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Dominance of the spin-dipolar NMR relaxation mechanism in fullerene superconductors

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We have performed *ab initio* calculations for the NMR relaxation rate in doped fullerenes and find that the spin-dipolar relaxation mechanism dominates the orbital and Fermi-contact mechanisms. The reason is that the states at the Fermi level are $pp\pi$-like so that the carbon orbitals have almost exclusively radial p character. With the values 7.2 and 8.1 states /(eV spin molecule) for the *bare* densities of states at the Fermi level for, respectively, K_3C_{60} and Rb_3C_{60}, plus the *ab initio* value 1.7 eV spin C atom for the effective Stoner exchange parameter, good agreement is obtained with the experimental relaxation rates.

The discovery of superconductivity in A_3C_{60} has stimulated enormous interest in the electronic structure of these molecular crystals.[1] For the superconductivity, one of the most important parameters is the value N of the electronic density of states at the Fermi level in the normal state. Several groups have performed local-density-functional-approximation (LDA) calculations of this quantity and, for ordered K_3C_{60}, the most reliable results scatter between 6.5 and 9.5 states/[eV spin (K_3C_{60} molecule)].[2,3] For Rb_3C_{60}, the calculated value is about 20% larger due to the increased lattice constant. But how reliable are such calculations? Electronic correlation effects may be important, orientational order may be lacking even at low temperatures, and the significant scatter within the LDA calculations for the same structure is due to basis-set incompleteness for the long intermolecular distances found in A_3C_{60}. Hence, the importance of experimental determinations. For A_3C_{60}, measurements of the electronic specific-heat coefficient and magnetic susceptibility do not give much information about N because the former is affected by the presence of soft, rotational phonons,[4] and the latter contains a large core contribution plus a Landau diamagnetic term.[5,6]

Another possibility is provided by the NMR spin-lattice relaxation rate $1/T_1$. Measurements of ^{13}C NMR in the normal state have been reported by Tycko *et al.*,[7] who obtained $1/(TT_1) = 0.0061/(\mathrm{K\,sec})$ for K_3C_{60}, and by Wong *et al.*[5] obtaining $1/(TT_1) = 0.0047/(\mathrm{K\,sec})$. These authors interpreted their relaxation rates in terms of the *Fermi-contact interaction,* which is proportional to the square of the electronic density of states at the Fermi level and at the carbon nucleus, that is, to $|\psi(\mathbf{r}=\mathbf{0})|^4 N^2$. In order to extract N, Tycko *et al.*[8] estimated $|\psi(\mathbf{0})|^2$ from Hartree-Fock calculations of the probability density at a carbon nucleus, averaged over the three t_{1u} orbitals, and arrived at the rather large values: $N\sim 17$ and 22 states/(eV spin molecule) for, respectively, K_3C_{60} and Rb_3C_{60}. It was noticed, that these relaxation rates are considerably larger than expected from the Fermi-contact mechanism and the measured Knight shifts. Other relaxation mechanisms may therefore be important. In fact, both the dipolar and the orbital mechanisms, which are mainly determined by the p, rather than the s, partial-wave projection of the density of states, might be important in A_3C_{60} whose conduction band is $pp\pi$-like and formed by carbon p_r orbitals pointing radially outwards from the nearly spherical molecule. In such a case, the s partial–wave projection may be thought of as arising from the expansion around the nucleus of the tails of the p orbitals centered on the neighboring atoms (that is, through rehybridization, in the terminology of quantum chemistry). If, furthermore, the radius of the molecule as large compared with the intramolecular bond length ($R/b = 2.48$ in C_{60}), the s-projection would vanish. In that case, not only the Fermi contact, but also the orbital mechanism would be ineffective, because the orbital angular momentum would be quenched.

In this paper we evaluate the relaxation rates for K_3C_{60} and Rb_3C_{60} using an *ab initio* LDA calculation. We shall find that the *spin-dipolar* relaxation rate is about *five* times larger than the orbital rate, and nearly *twenty* times larger than the Fermi-contact rate. Still, our calculated total rates agree well with those measured,[5,7] thus indicating that the calculated LDA density of states is basically correct.

