

Ab Initio treatment of molecular magnets using AFQMC

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Abstract

Molecular magnets have seen significant attention due to their potential applications in quantum information / quantum computing. A delicate balance of electron correlation, spin-orbit coupling (SOC), ligand field splitting, and other effects produces a persistent magnetic moment within each molecular magnet unit. The competition among these effects poses a challenge for theoretical treatments. Electron correlation effects play a central role since d-, or f-element ions provide the magnetic states in molecular magnets requiring explicit many-body treatments in general. In addition, the explicit inclusion of SOC expands the dimensionality of the Hilbert space that must be treated. Furthermore, molecular magnets are large systems involving tens of atoms in even the smallest systems. Auxiliary-field quantum Monte Carlo (AFQMC) has demonstrated a high degree of reliability in correlated-electron systems with computational cost that scales as a low order polynomial making applications to large systems feasible. Recent advances in AFQMC technology allow an *ab initio* treatment in molecular magnets where electron correlation, SOC, and material specificity are included accurately and on an equal footing. We demonstrate the approach by applying AFQMC to compute the zero-field splitting (ZFS) of a linear Co(II) complex.

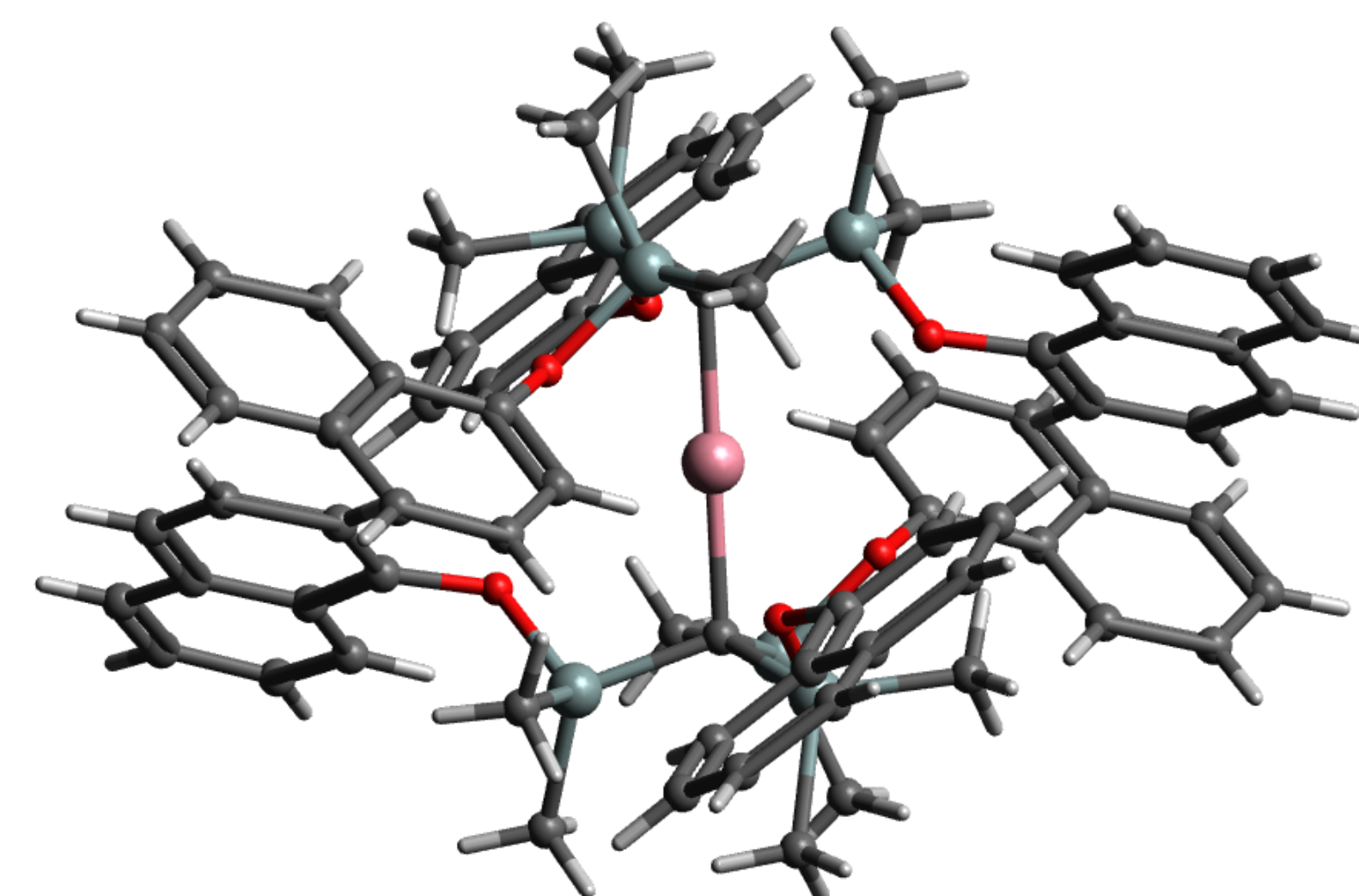
Co(C(SiMe₂ONaph)₃)₂

Previously experimentally realized / characterized [1]

- Near the theoretical limit of magnetic anisotropy
- magnetic hysteresis at low temperatures (up to 5 K)
- Record holder for magnetic reversal energy barrier (i.e. ZFS) – **L=3, S=3/2**

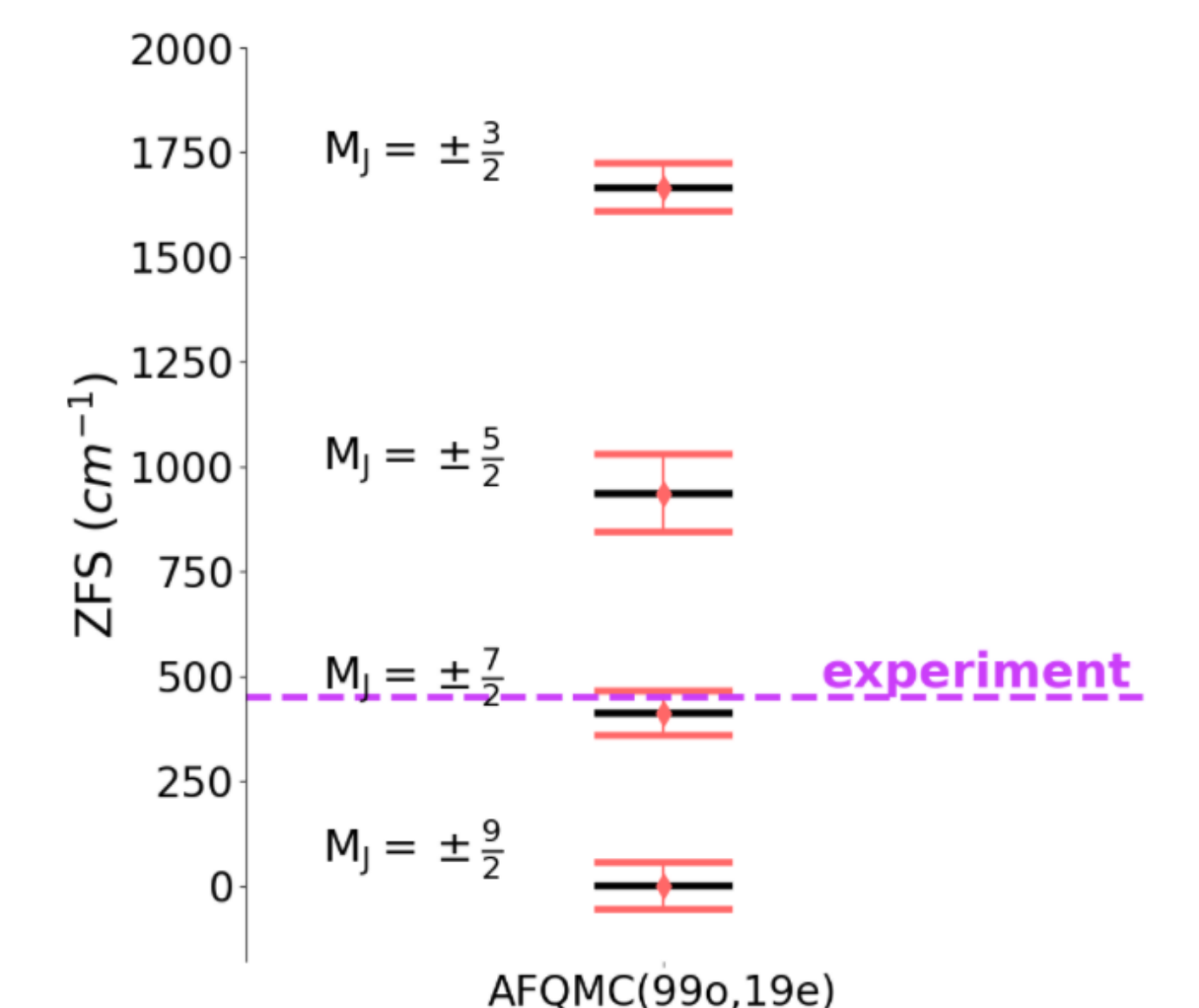
We computed the ZFS using AFQMC
(treatment details below)

