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On the use of cavity models to describe muonium in diamond, silicon and germanium

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The form of various cavity models are discussed with regard to their prediction of the isotropic hyperfine coupling constants of the "normal muonium" states in group IV elements. Neither the bulk dielectric constant nor the cavity radius seem to be as important as the detailed variation of the dielectric function very close to the trapped nucleus.

Key words: Cavity models — muon — μSR

Introduction

Recently Holzschuh et al. [1] questioned the validity of "cavity models" to explain "normal muonium" states in diamond, silicon and germanium. "Normal muonium" states are characterised by exhibiting isotropic hyperfine coupling constants, determined by muon spin rotation (μSR) spectroscopy, which are of the order of that expected for the free muonium atom (see Table 1 for the fractional values). It is the purpose of this paper to discuss the details of the dielectric function used in these models and to suggest the origin and resolution of the difficulties encountered.

Description of "cavity models"

In this paper a cavity in a material is defined as that region where the dielectric constant is less than the bulk dielectric constant (see Table 1). The muonium atom is placed at the centre of the cavity, which is always assumed to be spherical.

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Table 1. Data used for diamond, silicon and germanium crystals. f is the ratio of the observed muon isotropic hyperfine coupling constant with that of the free muonium atom. All distances are in atomic units (a_0)

Element	Dielectric constant ε'	Cavity radius R	Hyperfine interaction f
C	5.7	1.45	0.829
Si	11.9	2.22	0.450
Ge	16.0	2.31	0.520

The simplest model of all is to assume that the dielectric constant within the cavity is uniform with a value of unity. It is possible to solve numerically the Schrödinger equation for the hydrogen atom with the spherical potential function, modified by the dielectric function. This has been done for all the calculations described here.

Solving the Schrödinger equation for the case of the square well dielectric function, $\varepsilon(r) = 1$ for $r < R$, R being the radius (in units a_0, $1a_0 = 0.529$ Å) of the cavity, and $\varepsilon(r) = \varepsilon'$, for $r > R$, where ε' is used to denote the bulk dielectric constant, we obtain the following f values (and, in parentheses, energies in Hartrees)

C 1.45 (−0.350), Si 1.21 (−0.455), Ge 1.19 (−0.461).

The symbol f is the fractional hyperfine interaction calculated by dividing the calculated (or observed) hyperfine coupling constant by the value obtained for the muonium atom in its "free" (vacuum) state. f values larger than unity clearly demonstrate the "squeezing" effect of the cavity as it forces the electron into the relatively low potential energy of the cavity interior.

This squeezing is not universally applicable since the size of the cavity relative to the "size" of the muonium atomic orbital is very important (see Table 2). Using a dielectric constant appropriate for diamond ($\varepsilon' = 5.7$) a cavity larger than $5a_0$ has a negligible effect. As R decreases there is a rapid increase in the f value which peaks at a cavity radius of about $1a_0$ (the radius of maximum probability for the muonium atomic orbital) before a rapid decrease to the small limiting value for a cavity of zero size (that is, a muonium atom in a uniform medium with $\varepsilon' = 5.7$). The smaller the cavity the higher is the energy. The interpretation is quite clear. For large cavities the electron density is easily "squeezed" into the cavity, although at the expense of a slight increase in the kinetic energy. However a limit is reached when it is better for the electron to occupy regions of relatively high potential energy rather than to increase the kinetic energy. In other words the wave functions is forced to spread further outside the cavity.

Nevertheless, assuming the cavity size is related to the crystal lattice parameters, there is no way that the experimental f values (Table 1) can be correlated with the results of Table 2 since the former pass through a minimum with increasing cavity size whereas the latter pass through a maximum. It is difficult to believe

Table 2. Results obtained for the hydrogen (muonium) atom in a spherical cavity of radius R where the dielectric constant is 1 inside and 5.7 outside. The radial electron density function peaks at $d_{\max}$, f is the ratio of the isotropic hyperfine coupling constant with that of the free atom and the energy is in Hartrees. All distances are in atomic units (a_0)

R	$d_{\max}$	f	Energy
0	5.61	0.006	−0.015
0.5	3.58	0.108	−0.022
0.6	2.11	0.311	−0.033
0.7	1.01	0.678	−0.056
0.75	0.75	0.898	−0.073
1.0	0.79	1.450	−0.188
1.45	0.87	1.454	−0.350
2.0	0.94	1.249	−0.441
5.0	1.00	1.005	−0.499
∞	1.00	1.000	−0.500

that this simple model can be in error solely due to poor choices of values for the cavity radii or the bulk dielectric constants. This forces us to consider the variation of the dielectric *within* the cavity.

