Exploiting Multiple Symmetry-Broken SCF Solutions to Describe Ground and Excited States of Transition-Metal Complexes

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Low-Lying UHF Solutions and NOCI Wavefunctions of Model Octahedral $[VF_6]^{3-}$

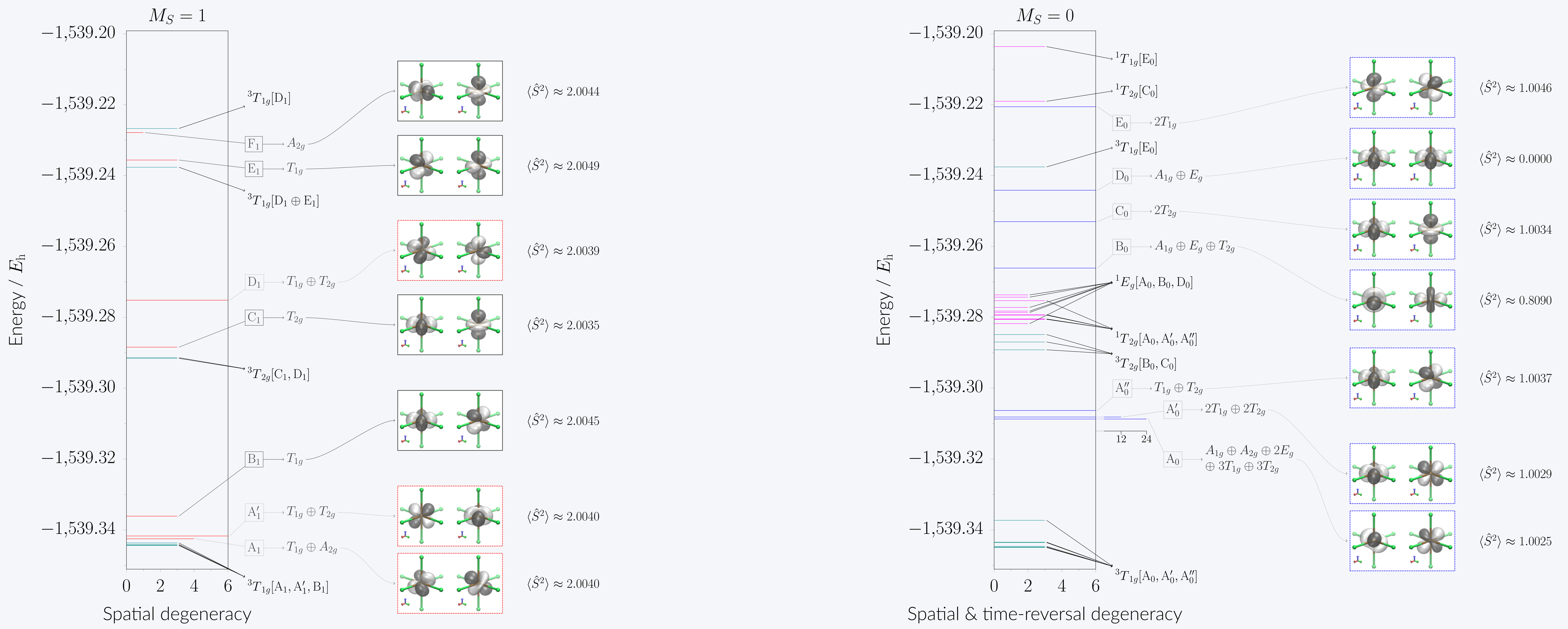
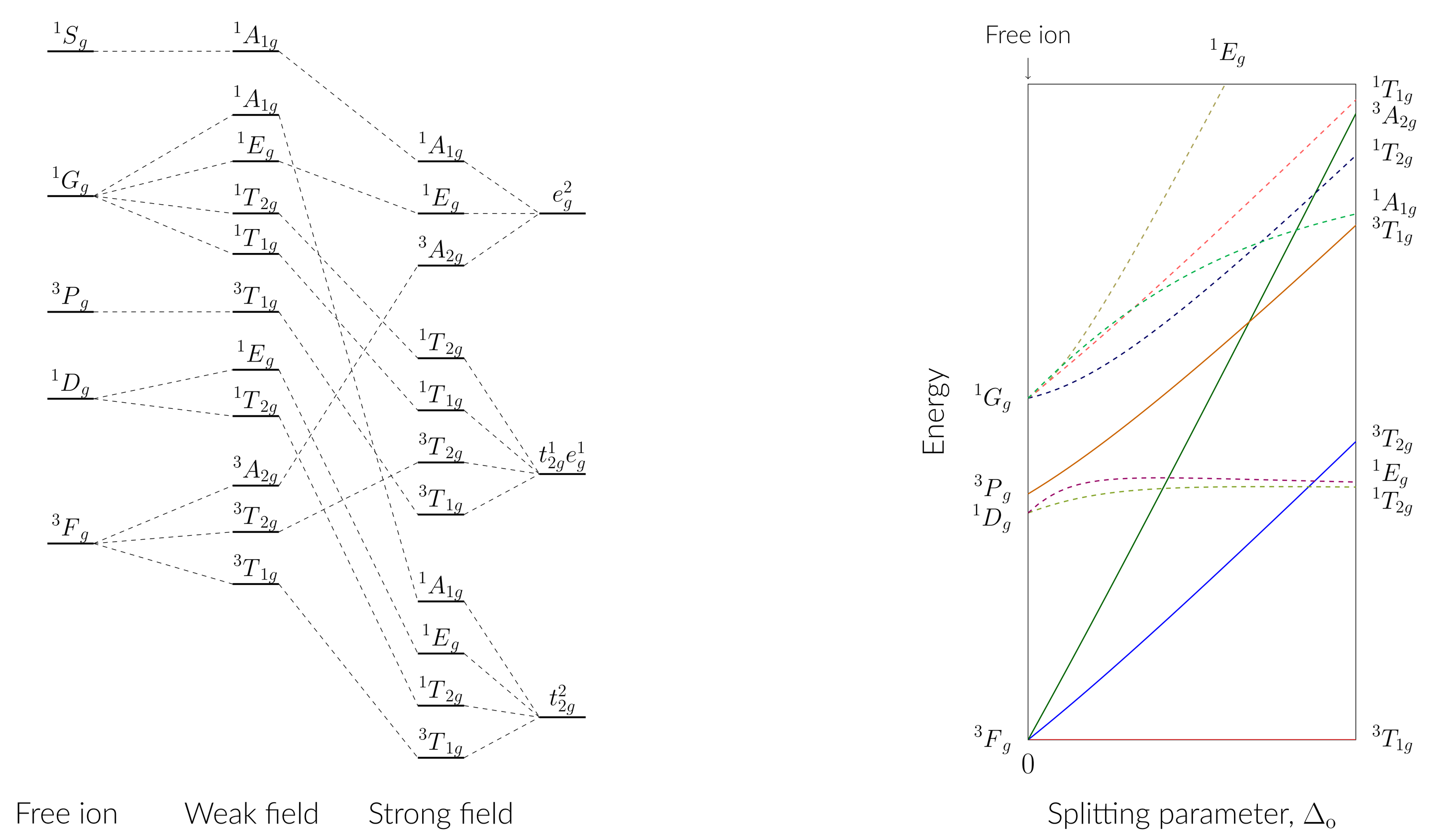