Since the symmetry around a carbon nucleus in A_3C_{60} is low, the common technique for computing the NMR relaxation rate in a cubic or hexagonal metal (see, e.g., Ref. 9) cannot be applied. Moreover, since there seems to be a need for making the numerics transparent, we start from basic principles[10] and specify the details: The relaxation is caused by the dipole interaction $-\boldsymbol{\mu}\cdot\mathbf{H}$ between the nuclear magnetic moment $\boldsymbol{\mu}=(\mu/I)\mathbf{I}$ and the hyperfine field $\mathbf{H}$ produced at the site of the nucleus by the conduction electrons. For the ^{13}C nucleus, the spin is $I=\frac{1}{2}$ and $\mu=0.702\mu_n$, with $\mu_n=e\hbar/2m_pc=\gamma_n\hbar/2$ being the nuclear magneton. The interaction may be split in three terms: the interaction with the electronic orbital moment, the dipole interaction with the electronic spin, and the Fermi-contact interaction:

$$\mathbf{H} = \mathbf{H}^o + \mathbf{H}^d + \mathbf{H}^F = 2\beta\left[\frac{-\mathbf{l}}{r^3} + \frac{\mathbf{s} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}}\cdot\mathbf{s})}{r^3} - \frac{8\pi\mathbf{s}\delta(\mathbf{r})}{3}\right].$$

Here, we have used the one-electron approximation and $\beta = 1836\,\mu_n = \gamma_e\hbar/2$ is the Bohr magneton. $\mathbf{r} \equiv r\hat{\mathbf{r}}$ and

$\hbar\mathbf{l}$ are, respectively, the position and angular momentum operators of the electron with respect to the site of the nucleus and $\hbar\mathbf{s}$ is the electronic spin operator. In addition to the terms mentioned, there could be a contact term due to spin polarization of the inner s-shell electrons, as well as an interaction between the nuclear quadrupole moment and the electric field gradient. These latter terms vanish for A_3C_{60} because the ^{13}C nucleus has no quadrupole moment, and the former one is small because the $1s$ and the $2s$ shells polarize in the opposite direction.[11]

After the applied magnetic field is turned off, the nuclear magnetization relaxes with a rate which is twice the transition probability of a nuclear spin flip and is therefore given in terms of the Fermi golden rule as

$$\frac{1}{T_1} = \frac{4\pi}{\hbar}\sum_{\mathbf{k},\mathbf{k}'} f(\epsilon_\mathbf{k})[1 - f(\epsilon_{\mathbf{k}'})]\delta(\epsilon_{\mathbf{k}'} - \epsilon_\mathbf{k}) \times |\langle \mathbf{k}\uparrow |2\mu\mathbf{I}\cdot\mathbf{H}|\,\mathbf{k}'\downarrow\rangle|^2 .$$

Here, the electronic states are $|\mathbf{k}\rangle$, with $\mathbf{k}$ being a joint label for the Bloch vector and a band index n, which takes two values for each band in case of Kramers degeneracy. The electronic states are normalized to unity in a cell volume V. The energy bands are $\epsilon_\mathbf{k}$, with the energy zero chosen at the Fermi level. Expansion of the Fermi functions, use of $\mathbf{I}\cdot\mathbf{H} = I_zH_z + \frac{1}{2}(I_+H_- + I_-H_+)$, and subsequent integration over the nuclear spin variable, yields

$$\frac{1}{T_1} = \frac{4\pi k_BT}{\hbar}\mu^2 \sum_{\mathbf{k},\mathbf{k}'} \delta(\epsilon_\mathbf{k})\delta(\epsilon_{\mathbf{k}'})\,|\langle \mathbf{k}\,|H_-|\,\mathbf{k}'\rangle|^2 .$$

Introducing now the density-of-states matrix at the Fermi level $\langle \mathbf{k}\,|N|\,\mathbf{k}'\rangle \equiv \delta(\epsilon_\mathbf{k})\delta_{\mathbf{k}\mathbf{k}'}$, the relaxation rate may be expressed as

$$\frac{1}{TT_1} = \frac{4\pi k_B}{\hbar}\mu^2 \mathrm{Tr} H_- N H_+ N, \tag{1}$$

which is *in*dependent of the representation chosen for the electronic variables; $\mathbf{H}$ and N are electronic operators. Since the samples are polycrystalline, we have to average over all crystallographic directions, or over all directions of the applied field. This is most conveniently done using tensor notation, that is, using the spherical vector components $H_{-1} \equiv H_-/\sqrt{2}$, $H_0 \equiv H_z$, and $H_{+1} \equiv -H_+/\sqrt{2}$. As a result