Realistic Application: Linear Co(II) Complex



Methodology applicable to other
molecular magnets

AFQMC Zero-Field Splitting (ZFS)



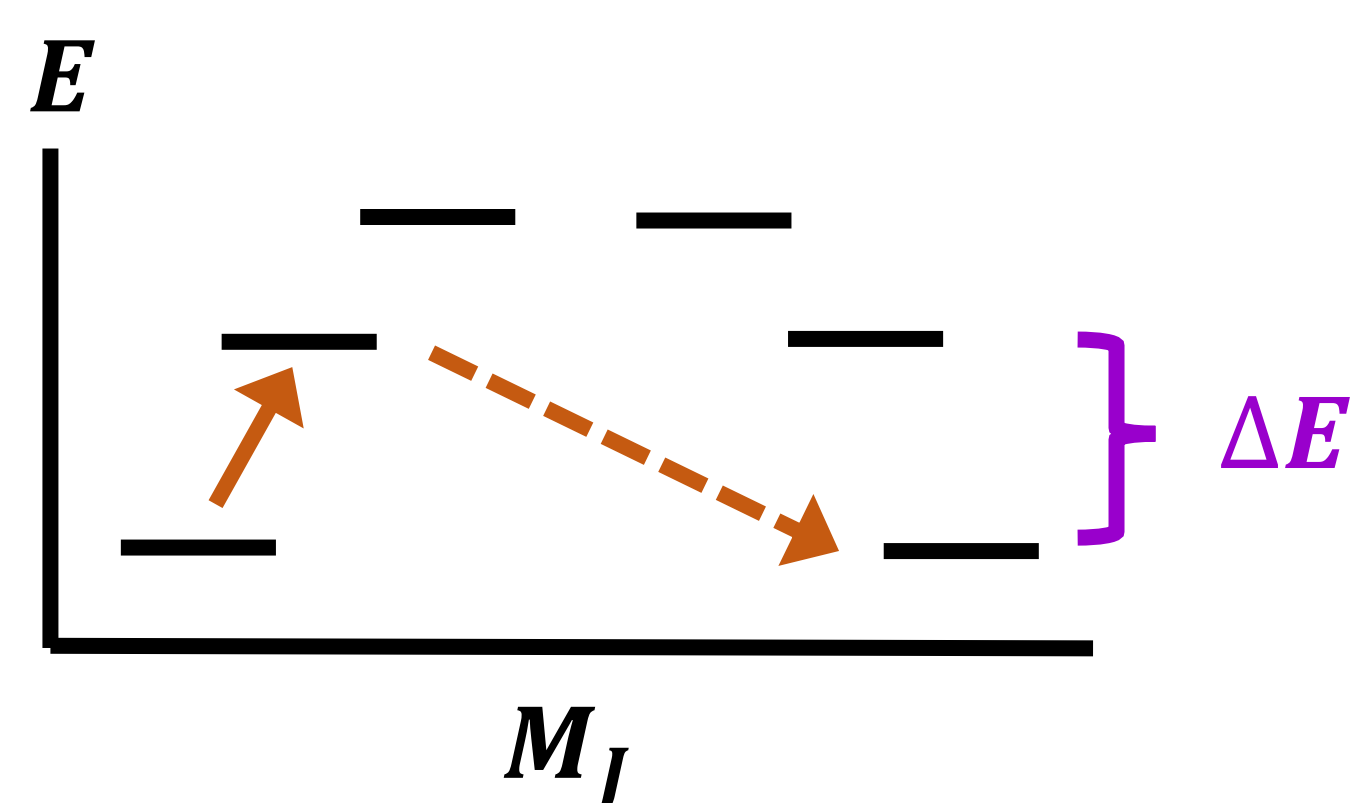
Computational details: Co : CRENBL ECP and basis, all other atoms cc-pVDZ basis; Frozen embedding density from ROKS DFT (PBE0); AFQMC trial wavefunction SHCI(70,11e) including SOC. SHCI calculations performed using the Dice code [7].

