ethyl radical, with major spin density in a  $2p_z$  orbital on one carbon atom, at the "radical centre".*

In these paramagnetic species, there is again a hyperfine interaction between the muon and the unpaired electron. It is much smaller than in muonium, since the wavefunction of the unpaired electron is centred not on the muon but elsewhere in the molecule. A *molecular orbital* description is appropriate:

$$\psi = \sum_i \alpha_i \psi_i + \alpha_s \psi_s. \quad (10)$$

In the addition reaction, the double bond is broken or it reduced, saturating one carbon atom and leaving an unpaired electron spin located, largely, on the other.<sup>10</sup> The notation  $\dot{C}H_2 \cdot CH_2Mu$  and the sketch showing the unpaired electron occupying a  $2p_z$  orbital on this carbon atom give a rather misleading picture of total localization. This is in fact just the leading term of the LCAO (10), with spin density "leaking" over the entire molecular frame.

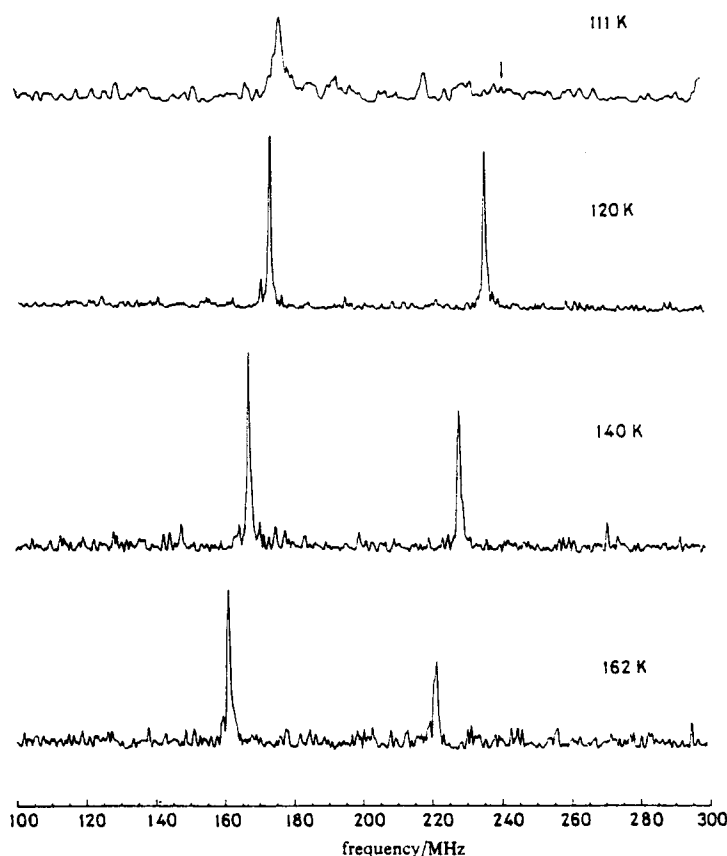
Another favourite and much studied example is the muonium-substituted *cyclohexadienyl* radical, formed in benzene. *Conjugation* of the bonds results in extensive delocalisation of the electronic spin around the ring [20].

<sup>8</sup>The ethyl radical, in common with all those discussed below, has an electronic doublet ground state, with g-factor close to 2, indicating that the electronic spin is the dominant contribution to the magnetic moment.

<sup>9</sup>Both nomenclatures are to be found in the literature but *muonium-substituted* is to be preferred, *muonic* being used also for species containing negative muons.

<sup>10</sup>Roughly stated, the addition reaction leaves a *dangling bond* on this atom. LCAO (10) is the same as LCAO (1), but rearranged – and with the muonium 2p term omitted altogether – to emphasize that the spin density on the muon is small.

