Tailoring Hyperfine Coupling through Ligand Tuning

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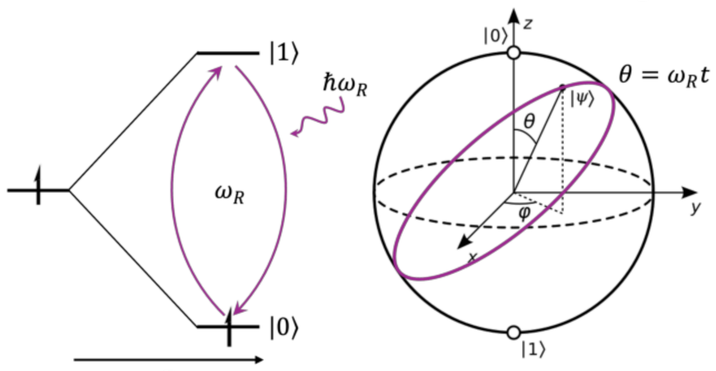
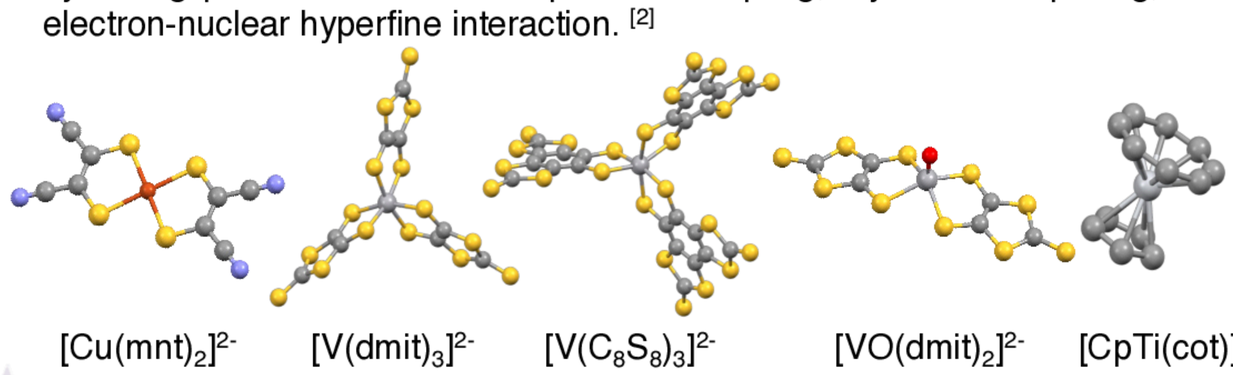
Molecular Quantum Sensors

Molecular quantum sensors exploit two-level electron spin states to detect external disturbances thanks to their strong sensitivity.[1]



Performance is dictated by **coherence time**, which can be further optimized by tuning parameters such as spin-orbit coupling, crystal field splitting, and electron-nuclear hyperfine interaction. [2]



