



A PERTURBATIVE APPROXIMATION TO RAS- n SF FOR EXCITED STATES AND STRONG CORRELATIONS

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INTRODUCTION

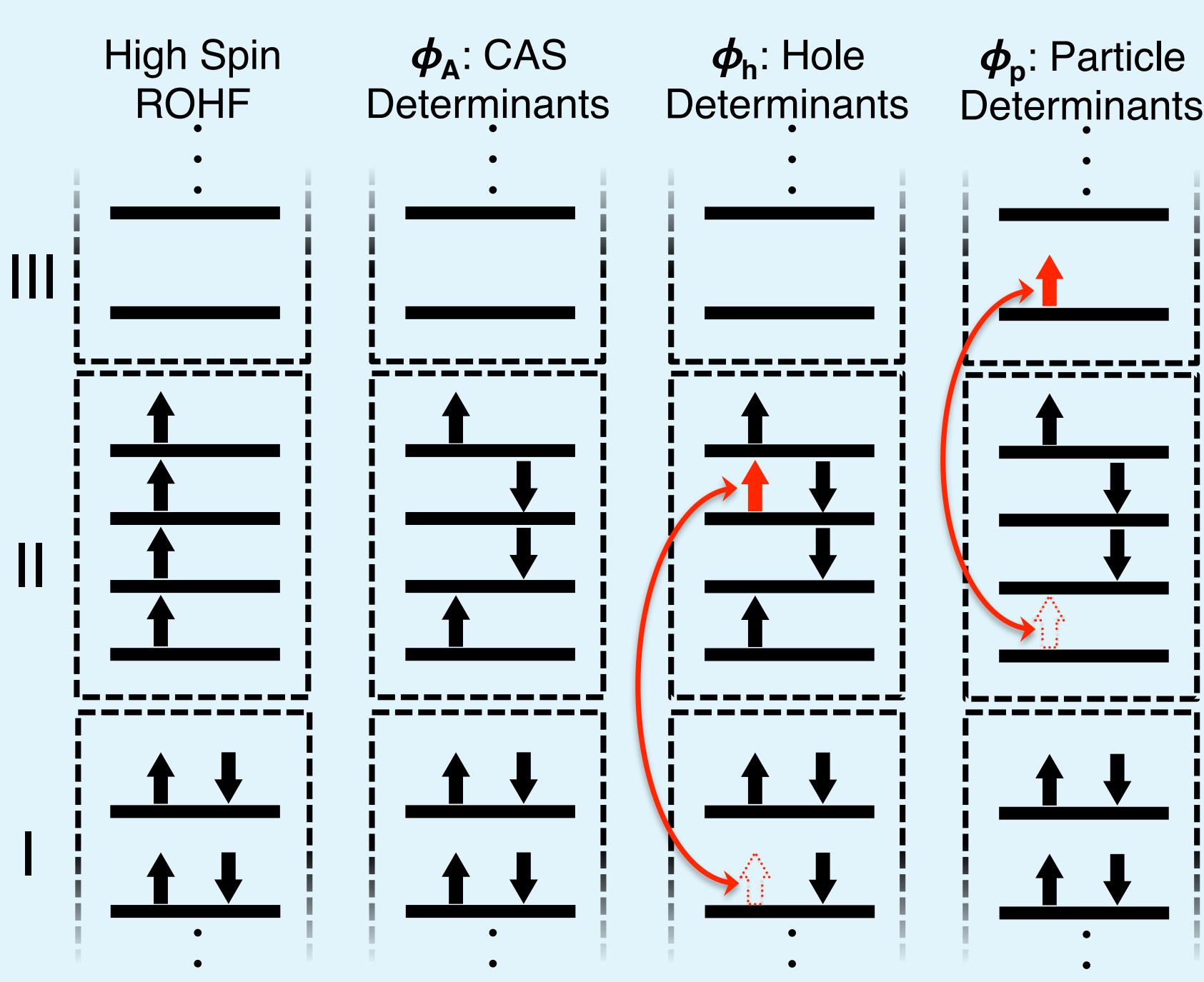
Desirable reactive, magnetic, or optical properties of molecular systems, are often a direct result of an underlying electronic structure that is relatively complex (spin-coupled atoms, low-lying excited states, etc.). Unfortunately, these are the same scenarios in which traditional approaches to electronic structure break-down. Until somewhat recently, the only recourse to study such a “strongly correlated” system, was to use a multireference approach such as CASSCF/CASPT2. These methods require significant user input (active space definition, state-averaging) and are often plagued by numerical issues (difficult orbital convergence, intruder-state problems).