Molecular Magnetism

- Have a **persistent magnetic moment** within each molecular unit
- Many possible applications including:

- Quantum computing
- High-density classical memory devices
- Artificial magnetic materials
- More!

- For example, Grover's algorithm has been implemented on a single TbPc₂ molecule [2]



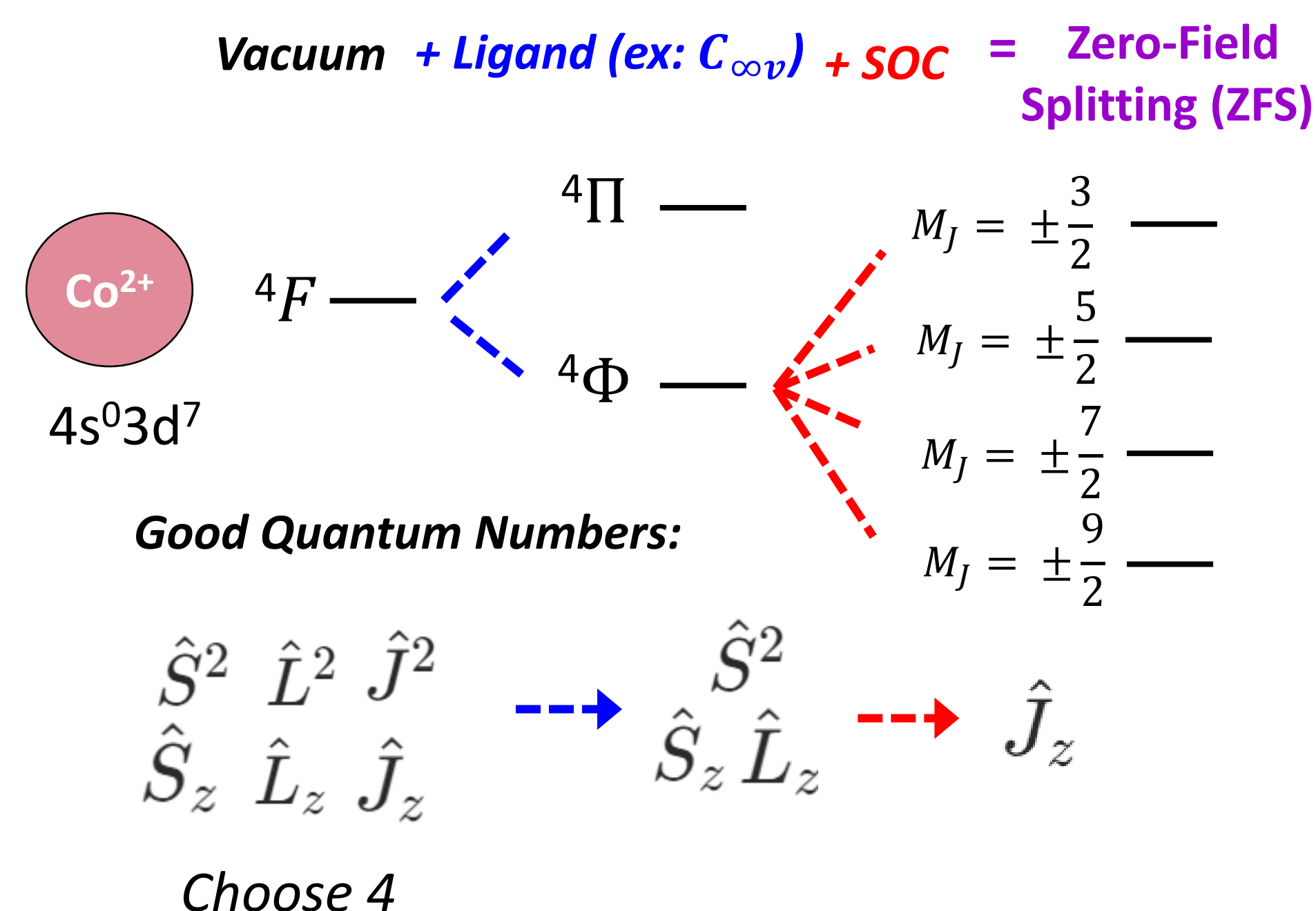
- Magnetic reversal is blocked via **electronic energy barrier**
- Several **relaxation pathways** exist
 - Electron-phonon processes
 - **Direct thermal excitation**
 - Others
- Large Gap / **Zero-Field Splitting (ZFS)** is one key predictor of molecular magnet behavior

- magnetic moments are supplied by d-, or f-element ion(s) - **explicit many-body methods required in general**
- Molecular magnets typically consist of at least 80 atoms – **very large many-body problem**

Details of Zero-Field Splitting (ZFS)