The muon-electron hyperfine interaction for such species is expected to be anisotropic, so that equations (2-4) apply. The isotropic component (4) is a measure of the contact interaction, including the direct term representing the density of the singly-occupied molecular orbital at the muon, plus any indirect term representing spin-polarization of the bonding (doubly-occupied) orbitals. In the ethyl and cyclohexadienyl radicals it is of order one tenth the muonium value. The anisotropy represents the dipolar interaction from an electron distribution which, in molecular species, is rarely symmetric about the muon site. Being a traceless term, however, it has the property of being averaged to zero by fast tumbling of the molecules in the fluid phases. Liquid and gas phase spectra therefore give the isotropic term directly. In high field spectra it is just the sum of the two frequencies.



*Fourier transform spectra for the  $\text{CH}_2\cdot\text{CH}_2\text{Mu}$  radical in liquid ethylene (anisotropy broadening is apparent near the freezing point) [21].*

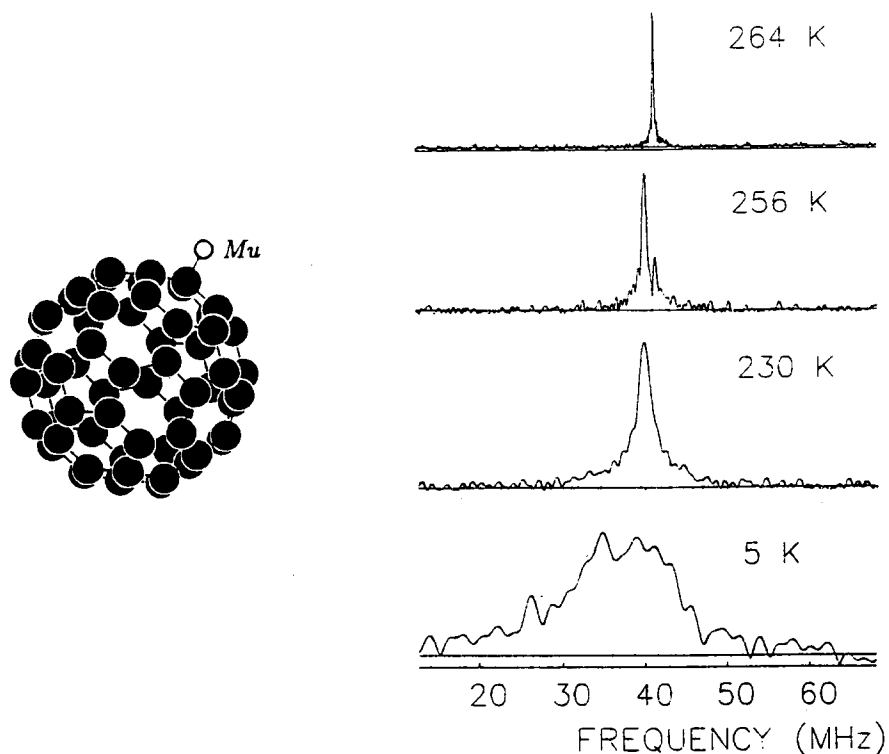
Radical formation by muonium addition at multiple bonds involving oxygen and nitrogen is also known. The temperature dependence of the hyperfine constant is informative on low-lying internal modes of vibration (in the muonic ethyl radical, for instance, on the torsional libration or hindered rotation about the C-C bond) [21, 22]. Level crossing resonance can be used to measure the hyperfine coupling to the other nuclei, *i.e.* to map out the spin density throughout the molecule [22, 15]. Many of the radicals are highly reactive transient species, and  $\mu\text{SR}$  detection serves also to determine their chemical

lifetimes, in studies of reaction kinetics [1, 22]. Gas phase studies of complex radicals by conventional ESR prove impossible, so here  $\mu$ SR studies of the muonium-substituted counterparts are particularly noteworthy.

#### 4.4 $C_{60}Mu$

A topical example of a particularly interesting species is  $C_{60}Mu$ , the muonium *adduct* of  $C_{60}$  fullerene. This is distinct from the endohedral complex,  $Mu@C_{60}$ , describe in Section 2.4.<sup>11</sup>  $C_{60}Mu$  is the result of external addition, muonium attacking one of the double bonds much as in the reaction with ethylene, so that the muon is located outside the fullerene cage, covalently bound to a single (saturated) carbon atom.  $C_{60}Mu$  is the analogue of the monohydride of  $C_{60}$ ; it has the distinction of having been detected in  $\mu$ SR studies *before*  $C_{60}H$  was recognised in ESR studies.

