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 $[VF_6]^{3-}$

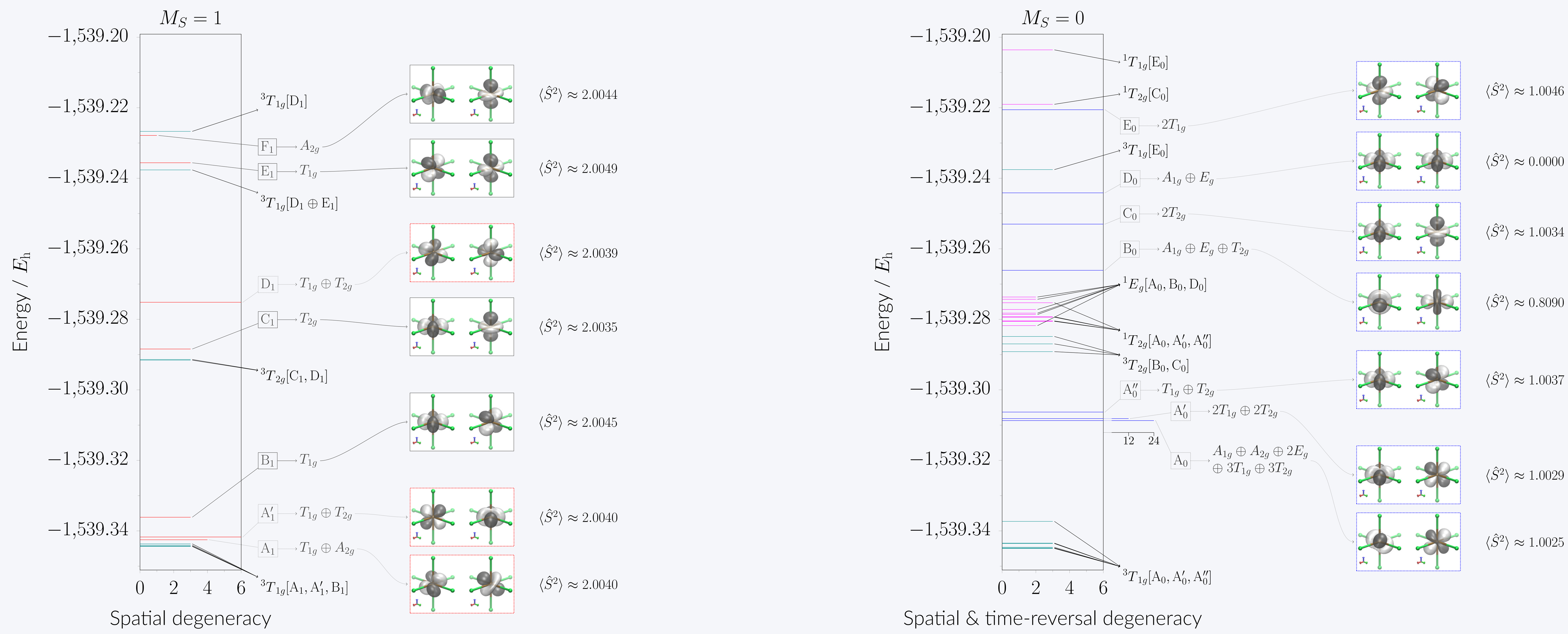
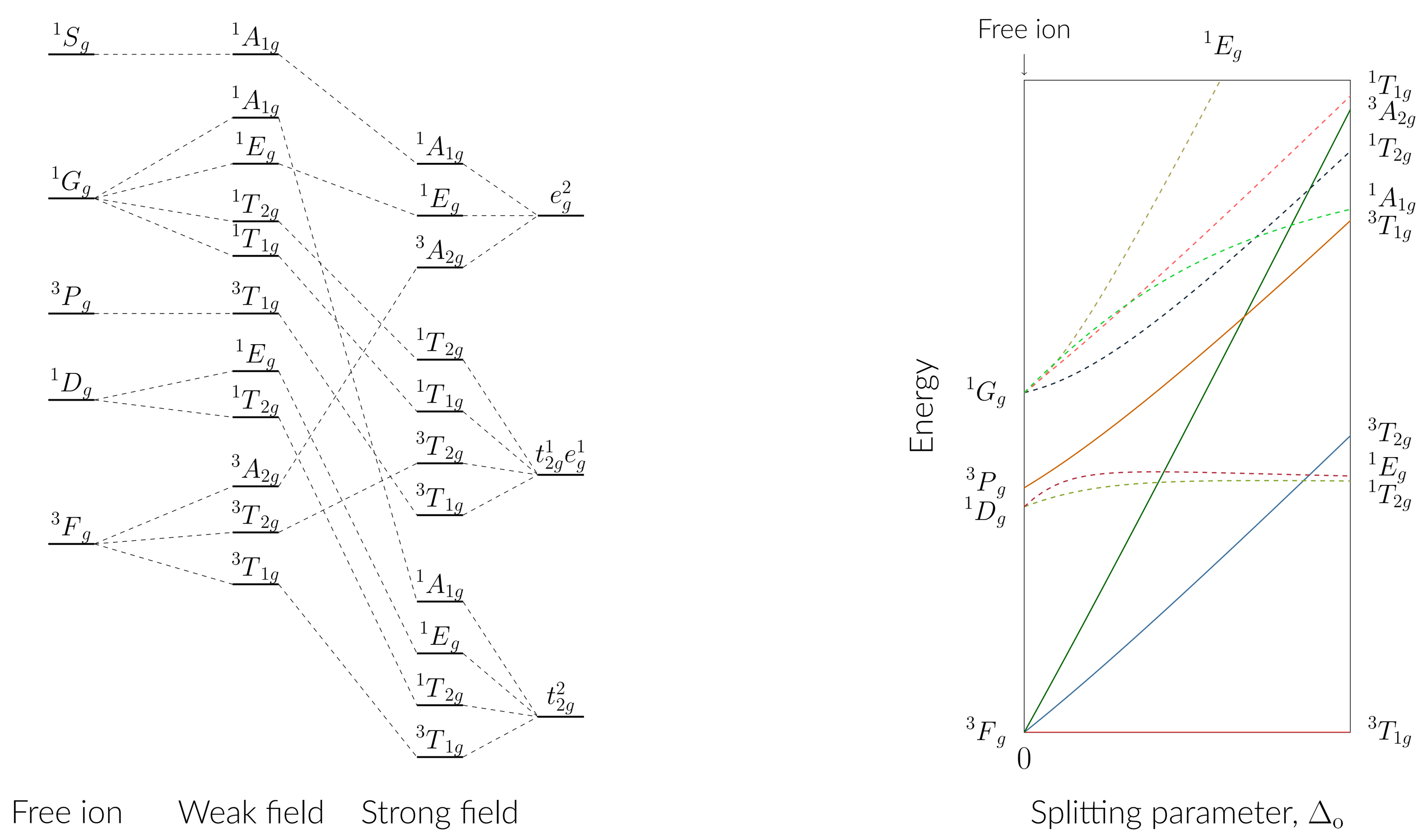


