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. Fluids 25 (1982) 736.

THE SPIN–ROTATION INTERACTION OF ATOMS WITH HALF-FILLED ELECTRON SHELLS

W. HAPPER, K.D. BONIN and T.G. WALKER

Department of Physics, Princeton University, Princeton, NJ 08544, USA

An important relaxation mechanism for spin polarized atoms with half-filled shells in noble gases is the spin–rotation interaction. A simple formula for the spin–rotation coupling constant is presented.

Recently Ferrante and Stwalley [1,2] called attention to the possibility of forming a van der Waals crystal from spin polarized nitrogen atoms. Recombination into N_2 molecules would be hindered by the repulsive nature of the $^7\Sigma$ potential curves for pairs of N atoms. However the magnetic dipole–dipole interaction between the spins of nitrogen atoms may cause such rapid spin relaxation that it would be difficult to form the crystals [3]. It might still be interesting to study dense spin polarized N atoms which are isolated from each other by a diamagnetic matrix, for example frozen argon, neon, or hydrogen, where relaxation times may be much longer.

Early experimental work by Holloway and Novick [4] and by Anderson et al. [5] showed that the spin relaxation rates of N atoms in diamagnetic buffer gases were much smaller than gas kinetic collision rates, but no quantitative measurements of the rates were made. In the case of alkali atoms colliding with noble gas atoms Bernheim [6] pointed out that the observed spin relaxation was probably due to the spin–rotation interaction

$$V_{SR} = \gamma S \cdot N , \tag{1}$$

between the spin S of the alkali metal atom and the rotational angular momentum N of the alkali metal atom and the noble gas atom about each other. The same spin–rotation interaction (1) will also cause relaxation of spin polarized N atoms in diamagnetic gases. In this paper we point out that the spin–rotation coupling constant γ can be estimated for N atoms or for any atom with a half closed shell

by the simple formula first given by Wu et al. [7]:

$$\gamma = -\frac{mG}{4\pi MR} \frac{\mathrm{d}}{\mathrm{d}R} \left| \frac{P_\lambda(R)}{R} \right|^2 . \tag{2}$$

Here m and M are the electron mass and the reduced mass of the atomic pair, R is the internuclear separation, and P_λ is the radial wavefunction for a valence electron of the paramagnetic atom

$$\phi_{1\lambda\mu}(R, \theta, \varphi) = Y_{\lambda\mu}(\theta, \varphi) \frac{P_\lambda(R)}{R} . \tag{3}$$

Also, $Y_{\lambda\mu}$ is a spherical harmonic of angular momentum λ and azimuthal quantum number μ, and the spherical coordinates of the electron with respect to the nucleus of the paramagnetic atom are R, θ, and φ. The quantity G depends only on the nature of the noble gas atom and it is a measure of the strength of the spin–orbit interaction of a low energy electron scattering in the core of the noble gas atom. Walker et al. [8] have shown that the amplitude for scattering slow electrons from an initial state with momentum $\hbar k_i$ and spin projection μ_i to a final state with momentum $\hbar k_f$ and spin quantum numbers μ_f is simply

$$\langle k_f \mu_f | f | k_i \mu_i \rangle = \frac{mG}{2\pi i \hbar^2} k_i \times k_f \cdot \langle \mu_f | S | \mu_i \rangle . \tag{4}$$

To calculate the magnitude of G, the wavefunction of slow electrons in the core of the noble gas atom must be known. Walker et al. [8] show that the wavefunction can be conveniently estimated in two ways: by orthogonalizing the free-electron wavefunc-

tion to the core orbitals of the noble gas atom, as is done in many pseudopotential calculations, or by solving the Schrödinger equation for low energy electrons in a conventional partial-wave calculation. Both methods yield similar estimates for G. We find it convenient to use the orthogonalization procedure in this paper.

Physically, (2) implies that the spin–rotation coupling constant γ is mainly due to the spin–orbit interaction of the valence electrons in the core of the noble gas and that the contribution to γ of the spin–orbit interactions in the core of the paramagnetic atom, which were considered by Herman [9], are not very important. Experiments show that for alkali atoms (2) works well for the heavier noble gases Ar, Kr, and Xe. Eq. (2) should also give the contribution to γ of spin–orbit interactions within the cores of Ne and He, but the experimental facts are less clear for these light noble gases which do not readily form van der Waals molecules.

In the remainder of this paper we will show that eq. (2) is not restricted to alkali–noble-gas pairs, but it also describes the contribution to γ of spin–orbit interactions in the core of a noble gas atom paired with any atom with a half-filled shell of valence electrons. For convenience we refer to these as "paramagnetic" atoms. Examples of paramagnetic atoms in this restricted sense are alkali metal atoms with half-filled s shells, N, P, and As atoms with half-filled p shells, Mn atoms (or Mn^{2+} ions in solution) with half-filled d shells.