$$\frac{1}{TT_1} = \frac{8\pi k_B}{\hbar}\mu^2 \mathrm{Tr}\frac{1}{3}\sum_{\nu=-1}^{1} (-)^\nu H_{-\nu} N H_\nu N$$
$$= (8\pi k_B/\hbar)\mu^2 \mathrm{Tr}\,|\mathbf{H}N|^2/3, \tag{2}$$

where the numerical value of the relevant prefactor is

$$(8\pi k_B/\hbar)(\mu\beta)^2 = (0.063/\mathrm{K\,sec})(\mathrm{a}_0^3\,\mathrm{eV})^2, \tag{3}$$

and a_0 is the Bohr radius.

In order to evaluate Eq. (2), we express the Bloch states as partial-wave expansions around the site of the nucleus[12] and, assuming that the one-electron potential has spherical symmetry in the relevant range, these expansions become $|i\mathbf{k}m_s\rangle = \sum_{lm} \varphi_l(\epsilon_{i\mathbf{k}}, r) Y_{lm}(\hat{\mathbf{r}}) c_{lm,i\mathbf{k}} |m_s\rangle$, where i labels the paramagnetic bands, $\mathbf{k}$ is the Bloch vector, and $m_s = \pm\frac{1}{2}$. The solution at energy ϵ of the radial Schroedinger equation is $\varphi_l(\epsilon, r)$, and at the Fermi energy, it is $\varphi_l(r)$. For a paramagnet, and neglecting the spin-orbit coupling, the density-of-states matrix is diagonal in spin, i.e., $N_{Lm_s,L'm_s'} = N_{LL'}\delta_{m_s,m_s'}$ with $L \equiv lm$. Here, the orbital part,

$$N_{LL'} = \frac{V}{8\pi^3}\sum_i \int d^3k\, c_{L,i\mathbf{k}}\delta(\epsilon_{i\mathbf{k}}) c^*_{L',i\mathbf{k}}, \tag{4}$$

is the carbon on-site density-of-states matrix per spin and at the Fermi level.

The orbital field $-2\beta\mathbf{l}/r^3$ is diagonal in spin, and the $|\mathbf{H}^o N|^2$ contribution to the relaxation rate (2) is therefore calculated by first performing the trace ($\mathrm{Tr}{=}\mathrm{Tr}_r\mathrm{Tr}_s$) over spin, yielding: $\mathrm{Tr}_s 1 = 2$. Since the matrix elements in orbital space are $\langle L\,|l_{-1}|\,L'\rangle = \delta_{l,l'}\delta_{-1,m-m'}\sqrt{(l-m)(l+m+1)/2}$, $\langle L\,|l_0|\,L'\rangle = \delta_{l,l'}\delta_{m,m'}m$, and $\langle L\,|l_1|\,L'\rangle = -\delta_{l,l'}\delta_{1,m-m'}\sqrt{(l+m)(l-m+1)/2}$, the orbital contribution is readily found to be

$$\frac{1}{3}\mathrm{Tr}\,|\mathbf{H}^o N|^2 = \frac{8}{3}\beta^2 \sum_{\Lambda L} \langle r^{-3}\rangle_{\lambda\lambda} \langle r^{-3}\rangle_{ll} \,[\mu m\,|N_{\lambda\mu,lm}|^2$$
$$+\sqrt{(\lambda-\mu)(\lambda+\mu+1)(l-m)(l+m+1)}\,\mathrm{Re}N_{\lambda\mu,lm}N_{l(m+1),\lambda(\mu+1)}], \tag{5}$$

where

$$\langle r^{-3}\rangle_{ll'} \equiv \int_0^\infty \varphi_l(r) r^{-3} \varphi_{l'}(r) r^2 dr \tag{6}$$

and $\Lambda \equiv \lambda\mu$. Only non-$s$ terms are seen to contribute. Moreover, if at the Fermi level, there were only $m{=}0$ partial waves, the orbital relaxation mechanism would vanish. This would be the case if the curvature of the carbon molecule were very large and the conduction states had pure $pp\pi$ character [provided that the high-l components can be neglected in the range picked up in the integral (6)].