This was first recognised by Reiss [2] who proposed that the electrostatic potential around the hydrogen nucleus (muon) should be

$$V=\frac{e}{r}-\frac{e}{R}\left(1-\frac{1}{\varepsilon'}\right), \qquad 0\le r\le R$$

$$V=\frac{e}{\varepsilon' r} \qquad R\le r\le\infty.$$

This function defining the variation of the dielectric within the cavity was chosen to remove the discontinuity in the square well potential (above) at the cavity surface. The effect on the results is quite dramatic (see Table 3, Reiss function). There is a reversal in the order of f compared to the square well potential and agreement with experiment is now generally worse. In fact this reversal is also found in calculations using a dielectric function calculated from the experimental band structure of each material [3] (Table 3, Hermanson function), and also using the model proposed by Resta [4] (who solved the linearised Thomas–Fermi equation)

$$\varepsilon(r)=\varepsilon' qR/[\sinh q(R-r)+qr], \qquad r\le R$$

$$\varepsilon(r)=\varepsilon', \qquad r>R$$

where q is 1.36, 1.10 and 1.08 and the screening radius $R(a_0)$ is 2.76, 4.28 and 4.71 for diamond, silicon and germanium respectively.

Table 3. Comparison of calculations of the hydrogen (muonium) atom in cavities for different dielectric functions. The slope is measured at the cavity centre and the energies are in Hartrees. The radial electron density function peaks at d_{max} and f is the ratio of the calculated isotropic hyperfine coupling constant with that of the free atom. All distances are in atomic units (a_0)

Element	Reiss function				Hermanson		Resta function				Exptl.
	Slope	Energy	d_{max}	f	Energy	f	Slope	Energy	d_{max}	f	f
C	0.81	−0.051	1.25	0.414	−0.076	0.381	1.305	−0.027	2.76	0.114	0.829
Si	0.49	−0.109	1.03	0.838	−0.058	0.428	1.114	−0.016	2.01	0.157	0.450
Ge	0.46	−0.112	1.02	0.863	−0.065	0.487	1.083	−0.013	1.89	0.172	0.520

Table 4. Results obtained for the hydrogen (muonium) atom in a cavity of radius R. Within the cavity ($r \leq R$) the dielectric function is given by $\varepsilon(r) = 1 + mr$ and outside the cavity ($r > R$) has the value ε'. The ground state energies are in Hartrees (27.2 eV). f is the ratio of the calculated isotropic coupling constant with that of the free atom. The radial electron density function peaks at d_{max}. All distances are in atomic units (a_0)

m	$R = \infty$			Diamond $R = 1.45$	$\varepsilon' = 5.7$		Silicon $R = 2.22$	$\varepsilon' = 11.9$		Germanium $R = 2.31$	$\varepsilon' = 16.0$	
	Energy	d_{max}	f	Energy	d_{max}	f	Energy	d_{max}	f	Energy	d_{max}	f
0.0	−0.500	1.00	1.000	−0.350	0.87	1.454	−0.455	0.95	1.214	−0.461	0.96	1.191
0.2	−0.344	1.03	0.929	−0.236	0.92	1.217	−0.311	0.99	1.081	−0.314	0.99	1.078
0.4	−0.244	1.08	0.803	−0.162	0.98	0.973	−0.215	1.04	0.931	−0.217	1.04	0.933
0.6	−0.175	1.16	0.676	−0.133	1.06	0.752	−0.149	1.11	0.778	−0.151	1.11	0.774
0.8	−0.126	1.25	0.559	−0.081	1.15	0.559	−0.103	1.19	0.632	−0.104	1.20	0.633
1.0	−0.091	1.37	0.452	−0.060	1.27	0.409	−0.071	1.30	0.496	−0.070	1.30	0.517
1.2	−0.066	1.50	0.355	−0.039	1.38	0.373	−0.048	1.42	0.391	−0.047	1.41	0.401

We have studied the properties of these functions, where possible, and have looked for characteristics which tend to dominate the calculated value of f. In all these calculations we conclude that the slope of the dielectric function at the cavity centre seems to be a significant factor in determining f, since the larger the slope, the smaller is f. It is easy to demonstrate this using the simple dielectric functions, $\varepsilon(r)=1+mr$, inside the cavity and the bulk dielectric constant, ε', outside the cavity. The results are shown in Table 4. A physical justification for this form of dielectric is suggested below.