We may describe the ground state of the unperturbed paramagnetic atom by the electron wavefunction

$$\Psi_{1SM} = \Phi_1(r_1, r_2, ..., r_{2\lambda+1})$$
$$\times \chi_{SM}(\sigma_1, \sigma_2, ..., \sigma_{2\lambda+1}) , \tag{5}$$

where λ is the orbital angular momentum of single electrons in the half-filled shell. The function Φ_1 depends on the spatial coordinates $r_1, r_2, ..., r_{2\lambda+1}$ of the $2\lambda+1$ different single electron orbitals of the form (3) with $\mu = -\lambda, -\lambda+1, ..., \lambda$. The spin function χ depends on the $2\lambda+1$ spin variables $\sigma_1, \sigma_2, ..., \sigma_{2\lambda+1}$, and it is the totally symmetric function of total spin angular momentum $S = \lambda + \frac{1}{2}$ and azimuthal quantum number $|M| \leq S$.

The valence electrons of the paramagnetic atom

will scatter in the core of a passing noble gas atom, and this scattering gives rise to the spin–rotation interaction (1). The valence electron orbitals of the paramagnetic atom are strongly distorted in the neighborhood of the noble gas nucleus, and we will approximate the orbitals, as was done in ref. [7], by orthogonalizing them to the moving core orbitals of the noble gas atom, i.e.

$$\phi_{\lambda\mu} \simeq \phi_{1\lambda\mu} - \sum_n \psi_{np} \cdot A_{\lambda\mu} C_{np} , \tag{6}$$

where $\psi_{np} = \psi_{np_x}\hat{x} + \psi_{np_y}\hat{y} + \psi_{np_z}\hat{z}$ is a cartesian vector formed from the p-orbitals of the noble gas (cf. eq. (5) of ref. [7]). The overlap coefficients (cf. eq. (3) of ref. [7]) are

$$C_{np} = \int_0^\infty z\psi_{np_z}(r) \, d^3r , \tag{7}$$

and the vector coefficients (cf. eq (7) of ref. [7]) are

$$A_{\lambda\mu} = \nabla \phi_{1\lambda\mu} - \frac{iMv}{\hbar}\phi_{1\lambda\mu} . \tag{8}$$

Here v is the velocity of the noble gas atom with respect to the paramagnetic atom. The wavefunction of the perturbed paramagnetic atom can therefore be written as

$$\Psi_{SM} = \Phi(r_1, r_2, ..., r_{2\lambda+1}) \chi_{SM}(\sigma_1, \sigma_2, ..., \sigma_{2\lambda+1}) , \tag{9}$$

where Φ is the Slater determinant formed from the $2\lambda+1$ orthogonalized orbitals (6). Consider the spin–orbit interaction for the $2\lambda+1$ valence electrons

$$V_{SO} = \frac{\mu_B}{emc} \sum_{\mu=-\lambda}^{\lambda} \nabla V(r_\mu) \times p_\mu \cdot s_\mu . \tag{10}$$

Here $V(r_\mu)$ is the self-consistent (attractive) electrostatic potential energy of the μth electron, s_μ is the spin operator of the electron, p_μ is the momentum operator of the electron and μ_B, e, and c are the Bohr magneton, the electronic charge (>0), and the speed of light. The matrix elements of V_{SO} between states of the form (9) are readily shown to be

$$\langle \Psi_{SM'} | V_{SO} | \Psi_{SM} \rangle = \frac{\mu_B}{emc(2\lambda+1)}$$
$$\times \left[\sum_{\mu=-\lambda}^{\lambda} \int d^3r \, \phi_{\lambda\mu}^*(r) \nabla V(r) \times p\phi_{\lambda\mu} \right]$$
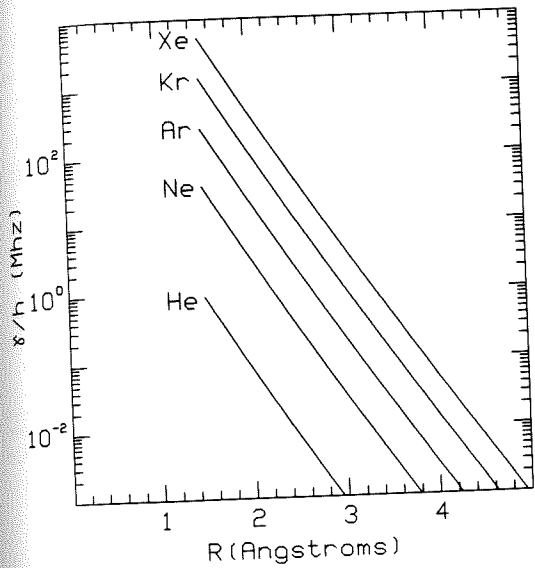$$\cdot \langle SM' | S | SM \rangle . \tag{11}$$

Fig. 1. The spin–rotation coupling constant γ versus internuclear separation R for nitrogen–noble-gas atomic pairs.