Figure 1. Energy and symmetry of low-lying UHF solutions and NOCI wavefunctions constructed from them in octahedral $[VF_6]^{3-}$.
$\boxed{S_{M_S}}$: symmetry-conserved UHF set S with $\hat{S}_z$ eigenvalue M_S. $\boxed{S_{M_S}}$: spatial or spin symmetry-broken UHF set S with $\hat{S}_z$ eigenvalue 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 by virtue of d electrons. 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 are therefore expected to admit multiple low-lying and degenerate or nearly degenerate solutions that are physically significant.

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

Each degenerate set of exact solutions to the spinless electronic Schröndinger equation *must* transform as a single irreducible representation (irrep) of the underlying point group $\mathcal{B}$, the spin rotation group $\mathsf{SU}(2)$, and the time reversal group $\mathcal{T}$.

However, UHF wavefunctions are not necessarily eigenfunctions of $\hat{S}^2$ nor do they and their degenerate partners have to transform as a single irreducible representation of $\mathcal{B}$.

Thus, consider a degenerate set $\mathrm{S} = \{{}^w\Psi \mid w = 1, 2, \ldots\}$ 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 a representation that can be reduced to 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.

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

As shown in Figure 3, the symmetry-broken UHF A_1 and A_1' solutions fail to exhibit reasonable minima expected for the $T_{1g} \otimes e_g$ Jahn–Teller distortion. The ${}^3T_{1g}[A_1 \oplus A_1']$ NOCI wavefunctions, however, do and also give the correct degeneracy splitting.

