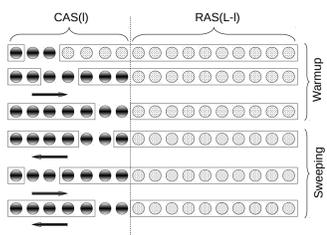


Motivation

- In light of tremendous progress in the past decade in transition metal chemistry, photosynthesis, single molecular magnets, and relativistic chemistry for compounds including heavy elements there is a high demand for a generally applicable method to efficiently treat strong electronic correlations and reveal solutions with chemical accuracy.
- Although the main features of the electronic states are often characterized by the static correlations, contributions of an intractable number of high energy excited configurations with small weights, i.e., dynamical effects, can be crucial for an accurate theoretical description in light of experimental data.
- Quite recently, a cross-fertilization of the conventional restricted active space (RAS) scheme with the density matrix renormalization group (DMRG) method [2, 3] has emerged as a new powerful method [1] to capture both static and dynamic correlations.
- Here, we present a new theoretical analysis and introduce a new extrapolation procedure [4], free of empirical parameters and fully ab-initio, which reveals the ground state energy of systems with full Hilbert space dimensions up to 2.48×10^{31} within chemical accuracy (1 kcal/mol or 0.0016 a.u.).

The N-electron Hilbert space for the the DMRG-RAS method



Partitioning of the orbitals into l CAS orbitals and $L - l$ RAS orbitals, with $N/2 \leq l \leq L$, in the DMRG-RAS method using the blocking structure introduced via the dynamically extended active space (DEAS) procedure. Filled circles stand for orbitals with four dimensional local Hilbert space, while orbital space built from dashed orbitals is restricted to an excitation threshold $k \leq N$. Arrows indicate the DMRG sweeping procedure and the vertical line shows the turning point of the forward sweep as the RAS orbitals are treated as a single site.

The N -electron Hilbert space for the DMRG-RAS method is then given by

$$\mathcal{H}(\ell, k) = \mathcal{H}_{\text{CAS}}(\ell) \oplus \mathcal{H}_{\text{RAS}}(L - \ell, k)$$

where the CAS Hilbert space is the full N -electron Hilbert space of the CAS orbitals,

$$\mathcal{H}_{\text{CAS}}(\ell) = \bigwedge_{i=1}^N \text{span}\{\varphi_1 \uparrow, \varphi_1 \downarrow, \dots, \varphi_\ell \uparrow, \varphi_\ell \downarrow\},$$

and the RAS Hilbert space is spanned by all Slater determinants which are at least singly and at most k -fold excited with respect to some CAS Slater determinant,

$$\mathcal{H}_{\text{RAS}}(L - \ell, k) = a_{a_1 \sigma_1}^\dagger \dots a_{a_k \sigma_k}^\dagger \mathcal{H}_{\text{CAS}} \oplus \dots \oplus a_{a_1 \sigma_1}^\dagger \dots a_{a_k \sigma_k}^\dagger \mathcal{H}_{\text{CAS}}.$$

Thus the method has two parameters, l (number of CAS orbitals) and k (RAS excitation threshold). While there is considerable freedom in choosing l , the standard choice for k (and the one investigated in this paper) is $k = 2$.

Optimization task to obtain the ground state

obtained from the Rayleigh-Ritz principle,

$$E^0(\ell, k) = \min_{\Psi \in \mathcal{H}(\ell, k): \langle \Psi, \Psi \rangle = 1} \langle \Psi, H \Psi \rangle, \quad (1)$$

where H is the (non-relativistic, Born-Oppenheimer) electronic Hamiltonian of the system

$$H = \sum_{ij\sigma} t_{ij\sigma} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{k\sigma} a_{l\sigma'},$$

where t_{ij} denotes the matrix elements of the one-particle Hamiltonian, which is comprised of the kinetic energy and the external electric potential of the nuclei, and V_{ijkl} stands for the matrix elements of the electron repulsion operator.