Calculations which use $\varepsilon(r)=1+mr$ for all r, that is, $R=\infty$, clearly show that this function tends to spread out the wave function for all positive values of the slope, m. This dielectric function by itself does not seem to introduce a "cavity effect" as is indicated by the f values which are all less than 1, and further, by the orbital "size", $d_{\max}$, which is larger than $1a_0$. The superposition of this dielectric function onto the square well models appropriate to diamond, silicon and germanium in fact reduces the cavity effect of the square well model with the general result that the larger we choose m the larger is $d_{\max}$ and the smaller is f. It is interesting, although of no quantitative significance, to note that for $m=0.4$ the f values for C, Si and Ge follow the sequence found experimentally. At least this shows that even a simple extension to the cavity model can give the right qualitative order in the f values. Of course there is no reason to believe that the slope at the cavity centre should be the same for all three crystals, or indeed that the slope should be constant within the cavity.

In fact the slope at the centre will probably be less than the average slope of $\varepsilon(r)$ in the cavity. For example, referring to table 3, the Reiss function for diamond has a slope of 0.81 which corresponds approximately to $m=1$ in Table 4. Similarly the Reiss slopes for silicon (0.49) and germanium (0.46) correspond to $m=0.5$ in Table 4. The very different Resta function with its large slope at the cavity centre leads to very small f values, predicted using Table 4 for $m>1.2$. This confirmation of the correlation of f to the slope of the dielectric in the cavity prompts an investigation as to the importance of this relative to the cavity radius and the bulk dielectric constant. If it should prove that the variation of $\varepsilon(r)$ near the cavity centre is the more important it will show that the difficulty with the cavity models lies in the determination of $\varepsilon(r)$ only in the region of the cavity centre. In other words, for deep levels in semi-conductors the bulk dielectric constant and cavity size may be of only secondary importance.

Spherical step function

Since most of the functional forms of $\varepsilon(r)$ already used in the literature are very restricted, we have looked for a general mathematical function which has sufficient parameters to simulate any of the previously used functions. The nature of the cavity is essentially a "step" function. One of the most commonly used forms for this is

$$\varepsilon(r)=\varepsilon''+x\tan^{-1}(y(r-D))$$

where y is a parameter which governs the slope of the step

$$\frac{\partial \varepsilon(r)}{\partial r}=\frac{xy}{1+y^2(r-D)^2}$$

D is not strictly the cavity radius, something which is only clearly defined using a square well function, but it is that distance from the cavity centre where the dielectric is ε''. If

$$x=(\varepsilon'-1)/(\pi/2-\tan^{-1}(-yD))$$

then

$$\varepsilon''=(\varepsilon'-x\pi/2).$$

If y is sufficiently large then $\varepsilon''=1+(\varepsilon'-1)/2$, that is, half-way between the initial value 1 and and final value ε'. In this case the step function will closely approximate the square well function. For example, if $y=100$ using $\varepsilon'=5.7$ and $D=1.45a_0$ (the diamond parameters) the square well results are closely reproduced. If we use $y=2.5$, giving a slope at the cavity centre of 0.289, the function gives an f value of 0.839, which is sufficiently close to the experimental value to choose this value of y for a series of calculations. Using

$$\varepsilon(r)=\varepsilon''+x\tan^{-1}(2.5(r-1.45)) \quad \text{for } r<R$$

$$\varepsilon(r)=5.7 \quad \text{for } r>R$$

the results in Table 5 were obtained.

