Parity nonconserving corrections to the spin-spin coupling in molecules

John Blanchard, Dmitry Budker, Jonathan King, Tobias Sjolander, and Mikhail Kozlov

SNPCCM

Mainz 2018

J-coupling in molecules

- Tensor form of the direct dipole-dipole interaction:

$$I_1 T^{(2)} I_2$$

- Direct dipole-dipole interaction between nuclear magnetic moments is of the order of

$$\alpha^2 \left(\frac{m_e}{m_p}\right)^2 \frac{1}{R^3} \sim \text{MHz}$$

- Indirect nuclear spin-spin interaction (*J-coupling*):

$$I_1 J I_2; \qquad J = J^{(0)} + J^{(1)} + J^{(2)}$$

- Indirect nuclear spin-spin interaction is of the order of
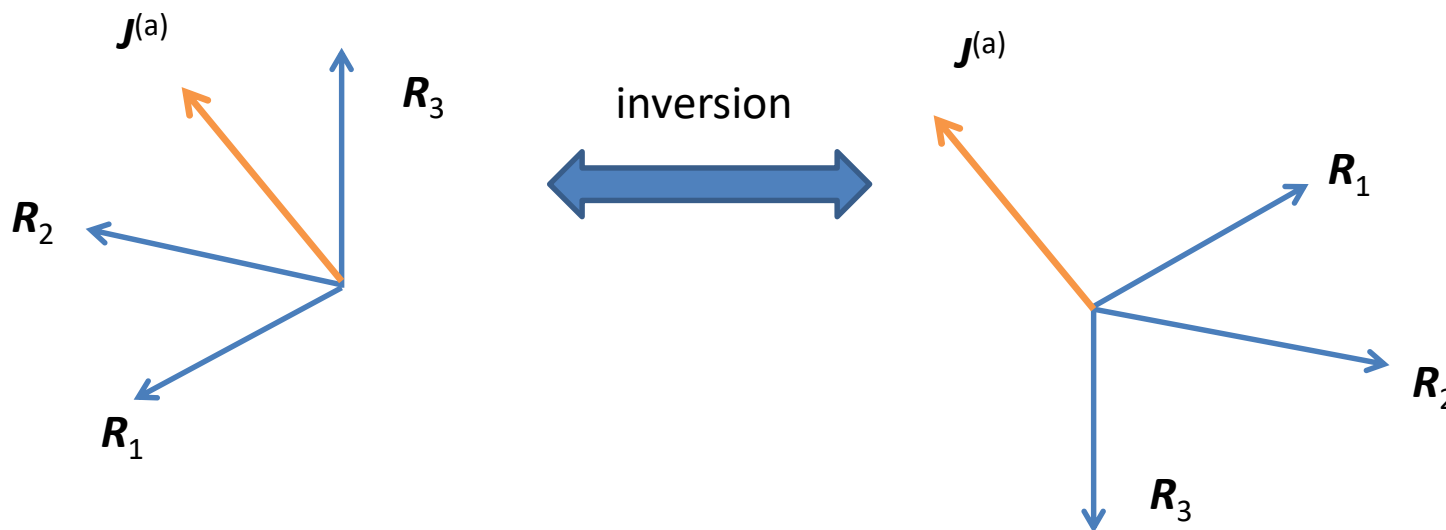
$$\alpha^4 \left(\frac{m_e}{m_p}\right)^2 Z_1 Z_2 < 100 \text{kHz}$$

- Only scalar J-coupling survives averaging over molecular rotation.

Vector coupling without P-odd interaction

$$I_1 J^{(1)} I_2 = I_1 \times I_2 \cdot J^{(a)}$$

If parity is conserved, then $J^{(a)}$ must be an axial vector. Non-degenerate electronic state is described only by polar vectors, such as nuclear radii R_i, therefore $J^{(a)} = 0$.
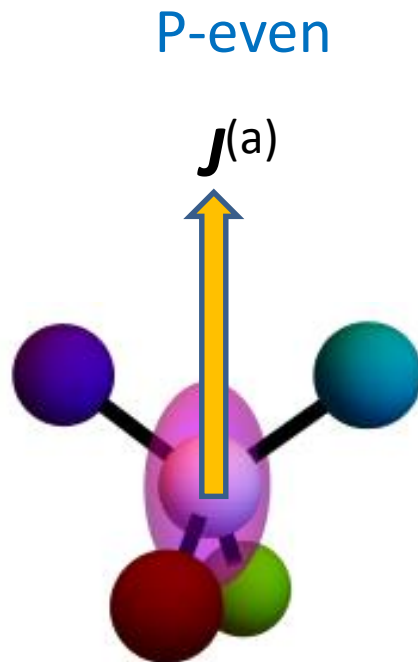

