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 $[VF_6]^{3-}$

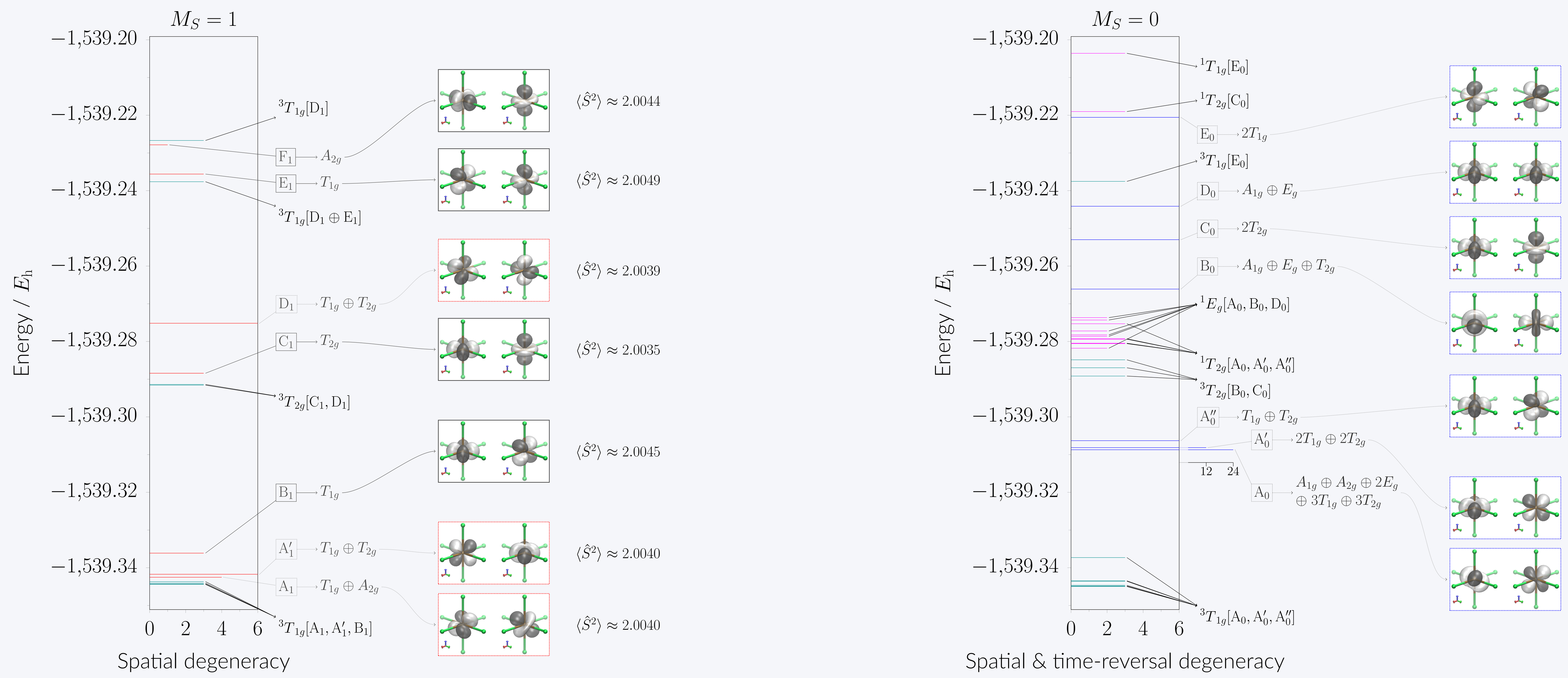
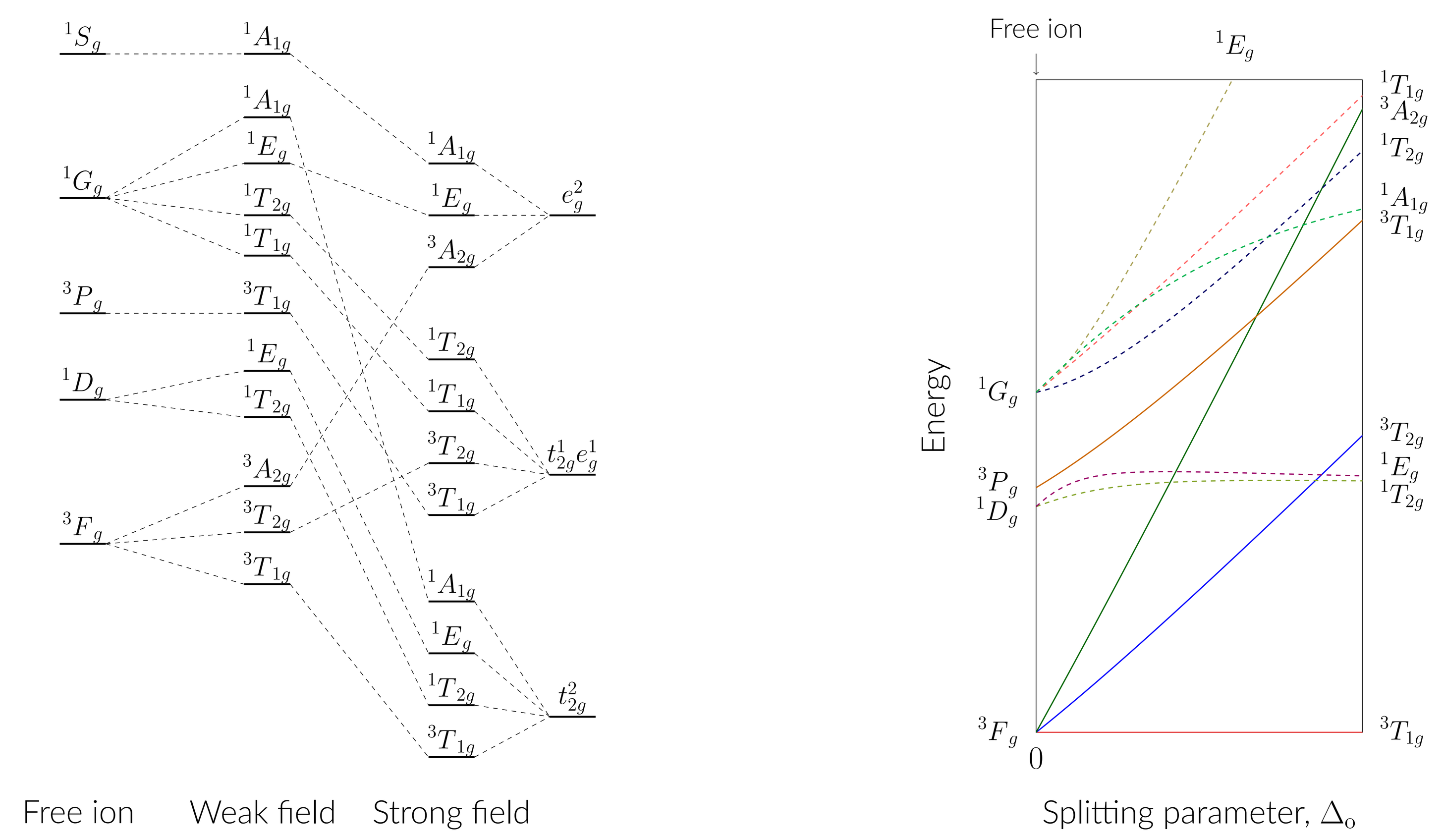