If we choose $R=1.45a_0$, $\varepsilon(1.45)=3.13$, much less than the bulk dielectric constant, a discontinuity has been introdcued into $\varepsilon(r)$. But this does not cause a significant change in f when compared with calculations using much larger values

Table 5. Results obtained for the hydrogen (muonium) atom in a cavity where the dielectric function is $\varepsilon(r)=\varepsilon''+x\tan^{-1}(2.5(r-1.45))$ for $r\leq R$ and $\varepsilon(r)=\varepsilon'$ for $r>R$. The slope at the cavity centre is 0.289. The energies are in Hartrees and the radial electron density distribution peaks at $d_{\max}$. f is the ratio of the calculated isotropic coupling constant with that of the free atom. All distances are in atomic units (a_0)

ε'	Energy	$d_{\max}$	f	R
5.7	−0.082	0.95	0.764	1.1
5.7	−0.092	0.96	0.808	1.2
5.7	−0.100	0.97	0.823	1.3
5.7	−0.107	0.98	0.847	1.45
5.7	−0.115	0.99	0.859	2.0
5.7	−0.117	0.99	0.853	3.0
5.7	−0.118	0.99	0.839	∞
11.9	−0.087	0.95	0.889	1.45

Table 6. Solutions of the Schrödinger equations for a hydrogen atom using the Coulomb potential screened by the fitted dielectric functions of Walter and Cohen [6] (WC) and of Vinsome and Richardson [7] (VR). All results, except the slopes of $\varepsilon(r)$ at the cavity centre, are taken from Table 2 of Wang and Kittel [5]

	Silicon				Germanium			
	Slope	Q_D	ε'	f	Slope	Q_D	ε'	f
WC	0.836	0.9153	11.47	0.427	0.808	0.8702	14.00	0.453
VR	0.835	0.9921	10.53	0.429	0.782	0.8377	14.95	0.478

of R. For $R < 1.45a_0$ the changes in f are more significant, but not dramatically so. In addition, if the bulk dielectric constant is more than doubled from 5.7 to 11.9, the value for silicon, the change is less than 5% for $R = 1.45a_0$. Overall, from many other calculations, it is clear that the f values are dependent on the form of $\varepsilon(r)$ only in the region of the cavity centre and quite insensitive beyond a_0. This might suggest that the least-squares fitting procedure used by Wang and Kittel [5] to obtain $\varepsilon(r)$ from $\varepsilon(q)$ calculated from experimental data by Walter and Cohen [6] and Vinsome and Richardson [7] might be reconsidered. Our work would seem to suggest that the least-squares fit should be strongly weighted towards small values of r. This may be even more important in the case of diamond [1] where the calculated f value from such a dielectric function is too small by a factor of more than 2. To re-emphasise the importance that the slope seems to have on the value of f we have reproduced in Table 6 some results from Wang and Kittel and supplemented them with the slopes of the dielectric function at the cavity centre. Even though Q_D and ε_0 differ for Si the slopes are very close as are the corresponding values of f.

Other calculations [8]

The molecular electrostatic potential, that is, the field sensed by a positive test charge, within the diamond lattice is not spherical. However at the centre of the tetrahedral cavity in the diamond lattice the potential is positive, V_0. If we assume that, after spherical averaging, the potential can be represented by

$$V = V_0 + \tfrac{1}{2}kr^2$$

then

$$\frac{1}{\varepsilon(r)r} = \frac{1}{r} - V$$

or

$$\varepsilon(r) \approx 1 + V_0 r + V_0^2 r^2 + (\tfrac{1}{2}k + V_0^3) r^3 \cdots, \qquad (r < 1/V_0).$$

This clearly indicates that there is a significant variation in the dielectric close to the cavity centre. Crudely the m in $\varepsilon(r) = 1 + mr$ can be regarded as a kind of averaged V. In any event it helps to explain why all observed f values are less than unity for crystals of these Group IV elements. It may seem at first sight that a simple cavity model cannot realistically simulate behaviour at distances less than $1a_0$. Neverthless, since the muonium is caught in the potential field of the crystal at a point where the electron density of the rest of the lattice is very small, it will respond to this potential and this is summarized by $\varepsilon(r)$. In addition cavity models have long been used in helping to rationalise the properties of these and similar solids and we have attempted to maintain the spirit of the model. However more detailed ab initio self-consistent-field calculations on atom clusters representing the crystal structure have already been done [9, 10] and similar calculations of the molecular electrostatic potential will be reported later [8].

Conclusions

The wave function of a hydrogen (muonium) atom trapped in a cavity depends critically on the form of the dielectric function within $1a_0$ of the nucleus. Neither the bulk dielectric constant nor the cavity radius when this is larger than about $1.3a_0$ seem to be important.

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