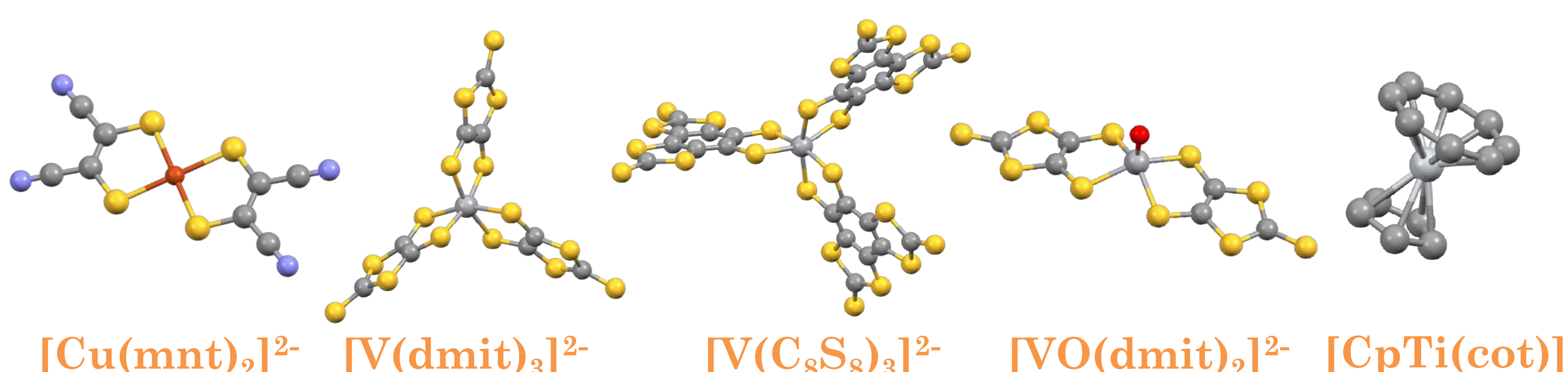


Molecular Qubits

Qubits are the quantum unit of their classical counterpart, the bit. Unlike the latter, the qubit is characteristic for being a two-state system, like the spin of an electron, where not only two outputs can be obtained, but also a quantum superposition state, known as **coherence**. This property is key to the performance of molecular qubits.



Coherence

Spin – Lattice (T₁)

Loss of coherence through the vibrations of the environment.

Spin – Spin (T₂)

Interactions that lead to 'dephasing' between spins.

Hyperfine Coupling

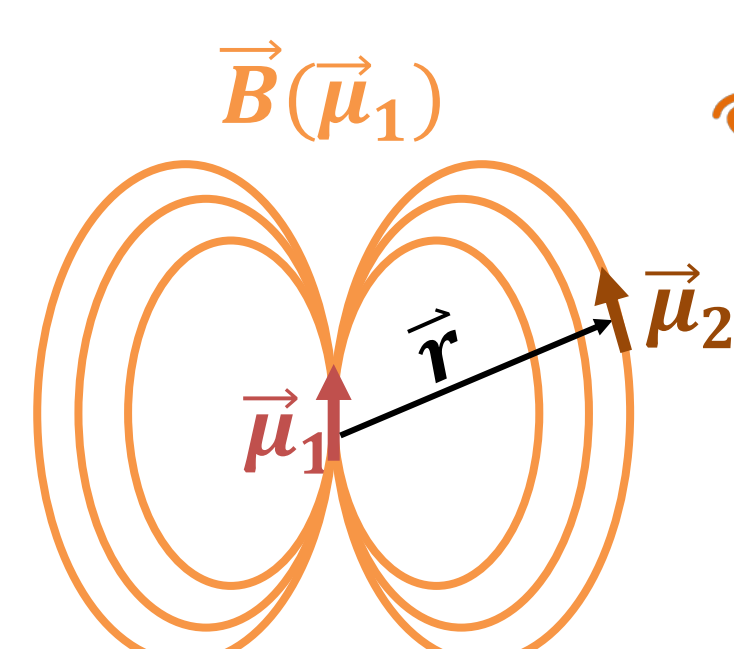
Hyperfine coupling plays an important role in spin-spin relaxation as it describes interactions between the electronic and nuclear spins of the same atom.