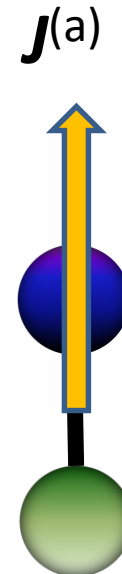*To have vector coupling $J^{(a)}$ we need chiral molecule with two degenerate states linked by inversion.*

Vector coupling with P-odd interaction

$$I_1 \times I_2 \cdot J^{(a)}$$

- If parity is not conserved, then $J^{(a)}$ can be a polar vector, which is fixed in molecular frame. In this case we can have vector coupling already in diatomic molecules, where $J^{(a)} \sim R_{12}$.

P-even

$J^{(a)}$

P-odd

$J^{(a)}$

Experiment to observe vector coupling

$$\boldsymbol{I}_1 \times \boldsymbol{I}_2 \cdot \boldsymbol{J}^{(a)}$$

- In the molecular stationary state expectation value is zero. We need to look at the correlation signal rather than frequency shift.

- Correlation $\boldsymbol{I}_1 \times \boldsymbol{I}_2 \cdot \boldsymbol{J}^{(a)}$ is similar to P-odd correlation $\boldsymbol{I}_1 \times \boldsymbol{S} \cdot \boldsymbol{n}$, which can be observed in diatomic radicals [Yale group: S Cahn, D DeMIlle *et al*].

- We can polarize molecule in electric field, then $\langle \boldsymbol{J}^{(a)} \rangle \sim \boldsymbol{E}$. We also need to decouple spins from each other.

Recent proposal of NMR experiment
[JP King, TF Sjolander, & JW Blanchard, *J.Phys.Chem.Lett.,* **2017***, 8*, 710]
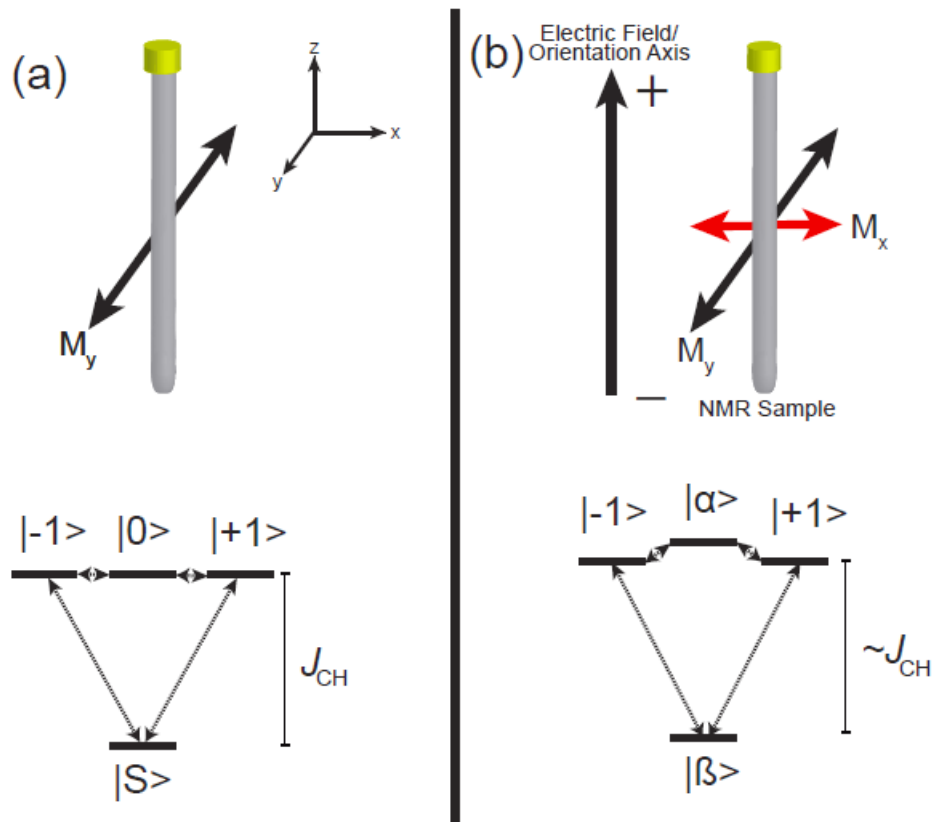
PV interaction in nonrelativistic approximation

