What is required for solving chemical problems on a quantum computer?

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K. Bourzac, C&EN, 2017, 95 (43), pp 27-31, October 30, 2017

Quantum Chemistry on Traditional Computers

1. Wave function methods
2. CI, CC, MCSCF, DMRG, (FCIQMC)

Non-Relativistic Many-Electron Hamiltonian

- many-electron Hamiltonian in position space (Hartree atomic units)

$$H_{el} = \sum_{i}^{N} \left(-\frac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}} \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{1}$$

  with $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ and N being the number of electrons.

- eigenvalue equation: electronic Schrödinger equation

$$H_{el}\ \Psi_{el}^{\{\boldsymbol{R}_I\}}(\{\boldsymbol{r}_i\}) \ = \ E_{el}(\{\boldsymbol{R}_I\})\ \Psi_{el}^{\{\boldsymbol{R}_I\}}(\{\boldsymbol{r}_i\}) \tag{2}$$

- central in electronic structure theory: how to approximate Ψ_{el} ?

Standard Procedure: Construction of Many-Electron Basis

- Construct many-electron (determinantal) basis set $\{\Phi_I\}$ from a given (finite) one-electron (orbital) basis set ϕ_i
- Orbital preparation: solution of Roothaan–Hall equations yields n orbitals from n one-electron basis functions.
- From N orbitals with lowest energy, the Hartree–Fock (HF) Slater determinant Φ_0 is constructed.
- The other determinants (configurations) are obtained by subsequent substitution of orbitals in the HF Slater determinant Φ_0:

$$\{\Phi_I\} \rightarrow \Phi_i^a \rightarrow \Phi_{ij}^{ab} \rightarrow \Phi_{ijk}^{abc} \ldots \tag{3}$$

- Determinants are classified by number of 'excitations' (= substitutions in HF reference determinant).

Standard Full Configuration Interaction (FCI)

- The number of possible determinants is determined by the number of virtual orbitals $n - N$.
- Including all possible excited Slater determinants for a finite or infinite one-electron basis set leads to the so-called **full CI** approach.
- Number of Slater determinants n_{SD} for N spin orbitals chosen from a set of n spin orbitals (slang: N electrons in n spin orbitals):

$$n_{\mathrm{SD}} = \binom{n}{N} = \frac{n!}{N!(n-N)!} \tag{4}$$

  Example: There are $\approx 10^{12}$ different possibilities to distribute 21 electrons in 43 spin orbitals.

- *In Physics: FCI is exact diagonalization*.

Determination of the CI Expansion Coefficients C_I

The CI expansion coefficients C_I determined by variational principle:

- write down the expectation value for the energy
- introduce the determinantal basis set
- vary the energy in order to minimize it

Expectation value for the CI electronic energy:

$$E_{el}^{\mathrm{CI}} = \frac{\left\langle \Psi_{el}^{\mathrm{CI}} \right| H_{el} \left| \Psi_{el}^{\mathrm{CI}} \right\rangle}{\left\langle \Psi_{el}^{\mathrm{CI}} \right| \left. \Psi_{el}^{\mathrm{CI}} \right\rangle} \tag{5}$$

Insert expansion of Slater determinants:

$$E_{el}^{\mathrm{CI}} = \frac{\sum_{K,L} C_K^* C_L \left\langle \Phi_K \right| H_{el} \left| \Phi_L \right\rangle}{\sum_{K,L} C_K^* C_L \left\langle \Phi_K \right| \left. \Phi_L \right\rangle} \tag{6}$$

The CI Eigenvalue Problem

Calculate all derivatives $\partial E_{el}^{\mathrm{CI}} / \partial C_K^*$ and set them equal to zero, which yields the **CI eigenvalue problem:**

$$\boldsymbol{H} \cdot \boldsymbol{C} = \boldsymbol{C} \cdot \boldsymbol{E}_{el} \tag{7}$$

Essential: H is constructed from matrix elements $\langle \Phi_K | H_{el} | \Phi_L \rangle$ in the pre-defined determinantal basis $\{\Phi_K\}$ in orbital basis $\{\phi_i\}$

By solving the CI eigenvalue problem, ground and excited electronic states of the system are obtained.

$\boldsymbol{E}_{el}$ is diagonal matrix with total energies of all electronic states that can be expressed in basis given (M determinants yield M electronic states).

Truncated CI Wave Functions

Standard recipe to avoid the factorial scaling of the many-electron basis-set size: **truncate basis**! *Note: basis is pre-defined!*

Assumption: Substitution hierarchy is a useful measure to generate a systematically improvable basis set.