Figure 1. Energy and symmetry of low-lying UHF solutions and NOCI wavefunctions constructed from them in octahedral $[VF_6]^{3-}$.
$\boxed{S_{M_S}}$: symmetry-conserved UHF set S with $\hat{S}_z$ eigenvalue M_S. S_{M_S}: spatial or spin symmetry-broken UHF set S with $\hat{S}_z$ eigenvalue M_S.
$\Gamma[A \oplus B \oplus C]$: a specific NOCI set of symmetry Γ constructed from all of A, B, and C. $\Gamma[A, B, C]$: multiple NOCI sets of symmetry Γ constructed from all non-trivial combinations of A, B, and C.

Introduction

Transition-metal complexes are strongly correlated as they have many low-energy electronic states that exhibit high degrees of degeneracy. Figure 2 gives such states for octahedral d^2 as an example.



(a) Correlation diagram (not to scale) (b) Tanabe–Sugano diagram

Figure 2. All electronic terms of a true d^2 system in an octahedral field.

The non-linear HF equations for these complexes therefore admit multiple low-lying solutions that are degenerate or nearly degenerate.

We have located these solutions using SCF metadynamics and investigated their symmetry properties in a model octahedral d^2 system, $[VF_6]^{3-}$ (Figure 1).

Symmetry Breaking in HF

Degenerate eigenfunctions of the spinless Hamiltonian *must* transform as a single irreducible representation (irrep) of the underlying point group $\mathcal{B}$, the spin rotation group SU(2), or the time reversal group $\mathcal{T}$.

HF wavefunctions do not have to obey this due to their approximate nature. Thus, consider a set of degenerate HF solutions $S = \{{}^w\Psi \mid w = 1, 2, \ldots\}$ and a particular group $\mathcal{G}$:

- if S spans a single irrep in $\mathcal{G}$, then S is symmetry-conserved in $\mathcal{G}$;
- if S spans multiple irreps in $\mathcal{G}$, then S is symmetry-broken in $\mathcal{G}$.

HF solutions break symmetry to become lower in energy and possibly recover some electron correlation. Restoring symmetry of symmetry-broken HF solutions allows us to form physically meaningful wavefunctions while incorporating said correlation.

Restoring Symmetry: Non-Orthogonal CI (NOCI)

For a complete symmetry-broken set $S = \{{}^w\Psi \mid w = 1, 2, \ldots\}$, solving the generalised eigenvalue equation

$$\boldsymbol{HA} = \boldsymbol{SAE} \quad \text{where} \quad (\boldsymbol{H})_{wx} = \langle {}^w\Psi | \hat{\mathscr{H}} | {}^x\Psi \rangle \text{ and } (\boldsymbol{S})_{wx} = \langle {}^w\Psi | {}^x\Psi \rangle$$

gives coefficients A_{wm} such that the NOCI wavefunctions

$${}^m\Phi = \sum_w {}^w\Psi A_{wm}$$

conserve symmetry and can be used to approximate corresponding electronic terms.

UHF vs. NOCI: Jahn–Teller Distortion

Consider the $T_{1g} \otimes e_g$ Jahn–Teller distortion in octaheral $[VF_6]^{3-}$. Figure 3 shows that:

- the UHF A_1 and A_1' solutions fail to exhibit the expected energy minima;
- the ${}^3T_{1g}[A_1 \oplus A_1']$ NOCI wavefunctions do show the expected stabilisation and give the correct degeneracy splitting upon symmetry descent.