(I) Nuclear Spin

$$H_{HFC} = I \cdot A \cdot S \quad (A) \text{ Hyperfine Coupling Tensor}$$

(S) Electron Spin

This phenomenon has three major components: **Fermi Contact**, **Spin-Dipole Interaction** and **Spin-Orbit Coupling**.^[1]

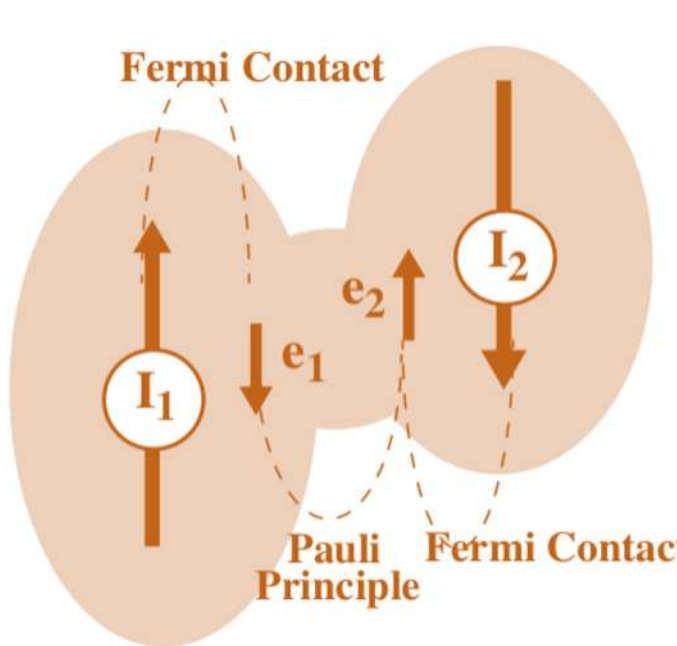


Spin-Dipole Interaction

$$A_{\mu\nu}^{dip}(N) = P_N \sum_{kl} \rho_{kl} \langle \phi_k | r_N^{-5} (3\vec{r}_{N\mu} \vec{r}_{N\nu} - \delta_{\mu\nu} r_N^2) | \phi_l \rangle \quad (1)$$

Set of basis functions (ϕ_i)

Spin density matrix (ρ_{kl})



Fermi Contact

$$A_{iso}(N) = \left(\frac{4}{3}\pi\langle S_z \rangle^{-1}\right) g_e g_N \beta_e \beta_N \rho(\vec{R}_N) \quad (2)$$

Spin density at the nucleus ($\rho(\vec{R}_N)$)

Expectation value of the z-component total spin ($\langle S_z \rangle$)

Spin-Orbit Coupling

$$A_{\mu\nu}^{SOC2} = -P^A \left\{ \sum_i \Delta_{I_i}^{-1} \sum_{\kappa, \tau \neq x, y, z} \varepsilon_{\kappa\tau\mu} F_{\kappa\nu}^{io} L_{1\tau}^{io} - \sum_a \Delta_{II_a}^{-1} \sum_{\kappa, \tau \neq x, y, z} \varepsilon_{\kappa\tau\mu} F_{\kappa\nu}^{ao} L_{1\tau}^{ao} \right\} \quad (3)$$

One-center reduced field gradient integrals ($F_{\kappa\nu}^{xo}$)

One-center angular momentum integrals ($L_{1\tau}^{xo}$)

Computational Details

- Turbomole 7.7 & ORCA 5.0.4 packages were employed.
- B3LYP, PBE0, PBE-40HF and ω B97X functionals were tested upon alongside x2c-TZVPall, x2c-TZVPPall, x2c-QZVPPall, x2c-QZVPPall-s, def2-QZVPP, UGBS, ANO-DK3 and IGLO-III basis set.
- Relativistic approximations (X2C & ZORA) were used.

