Parity nonconserving corrections to the spin-spin coupling in molecules

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J-coupling in molecules

- Tensor form of the direct dipole-dipole interaction:

$$\boldsymbol{I}_1\boldsymbol{T}^{(2)}\boldsymbol{I}_2$$

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

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

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

$$\boldsymbol{I}_1\boldsymbol{J}\boldsymbol{I}_2; \qquad \boldsymbol{J}=\boldsymbol{J}^{(0)}+\boldsymbol{J}^{(1)}+\boldsymbol{J}^{(2)}$$

- Indirect nuclear spin-spin interaction is of the order of

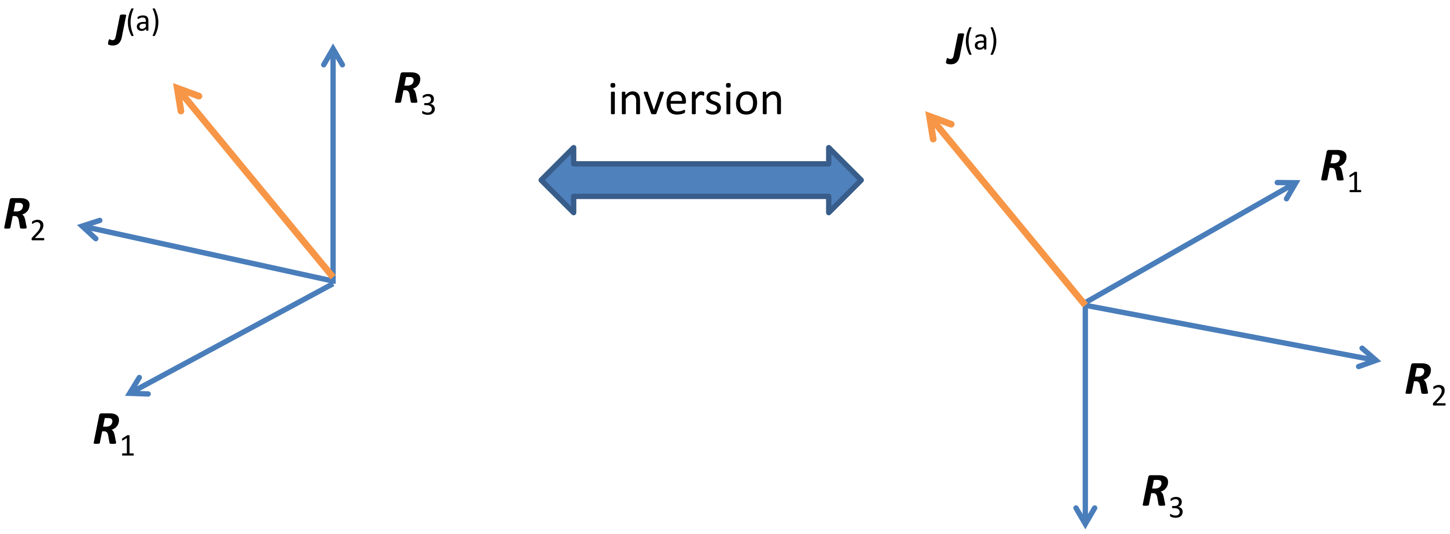
$$\alpha^4\left(\frac{m_e}{m_p}\right)^2 Z_1Z_2<100\mathrm{kHz}$$

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

Vector coupling without P-odd interaction

$$\boldsymbol{I}_1 J^{(1)} \boldsymbol{I}_2 = \boldsymbol{I}_1 \times \boldsymbol{I}_2 \cdot \boldsymbol{J}^{(a)}$$