Atomic units: $\hbar = m_e = |e| = 1$

Nuclear-spin-dependent PV interaction:

$$H_{\text{PV}}^{(2)} = \frac{G\alpha}{2\sqrt{2}} \sum_{i,K} g_K^{(2)} \boldsymbol{I}_K \left[\boldsymbol{p}_i, \delta(\boldsymbol{r}_i - \boldsymbol{R}_K) \right]_+$$

In the external magnetic field

$$\boldsymbol{p}_i \rightarrow \boldsymbol{\pi}_i = \boldsymbol{p}_i + \alpha \boldsymbol{A}$$

$$\boldsymbol{A}_L = \gamma_L \frac{\boldsymbol{I}_L \times (\boldsymbol{r} - \boldsymbol{R}_L)}{|\boldsymbol{r} - \boldsymbol{R}_L|^3}$$

PV interaction in the magnetic field of a nucleus

$$H_{\mathrm{PV}}^{(2)} = \frac{G\alpha}{2\sqrt{2}} \sum_{i,K} g_K^{(2)} \boldsymbol{I}_K \left[\boldsymbol{p}_i, \delta(\boldsymbol{r}_i - \boldsymbol{R}_K) \right]_+$$

$$+ \frac{G\alpha^2}{\sqrt{2}} \sum_{i,K,L} g_K^{(2)} \gamma_L \frac{\boldsymbol{I}_K \cdot \boldsymbol{I}_L \times (\boldsymbol{R}_K - \boldsymbol{R}_L)}{|\boldsymbol{R}_K - \boldsymbol{R}_L|^3} \delta(\boldsymbol{r}_i - \boldsymbol{R}_K)$$

Second term gives direct contribution to antisymmetric *J*-coupling!
[Barra & Robert, MP, 88, 875 (1996)]

PV contribution to *J*-coupling

$$\boldsymbol{J}^{(a)}(K,L) = \frac{G\alpha^2}{\sqrt{2}} \left(\gamma_K g_L^{(2)} \langle \Psi_e | \sum_i \delta(\boldsymbol{r}_i - \boldsymbol{R}_L) | \Psi_e \rangle \right.$$

$$\left. + g_K^{(2)} \gamma_L \langle \Psi_e | \sum_i \delta(\boldsymbol{r}_i - \boldsymbol{R}_K) | \Psi_e \rangle \right) \frac{\boldsymbol{R}_K - \boldsymbol{R}_L}{|\boldsymbol{R}_K - \boldsymbol{R}_L|^3}$$

Electronic ME does not include spin, or momentum.
Therefore, the main contribution comes from 1s shell.

$$\langle \Psi_e | \sum_i \delta(\boldsymbol{r}_i - \boldsymbol{R}_K) | \Psi_e \rangle = \rho_e(\boldsymbol{R}_K) \approx \frac{2}{\pi} Z_K^3$$

Estimate of PV contribution to *J*-coupling

Typical internuclear distance *R* is few a.u. Assuming *R*=4 and *Z*=80 we get:

$$J^{(a)} \sim \frac{G\alpha^3}{\sqrt{2}} \frac{m_e}{m_p} g^{(2)} \frac{1}{8\pi} Z^3$$

$$\frac{1}{g^{(2)}} J^{(a)} \sim 6.8 \times 10^{-20} \, \mathrm{a.u.} = 0.45 \, \mathrm{mHz}$$

Contribution of the first term of PV interaction to J-coupling

The second-order expression for the $J^{(a)}$ has the form:

$$J^{(a)} \sim \sum_n \frac{\langle 0 | H_{\mathrm{PV}}^{(2)} | n \rangle \langle n | H_{\mathrm{HF}} | 0 \rangle}{E_0 - E_n}$$

$$H_{\mathrm{PV}}^{(2)} \sim \frac{G\alpha Z^2}{2\sqrt{2}\pi} g^{(2)} \qquad H_{\mathrm{HF}} \sim \alpha^2 \frac{m_e}{m_p} Z$$

$$\boxed{J^{(a)}(K, L) \sim \frac{G\alpha^3 Z_K^2 Z_L}{2\sqrt{2}\pi} \frac{m_e}{m_p} g_K^{(2)}}$$

For $Z_L \ll Z_K$ this is smaller than first order term.

