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Citation: [The Journal of Chemical Physics](#) **72**, 5786 (1980); doi: 10.1063/1.439007

View online: <http://dx.doi.org/10.1063/1.439007>

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Analytic formula for chemically induced magnetic polarization by $S-T_{\pm 1}$ mixing in a strong magnetic field^{a)}

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(Received 17 December 1979; accepted 5 February 1980)

Recently we reported a theory of chemically induced magnetic polarization due to mixing of the singlet (S) and $M_S = \pm 1$ triplet sublevels ($T_{\pm 1}$) of a diffusing radical pair in a strong magnetic field,¹ which paper is henceforth referred to as AM. The polarization, due almost completely to $S-T_{\pm 1}$ mixing in the level crossing region, was expressed as a complicated series which had to be evaluated numerically. Here, we derive an analytic formula for this polarization, whose very strong field limit corresponds to Alexandrov's result for nonadiabatic transitions between two linearly intersecting energy levels.²

By Eq. (35) of AM, the $t \rightarrow \infty$ limit of the polarization produced by $S-T_{\pm 1}$ mixing is

$$\mathcal{P}_{\infty}(S-T_{\pm 1}) = \frac{a^2}{2H^2} - \frac{a^2}{4} \int_{r_0=1}^{\infty} dp \int_{r_0=1}^{\infty} dq \times [G_{+,t}(p, q) + G_{*,t}(p, q)], \quad (1)$$

where a and H are, respectively, related to the hyperfine interaction, which mixes the S and $T_{\pm 1}$ states, and the magnetic field [cf. Eq. (6) of AM], and $G_{*,t}$ is a Green function. The $S-T_{\pm 1}$ polarization is obtained by changing the sign of the rhs of Eq. (1) and also the sign of H , where the dependence of $G_{*,t}$ on H will be given momentarily.

We now replace the truncated Green function $G_{*,t}$ in Eq. (1) by the complete function $G_{*,t}$, and drop the $a^2/2H^2$ term, which is included in $G_{*,t}$ but had to be treated separately in AM because of integral convergence problems. Usually, the exponentially decaying exchange interac-

tion, which splits the S and T states, will be very large at the minimum interrational separation [i.e., $(J_0 e^{-\lambda r})_{r=1} \rightarrow \infty$], in which case Eq. (23) of AM shows that

$$G_{*,t}(p, q) = -\frac{2}{\lambda} \int_0^{\infty} \frac{x \mathcal{J}_{\nu}(x | \omega | e^{-\lambda p/2}) \mathcal{J}_{\nu}(x | \omega | e^{-\lambda q/2}) dx}{x^2 + i}, \quad (2)$$

where \mathcal{J}_{ν} is the Bessel function of order ν , and by Eqs. (15) and (18) of AM with $s \rightarrow 0$, which corresponds to the long-time limit,

$$\omega = (4J_0/\lambda^2)^{1/2} e^{-i\tau/4}; \quad \nu = (4H/\lambda^2)^{1/2} e^{-i\tau/4}. \quad (3)$$

TABLE I. $(S-T_{\pm 1})$ polarization as a function of H_0 and λ . Other parameters are $D = 2(10)^{-6}$ cm/sec, $\sigma = 2(10)^{-8}$ cm, $\tilde{r}_c = \sigma r_c$, $\tilde{\lambda} = \lambda/\sigma$, and $2\tilde{J}_0 e^{-\tilde{\lambda}\sigma} = 4(10)^{13}$ rad/sec.

$\Delta \mathcal{P}_{\infty}(S-T_{\pm 1})/a^2$						
H_0 G	λ	r_c	$\nu/e^{-i\tau/4}$	Eq. (6) $ \nu \rightarrow \infty$	Eq. (6) \equiv AM	
850	2	4.944	0.547	12.98	13.59	
3400	2	4.251	1.094	2.79	2.82	
13600	2	3.588	2.187	0.58	0.58	
850	4	2.972	0.273	3.90	4.56	
3400	4	2.626	0.547	0.86	0.90	
13600	4	2.279	1.094	0.19	0.19	
850	8	1.986	0.137	1.30	1.79	
3400	8	1.813	0.273	0.30	0.34	
13600	8	1.639	0.547	0.067	0.069	
850	16	1.493	0.068	0.49	0.80	
3400	16	1.406	0.136	0.12	0.15	
13600	16	1.320	0.273	0.027	0.030	

G^* is readily derived from Eq. (2), as are the corresponding functions for the $S-T_1$ case after noting from Eq. (3) that $\nu(-H) = \nu^*(H)$. We combine the expressions for the $S-T_{-1}$ and $S-T_1$ polarizations, obtaining the net polarization as

$$\Delta\phi_\infty(S-T_{\pm 1}) = \text{Im} \left[-\frac{16a^2}{\lambda^4} \int_0^\infty dx \frac{x}{x^4+1} \times \int_0^\infty dP \ln \left(\frac{P}{x|\omega|} \right) \frac{J_\nu(P)}{P} \int_0^\infty dQ \frac{J_\nu(Q)}{Q} \right] \quad (4)$$

after the following steps: (1) Interchange of the orders of integration; (2) The variable changes $P = x|\omega|e^{-\lambda P/2}$ and $Q = x|\omega|e^{-\lambda Q/2}$; (3) Noting that the upper limit of the integrations over P and Q , $x|\omega|e^{-\lambda/2}$, may be approximated as ∞ for $J_0 e^{-\lambda}$ large, except when x is very small, which region is unimportant because of the $x/(x^4+1)$ term in the integration over x .