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



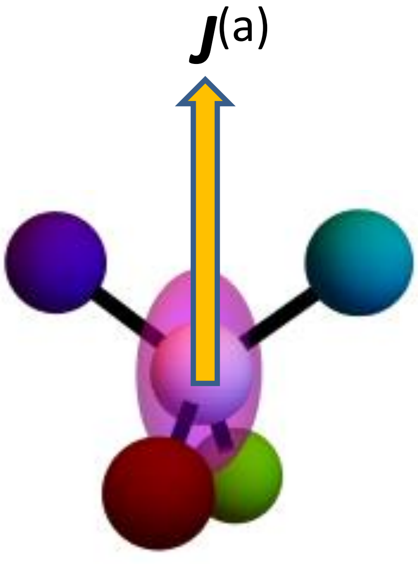
To have vector coupling $\boldsymbol{J}^{(a)}$ we need chiral molecule with two degenerate states linked by inversion.

Vector coupling with P-odd interaction

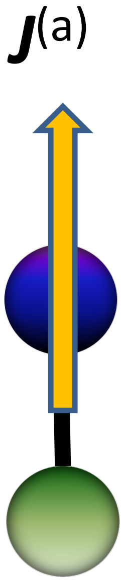
$$\boldsymbol{I}_1 \times \boldsymbol{I}_2 \cdot \boldsymbol{J}^{(a)}$$

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

P-even



P-odd



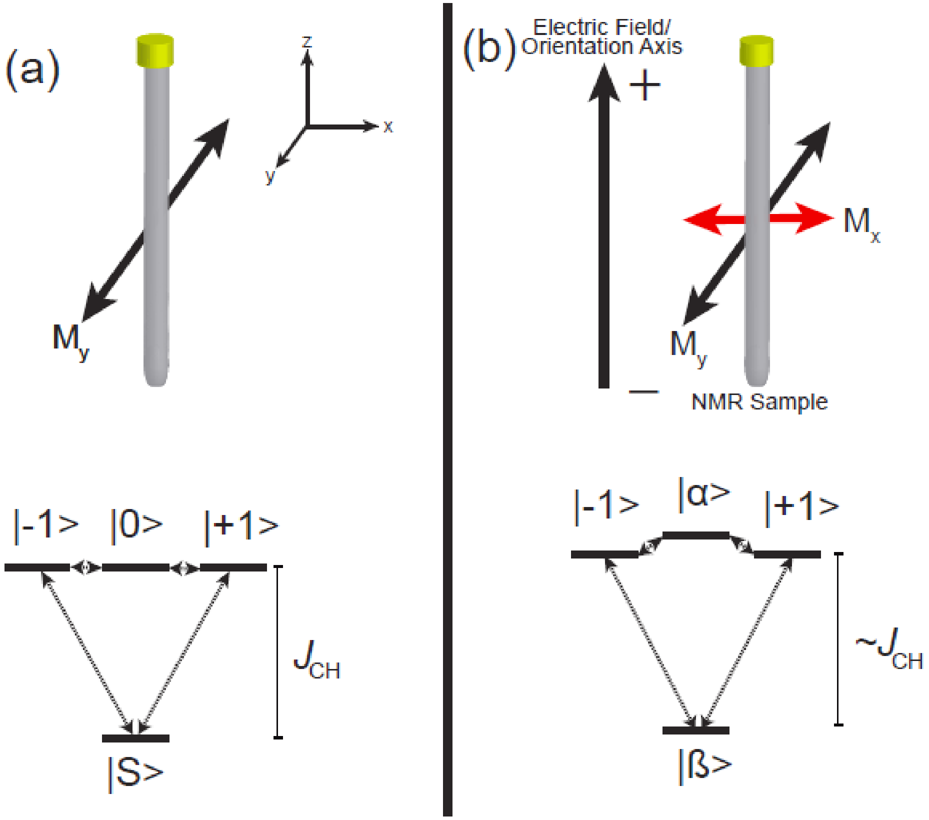
Experiment to observe vector coupling

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

- 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:

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

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

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

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

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 2*mc*^{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

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

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

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

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

Two examples

TlF

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

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

HF

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

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

Collaborators

- John Blanchard
- Dmitry Budker
- Jonathan King
- Tobias Sjolander

Thank you!