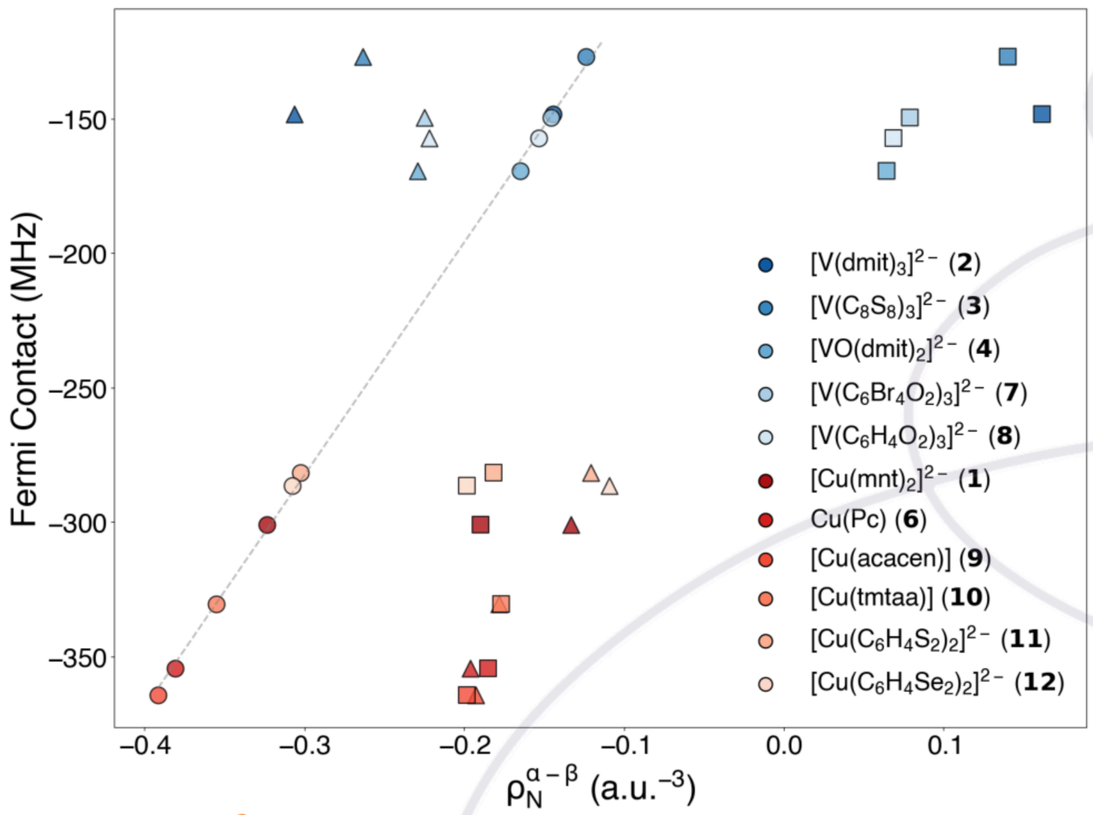
Electron-nuclear hyperfine interaction (HFC) has three major components: **Fermi Contact**, **Spin-Dipole Interaction** and **Spin-Orbit Coupling** which have been calculated at a DFT level including relativistic corrections using ZORA for the systems shown above.[3]

Hyperfine Coupling Analysis

$$A_{\mu\nu}^{(A)} = \left(\frac{4}{3}\pi\langle S_z\rangle^{-1}\right) P^A \rho_A^{\alpha-\beta}(R_A)\delta_{\mu\nu} + \frac{1}{2S}P_d \sum_i c_{Ai}^2 \langle d_i|f_{\mu\nu}|d_i\rangle + P_d \Delta g_{\mu\nu} - P_d \sum_i \sum_j \Delta_{ij}^{-1}(-1)^{\rho_{ij}} \zeta_{ij} c_{Mi}^2 c_{Mj}^2 \cdot \sum_{\kappa,\tau=x,y,z} i\varepsilon_{\kappa\tau\mu}\langle d_j|f_{\kappa\nu}|d_i\rangle\langle d_i|l_\tau^M|d_j\rangle$$

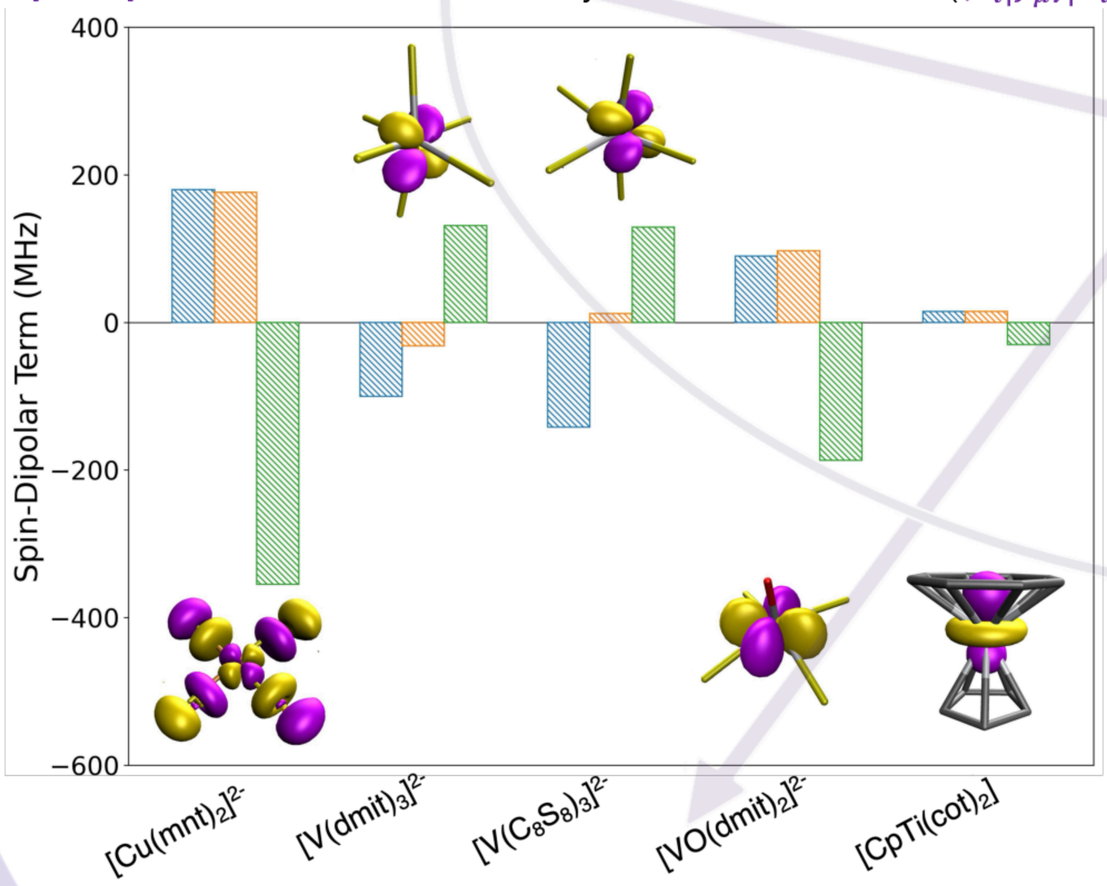
Fermi contact is an **isotropic** term composed by:

▲ Inner-shell contributions ■ Valence-shell contributions



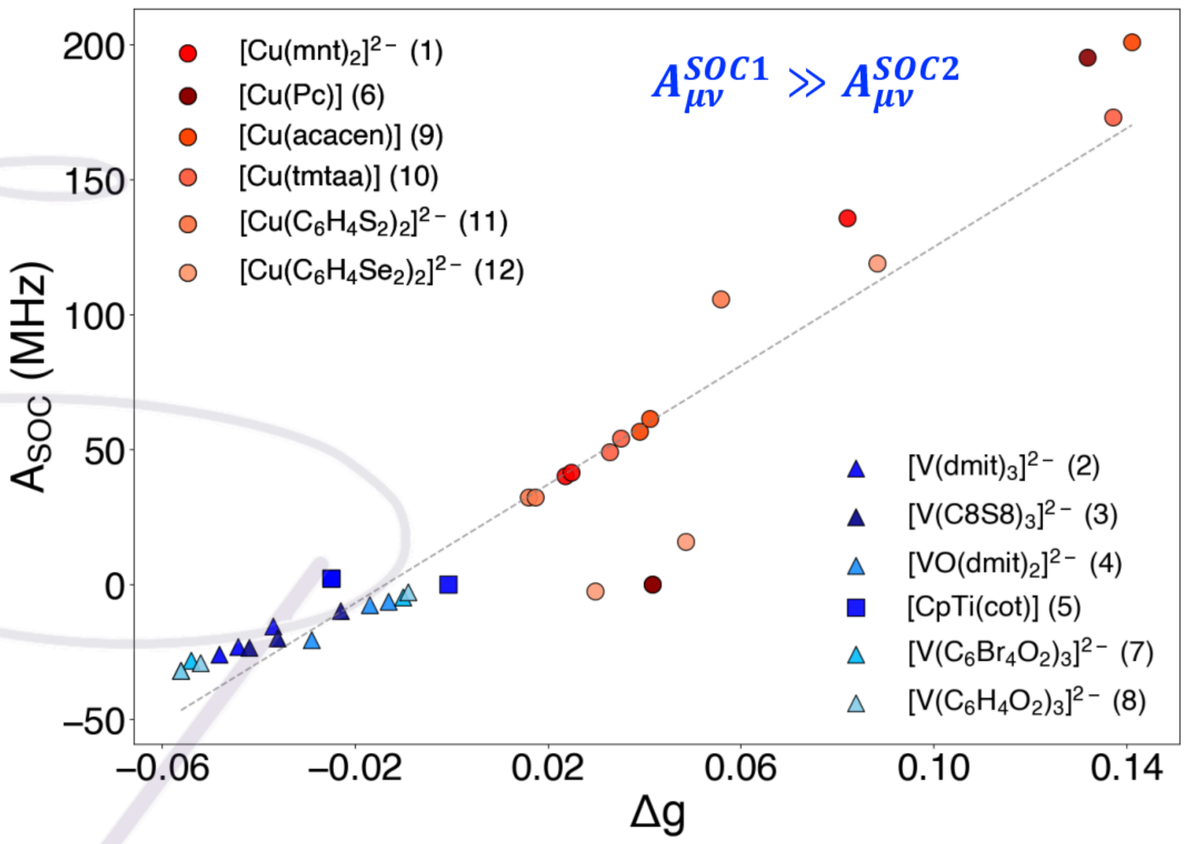
Spin density $\rho_A^{\alpha-\beta}$ is affected by **covalence** lowering inner-shell contributions in d⁹ metal centres while competing contributions were observed in d¹ metal centers.