Spin-flip methods, offer an attractive alternative for many strongly correlated systems. SF uses orbitals optimized for a higher-spin HF state (which is truly single reference), and applies a CI operator which flips one or more electron spins to return states of the desired total spin, providing a multideterminantal wavefunction, from a single determinant reference.

In this work, we present a perturbative approximation to RAS- n SF which has significant computational advantages, while introducing minimal additional error.

RAS-SF

The RAS- n SF method is a cost-effective member of the “spin-flip” family of CI methods which has the advantage of being defined for an arbitrary number of spin flips, while providing both size intensive and spin-pure states. Although, the computational cost increases factorially with number of spin-flips, the complexity increases only moderately with system size (linear in number of CI coefficients).



Built from a high-spin ROHF set of orbitals, the RAS- n SF wavefunction can be thought of as a CAS-CI wavefunction in a different spin block (hence the spin-flip), augmented with excitations into (*holes*), and out of (*particles*), the active space.

As with all spin-flip methods, the use of high-spin orbitals eliminates the need for orbital-optimization of a multi-determinantal electronic state.

However, use of only the active space spin flip wavefunction (SF-CAS-CI) is not quite sufficient. The reference orbitals have been optimized for the high spin state, the low spin states are not described with an equal amount of variational flexibility. Thus the hole and particle states are included which allow the low spin states to relax subject to core and virtual mixing. The RAS-SF wavefunction is defined as:

$$\Psi_s^{RAS} = \sum_A c_A^s \phi_A + \sum_h c_h^s \phi_h + \sum_p c_p^s \phi_p, \quad (1)$$

SF-CAS(h,p) $_n$

Here, we take the SF-CAS-CI wavefunction as our 0th-order wavefunction (A space) and include the hole, and particle states (X space) via 2nd-order perturbation theory. Using the Löwdin partitioning technique, we partition the hamiltonian as:

$$\mathbf{H}^{(0)} = \begin{pmatrix} \hat{H} & \hat{0} \\ \hat{0} & \hat{F} + \langle |\hat{V}| \rangle \end{pmatrix} \quad \mathbf{H}^{(1)} = \begin{pmatrix} \hat{0} & \hat{H} \\ \hat{H} & \hat{V} - \langle |\hat{V}| \rangle \end{pmatrix}, \quad (2)$$

where $|\rangle$ is taken to be the ground-state of the 0th-order Hamiltonian.

•SF-CAS(h,p):

$$E_s^{\text{SF-CAS}(h,p)} = E_s^{\text{SF-CAS}} + \mathbf{C}_{A,s}^{(0)\text{T}} \frac{\mathbf{H}_{AX}^{(1)} \mathbf{H}_{XA'}^{(1)}}{E_s - \mathbf{H}_{XX}^{(0)}} \mathbf{C}_{A',s}^{(0)} \quad (3)$$

•SF-CAS(h,p) $_0$:

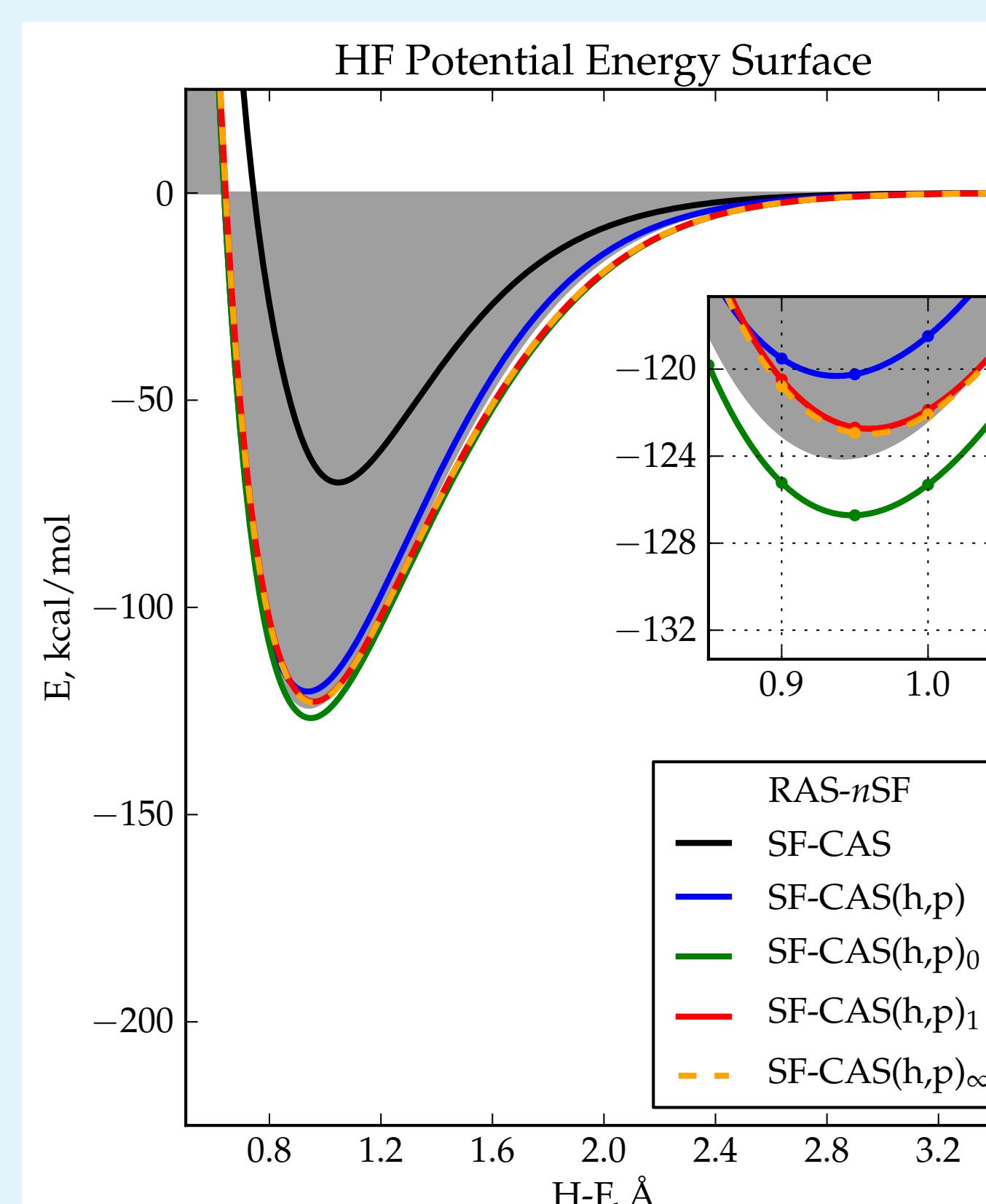
$$\mathcal{H}_{AA'} = \mathbf{H}_{AA'}^{(0)} - \frac{\mathbf{H}_{AX}^{(1)} \mathbf{H}_{XA'}^{(1)}}{\langle X | \hat{F} | X \rangle - \langle |\hat{F}| \rangle} \quad (4)$$

•SF-CAS(h,p) $_1$:

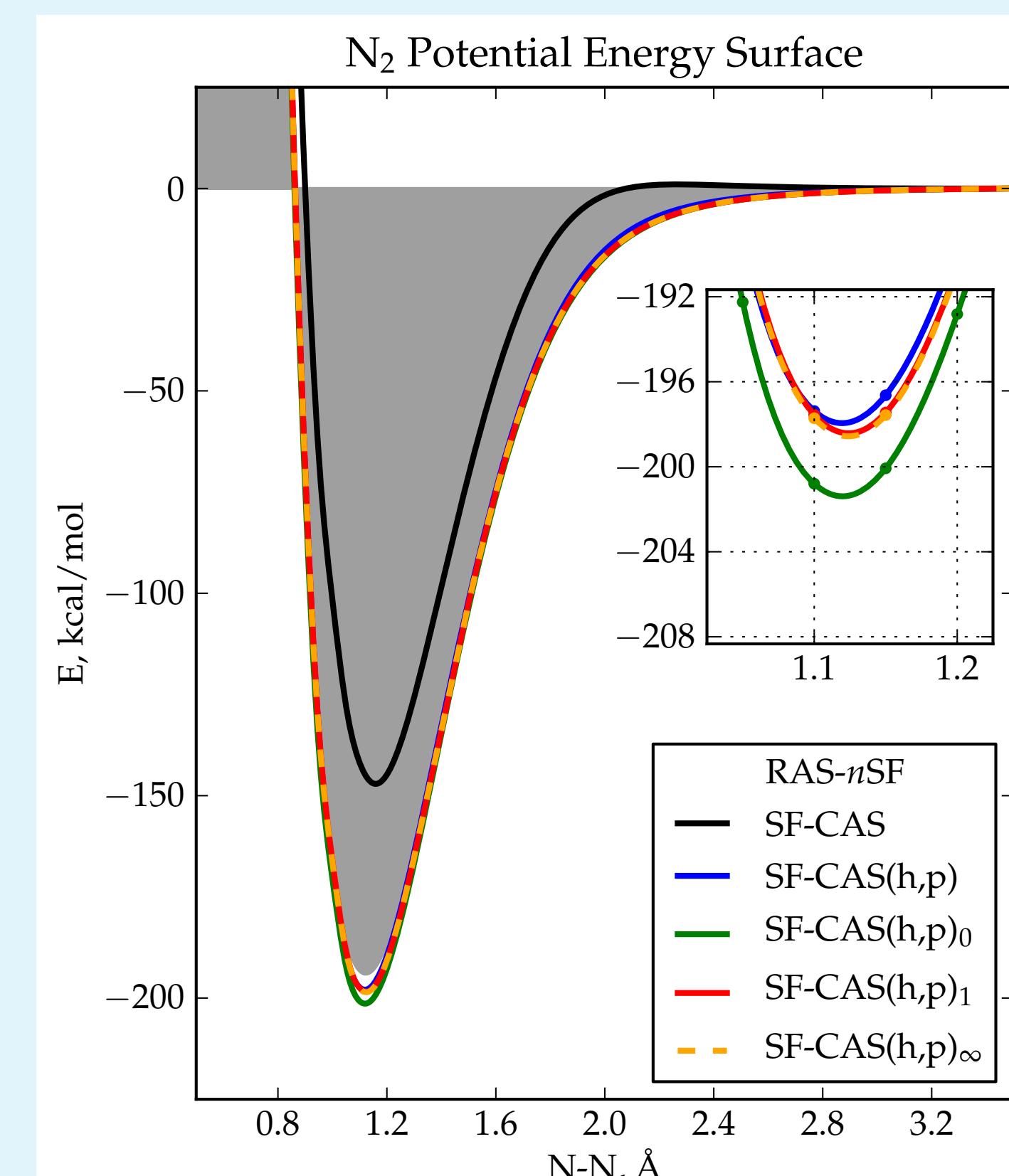
$$\mathcal{H}_{AA'} = \mathbf{H}_{AA'}^{(0)} - \frac{\mathbf{H}_{AX}^{(1)} \mathbf{H}_{XA'}^{(1)}}{\langle X | \hat{F} | X \rangle - \langle |\hat{F}| \rangle} + E_0^{(0)} \frac{\mathbf{H}_{AX}^{(1)} \mathbf{H}_{XA'}^{(1)}}{(\langle X | \hat{F} | X \rangle - \langle |\hat{F}| \rangle)^2} \quad (5)$$

$$S_{AA'} = \mathbf{I}_{AA'} + \frac{\mathbf{H}_{AX}^{(1)} \mathbf{H}_{XA'}^{(1)}}{(\langle X | \hat{F} | X \rangle - \langle |\hat{F}| \rangle)^2} \quad (6)$$