Partitioning of the full Hamiltonian into a reference Hamiltonian associated with the CAS energy and a remainder. We propose the following choice:

$$H = H_0 + H' \quad \text{with} \quad (2)$$

$$H_0 = PHP + (E_0 + \Delta)Q \quad (3)$$

$$H' = H - PHP - (E_0 + \Delta)Q \quad (4)$$

where P is the projector of H onto the CAS Hilbert space $\mathcal{H}_{\text{CAS}}(\ell)$, $Q = I - P$ is the projector onto its orthogonal complement $\mathcal{H}_{\text{RAS}}(L - \ell, N)$ within the full N -electron Hilbert space $\mathcal{H}(\ell, N)$, E_0 is the CAS ground state energy, i.e.

$$E_0 = E_{\text{CAS}}^0(\ell), \quad (5)$$

and $\Delta > 0$ is a parameter to be chosen later.

$$H - PHP = \underbrace{QHP}_{\mathcal{H}_{\text{CAS} \rightarrow \text{RAS}}} + \underbrace{PHQ}_{\mathcal{H}_{\text{RAS} \rightarrow \text{CAS}}} + \underbrace{QHQ}_{\mathcal{H}_{\text{RAS} \rightarrow \text{RAS}}}$$

Error scaling for interacting systems via dressed CAS ground state

By this we mean the normalized projection of the full FCI ground state Ψ_{FCI} onto the CAS,

$$\tilde{\Psi}_0 = \frac{P\Psi_{\text{FCI}}}{\|P\Psi_{\text{FCI}}\|}. \quad (6)$$

This state gives rise to the dressed CAS ground state energy

$$\tilde{E}_0 = \langle \tilde{\Psi}_0 | H_0 | \tilde{\Psi}_0 \rangle$$

and dressed perturbation contributions leads to:

$$\varepsilon_{\text{RAS}}(\ell) = O(\tilde{E}^{(3)} + \|H'\tilde{\Psi}_0\|^4 + \|H'\tilde{\Psi}_0\|^2(\tilde{E}_0 - E_0)) \quad (7)$$

as $H'\tilde{\Psi}_0 \rightarrow 0$.

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New extrapolation method

- Suppose we have numerically calculated the CAS energy $E_{\text{CAS}}^0(\ell)$ and the DMRG-RAS energy $E^0(\ell, 2)$ for a few values of ℓ .
- The scaling law now gives some information about the (unknown) FCI energy, namely

$$E^0(\ell, 2) - E^{\text{FCI}} \approx a(E_{\text{CAS}}^0(\ell) - E^{\text{FCI}})^p \quad \text{for some } p > 1. \quad (8)$$

- For careful numerical validation of this scaling law in real systems, with exponents p differing from system to system as expected from theory, see the next section.
- This is achieved by minimizing the mean squared regression error of RAS versus CAS error in a log log plot,

$$\text{MSE} = \frac{1}{n} \sum_{\ell} (y_{\ell} - (p \cdot x_{\ell} + \log a))^2 \quad (9)$$

- The predicted FCI energy is then

$$E_{\text{RAS-X}} = \arg \min_{E^{\text{FCI}}} \text{MSE}.$$

Demonstration of the new extrapolation method

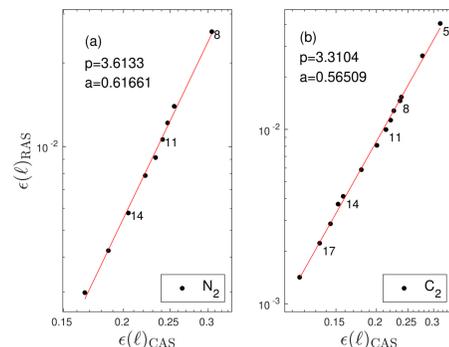


Figure: $\varepsilon(\ell)_{\text{RAS}}$ as a function of $\varepsilon(\ell)_{\text{CAS}}$ shown on a double logarithmic scale for the (a) for the N_2 molecule at $d = 2.118a_0$ in the cc-pVDZ basis corresponding to CAS(14,28). (b) Similar to (a) but for the C_2 molecule at $d = 1.25$ in the frozen core cc-pVTZ basis corresponding to CAS(8,58).