CIS: all singly-(S)-excited determinants are included:

$$\Psi_{el}^{\mathrm{CIS}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} \Phi_i^a \tag{8}$$

CISD: all singly- and doubly-(D)-excited determinants are included:

$$\Psi_{el}^{\mathrm{CISD}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} \Phi_i^a + \sum_{(ai)(bj)} C_{(ai,bj)} \Phi_{ij}^{ab} \tag{9}$$

$$C_0, C_{(ai)}, C_{(ai,bj)} \in \{C_I\} \tag{10}$$

Standard 'Technical' Trick: Second Quantization

Operators and wave functions are expressed in terms of creation and annihilation operators to implement the Slater–Condon rules for the evaluation of matrix elements $\langle \Phi_K | H_{el} | \Phi_L \rangle$ directly into the formalism.

H_{el} in second quantization (i, j, k, l are spin orbital indices):

$$\Rightarrow \qquad H_{el} = \sum_{ij} \langle \phi_i | h(1) | \phi_j \rangle a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} \langle \phi_i(1) \langle \phi_k(2) | g(1,2) | \phi_l(2) \rangle \phi_j(1) \rangle a_i^\dagger a_k^\dagger a_l a_j \quad (11)$$

CI wave function in second quantization:

$$\Psi_{el}^{\mathrm{FCI}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} a_a^\dagger a_i \Phi_0 + \sum_{(ai)(bj)} C_{(ai,bj)} a_b^\dagger a_j a_a^\dagger a_i \Phi_0 \cdots \quad (12)$$

CI Energy in Second Quantization

$$E_{el}^{\mathrm{CI}} = \left\langle \Psi_{el}^{\mathrm{CI}} \middle| H_{el} \middle| \Psi_{el}^{\mathrm{CI}} \right\rangle \tag{13}$$

$$= \sum_{ij}^{n} \underbrace{\sum_{KL} C_K^* C_L t_{ij}^{KL}}_{\gamma_{ij}} \underbrace{\langle \phi_i(1) | h(1) | \phi_j(1) \rangle}_{\equiv h_{ij}}$$

$$+ \sum_{ijkl}^{n} \underbrace{\sum_{KL} C_K^* C_L T_{ijkl}^{KL}}_{\Gamma_{ijkl}} \underbrace{\langle \phi_i(1) \langle \phi_k(2) | g(1,2) | \phi_l(2) \rangle \phi_j(1) \rangle}_{g_{ijkl}} \tag{14}$$

$$= \sum_{ij}^{n} \gamma_{ij} h_{ij} + \sum_{ijkl}^{n} \Gamma_{ijkl} g_{ijkl} \tag{15}$$

t_{ij}^{KL} or T_{ijkl}^{KL} are matrix elements of determinantal basis functions over pairs or quadruples of elementary operators $a^\dagger$ and a.

γ_{ij} are Γ_{ijkl} are density matrix elements.

Is there a better way to construct the finite-dimensional determinantal basis set in order to avoid the factorial scaling?

Coupled-Cluster — An Advanced CI-type Wave Function

Ansatz:

$$\Psi_{\mathrm{el}}^{\mathrm{CC}} = \exp\left(T\right) \Phi_{\mathrm{el}}^{\mathrm{HF}} \tag{16}$$

Excitation operator:

$$T = T_1 + T_2 + T_3 + \cdots \tag{17}$$

where

$$T_\alpha = \sum_{\underbrace{ab\cdots}_{\alpha \text{ times}}\underbrace{ij\cdots}_{\alpha \text{ times}}} \overbrace{t_{ij\ldots}^{ab\cdots}}^{\text{cluster-amplitudes}} \underbrace{\cdots a_b^\dagger a_j a_a^\dagger a_i}_{\alpha \text{ pairs } a^\dagger a} \quad \Rightarrow \quad T_1 = \sum_{ai} t_i^a a_a^\dagger a_i \tag{18}$$

Notation:

CCS ($T = T_1$), CCSD ($T = T_1 + T_2$), CCSDT ($T = T_1 + T_2 + T_3$) ,$\cdots$

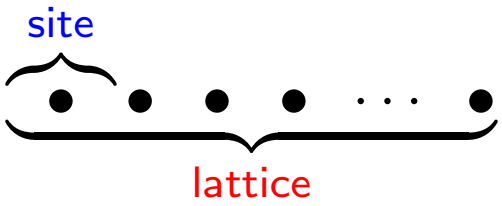
Coupled-cluster improves on truncated CI, because certain (disconnected) higher excited configurations (e.g., $t_i^a a_a^\dagger a_i t_{jk}^{bc} a_c^\dagger a_k a_b^\dagger a_j$) are included.