For the dipole field, we first factorize the space and spin variables according to

$$s_\nu - 3\hat{r}_\nu \hat{\mathbf{r}}\cdot\mathbf{s} = \sqrt{8\pi} \sum_{\substack{|\omega|\le 2\\ |\nu'|\le 1}} (2\omega, 1\nu' \mid 1\nu) Y_{2\omega}(\hat{\mathbf{r}}) s_{\nu'}, \tag{7}$$

where $(j_1m_1, j_2m_2 \mid jm)$ are the vector-coupling coefficients. In order to evaluate the $|\mathbf{H}^d N|^2$ contribution to the relaxation rate, we substitute (7) in (2) and then perform the trace over spin: $\mathrm{Tr}_s s_{-\nu} s_{\nu'} = (-)^\nu \delta_{\nu\nu'}/2$. Since $\sum_\nu (2\omega, 1(\nu-\omega) \mid 1\nu)^2 = \frac{3}{5}$ for $|\omega| \le 2$, and zero otherwise, we find that

$$\frac{1}{3}\mathrm{Tr}\left|\mathbf{H}^d N\right|^2 = \frac{16\pi}{5}\beta^2 \mathrm{Tr}_r \sum_{\omega} \frac{Y^*_{2\omega}(\hat{\mathbf{r}})}{r^3} N \frac{Y_{2\omega}(\hat{\mathbf{r}})}{r^3} N.$$

Evaluation of the trace in the partial-wave representation yields the following result for the dipole relaxation rate:

$$\begin{aligned}\frac{1}{3}\mathrm{Tr}\left|\mathbf{H}^d N\right|^2 = 4\beta^2 \sum_{\Lambda\Lambda'}\sum_{LL'} &\delta_{\mu-\mu',m-m'} \\ &\times \left\langle r^{-3}\right\rangle_{\lambda\lambda'} c^2_{\Lambda\Lambda'} N_{\Lambda L} \\ &\times \left\langle r^{-3}\right\rangle_{ll'} c^2_{LL'} N_{L'\Lambda'}. \end{aligned} \qquad (8)$$

Here $c^k_{LL'} \equiv \sqrt{\frac{4\pi}{2k+1}} \int Y_{k\,m-m'}(\hat{\mathbf{r}}) Y^*_L(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{r}}) d^2\hat{r} = (-)^{m-m'} c^k_{L'L}$ are the Gaunt coefficients, which for $l, l' \leq 2$ have nonvanishing *pp, sd,* and *dd* components. These, then couple N_{pp}, N_{sp}, N_{pd}, N_{ss}, N_{dd}, and N_{sd}. For the simple $pp\pi$ model, $N_{\lambda\mu,lm} = \delta_{\lambda 1}\delta_{l1}\delta_{\mu 0}\delta_{m0}N_{zz}$, and since $c^2_{10,10} = \frac{2}{5}$, we obtain

$$\frac{1}{3}\mathrm{Tr}\left|\mathbf{H}^d N\right|^2 = \beta^2 \left(\frac{4}{5}\left\langle r^{-3}\right\rangle_{pp} N_{zz}\right)^2. \qquad (9)$$

For the Fermi-contact mechanism, the result is

$$\frac{1}{3}\mathrm{Tr}\left|\mathbf{H}^F N\right|^2 = \frac{\beta^2}{2}\left(\frac{4}{3}\varphi^2_s(0) N_{ss}\right)^2, \qquad (10)$$

since $\mathrm{Tr_s s^2} = \frac{3}{2}$. With the notation used in the introduction, $N\left|\psi(\mathbf{0})\right|^2 = N_{ss}\varphi^2_s(0)/4\pi$. The Fermi-contact term vanishes for the $pp\pi$ model.

The cross terms in the relaxation rate (2) all vanish: the $\mathbf{H}^o N\cdot\mathbf{H}^d N$ and $\mathbf{H}^o N\cdot\mathbf{H}^F N$ terms, because $\mathrm{Tr}_s\mathbf{s} = \mathbf{0}$, and the $\mathbf{H}^F N\cdot\mathbf{H}^d N$ term, because $\mathbf{s}$ and N commute and because $\mathrm{Tr}_s\mathbf{s}\cdot[\mathbf{s}-3\hat{\mathbf{r}}(\hat{\mathbf{r}}\cdot\mathbf{s})] = \mathrm{Tr}_s[s^2 - 3(\mathbf{s}\cdot\hat{\mathbf{r}})^2] = 0$. The relaxation rate (2) for a polycrystal is thus given by the sum of the orbital (5), the dipolar (8), and the Fermi-contact (10) terms.