The  $\mu$ SR spectrum is remarkable in showing strong narrow lines over a considerable temperature range, for *solid state, powder* samples of  $C_{60}$ . For the other muonic radicals the solid state spectra, unless from single-crystal samples, are broadened and weakened by the hyperfine anisotropy, often beyond detection. In solid  $C_{60}$ , however, the individual molecules can reorient, whilst their centres of mass remain fixed on the lattice structure. The result is a progressive *motional narrowing* of the  $\mu$ SR line-widths in the phase between 90 and 260 K, from which the correlation time for the reorientation can be deduced, with extreme narrowing corresponding to liquid-like rotational diffusion in the phase (still solid) above 260 K.



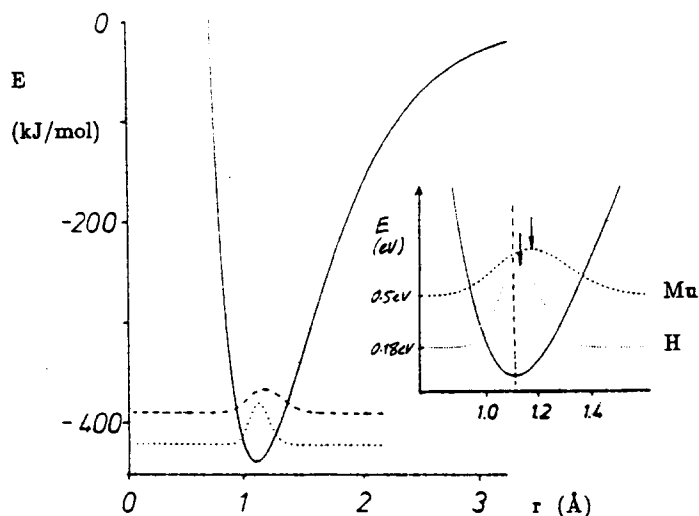
*$C_{60}Mu$  and motional narrowing of one of its spectral lines [29].*

<sup>11</sup>The endohedral state,  $Mu@C_{60}$ , provides another remarkable example of metastability in muonium studies: some potential barrier prevents reaction with the cage structure from inside. Its signal coexists with that of  $C_{60}Mu$  in the  $\mu$ SR spectrum.

#### 4.5 The hyperfine isotope effect

In the muonium-substituted organic radicals, the spin density on the muon is invariably greater than it is on the equivalent proton in the unsubstituted radical.<sup>12</sup> This is revealed by comparing the *reduced hyperfine constant*  $A_{\mu} \cdot \mu_P / \mu_{\mu}$  from the  $\mu$ SR measurement with the proton hyperfine constant  $A_p$  from the ESR measurement. ( $\mu_P / \mu_{\mu} = \gamma_p / \gamma_{\mu}$  is the ratio of the magnetic moments of proton and muon.)

The radicals  $C_{60}X$  ( $X = H, Mu$ ) are ideal for a discussion of the origin of this effect. Both H and Mu are light atoms bonded to the heavy  $C_{60}$  substrate. Their normal modes of vibration are therefore very similar; we focus attention on the bond-stretching mode. A Morse potential describes the total energy of the molecule as a function of the bond length. This is just a 1D cut through the potential energy surface which governs the proton or muon dynamics; within the Born-Oppenheimer or adiabatic approximation it is the same for all isotopes.<sup>13</sup> If there were a hydrogen isotope with infinite mass it would sit at the *equilibrium* position at the bottom of this well, i.e. the bond length would be well defined. By virtue of its light mass and zero point energy, the bond length for hydrogen is not fully determinate, but must be described by a spread in the *proton* wavefunction. The zero point energy for muonium and rms spread of the *muon* wavefunction are higher still. The situation may be compared with the harmonic oscillator potential sketched in Section 2.4. The result of a degree of *anharmonicity* in the Morse potential is that the mean bond length (as well as its variance) is slightly greater for  $X = Mu$  than for  $X = H$ .