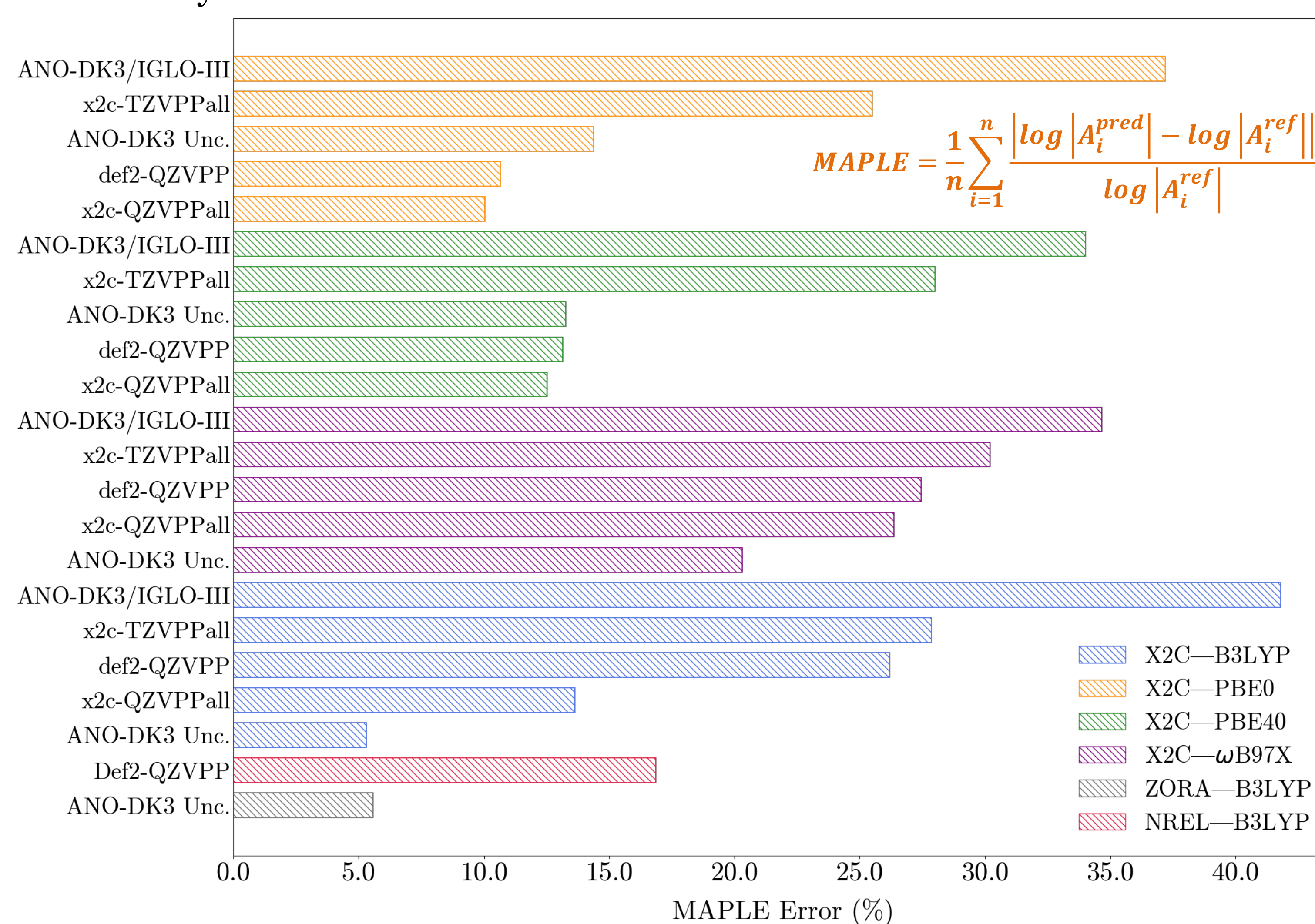
Project TED2021-129593B-I00 funded by:



