Electric field gradient antishielding for HD and D$_2$

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We calculate the electric field gradient (efg) antishielding factors for the nuclei of HD and D$_2$ in their $J=0$ and $J=1$ states using perturbation theory. For $J=1$, the factor depends on the m_j state. Since the antishielding factor is quite large, the effective efg felt by the nuclei can be more than an order of magnitude greater than the bare efg on, say, an H atom. Combined with NMR results on deuterium nuclei, this yields a compelling argument that the isolated molecular hydrogen in a-Si:H(D) resides in sites of approximate cubic symmetry, such as the amorphous analogue of tetrahedral sites. We also report on a variational calculation for axial field gradients of arbitrary magnitude.

I. INTRODUCTION

Recently, it has been suggested[1–4] that a substantial fraction of the hydrogen in amorphous hydrogenated silicon [a-Si:H(D)] lies in the analogue of isolated *T*-like sites. In crystalline Si, the tetrahedral or *T* site lies at the center of the large open volume in the lattice and the site has tetrahedral symmetry with respect to the four Si atoms that are nearest to it. Since the site is the center of a large open space, it is rather easy for hydrogen molecules to reside there. In a-Si:H, there are also large open volumes that are the amorphous analogue of the crystalline *T* site, although they no longer possess, tetrahedral symmetry. Related experiments also indicate that H$_2$(D$_2$) resides in the *T* sites in c-Si.[5] Since proton spins ($I=\frac{1}{2}$) are totally insensitive to their electrical environment, NMR on deuterons ($I=1$) is necessary to obtain detailed information on the electrical environment of the molecules. However, the molecular state can have an enormous effect on the nuclear spin relaxation time called T_1, and can also effect nuclear spin lineshapes through the dipolar interaction. Further more, in infrared experiments, the perturbation on hydrogens from efg's can affect the spectrum. Finally, molecular hydrogen is used to probe surfaces and study two-dimensional models on surfaces of various materials.[6]

In particular, the electrical environment affects the deuteron nuclear spin through its quadrupole moment, and the interaction is directly proportional to the efg and the nuclear quadrupole moment. However, besides the direct effect of the efg on a nucleus, there can be an indirect effect that, in general, is much larger than the direct effect. For some nuclei, the indirect effect can be hundreds of times greater than the direct effect, and the ratio of the two is called the Sternheimer antishielding factor[7] because the indirect effect invariably has the opposite sign from the direct effect. For a hydrogen molecule one can physically think of the efg inducing changes in the electronic (angular momentum) wave function which, in turn, causes an additional efg at the nucleus. For a free or chemically bonded H atom there is no indirect effect. For molecular hydrogen the indirect effect turns out to be between one and two orders of magnitude larger than the direct effect. If it is not taken into account errors in interpretation of experiments can arise that are also between one and two orders of magnitude and can totally

distort the results. For these reasons, we have calculated the efg antishielding factor for D$_2$ and HD by perturbation theory for an arbitrarily oriented set of efg's. We have also calculated the antishielding for an arbitrary large axial efg on the ground state of the molecule.

In Sec. II we shall calculate the antishielding factor by perturbation theory for a diatomic molecule in the $J=0$ and $J=1$ states. Section III will contain a variational calculation for an arbitrary axial efg. The results will be discussed with respect to HD and D$_2$ in a-Si:H(D) in Sec. IV. In the remainder of the present section we shall review some theoretical details needed for the calculation.

The interaction of a spin (nuclear) I with an efg can be written as[8]

$$\mathcal{H}=(eQ_e/4I(2I-1))$$
$$\times\{V_{zz}(3I_z^2-I(I+1))+(V_{xx}-V_{yy})(I_x^2-I_y^2)\}, \quad (1)$$

where the V_{ii} are the efg's in the principal axis system where the off-diagonal efg's $V_{ij}(i\neq j)$ vanish, Q_e is the electric quadrupole moment of the nucleus, and I is the nuclear spin where $I\geqslant 1$. The above equation applies to a simple nuclear spin, a compound nucleus such as HD or D$_2$, and actually also for the electronic part of an atom or molecule where I becomes J, the angular momentum. It is this Hamiltonian that is used to calculate the NMR lineshape of nuclei with a quadrupole moment.

For the hydrogen molecule, the efg mixes higher J states into the $J=0$ or $J=1$ state and the dimensionless perturbation parameter is $P=eQ_eV/B$, where V is the magnitude of the efg and B is defined in terms of the unperturbed molecular energy levels

$$E(J)=BJ(J+1). \quad (2)$$

Fortunately, the J dependence of Q_e is negligible. As a charged entity gets closer to a hydrogen molecule, the efg V increases as one divided by the cube of the distance separating the two. By considering the efg due to a simple point charge of magnitude e, one can see that P becomes of order one when the molecule gets about 4 Å from a point charge.