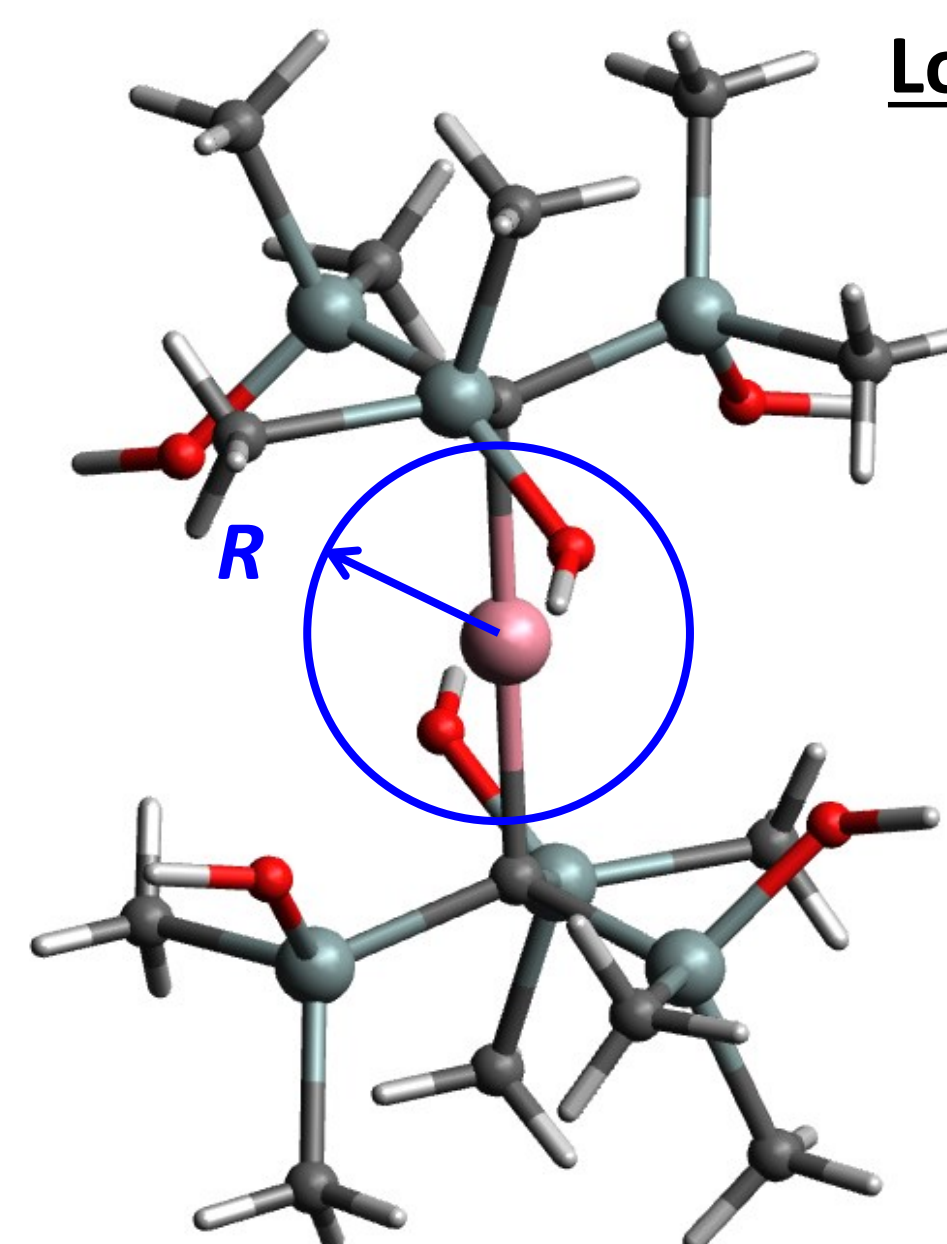
Consider an open shell ion in **vacuum** (ex: Co 2+ ion)

- **Electron Correlation** determines the ground state LS term
- Adding a **ligand field**, spherical symmetry is broken
- Next, considering **SOC**, spin-symmetry is broken as well



AFQMC / Many-Body Treatment

Local Embedding (Correlation + Ligand Field)



- Molecular magnets are **large**
- Use local embedding to focus computational effort on magnetic ions [3]
- Yields accurate relative energies, systematically improvable based on simple localization Radius, **R**
- **Orbitals** are included in active space based on local criteria
- **"Inactive space"** left at DFT level

$$\Psi \approx \mathcal{A}(\Psi_I \Psi_A) \quad E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_A | \hat{H}_A | \Psi_A \rangle$$

$$\hat{H}_A = \sum_{\mu\nu \in \Delta} K_{\mu\nu} \hat{c}_\mu^\dagger \hat{c}_\nu + \sum_{\mu\nu\gamma\delta \in \Delta} V_{\mu\nu\gamma\delta} \hat{c}_\mu^\dagger \hat{c}_\nu^\dagger \hat{c}_\gamma \hat{c}_\delta + \sum_{\mu\nu \in \Delta} V_{\mu\nu}^{\text{I-A}} \hat{c}_\mu^\dagger \hat{c}_\nu + E_{\text{I}} + \sum_{\mu\nu \in \Delta} K_{\mu\nu}^{\text{SOC}} \hat{c}_\mu^\dagger \hat{c}_\nu$$