Figure 1. Energy and symmetry of low-lying UHF solutions and NOCI wavefunctions constructed from them in octahedral $[VF_6]^{3-}$.
$\boxed{S_{M_S}}$: symmetry-conserved UHF set S with $\hat{S}_z$ eigenvalue M_S. $\boxed{S_{M_S}}$: spatial or spin symmetry-broken UHF set S with $\hat{S}_z$ eigenvalue 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 $[VF_6]^{3-}$ system (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 $\mathrm{S} = \{{}^w\Psi \mid w = 1, 2, \ldots\}$ and a 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.

References

1. Thom, A. J. W. & Head-Gordon, M. *Physical Review Letters* **101,** 193001 (November 2008).
2. Thom, A. J. W. & Head-Gordon, M. *The Journal of Chemical Physics* **131,** 124113 (September 2009).
3. Huynh, B. C. & Thom, A. J. W. (Manuscript in preparation).

Non-Orthogonal Configuration Interaction (NOCI)

For a symmetry-broken set S, 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

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

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

UHF vs. NOCI: Jahn–Teller Distortion

Figure 3 shows that:

- the symmetry-broken UHF A_1 and A'_1 solutions fail to exhibit minima expected for the $T_{1g} \otimes e_g$ Jahn–Teller distortion;
- the ${}^3T_{1g}[\mathrm{A}_1 \oplus \mathrm{A}'_1]$ NOCI wavefunctions do show the expected minima and give the correct degeneracy splitting.