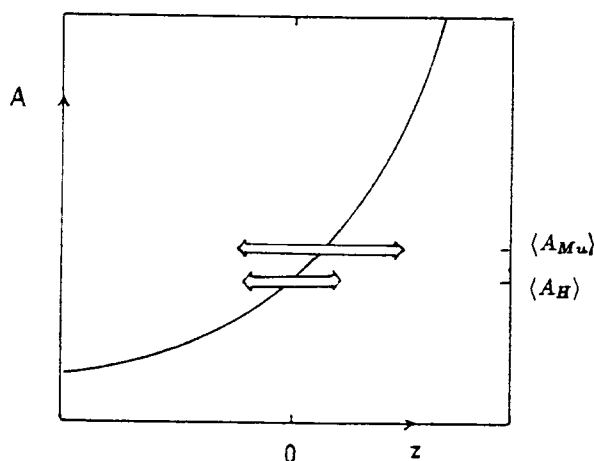


*Morse potential for the C-X bond and zero-point energies for X=H and X=Mu [24].*

<sup>12</sup>Note that this *isotope effect* in the organic radicals is in the opposite sense to that for the interstitial atoms in dielectrics (section 2.4) where spin density on the muon is smaller than on the proton.

<sup>13</sup>Despite the low muon mass, the Born-Oppenheimer approximation, involving separation of the electronic and nuclear wavefunctions, appears to be valid, in that no significant effects of its breakdown have been demonstrated in molecular species. It is in muon diffusion in metals at low temperatures where non-adiabatic behaviour is most clearly observed (Section 5.3) [19].

The relevance of this to hyperfine coupling is that spin density on the nucleus X is also a function of bond length. This function, like the Morse curve, is also common to all isotopes X. In fact it is a non-linear, rapidly accelerating function: one can imagine that stretching the bond corresponds to withdrawing a hydrogen or muonium atom from the molecule, so that spin density on the proton or muon rapidly approaches the free atom value. The measured hyperfine constant corresponds to an average value, weighted by the nuclear density (the square of the nuclear wavefunction). It is greater for X = Mu than for X = H both by virtue of the longer mean bond length and (since the function is non-linear) the greater variance.



*Variation of spin density on X with C-X bondlength  
and the different averages to be taken for X = H, X = Mu [25].*

The hyperfine isotope effect between  $C_{60}H$  and  $C_{60}Mu$  is relatively small: calculations and experiments suggest rather less than 10%. This example is given since it involves only the ground states, i.e. lowest energy levels, of a particularly simple vibrational mode. In other radicals with less rigid structures, different low-lying modes with a number of thermally accessible levels complicate the description. A case in point is the ethyl radical system,  $CH_2CH_2X$ , where the hindered internal rotation about the C-C bond must be considered [22]. The hyperfine isotope effect is then commonly closer to 20% and can be higher, although the various contributions can usually each be traced to the effects of nuclear zero-point energy.

## 5. METALS

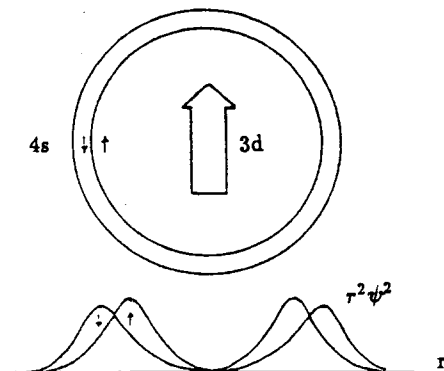
### 5.1 Screening

Muonium is not formed in simple metals. This seems paradoxical, in that conduction electrons are always at hand, apparently available to be picked up by the muon. In fact the conduction electron density is too high to allow a bound state with a single electron to be formed. The density of these mobile charges adjusts in response to the muon's presence to screen its Coulomb potential.<sup>14</sup> The muonium binding energy is reduced,

<sup>14</sup>An exception is  $C_{60}$ , where the muonium signal persists in material which is doped to become metallic or superconducting. Inside the cage, the muon is insulated from the mobile charges outside.



not exactly to zero, but to such a shallow level that the lifetime broadening exceeds its depth. Electrons hop and off the muon, so to speak, in rapid succession.<sup>15</sup> Some of the electrons have spin-up, some spin-down. In magnetic metals in their ordered state, the conduction electron polarization can be considerable, and give rise to huge hyperfine fields at the muon [26].