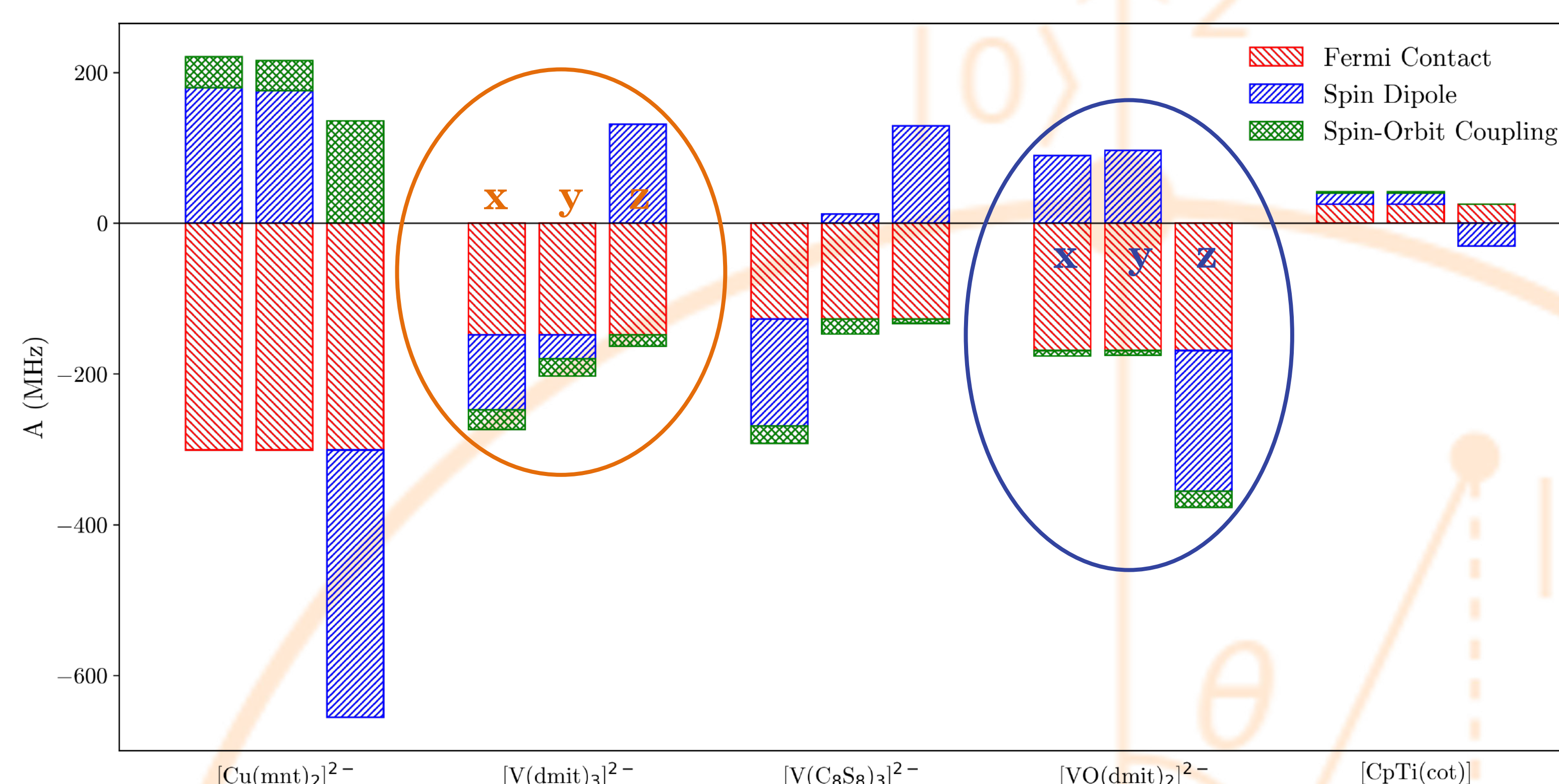
Project TED2021-129593B-I00 funded by MICIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR