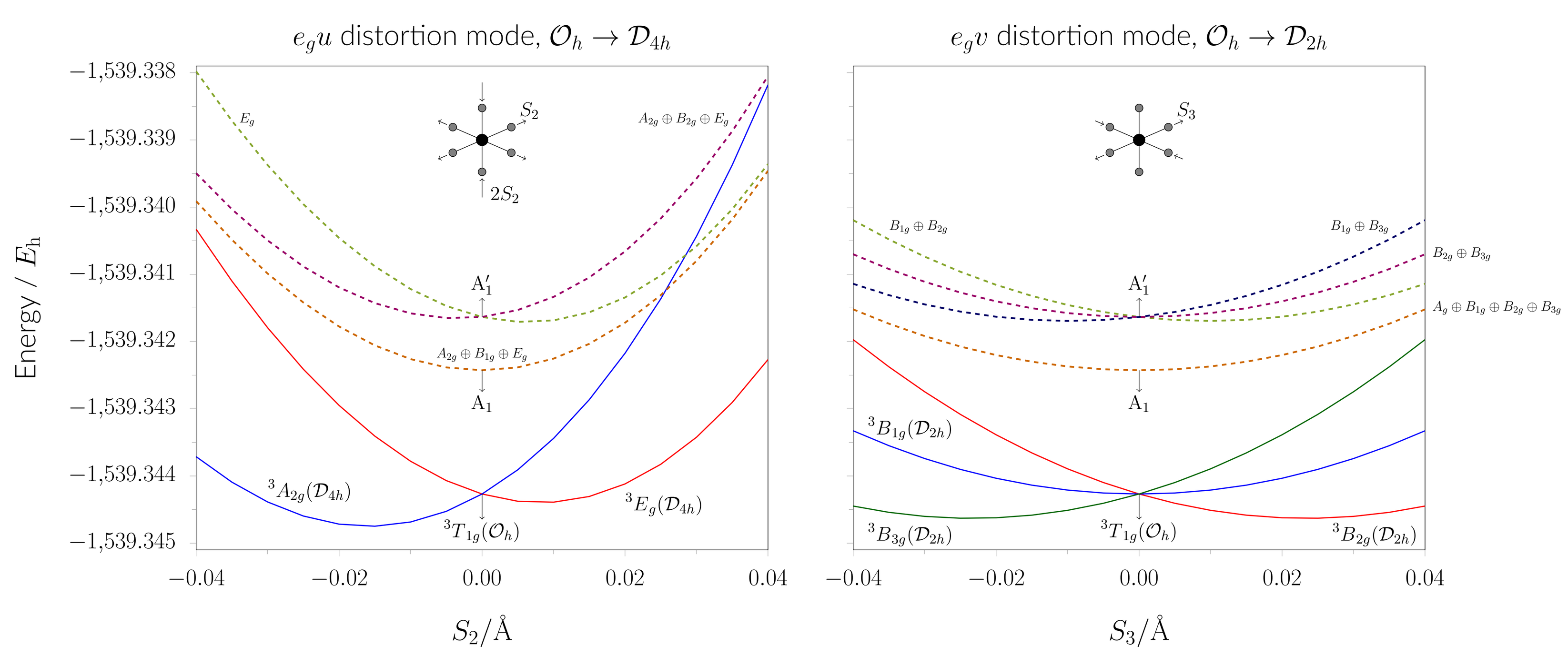
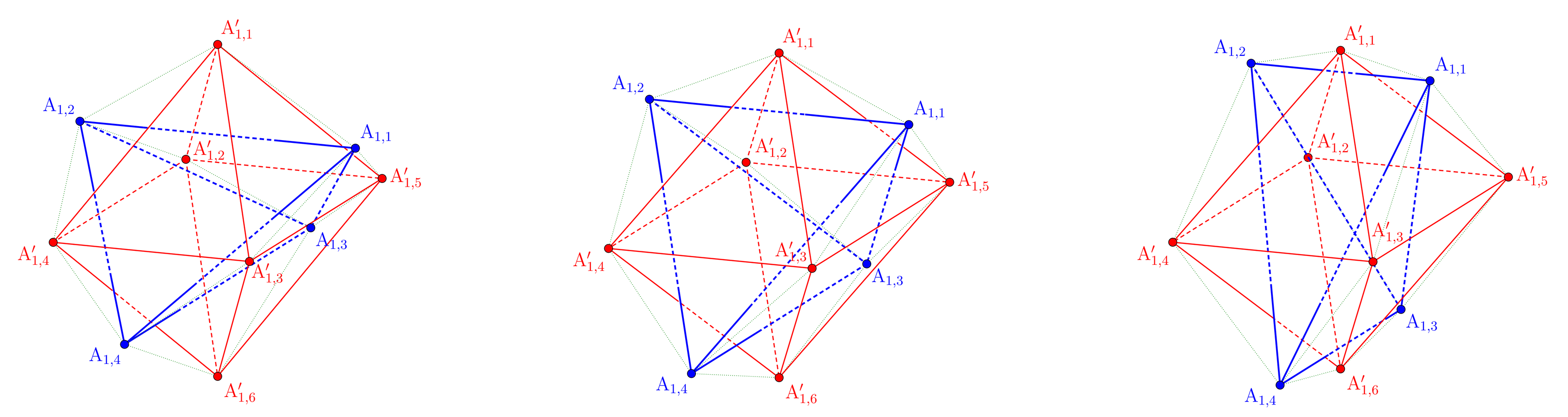


Figure 3. State energy in the $T_{1g} \otimes e_g$ Jahn–Teller distortion of octahedral $[VF_6]^{3-}$.
Dashed curves: symmetry-broken UHF A_1 or A_1' solutions. Solid curves: ${}^3T_{1g}[A_1 \oplus A_1']$ NOCI wavefunctions.

Solution Topology: Euclidean Realisation of State Distances

By realising the distance matrices between symmetry-broken HF solutions to give polytopes showing their arrangements in Euclidean space (Figure 4), we hope to gain insight into the nature of their symmetry breaking.



(a) $S_2 = -0.04$ Å (b) $S_2 = 0$ (c) $S_2 = 0.04$ Å

Figure 4. Three-dimensional projections of polytopes of A_1 and A_1' solutions along the $e_g u$ distortion.

In a Nutshell

- There exist many low-lying HF solutions in transition-metal complexes.
- Some solutions break symmetry, spin or spatial or both.
- NOCI can restore symmetry to give proper physical behaviours, *e.g.*, vibronic coupling.
- There are clear patterns in symmetry breaking that need further understanding.

References

1. Thom, A. J. W. & Head-Gordon, M. *Physical Review Letters* **101**, 193001 (November 2008).
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