Spin-dipolar interaction is defined by the **SOMO character** ($\langle d_i|f_{\mu\nu}|d_i\rangle$).[4]



Jahn-Teller distortions disrupts **axial relationship** generating rhombicity due to orbital mixing.

Spin-orbit coupling can be dictated by g-factor shift ($\Delta g_{\mu\nu}$) ≫ excited states energy gap(Δ_{ij}^{-1})



$$\Delta g_1 \approx \Delta g_2 \neq \Delta g_3 \Longrightarrow A_1^{SOC} \approx A_2^{SOC} \neq A_3^{SOC}$$
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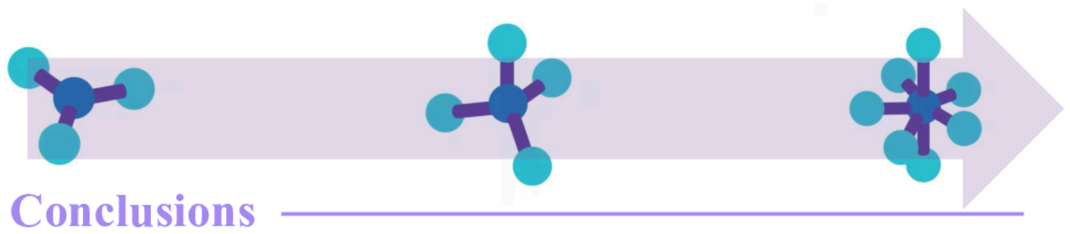
Coordination Environment Manipulation

	A_{FC}	A_{SD}			A_{SOC}			MHz
	A_{iso}	A_1	A_2	A_3	A_1	A_2	A_3	
Trigonal Planar	-357	106	93	-200	-10	-83	-60	
Vacant Tetrahedra	-225	96	110	-206	-10	-28	-70	
Square Planar	-312	111	111	-223	47	47	-11	
Tetrahedra	-90	-104	-104	209	-24	-24	-3	
Seesaw	-174	108	101	-209	-32	-34	-24	
Trigonal Bypiramid	-89	106	105	-210	-17	-76	-24	
Square Based Pyramid	-109	104	104	-208	-24	-24	-19	
Octahedra	-114	109	107	-216	-78	-82	-20	
Trigonal Prism	-74	-112	-113	225	-20	-20	-3	
Pentagonal Bypiramid	-126	116	86	-201	-8	-76	-24	
Capped Ocathedra	-128	107	101	-208	-10	-24	-40	



Conclusions

The **isotropic term** can be controlled by adjusting metal-ligand bond covalency, affecting s-shell contributions through **spin delocalization and polarization** mechanisms.

The **spin-dipolar term** responds to **SOMO character** and symmetry breaking modifications, such as **Jahn-Teller distortions**.

SOC contribution correlates with **Δg**; anisotropic molecules yield greater HFC shifts with rhombic character.

References

[1]. N. Aslam, H. Zhou, E. K. Urbach, M. J. Turner, R. L. Walsworth, M. D. Lukin, H. Park, *Nat. Rev. Phys.,* 2023, **5**, 157–169

[2] C. J. Yu, S. von Kugelgen, D. W. Laorenza and D. E. Freedman, *ACS Cent. Sci.*, 2021, **7**, 5, 712–723

[3] J. Cardona, A. Solè, P. Mella, D. Aravena, J. Ruiz-Hidalgo, S. Gómez-Coca and E. Ruiz*Chem. Sci.*, 2025,16, 11291-11303

[4] F. Neese and E. I. Solomon, Magnetism: Molecules to Materials IV, WIley-VCH., 2002, pp. 345-466

Acknowledgments

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