POTENTIAL ENERGY CURVES



(a) 1 Spin Flip - (6,4) Active Space



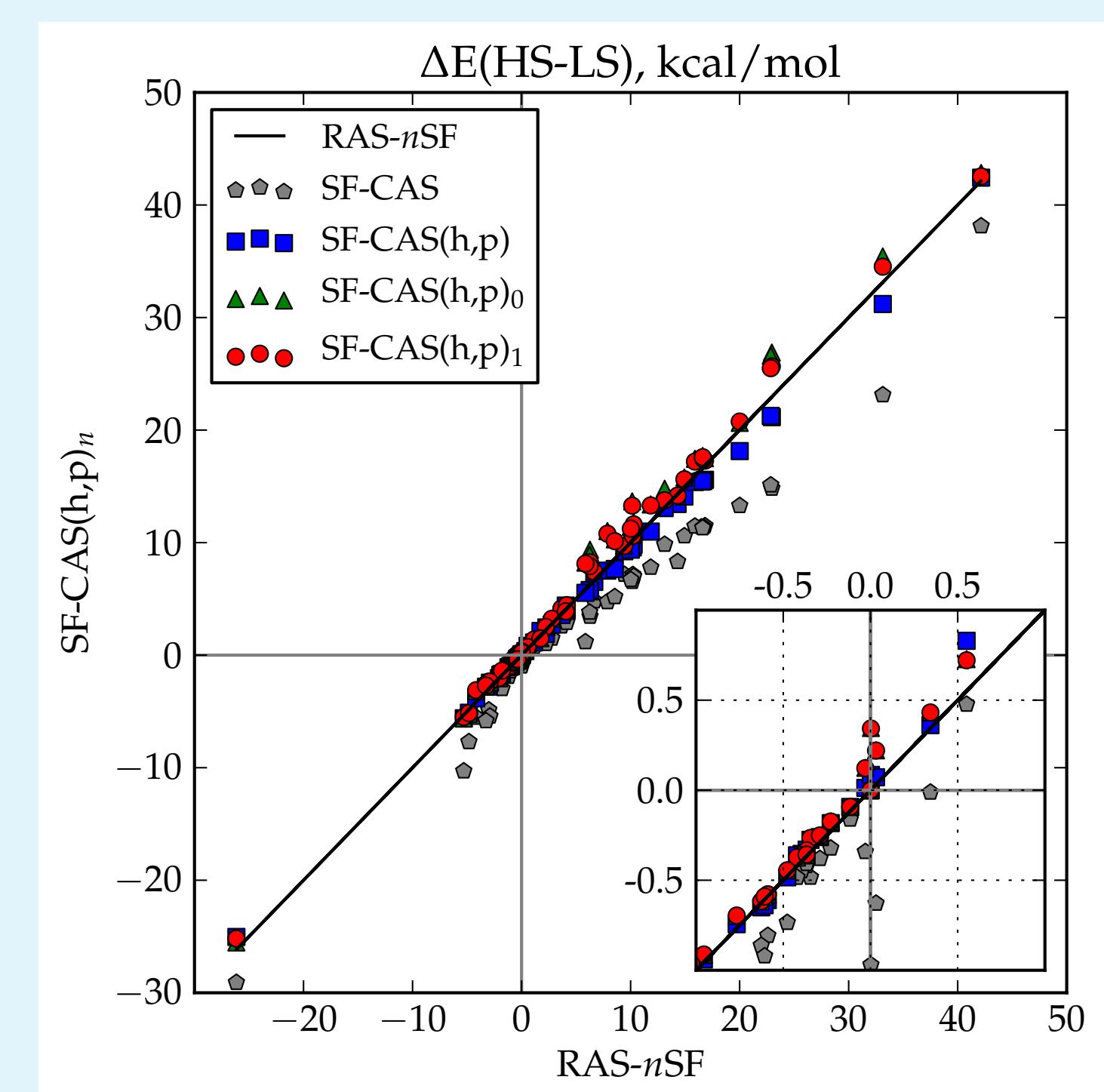
(b) 3 Spin Flip - (6,6) Active Space

Grey area: RAS- n SF. Black curve: SF-CAS. Blue curve: SF-CAS(h,p). Green curve: SF-CAS(h,p) $_0$. Red curve: SF-CAS(h,p) $_1$. Orange dotted line: SF-CAS(h,p) ∞ .