For our $pp\pi$ model, the relaxation rate is *entirely dipolar* and given by Eq. (9). Using in this expression the *free* carbon atom value, $\left\langle r^{-3}\right\rangle_{pp} \sim 1.7a_0^{-3}$, and N_{zz} ~(8/60) states/(eV spin C atom) as a representative value for the LDA density of states in K_3C_{60}, we find that the relaxation rate for the $pp\pi$ model is $1/(TT_1)$ ~0.002/(K sec), which is about one third the experimental low-temperature values of 0.0061 (Ref. 7) and 0.0047/(K sec).[5]

In order to obtain a more accurate estimate, we have performed LDA linear-muffin-tin-orbital (LMTO) method in the atomic-spheres-approximation (Ref. 13) calculations for K_3C_{60} (a=14.245 A) and Rb_3 C $_{60}$ (a=14.420 A), as described in Refs. 3 and 14. A fairly complete basis set, consisting of 1206 LMTOs per molecule contracted to 317 LMTOs per molecule, was used. Moreover, in order to obtain accurate wave functions at the Fermi level the linear partial-wave expansions were performed around $\epsilon_{\nu Rl} \equiv \epsilon_F$. For the accuracy of the present paper, it was sufficient to consider the fcc unidirectional crystal structure (space-group Fm = $\bar{3}$). The Brillouin-zone integrations were performed with the linear tetrahedron method and a mesh of 396 irreducible **k** points. We found that N =9.0 and 10.5 states/(eV spin molecule) for K_3C_{60} and Rb_3C_{60}, respectively. The coefficients $c_{lm,ik}$ used in Eq. (4) are defined so that the carbon partial waves $\varphi_l(\epsilon, r)$ be normalized in a sphere of radius $s_C = 1.60a_0$. Of course, the *products* like $N_{ll}\varphi^2_l$ do not depend on the choice of the radius.

The convergence of the sums over angular momenta in expressions (5) and (8) for the orbital and dipolar matrix elements is governed by the product of the radial integrals (6) and the matrix elements of the density of states. For K_3C_{60}, we find that $\langle(a_0/r)^3\rangle_{pp} = 3.71$ is much larger than $\langle(a_0/r)^3\rangle_{sd} = 0.47$ and $\langle(a_0/r)^3\rangle_{dd} = 0.54$. Since also N_{pp} =6.5 is much larger than N_{dd}= 0.25, and N_{ss}=0.05 states/(eV spin 60 C atom), where $N_{ll} \equiv \sum_m N_{lm,lm}$, the l convergence appears to be so good that we can truncate after the d waves. Since the above-mentioned radial integrals were, in fact, truncated outside the ^{13}C-centered sphere of radius s_C, this good convergence merely concerns the integrals inside the central sphere.[15] The integrals outside this sphere were not taken into account,[16] but we estimate the error associated herewith to be less than 5%.

With this procedure, we obtained the contributions to the relaxation rate given in Table I. The dipole mechanism is seen to dominate and the Fermi-contact mechanism is the least important. The relaxation rates were averaged over three kinds of carbon atoms, but the variation of the total rate was less than 10%, due to the dominance of N_{pp}. The relative variation of the Fermi-contact rate was larger because the small $|\psi(\mathbf{0})|^4$ is caused by the tails of the radial p orbitals and therefore sensitive to overlap from the neighboring molecule [$1/(TT^F_1)$ =0.00022, 0.00028, and 0.00039/(K sec) for, respectively, the top-hexagon-edge atoms, the contact atoms, and the remaining atoms]. The contributions from the d partial waves to the dipole and orbital relaxation rates were small, at the order of 1%.

The calculated dipole rate, 0.0054/(K sec), given in Table I is essentially what one obtains [0.0065/(K sec)] from the $pp\pi$ model (9) using for N_{zz} the calculated N_{pp} =6.5 states/(eV spin 60 C atom) and the calculated $\langle(a_0/r)^3\rangle_{pp}$=3.71. What increases the dipole rate from the one previously estimated by a factor 3, is the increase of the radial integral due to the compression of the wave function in the molecule ("renormalized-atom effect"). The Fermi-contact rate is very small due to the smallness of N_{ss}=0.05 states/(eV spin 60 C atom)≈ $N_{pp}/150$. This ratio (150) is particularly large for the t_{1u} orbital,[17] and is essentially a geometrical factor for a given orbital. The calculated value of $a^3_0\varphi^2_s(0)$ =81 is more than twice the value obtained from the free-atom 2p orbital, whose

TABLE I. Contributions to $(TT_1)^{-1}$ [10^{-4}/(K sec)].