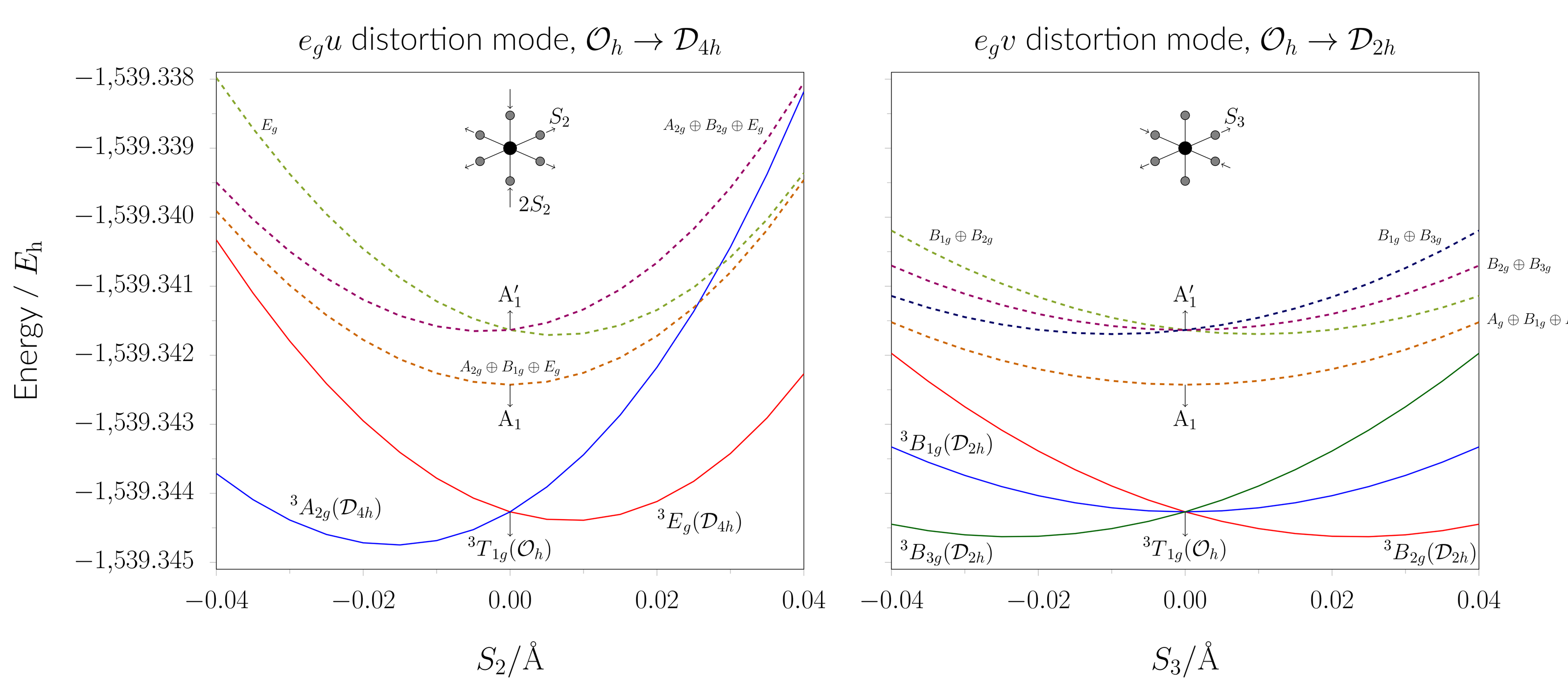


Figure 3. State energy in the $T_{1g} \otimes e_g$ Jahn–Teller distortion of octahedral $[VF_6]^{3-}$.
Dashed curves: symmetry-broken UHF A_1 or A_1' solutions. Solid curves: ${}^3T_{1g}[A_1 \oplus A_1']$ NOCI wavefunctions.

Solution Topology: Euclidean Representation of State Distances

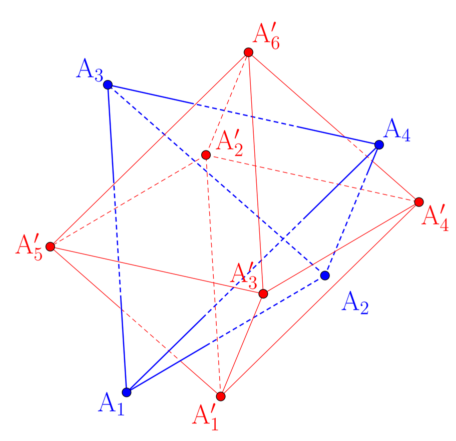


Figure 4

References

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2. Thom, A. J. W. & Head-Gordon, M. *The Journal of Chemical Physics* **131**, 124113 (September 2009).
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