*Exchange polarization of outer by inner electrons in magnetic metals.*

In diamagnetic metals the interaction is observed as a *Knight shift* – a small proportional change in the muon Larmor frequency from the value appropriate to the externally applied field [27]. The Zeeman energy  $\hbar\gamma_\mu HI_z$  calculated as though for a free muon becomes  $(1 + K)\hbar\gamma_\mu HI_z$ , with

$$K \propto \rho_\uparrow - \rho_\downarrow. \quad (12)$$

Expressing the electron spin density at the muon in an obvious notation, and with a judicious rearrangement of terms, one can write

$$\rho_\uparrow - \rho_\downarrow = n_\uparrow |\psi_\uparrow|^2 - n_\downarrow |\psi_\downarrow|^2 \quad (13)$$

$$= \frac{1}{2}(n_\uparrow - n_\downarrow)(|\psi_\uparrow|^2 + |\psi_\downarrow|^2) + \frac{1}{2}(n_\uparrow + n_\downarrow)(|\psi_\uparrow|^2 - |\psi_\downarrow|^2). \quad (14)$$

In simple treatments only the first term is retained, evaluated at the Fermi surface. The Knight shift is proportional to the difference in the *populations* of spin-up and spin-down states, *i.e.* the electronic susceptibility. The second term contributes when the spin-up and spin-down wavefunctions are not identical. It is analagous to the *spin polarization* effects noted for bonding electrons in semiconductors (Section 3.3) and organic radicals (Section 4.3).

## 5.2 The small polaron state

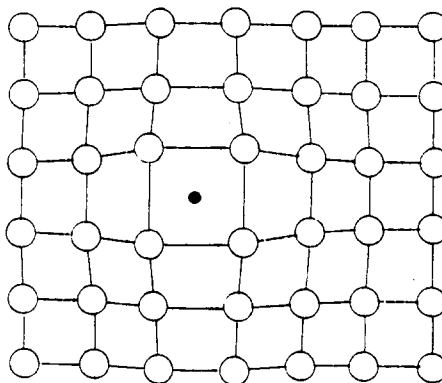
The local accumulation of conduction electron density largely screens the muon's positive charge within a distance comparable with the interatomic spacing. The absence of electrons with short enough wavelength to accomplish this smoothly results in oscil-

<sup>15</sup>Note that in muonium and in the muonic radicals, the electron spin states are usually long lived, so that the effective hyperfine field at the muon takes two discrete values,  $(2\pi/\gamma_\mu)A.S_z = \pm(\pi/\gamma_\mu)A$ , according as the electron is spin-up or spin-down. For short-lived spin states, or rapid *spin-exchange* the two spectral lines collapse to one, exhibiting a *paramagnetic shift*  $A.(S_z)$ .

lations or “diffraction haloes” at greater distances. The spin density oscillations lag in phase relative to the charge density oscillations. Modelling this response accurately is a severe test of screening theory and  $\mu$ SR data have provided a valuable stimulus in this area [27].

The muon site in metals is invariably interstitial, and the same as that adopted by the screened proton state of hydrogen in metals. The analogy makes implanted muon studies invaluable in modelling certain aspects of the behaviour of hydrogen in metals, especially in metals such as copper where hydrogen itself is too insoluble to be studied by conventional techniques [19]. Imperfect screening of the muon or proton charge implies that the neighbouring ion cores will be slightly repelled, producing a local elastic distortion on relaxation of the lattice.<sup>16</sup>

*Local elastic distortion.*



The lattice relaxation results in a lowering of the interstitial potential at the muon or proton site, favouring localisation. Muons and protons are said to *self-trap* in this manner. The whole entity, *i.e.* interstitial particle plus screening charge plus elastic distortion, is referred to as a *small polaron* state. Erudite works refer to the particle “dressed” with electron and phonon clouds.