	$d = 2.118a_0$	$d = 2.700a_0$	$d = 3.600a_0$
E_{CCSD}	-109.26762	-109.13166	-108.92531
E_{CCSDT}	-109.28032	-109.15675	-109.01408
E_{CCDTQ}	-109.28194	-109.16224	-108.99752
$E_{\text{RAS-X}}$	-109.2814	-109.1634	-108.9980
$p_{\text{RAS-X}}$	3.98	3.45	3.23
$a_{\text{RAS-X}}$	0.0007	0.0002	0.0001
p_{fit}	3.61	3.34	3.20
E_{DMRG}	-109.282165	-109.16359	-108.99807

Table: Full-CI ground state energies obtained by large-scale DMRG calculations with $M_{\text{min}} = 1024$, $M_{\text{max}} = 10000$ and $\chi = 10^{-6}$, together with CC reference energies taken from Ref. [5] and predicted values $E_{\text{RAS-X}}$, $p_{\text{RAS-X}}$ and $a_{\text{RAS-X}}$ via the DMRG-RAS-X method using $\ell = 8 \dots 16$ for various bond lengths for the N_2 dimer in the cc-pVDZ basis. The p_{fit} values correspond to direct fits of ε_{RAS} vs ε_{CAS} as shown in Fig. 1 using the full-CI reference energies.

Numerical results for strongly correlated diatoms

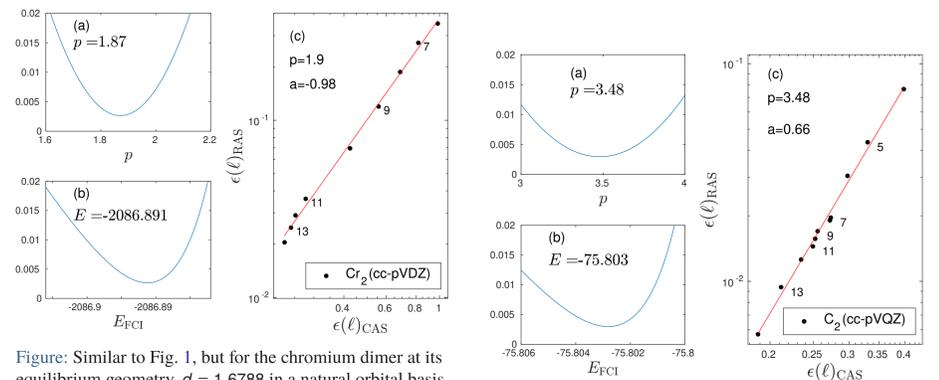


Figure: Similar to Fig. 1, but for the chromium dimer at its equilibrium geometry, $d = 1.6788$ in a natural orbital basis obtained from the cc-pVDZ atomic basis, corresponding to a full orbital space CAS(12,68). Here, first the extrapolation has been performed to obtain the predicted exponent $p_{\text{RAS-X}}$ and energy value $E_{\text{RAS-X}}$ as shown in panel (a) and (b), and the predicted energy was used to get the curve presented in panel (c).

Figure: Similar to Fig. 2, but for the significantly larger cc-pVQZ basis set with frozen cores for $d = 1.25$, corresponding to CAS(8,108). In the extrapolation procedure we have used $\ell = 4 \dots 14$.

Results for a large chemical complex: FeMoco

Non-extrapolated ground state energy values obtained by DMRG and FCIQMC methods presented in Refs. [6, 7], as well as our results, are summarized in Tab. 2.

Method	Ground state energy
i-FCIQMC-RDME	-13482.1746
i-FCIQMC-PT2	-13482.1785
sHCl-VAR	-13482.1604
sHCl-PT2	-13482.1734
DMRG	-13482.1768
DMRG(D=8192)	-13482.1718
DMRG(D=10240,NO)	-13482.1754
RAS(23)	-13482.1421
RAS(23,NO)	-13482.1544

Table: Top: Non-extrapolated ground state energies obtained by various methods [6, 7] for the FeMoco orbital space introduced in Ref. [8]. Bottom: our results, including data for natural orbitals as well.

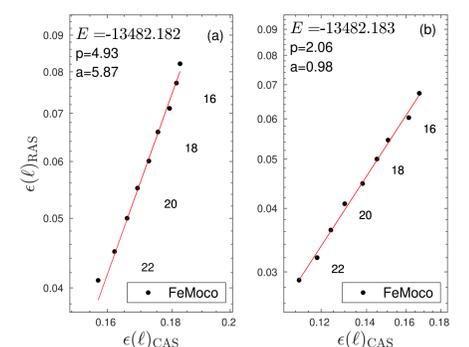


Figure: (a) Result of the DMRG-RAS-X extrapolation as function of ℓ for the FeMoco for the model space taken from Ref. [8] corresponding to CAS(54,54). (b) The same but for the natural orbital basis. The predicted exponents $p_{\text{RAS-X}}$, the constants $a_{\text{RAS-X}}$ and the energy values $E_{\text{RAS-X}}$ are also presented.