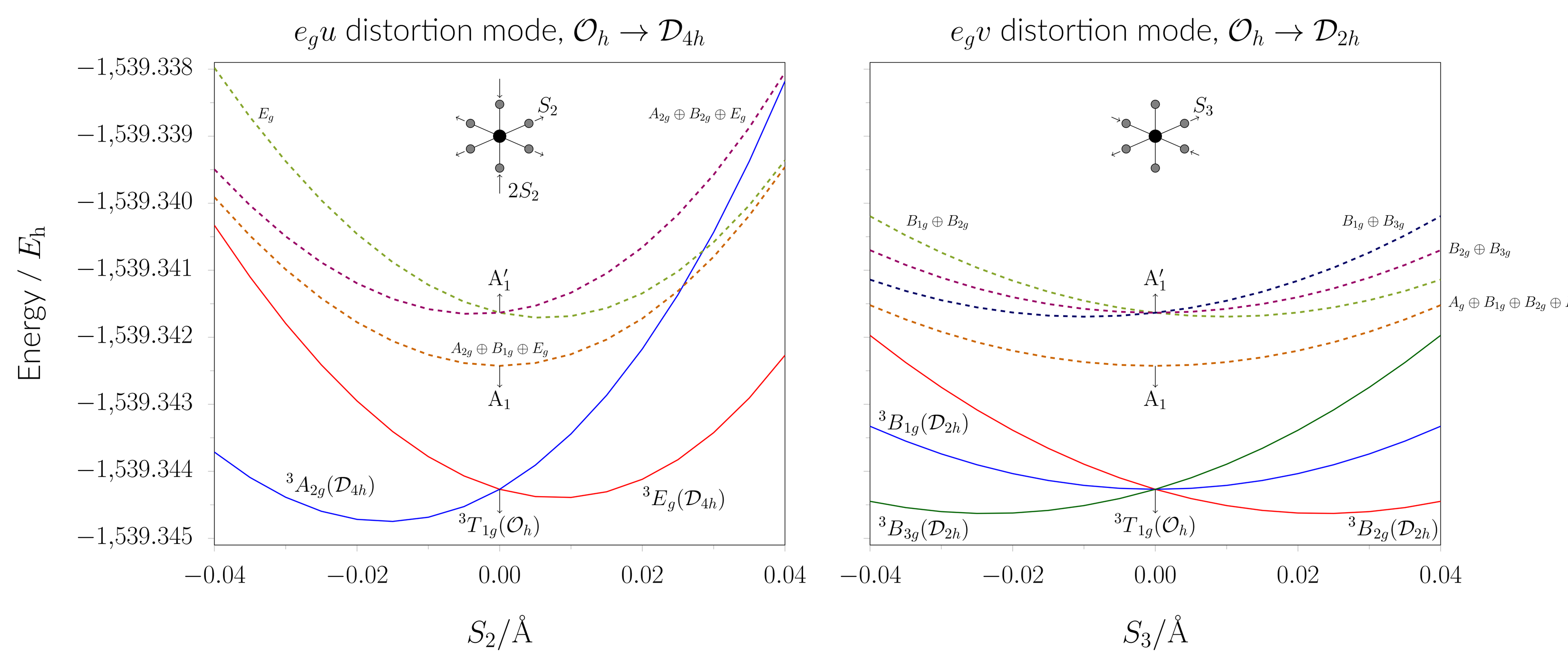


Figure 3. State energy in the $T_{1g} \otimes e_g$ Jahn–Teller distortion of octahedral $[VF_6]^{3-}$.
Dashed curves: symmetry-broken UHF A_1 or A'_1 solutions. Solid curves: ${}^3T_{1g}[\mathrm{A}_1 \oplus \mathrm{A}'_1]$ NOCI wavefunctions.

Solution Topology: Euclidean Representation of State Distances

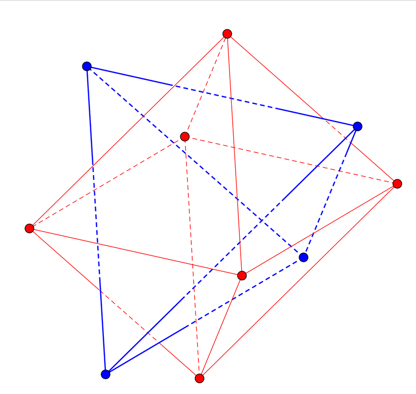


Figure 4