### 5.3 Quantum diffusion

The localisation or self-trapping does not imply that the small polaron state is necessarily immobile. In many metals, interstitial muons and protons diffuse with remarkable rapidity.  $\mu$ SR and other studies have been concerned with understanding the nature of the elemental step, *i.e.* the mechanism by which the small polaron state can move between adjacent sites. This is not expected to be identical for muons and protons, though the comparison of their mobility may be valuable, with the muon more likely to exhibit *quantum diffusion*: by virtue of its greater zero-point energy in the interstitial well, the muon is often able to tunnel through the intervening barrier to the next site more readily than the proton.

The necessity to transfer the elastic distortion is common to muons in metals and muonium in non-metals. Topical questions include how to distinguish *coherent* tunnelling (best described by band-like or propagating states, which are *scattered* by phonons and by defects) from *incoherent* tunnelling (best described by localised states moving step

<sup>16</sup>Phase transitions in the concentrated hydrides can sometimes be described in terms of this distortion exceeding the elastic limit.

by step in a random walk) and how to express the transition between the two. Thermal vibration impedes tunnelling at low temperature but assists it at high temperature, with the result that variation of mobility is not necessarily monotonic: it can show a remarkable minimum, generally between 50 K and 90 K for muonium in non-metals and at lower temperatures for muons in metals [5, 19]. The *quantum mobility* is modified in metals by the necessity to carry the screening charge, with evidence that, at very low temperatures, this no longer follows the muon motion adiabatically [19].

## 6 SUMMARY

### 6.1 Ionic *vs* covalent bonding, diamagnetic *vs* covalent states

In summary, the muon does not remain as a bare particle when implanted and thermalized in matter, but enters into chemical association with the host. An ionic description can sometimes be used; in metals this will imply an associated screening charge; in non-metals purely electrostatic considerations will be modified by varying degrees of covalency and consequent directional bonding. Muonium can exist as the trapped interstitial atom or react to become covalently bound in molecular species.

In diamagnetic metals and in closed-shell molecular species, the muon spin rotation or resonance spectrum displays a single frequency, displaced from the Larmor frequency by a small Knight shift (metals) or chemical shift (molecules).

When the wavefunction of unpaired or spin polarized electrons has some density at the muon site, large hyperfine fields can add or subtract to the external or distant-dipole fields which the muon experiences. Characteristic multiple frequencies appear in the  $\mu$ SR spectra when the electron spin states are long lived; an average paramagnetic shift results when they fluctuate rapidly, or when an ensemble of conduction electrons is involved.

Atomic muonium is itself paramagnetic, as are the open-shell molecules or radicals formed by muonium addition to unsaturated organic compounds. In the trapped atom state of muonium, the electronic moment and wavefunction are centred on the muon but subject to delocalization over the neighbouring atoms. In the  $\text{Mu}^*$  state, which appears unique to the tetrahedrally coordinated semiconductors (including diamond), and in the radicals, major spin density is located elsewhere, on neighbouring atoms. The isotropic component of the hyperfine tensor provides a measure of the spin density on the muon.

### 6.2 Carbon from soot to diamond

Muon states in the different allotropes of carbon illustrate most of these possibilities. In graphite, which is commonly used as a standard of asymmetry in  $\mu$ SR experiments to calibrate polarization, all implanted muons reach a diamagnetic state. A large and anisotropic Knight shift to the muon Larmor frequency reflects the almost 2D character of the electronic conduction in this material but still the screening is sufficiently effective to preclude muonium formation. Diamond, on the other hand, shows the trapped-atom  $\text{Mu}'$  state coexisting with the  $\text{Mu}^*$  state (in which muonium can be said to have reacted with the diamond lattice); thermal conversion from  $\text{Mu}'$  to  $\text{Mu}^*$  in diamond is evidence for the metastability of  $\text{Mu}'$ . The fullerenes also show the metastable trapped atom state, insulated by some potential barrier against reaction from within the cage. But reaction from outside the cage, by addition at a double bond, creates muonium adduct radicals similar to those formed in other unsaturated organic compounds.

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