Electron Correlation + Ligand Field + SOC

Active space Hamiltonian with explicit SOC treated using AFQMC

Explicit Spin-Orbit Coupling (SOC)

- explicit, two-component SOC was recently incorporated in AFQMC [4]

$$\hat{K}^{\text{SOC}} = \hat{W}_z^{\text{SOC}} \hat{S}_z + \hat{W}_+^{\text{SOC}} \hat{S}_+ + \hat{W}_-^{\text{SOC}} \hat{S}_-$$

$$[W_\lambda^{\text{SOC}}]_{ij} = \int d\vec{r} \phi_i^*(\vec{r}) \sum_A W_{A,\lambda}^{\text{SOC}} \phi_j(\vec{r}),$$

- 1-body SOC integrals can be expressed in a **spatial orbital basis** – can be added either before or after embedding transformation

AFQMC Method

Orbitally-based many-body method which uses the 2nd Quantization Hamiltonian – recent review for more detail [5]

$$\hat{H} = \hat{K} + \hat{V} = \sum_{\mu\nu} K_{\mu\nu} \hat{c}_\mu^\dagger \hat{c}_\nu + \sum_{\mu\nu\gamma\delta} V_{\mu\nu\gamma\delta} \hat{c}_\mu^\dagger \hat{c}_\nu^\dagger \hat{c}_\gamma \hat{c}_\delta$$

Many-Body states (**ground state, and excited states**) computed via projection

$$\lim_{\beta \rightarrow \infty} e^{-\beta \hat{H}} |\Psi_I\rangle = e^{-\tau \hat{H}} e^{-\tau \hat{H}} \dots e^{-\tau \hat{H}} |\Psi_I\rangle \rightarrow |\Psi_n\rangle$$

Use Trotter-Suzuki decomposition + Hubbard Stratonovich transformation

$$\hat{V} = \sum_\gamma \hat{v}_\gamma^2 \quad e^{-\tau \hat{H}} \approx \int d\sigma P(\sigma) B(\sigma), \quad \text{where } B(\sigma) = e^{-\tau \hat{K}/2} e^{\sqrt{\tau} \sigma \cdot \hat{v}} e^{-\tau \hat{K}/2}$$

Physical observables computed via stochastic sampling: $\sim O(N^3 - N^4)$

$$E_n = \frac{\langle \Psi_T | \hat{H} | \Psi_n \rangle}{\langle \Psi_T | \Psi_n \rangle} = \lim_{\beta \rightarrow \infty} \frac{\langle \Psi_T | \hat{H} e^{-\beta \hat{H}} | \Psi_I \rangle}{\langle \Psi_T | e^{-\beta \hat{H}} | \Psi_I \rangle}$$

Fermionic sign problem is controlled via importance sampling, and the phaseless approximation [6]

References

1. P. C. Bunting et al., *Science* **362**, eaat7319 (2018). DOI: 10.1126/science.aat7319
2. C. Godfrin, A. Ferhat, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, and F. Balestro *Phys. Rev. Lett.* **119**, 187702 (2017)
3. B. Eskridge, H. Krakauer, S. Zhang. *J. Chem. Theory Comput.* **15**, 7, 3949–3959 (2019)
4. B. Eskridge, H. Krakauer, H. Shi, S. Zhang. *J. Chem. Phys.* **156**, 014107 (2022)
5. M. Motta, S. Zhang, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **8**, e1364 (2018).
6. S. Zhang and H. Krakauer, *Phys. Rev. Lett.* **90**, 136401 (2003).
7. S. Sharma, et al, *J. Chem. Theory Comput.* **13**, 4, 1595–1604 (2017)

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