Benchmark

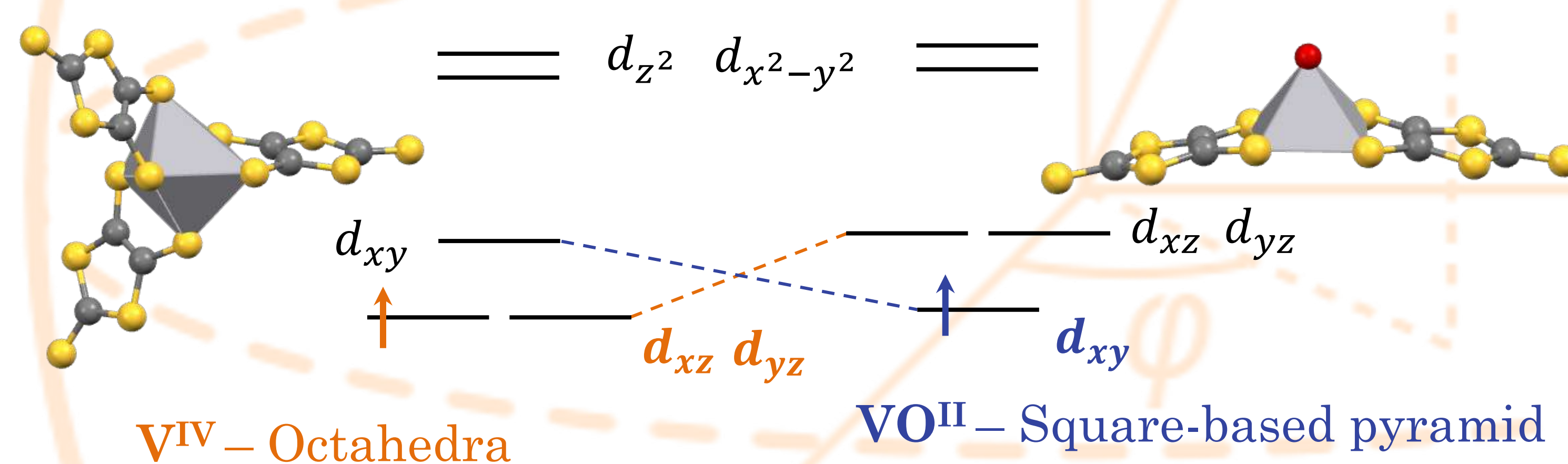
Hybrid functionals **B3LYP**, **PBE0**, **PBE40** yielded better constants when compared to long range hybrid ω B97X functional. **Relativistic basis** significantly improves hyperfine coupling prediction. Providing a **higher ζ** or an **uncontracted basis** has also enhanced prediction accuracy.



Term Decomposition



The main contribution to significant variations in hyperfine coupling can be attributed to the shifting of **spin dipole** (Eq. 1) values. These disparities stem from the **distinct geometries of the complexes**.



These geometrical differences influence the spatial distribution of the unpaired electron, reflected in the occupation of different **singly occupied molecular orbital (SOMO)**.

Conclusions

- Benchmark studies indicate that **B3LYP** hybrid functional performs best, in specific when paired with **uncontracted ANO-DK3** basis set.
- Term decomposition analysis demonstrates that the **localization of unpaired electrons in different orbitals** significantly impacts **spin-dipole interactions**, leading to distinct trends in VOII and VIV, respectively.