	Fermi	Orbital	Dipole	Total	Expt. (Ref. 5)	Expt. (Ref. 7)
K_3C_{60}	3	9	54	66	47	61
Rb_3C_{60}	4	13	75	92		100

energy is about 20 eV below the Fermi level.

The total relaxation rates, 0.0066 and 0.0092/(K sec), calculated for, respectively, K_3C_{60} and Rb_3C_{60} agree almost too well with the rates 0.0061/(K sec) and 0.0100/(K sec) measured at temperatures slightly above T_c.[7] An independent measurement for K_3C_{60} at 20 K yields 0.0047/(K sec).[5]

The LDA density of states does not include exchange-correlation enhancement. This we have estimated from the splitting of the bands in the Γ point due to an external magnetic field, and the result for the effective Stoner exchange parameter is $I \equiv \Delta E/m = 1.7$ eV spin C atom, in good agreement with the renormalized-atom value of 2.3 eV spin C atom sphere[3] (note that the first value should be used with the *total* density of states, while the second should be used with the density of states projected onto a carbon sphere). For K_3C_{60} and Rb_3C_{60}, the densities of states used for the relaxation rate should thus be enhanced by factors of $(1 - NI)^{-1}$ =1.34 and 1.42 (NI =0.26 and 0.30), respectively. The good agreement found with the experiments thus suggest that it is the *enhanced* densities of states which should take the values N =9.0 and 10.5 states/(eV spin molecule) for K_3C_{60} and Rb_3C_{60}. The corresponding *bare* LDA values should have been 7.2 and 8.1 states/(eV spin molecule), that is, 20% lower. This still lies within the range of LDA calculations[2] for the unidirectional structure. A physical, rather than computational, source of such an overestimation could be the effect of orientational disorder which would tend to smear out the peaks in the density-of-states function $N(\epsilon)$.

In conclusion, we have performed *ab initio* LDA calculations for the NMR relaxation rate in doped fullerenes. We find that the spin-dipolar relaxation mechanism dominates the orbital and Fermi-contact mechanisms, because the states at the Fermi level are $pp\pi$-like so that the carbon orbitals have almost exclusively radial p character. With the values 7.2 and 8.1 states/(eV spin molecule) for the bare densities of states at the Fermi level for K_3C_{60} and Rb_3C_{60}, plus the value 1.7 eV spin C atom for the effective Stoner exchange parameter, good agreement is obtained with the experimental relaxation rates.

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[11] This can be understood as follows: The hyperfine field due to core polarization may be written as $-2\beta(8\pi/3)\mathbf{s}\sum_n dm_n(\mathbf{0})/dM$, where m_n is the spin density of the nth shell on the nucleus, induced by a spin polarization M of the valence electrons, and the summation is over all occupied shells. In case of C_{60}, perturbation theory applied to the $1s$ and $2s$ shells yields the result that $dm_1(\mathbf{0})+dm_2(\mathbf{0})$ differs from 0, only when coupling with the unoccupied $3s$ and higher shells is included. A numerical free-atom calculation with $dM = 0.4\mu_B$ shows that this hyperfine field is less than 0.5% of the Fermi-contact field, thus providing the estimate for the corresponding contribution to the relaxation rate: $(0.005{*}N_{pp}/N_{ss})^2 \approx 0.5$ of the Fermi-contact rate.

[12] We do not use the total angular-momentum ljm_j representation, but the lmm_s representation because the spin-orbit coupling is negligible and we wish to discuss separately the orbital-, spin dipolar-, and Fermi-contact relaxation mechanisms. Note, that the density-of-states matrix N is not a *spherical* tensor operator of rank 0.

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[15] The partial waves of high l behave like r^l, so that $\langle (a_0/r)^3\rangle_{ll'} \to (a_0/s_C)^3[1 + 3/(l + l')]$, which is 0.58 for $ll' = pp$ and sd, and 0.40 for dd.

[16] The most practical way of doing so, would be to use the ASA, that is, to add the integrals over the remaining spheres. Such an integral would then be calculated by expanding the wave functions *and* the central operator around the new center. With such an approach, each partial-wave expansion converges well.

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