Is there a better way to construct the finite-dimensional determinantal basis set in order to avoid the factorial scaling?

Let's investigate FCI from a different perspective:

The (two-site) DMRG Algorithm: Terminology

- arrange all **spatial** orbitals as a one-dimensional lattice
- lattice consists of sites



(19)

- the sites of solid state physics are the orbitals in quantum chemistry
- divide lattice into system block, two single sites, environment block

(active subsystem) (explicitly treated subsystem) (complementary subsystem)

- joined systems (= complete active space, CAS) are called 'superblock'

The DMRG Algorithm: Initialization

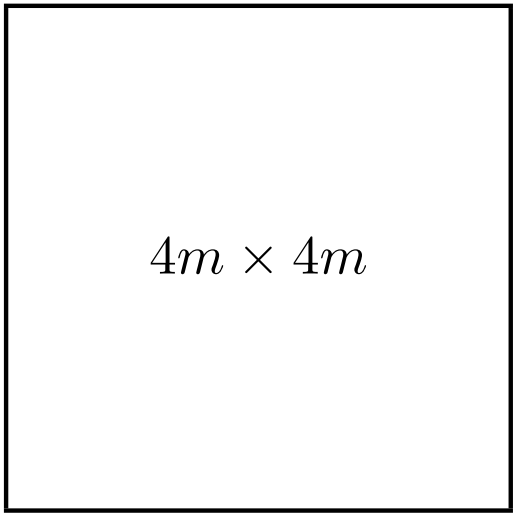
- Construct many-particle states explicitly on active subsystem

$\rightarrow$ actually: find matrix representation of elementary operators defined on this subsystem

- NB: For a total(!) system of N electrons, many-particle states with 0 to a maximum of N electrons need to be considered
- Hence, active subsystem can comprise only few orbitals (too many sites prohibitive because of factorial scaling of states)
- Find a way to increase the number of orbitals (blocking), while keeping the number of basis states on the active subsystem constant (decimation)

Pictorially: Diagonalization of the RDM

- reduced density matrix is diagonalized $\rightarrow 4m$ eigenpairs

$U =$ 

Pictorially: Diagonalization of the RDM

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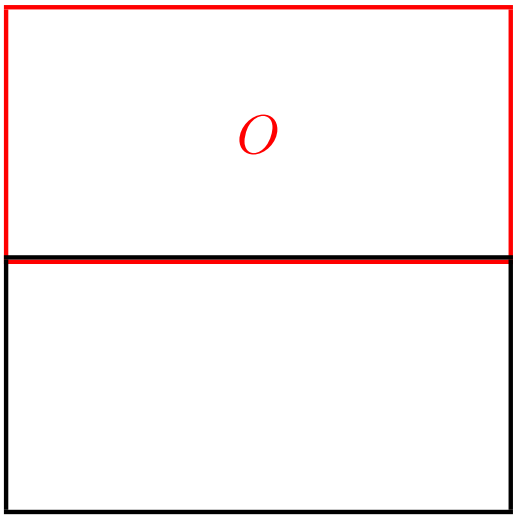
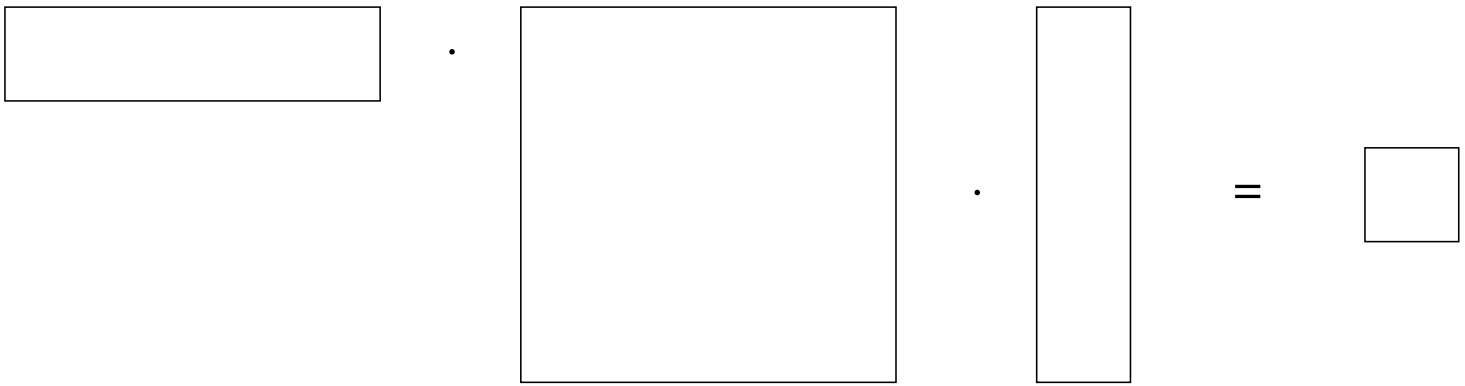
$U =$ 