The integral over Q is known³: $I_2 = \int_0^\infty Q^{-1} J_\nu(Q) dQ = 1/\nu$. The integral over P is $\int_0^\infty P^{-1} \ln(P/x|\omega|) J_\nu(P) dP = I_1 - \ln(x|\omega|) I_2 \cong I_1 - \nu^{-1} \ln|\omega|$, where the $\ln x$ term is neglected because $\ln|\omega| \gg |\ln x|$ for all x which contribute significantly to the x integrand $x/(x^4+1)$, and I_1 is

$$I_1 = \int_0^\infty P^{-1} \ln(P) J_\nu(P) dP = \frac{\Gamma(\frac{1}{2}\nu)}{4\Gamma(\frac{1}{2}\nu+1)} [\psi(\frac{1}{2}\nu) + \psi(\frac{1}{2}\nu+1) - \ln \frac{1}{4}], \quad (5)$$

where $\psi(z) = d \ln \Gamma(z) / dz = \ln(z) - \sum_{k=0}^\infty \{ (k+z)^{-1} - \ln[1 + (k+z)^{-1}] \}$.⁴ Finally, $\int_0^\infty x dx / (x^4+1) = \pi/4$.

Using the foregoing results for the integrals and Eq. (3) to evaluate Eq. (4) gives

$$\Delta\phi_\infty(S-T_{\pm 1}) = \frac{\pi a^2}{2\lambda H} \left\{ r_c - \frac{2}{\lambda} \text{Re} \left[\nu^{-1} - \sum_{k=0}^\infty \frac{1}{k + \frac{1}{2}\nu} \right] \right\}$$

$$- \ln \left(1 + \frac{1}{k + \frac{1}{2}\nu} \right) \Bigg\} \Bigg|_{\text{asymptotic}} = \frac{\pi A^2}{4\mu_B g H_0} \frac{\tilde{r}_c}{\lambda D}, \quad (6)$$

where $r_c = \lambda^{-1} \ln(J_0/H)$ is the level crossing separation, and the asymptotic limit on the far r.h.s. of Eq. (6) is in dimensioned variables. By Eq. (6) of AM these are: A is the hyperfine interaction constant, $2J_0 e^{-\lambda \tilde{r}}$ is the exchange interaction, $g\mu_B H_0$ is the triplet Zeeman splitting in the magnetic field H_0 , and D is the diffusion constant.

Table I compares $\Delta\phi_\infty$ calculated by the exact and asymptotic versions of Eq. (6) with the numerical results of AM. The exact Eq. (6) and AM yield identical results, whereas, the simple asymptotic expression gives very good results except for those combinations of low H_0 , large λ , and large D which make ν quite small. It should be noted, however, that an effect due to nonadiabatic mixing of the S and T_{-1} levels only would be less well represented by Eq. (6), because then one must also consider the effects of mixing in the Zeeman splitting region which are no longer cancelled by the $S-T_1$ term.

^aWork supported by the U. S. Department of the Navy, Naval Sea Systems Command, under Contract N00024-78-C-5384.

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On the many-body contributions to the OK binding energy of solid argon^{a)}

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(Received 18 September 1979; accepted 5 February 1980)

In the calculation of the binding energy of solid argon at OK, many-body effects are large and cannot be neglected. Recently,^{1,2,3,4} it has been the fashion to account for these many-body effects by including only the long-range third-order triple dipole energy term $(DDD)_3$. The reason for this is that it has been assumed that contributions of the many-body dipole interaction terms of fourth-order and above $(MBD)_{4-\infty}$ cancel those of higher multipole third-order terms $(DDQ)_3$, $(QQD)_3$, $(DDO)_3$, and $(QQQ)_3$. D , Q , and O refer to dipole, quadrupole, and octopole and subscripts 3 and 4 $\rightarrow \infty$ refer to third- and fourth to higher order of quantum perturbation theory. Agreement of the calculation

using only the $(DDD)_3$ term with experimental estimates^{5,6,7} of the heat of sublimation for argon at OK has been good. While it might be argued that the potential of Barker *et al.*³ (BFW) has been somewhat biased to fit the OK binding energy for argon on the assumption that the $(DDD)_3$ term alone accounts for the many-body effects, the work of Ref. 4 adds support to this assumption. In that paper, Gibbons *et al.* calculated solid state properties again assuming that the $(DDD)_3$ term solely accounted for the many-body interactions but using a potential⁸ derived from dilute gas properties alone (scattering, spectroscopy, and second virial data) and found agreement with experimental results.