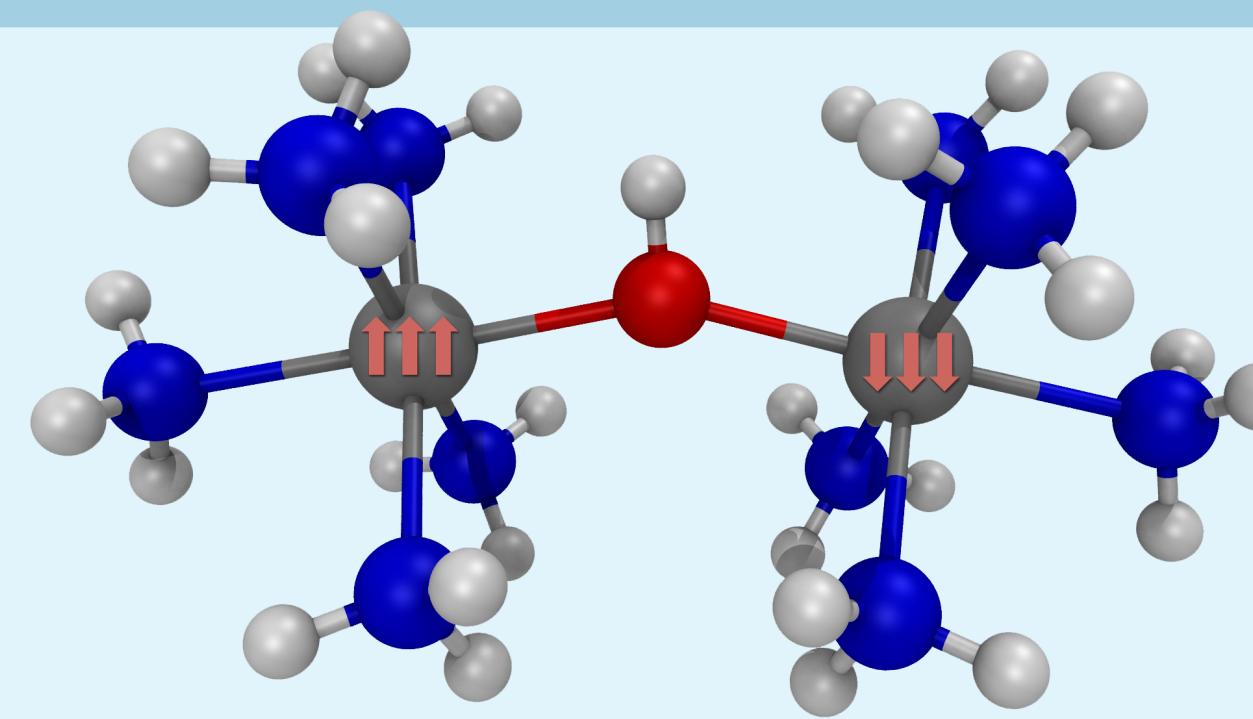
SPIN STATE ENERGY GAPS

The RAS- n SF method was found to be extremely reliable in predicting ground state spin multiplicities. Here we determine how well our perturbative approximation performs in reproducing the spin-state energy gaps. A set of 68 various T-S, Q-T, and Q-S gaps are shown plotted against the fully variational RAS- n SF results.

While the data covers a wide magnitude range, the SF-CAS-CI method provides a reasonable description of the spin gaps. However, upon inclusion of our perturbative correction, the performance is greatly enhanced for all PT methods, particularly for the non-degenerate SF-CAS(h,p) and the quasidegenerate SF-CAS(h,p) $_1$ methods.



COMPUTATIONAL COST



For n spin-flips and M_V virtual orbitals, the largest CI dimension usually corresponds to the particle states, consisting of $(\frac{2n}{n}) (\frac{2n}{n-1}) M_V$ determinants. For a fixed active space, RAS- n SF requires a diagonalization of the full space which scales as $\mathcal{O}(M_v^2)$ for a σ vector formation. SF-CAS(h,p) $_n$ requires only 1-2 matrix multiplications costing only $\mathcal{O}(M_v)$ each. Of course, both methods still scale factorially with active space.

	RAS-SF	SF-CAS(h,p)	SF-CAS(h,p) $_0$	SF-CAS(h,p) $_1$
Time(s)	45935	47	57	68
Time/State(s)	4594	5	6	7
Iterations	156*	—	—	—
Singlet (meV)	0.00	0.00	0.00	0.00
Triplet (meV)	0.87	0.99	1.09	1.09
Quintet (meV)	2.61	2.98	3.29	3.29
Heptet (meV)	5.23	5.97	6.59	6.59

FUTURE ISSUES

For several spin-flips, the factorially increasing coefficient in front of the above scalings will dominate. In the large molecule limit (few spin-flips), the evaluation of the $2e$ integrals becomes the bottleneck.

	Large Molecule	Large Active Space
RAS-SF Scaling	$\mathcal{O}(N^4)$	$\mathcal{O}(N^2) * C_{act}$
SF-CAS(h,p) $_n$ Scaling	$\mathcal{O}(N^3)$	$\mathcal{O}(N^1) * C_{act}$
SF-CAS(h,p) $_n$ Algorithm	✓ Exact Diag of $\mathcal{H}_{AA'}$	✗ Davidson Diag of $\mathcal{H}_{AA'}$
Improvements needed	Parallelize (underway)	Convert to matrix-vector algorithm
Collaborative Efforts	Sam Williams has provided design guidance	Xiaoye Sherry Li & Chao Yang to help with iterative solvers