- choose the m eigenvectors with the highest eigenvalues
- keep m variable to always adjust to the optimum number of relevant eigenvectors (Ö. Legeza: dynamic block-state selection DBSS)
- selected eigenvectors transform the many-particle basis of the (enlarged) system to a reduced basis

Pictorially: Renormalization of Operators

- transformation by selected eigenvectors yields new many-particle basis of the system (optimum reduced m-dimensional basis in a least-squares sense)
- operators are now transformed to the new basis, i.e. renormalized:



$$O^T \, \tilde{a}_{\text{new}} \, O \; = \; a_{\text{new}} \tag{20}$$

- columns of the transformation matrix O consist of the selected eigenvectors
- dimension of the operators is reduced from $4m$ to m

Features of the DMRG Algorithm

- DMRG is an FCI approach (in practice: CAS-CI/CAS-SCF)
- DMRG iterations increase AS orbital by orbital until the environment is completely absorbed into the system.
- Then, the iteration direction is reversed to optimize the environment representation.
- This defines a 'linear' algorithm, and explains why the orbital ordering can be important (convergence to local minima possible!).

  G. Moritz, B. A. Hess, M. Reiher, *J. Chem. Phys.* **2005** *122* 024107
- It was thought that DMRG is therefore only beneficial for pseudo-one-dimensional molecules.
- An FCI/CAS solution can be converged; but the basis cannot be completely known in terms of CSFs if DMRG shall be efficient

Determining Factors of DMRG Convergence

1. (Choice of the one-electron basis set for the representation of the molecular orbitals)
2. Size of the complete active (orbital) space (CAS)
3. Choice of the type of molecular orbitals
   (HF, NO's, localized orbitals, ..., DMRG-SCF)
4. Environment-state guess in the first sweep
   (CI-DEAS by Ö. Legeza or noise/perturbation added to RDM)
5. Ordering of orbitals (exploit entanglement measures, see below)
6. Number of renormalized subsystem states m

$\Rightarrow$ **All of these parameters must be documented in a report on DMRG results !**

S. Keller, M. Reiher, Chimia 68 **2014** 200-203 [arXiv: 1401.5497]

Instead of standard CI-type calculations by diagonalization/projection

$$\Psi_{el} = \sum_{i_1 i_2 \cdots i_n} C_{i_1 i_2 \cdots i_n} \; |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_n\rangle \tag{21}$$

construct CI coefficients from correlations among orbitals

$$\Psi_{el} = \sum_{i_1 i_2 \cdots i_n} C_{i_1 i_2 \cdots i_n} \; |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_n\rangle \tag{22}$$

$\Longrightarrow$ tensor construction of expansion coefficients

Some Early Tensor Network (TN) Approaches

... for spin Hamiltonians developed:

- 1-dimensional TN: **Matrix Product States** (MPS) / DMRG

  S. R. White, *Phys. Rev. Lett.* **1992** *69* 2863

  S. Römmer, S. Ostlund, *Phys. Rev. Lett.* **1995** *75* 3537

- 2-dimensional TN: **Projected Entangled Pair States** (PEPS)

  F. Verstraete, M. M. Wolf, D. Perez-Garcia, J. I. Cirac *PRL* **2006** *96* 220601

- higher-dimensional TN:
  Multiscale Entanglement Renormalization Ansatz (MERA)

  M. Aguado, G. Vidal, *Phys. Chem. Rev.* **2008** *100* 070404

MPS & DMRG

- Structure of White's DMRG wave function: Matrix Product States (MPS)

  S. Römmer, S. Ostlund, *Phys. Rev. Lett.* **1995** *75* 3537

$$\Psi_{el}^{\mathrm{MPS}} = \sum_{i_1 i_2 \cdots i_n} \left[A^{[i_1]} \dots A^{[i_n]} \right] |i_1 \otimes i_2 \otimes \cdots \otimes i_n\rangle \tag{23}$$

- **DMRG algorithm defines a protocol for the iterative improvement of the matrices A^{i_j} by using the reduced density matrix (RDM) for the AS of the total system.**
- Transformation matrices $A^{[i]}$ represent the change of the many-electron basis when adding to the *active subsystem* (AS) states on a single orbital taken from the *environment*.
- In the finite-CAS DMRG, the first and last matrices $A^{[i_1]}$ and $A^{[i:n]}$, resp., are actually vectors (of length 4 for spatial orbitals).