For our purposes, the interaction of an angular momentum state of the hydrogen molecule with an efg is written as

$$V_Q=\frac{1}{6}eQ_e\sum_i V_{ii}(3\gamma_i^2-1) \quad (3)$$

in the principal axis system where Q_e is the electronic quadrupole moment and γ_i is the angular momentum direction cosine in the Cartesian direction i. Thus the equation describes the coupling between the efg's V_{ii} and the angular momentum represented by the γ_i. Equation (3) will be used to calculate the perturbed J state.

The new wave functions can then be used to calculate the indirect effect on the nuclear spins. From Ramsey[9] we get the quadrupole interaction which will yield the effect of the angular momentum on the nuclear spins since $\vec{I}$ is the nuclear spin operator:

$$\mathcal{H}=-\frac{5}{2}\hbar d'_{Q1}X, \tag{4}$$

$$d'_{Q1}=eQ_1q/10I(2I-1),$$
$$X=3(\vec{I}\cdot\vec{\gamma})^2-\vec{I}\cdot\vec{I}, \tag{5}$$

where $\vec{\gamma}$ is the vector formed from the direction cosines and Q_1q is given in Ramsey's book. There is actually a small dipolar contribution to d'_{Q1} besides the quadrupolar contribution. However, as shown by Ramsey, this interaction takes exactly the same form as the above equations and is thus included in the definition of d'_{Q1}.

II. $J=0,1$ STATES

First we consider antishielding for a molecule in the $J=0$ state. The efg's can be oriented arbitrarily but we are working in the principle axis system, and the perturbation must be small. Since the quadrupole Hamiltonian connects states J to $J\pm2$, we shall need a set of $J=2$ states. We have found it easier to work with the Cartesian components rather than the spherical ones, and we thus denote the m manifold of $J=2$ with the convenient orthonormal set:

$$T_i=\sqrt{3\cdot5}\,\gamma_j\gamma_k \quad (i,j,k \text{ cyclic } 1,2,3),$$
$$T_4=(\sqrt{3\cdot5}/2)(\gamma_x^2-\gamma_y^2), \tag{6}$$
$$T_5=(\sqrt{5}/2)(3\gamma_z^2-1),$$

as well as the ground state with a wave function of one. Thus matrix elements consist of simple angular averages

$$\langle\alpha|M|\beta\rangle=\int\frac{d\Omega}{4\pi}T_\alpha T_\beta M(\Omega), \tag{7}$$

where, as usual, Ω represents the solid angle. The expectation of the perturbation in the ground state is zero and only T_α with $\alpha=4$ and 5 are connected to the ground state by the perturbation given by Eq. (3). Thus we have to first order in V_Q:

$$|g\rangle=|0\rangle+A_4|T_4\rangle+A_5|T_5\rangle, \tag{8}$$

where g is the new ground state and

$$A_\alpha=\langle T_\alpha|V_Q|0\rangle/(E(0)-E(2)),$$

$$A_4=-eQV_{zz}/12\sqrt{5}B, \tag{9}$$

$$A_5=-eQ(V_{xx}-V_{yy})/12\sqrt{15}B.$$

We now use this perturbed ground state to calculate the expectation value of $\mathcal{H}_Q$ given by Eq. (4), integrating out the angular momentum variables but, of course, not the spin operators. This will enable us to calculate the effects on the nuclear spins. Although it is far from obvious, since the $J=0$ state was originally spherically symmetric, the form of $\langle g|X|g\rangle$ is exactly the same as given by Eq. (1). A modest amount of algebra yields

$$\mathcal{H}_i=(eQR_o/4I(2I-1))$$
$$\times\{V_{zz}(3I_z^2-I(I+1))+(V_{xx}-V_{yy})(I_x^2-I_y^2)\}, \tag{10}$$

$$R_o=-eQ_1q/30B.$$

As noted, the equation has exactly the same form as the direct effect given by Eq. (1), but the effect is multiplied by R_o. Using the values in Ramsey's book for the relevant parameters we obtain $R_o=-40.5$ for D_2 and -27.5 for HD. The difference between the two is almost entirely due to the smaller value for B for the heavier D_2.

The calculation for the $J=1$ states is similar but considerably more tedious. Furthermore, there is technically no antishielding factor, since the form of the spin Hamiltonian depends on the m angular momentum state. Only after averaging over m states is the interaction in the form of Eq. (10).

As earlier, we find it easier to work in a Cartesian basis so for the $J=1$ subspace we use the orthonormal basis

$$T_i=\sqrt{3}\,\gamma_i, \quad i=1,2,3 \tag{11}$$

and for the $J=3$ space the states

$$T_{1i}=\sqrt{21/8}\,\gamma_i(5\gamma_z^2-1), \quad i=1,2,$$
$$T_{2i}=\sqrt{35/8}\,\gamma_i(\gamma_i^2-\gamma_j^2), \quad i=1,2 \text{ and } j=2,1,$$
$$T_0=\sqrt{7/4}\,\gamma_z(5\gamma_z^2-3), \tag{12}$$
$$T_{3a}=\sqrt{3\cdot5\cdot7/4}\,\gamma_z(\gamma_x^2-\gamma_y^2),$$
$$T_{3b}=\sqrt{3\cdot5\cdot7}\,\gamma_x\gamma_y\gamma_z.$$