The main contributions to (11) come from the neighbourhood of the noble gas nucleus. Indeed, it is well known that for a half-closed shell of unperturbed electrons the matrix elements of V_{SO} are zero. Substituting (6) into (11) we find that

$$\langle SM' | V_{SO} | SM \rangle$$

$$= \frac{iG}{2\lambda+1} \sum_\mu \boldsymbol{A}_{\lambda\mu} \times A^*_{\lambda\mu} \cdot \langle SM' | \boldsymbol{S} | SM \rangle , \qquad (12)$$

where (cf. eq. (2) of ref. [7])

$$G = \frac{1}{2} \left(\frac{\hbar}{mc} \right)^2 \int \left[\sum_n C_{np} R_{np}(r) \right]^2 \frac{1}{r} \frac{dV}{dr} dr . \qquad (13)$$

From the definition (8) we see that

$$\sum_\mu \boldsymbol{A}_{\lambda\mu} \times A^*_{\lambda\mu} = -\frac{im}{\hbar} \boldsymbol{v} \times \nabla \sum_\mu |\phi_{\lambda\mu}|^2$$

$$= i \frac{m(2\lambda+1)}{4\pi\hbar} \frac{\boldsymbol{R} \times \boldsymbol{v}}{R} \frac{d}{dR} |P_\lambda|^2 . \qquad (14)$$

Noting that $M\boldsymbol{R} \times \boldsymbol{v} = \hbar \boldsymbol{N}$ and substituting (14) into (12) we obtain (2).

Using the convenient analytic approximation to P_λ as given by Clementi and Roetti [10] and the tabu-

lated values of G from the partial wave calculations in ref. [8] we obtain the plots of γ as a function of internuclear separation R shown in fig. 1.

As a simple application of the above results, we estimate the strength of the spin–rotation interaction for the case of NAr and NXe molecules. The potential curves have been experimentally determined, and the equilibrium radii are 3.62 Å for NAr [12] and 3.76 Å for NXe [13]. From fig. 1, we estimate γ/h at these radii to be 0.013 MHz for NAr and 0.15 MHz for NXe. For comparison, the experimentally measured values for the molecules KAr [14] and KXe [7] are 0.24 MHz and 2.3 MHz. Thus nitrogen would have considerably longer spin-relaxation times due to the interaction (1) in the noble gases than potassium.

References

[1] R.F. Ferrante and W.C. Stwalley, J. Chem. Phys. 78 (1983) 3107.
[2] R.F. Ferrante and W.C. Stwalley, J. Chem. Phys. 85 (1986) 1201.
[3] W. Happer, K.D. Bonin and T.G. Walker, The stability of spin-aligned nitrogen crystals, to be published.
[4] W.W. Holloway and R. Novick, Phys. Rev. Lett. 1 (1958) 367.
[5] L.W. Anderson, F.M. Pipkin and J.C. Baird Jr., Phys. Rev. 116 (1962) 87.
[6] R.A. Bernheim, J. Chem. Phys. 36 (1962) 135.
[7] Z. Wu, T.G. Walker and W. Happer, Phys. Rev. Lett. 54 (1985) 1921.
[8] T.G. Walker, K.D. Bonin and W. Happer, Electron–noble-gas spin-flip scattering, to be published.
[9] R. Herman, Phys. Rev. 136 (1964) A1576.
[10] E. Clementi and Roetti, At. Data Nucl. Data Tables 14 (1974) 177.
[11] C.C. Bouchiat, M.A. Bouchiat and L.C.L. Pottier, Phys. Rev. 181 (1969) 144.
[12] B. Brunetti, G. Liuti, E. Luzzatti, F. Pirani and G.G. Volpi, J. Chem. Phys. 79 (1983) 273.
[13] L. Herman and R. Herman, J. Phys. Radium 24 (1963) 73.
[14] E.M. Mattison, D.E. Pritchard and D. Kleppner, Phys. Rev. Lett. 32 (1974) 507;
R.R. Freeman, E.M. Mattison, D.E. Pritchard and D. Kleppner, J. Chem. Phys. 64 (1976) 1194.