Relativistic operators

PV weak interaction has the form:

$$H_{\mathrm{PV}}^{(2)} = \frac{G}{\sqrt{2}} \sum_{i,K} g_K^{(2)} \boldsymbol{\alpha}_i \boldsymbol{I}_K \rho_K (\boldsymbol{r}_i - \boldsymbol{R}_K)$$

There is no dependence on the second spin here and we need to consider second-order expression with H_{HF}:

$$H_{\mathrm{HF}} = \sum_{i,K} \gamma_K \frac{\boldsymbol{I}_K \cdot \boldsymbol{\alpha}_i \times (\boldsymbol{r}_i - \boldsymbol{R}_K)}{(\boldsymbol{r}_i - \boldsymbol{R}_K)^3}$$

$$J^{(a)} \sim \sum_n \frac{\langle 0| H_{\mathrm{PV}}^{(2)} |n\rangle \langle n| H_{\mathrm{HF}} |0\rangle}{E_0 - E_n}$$

Relativistic expression for $J^{(a)}$

The sum over states includes positive and negative energy spectrum, $\sum_n = \sum_{n_e} + \sum_{n_p}$. In the second sum we can substitute energy denominator by $2mc^2$ and use closure:

$$\sum_{n_p} \frac{|n_p\rangle \langle n_p|}{E_0 - E_{n_p}} \approx \frac{\alpha^2}{2} \hat{I}$$

This gives us effective operator:

$$H_{\mathrm{PV}}^{\mathrm{eff}} = \frac{G\alpha^2}{\sqrt{2}} \sum_{i,K,L} g_K^{(2)} \gamma_L \frac{\boldsymbol{I}_K \cdot \boldsymbol{I}_L \times (\boldsymbol{R}_K - \boldsymbol{R}_L)}{|\boldsymbol{R}_K - \boldsymbol{R}_L|^3} \rho_K(\boldsymbol{r}_i - \boldsymbol{R}_K)$$

Relativistic correction

$$\rho_e(\boldsymbol{R}_K) \approx \frac{2}{\pi} Z_K^3 \ F_{\mathrm{rel}}$$

$$F_{\mathrm{rel}} = \frac{2(1+\gamma)(2ZR_{\mathrm{nuc}})^{2\gamma-2}}{\Gamma^2(2\gamma+1)}$$

$$\gamma = \sqrt{1-(\alpha Z)^2}$$

$$\boldsymbol{J}^{(a)}(K,L) = \frac{2G\alpha^2}{\sqrt{2}\pi} \frac{\boldsymbol{R}_{KL}}{R_{KL}^3}$$
$$\times \left(\gamma_K g_L^{(2)} Z_L^3 F_{\mathrm{rel},L} + g_K^{(2)} \gamma_L Z_K^3 F_{\mathrm{rel},K} \right)$$

Two examples

TlF

$Z=81,$
$R=2.08\text{Å}=3.9 \text{ a.u.}$
$\gamma_F=5.12\mu_N=2.0 \ 10^{-5}$
$F_{rel}=7.6$

$J^{(a)}/g^{(2)}{}_{Tl}=3.0 \ 10^{-18} \text{ a.u.}$
$= 20 \text{ mHz}$

HF

$Z=9,$
$R=0.92\text{Å}=1.7 \text{ a.u.}$
$\gamma_H=5.58\mu_N=2.2 \ 10^{-5}$
$F_{rel}=1.0$

$J^{(a)}/g^{(2)}{}_{H}=3.0 \ 10^{-21} \text{ a.u.}$
$= 20 \text{ μHz}$

Conclusions

- PV nuclear-spin-dependent interaction leads to antisymmetric vector coupling of nuclear spins in diamagnetic molecules.

- We can get analytical expression for this coupling. For heavy diatomic molecules it is of the order of 10 mHz.

- PV vector coupling can be observed in NMR experiment in the liquid phase in external electric field.

Thank you!