The rest of the calculation is a straightforward generalization of the $J=0$ calculation. The results can be expressed as follows. The average over all three m states yields the spin Hamiltonian given by Eq. (10) but with

$$R_0=-3eQ_1q/250B, \tag{13}$$

so that $R_0=-14.6$ for D_2 and -9.9 for HD. For the three states i given by Eq. (11), the results are [see Eqs. (4) and (5)]:

$$\langle X \rangle_z = -3(e/350B)$$

$$\times \left\{ \left(\frac{9}{5} \right) V_{zz}[3I_z^2 - I(I+1)] + (V_{xx} - V_{yy})(I_x^2 - I_y^2) \right\}, \tag{14}$$

$$X_x = -(e/250.7B) \left\{ 9V_{zz}[(3I_z^2 - I(I+1)) - (I_x^2 - I_y^2)] \right.$$

$$\left. + \frac{1}{4}(V_{xx} - V_{yy})[(3I_z^2 - I(I+1))] + 35[(I_x^2 - I_y^2)] \right\}, \tag{15}$$

$\langle X \rangle_y$ is given by $\langle X \rangle_x$ with x and y interchanged.

III. STRONG AXIAL EFG

Consider the ground state of a molecule in an arbitrarily large axial efg. The perturbation is now

$$V = V_0(3\gamma_z^2 - 1), \tag{16}$$

where $V_0 = eQV_{zz}/4$ and the unperturbed energy of the molecule in the state l is $Bl(l+1)$. The wave function for the state can be expanded as

$$|\psi\rangle = \sum_l a_l |f_l\rangle \Big/ \left(\sum_l a_l^2 \right)^{1/2}, \tag{17}$$

where the summation is from $l=0$ to $l=\infty$. Since the states l are described simply by the Legendre polynomials P_l, we have

$$f_l(\gamma_z) = ((2l+1)/2)^{1/2} P_l(\gamma_z); \tag{18}$$

and one can easily show that

$$\langle f_l | \gamma_z^2 | f_{l'} \rangle = A_0(l)\delta(l,l') + A_1(l)\delta(l',l+1),$$

$$A_0(l) = (8l^2 + 4l - 1)/(4l-1)(4l+3) \tag{19}$$

$$A_1(l) = (2l+1)(2l+2)/(4l+3)[(4l+5)(4l+1)]^{1/2},$$

where $\delta(l,l')$ equals one if $l=l'$ and is zero otherwise.

Furthermore, one can take the expectation value of the Hamiltonian given by Eq. (16) and get

$$\langle \psi | \mathcal{H} | \psi \rangle = \left[\sum_l (a_l^2 F(l)) + a_l a_{l+1} G(l) \right] \Big/ \sum_l a_l^2,$$

$$F(l) = 2B(2l+1) + 3V_0 A_0(l) - V_0,$$

$$G(l) = 6V_0 A_1(l). \tag{20}$$

This can be easily minimized using a conjugate gradient method.

IV. DISCUSSION AND CONCLUSION

We have computed the antishielding factors or induced efg at nuclear sites for arbitrarily oriented but weak efg's for the $J=0$ and $J=1$ states of HD and D_2 and for a strong axial efg on the $J=0$ state. For D_2 and HD in the $J=0$ states, the antishielding factors using perturbation theory are -40.5 and -27.5, respectively, and the indirect effect has exactly the same form as the direct effect. The net effect of the efg's is the sum of the direct effect plus the indirect effect. Thus the net effect for $J=0$ HD and D_2 is that the total efg felt at the nuclei is multiplied by a factor of $-39.5 = -40.5 + 1.00$ and $-26.5 = -27.5 + 1.00$, respectively. For the $J=1$ states, averaged over the m states, the factors are -13.6 and -8.9, respectively.

As noted in the Introduction, these calculations were motivated by DMR measurements[1] on a-Si:H(D), where one observes a sharp Pake doublet with a splitting of 66 kHz and a broad Gaussian-like line with a width of about 33 kHz. The claim is made that the Pake doublet arises from D chemically bonded to a Si atom, and the Gaussian arises from isolated HD and D_2 in the amorphous analogue of T-like sites. Because of the unique shape of this line, this claim for the bonded D has never been questioned and can be accepted as fact.

However, for the broad central line, one can ask why the molecules in an open space in the network can experience large enough efg's to allow it a width of $\frac{1}{2} - \frac{1}{3}$ of the bonded D! The answer is that the efg at the molecule is not that large. Since the line width of the molecular broad central line is two to three times narrower than the Pake doublet, the apparent efg for D_2 and HD is two to three times smaller than the efg for the bonded D. However, since the actual efg is being magnified by an amount between 27 and 40 (depending on the relative amounts of D_2 and HD), it is about 1% (a factor of 27 to 40 times 2 or 3) of that experienced by the bonded D. A neglect of this correction will lead to a determination of a ridiculously high efg at the molecular site. Thus molecular hydrogen resides at site with very small efg's, which makes the T-like site the prime candidate for the molecules to reside in.

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