DMRG with Matrix Product States (MPS) and Matrix Product Operators (MPO)

Our new MPO-based DMRG program: QCMaquis

Download: http://www.reiher.ethz.ch/software/maquis.html

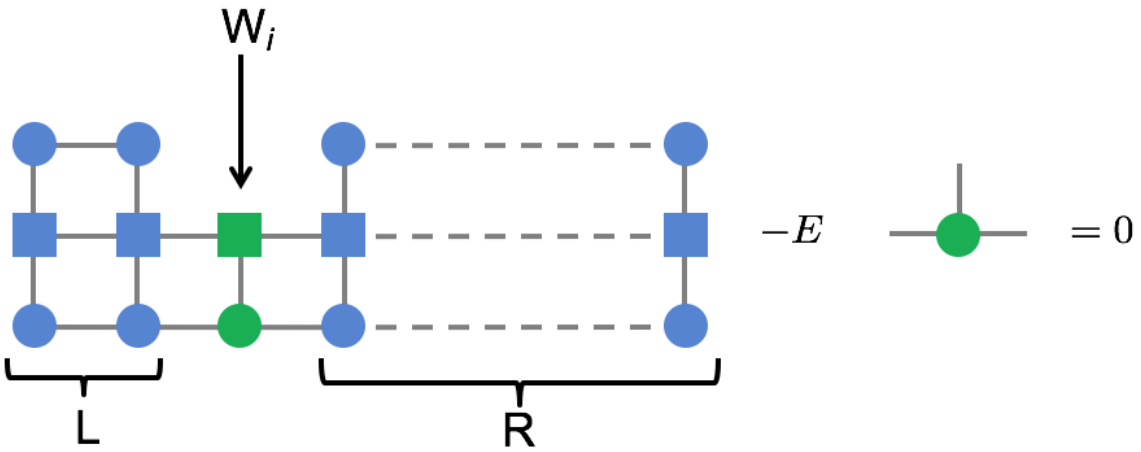
$$|\Psi\rangle = \sum_{\boldsymbol{\sigma}} c_{\boldsymbol{\sigma}} |\boldsymbol{\sigma}\rangle \quad \rightarrow \quad |\Psi\rangle = \sum_{\boldsymbol{\sigma}} \sum_{a_1,\ldots,a_{n-1}} M^{\sigma_1}_{1a_1} M^{\sigma_2}_{a_1 a_2} \cdots M^{\sigma_n}_{a_{n-1}1} |\boldsymbol{\sigma}\rangle$$

$$\widehat{\mathcal{W}} = \sum_{\boldsymbol{\sigma},\boldsymbol{\sigma'}} w_{\boldsymbol{\sigma}\boldsymbol{\sigma'}} |\boldsymbol{\sigma}\rangle\langle\boldsymbol{\sigma'}| \quad \rightarrow$$

$$\widehat{\mathcal{W}} = \sum_{\boldsymbol{\sigma}\boldsymbol{\sigma'}} \sum_{b_1,\ldots,b_{n-1}} W^{\sigma_1\sigma'_1}_{1b_1} \cdots W^{\sigma_l\sigma'_l}_{b_{l-1}b_l} \cdots W^{\sigma_n\sigma'_n}_{b_{n-1}1} |\boldsymbol{\sigma}\rangle\langle\boldsymbol{\sigma'}|$$

S. Keller, M. Dolfi, M. Troyer, M. Reiher, J. Chem. Phys. 143, 244118 (2015)

Local part of the eigenvalue problem



$$\sum_{\sigma_i'} \sum_{a_{i-1}' a_i'} \sum_{b_{i-1} b_i} L_{b_{i-1}}^{a_{i-1},a_{i-1}'} W_{b_{i-1},b_i}^{\sigma_i,\sigma_i'} R_{b_i}^{a_i,a_i'} M_{a_{i-1}',a_i'}^{\sigma_i'} - E M_{a_{i-1},a_i}^{\sigma_i'} = 0$$

- one-site DMRG
- $\mathbf{M}^{\sigma i}$ has dimension $4m^2$

↓ rewrite $\mathbf{M}^{\sigma i}$ as vector v

$$H\nu - E\nu = 0$$

U. Schollwöck, *Ann. Phys.* (**2011**), *326*, 96.

DMRG – ground state search

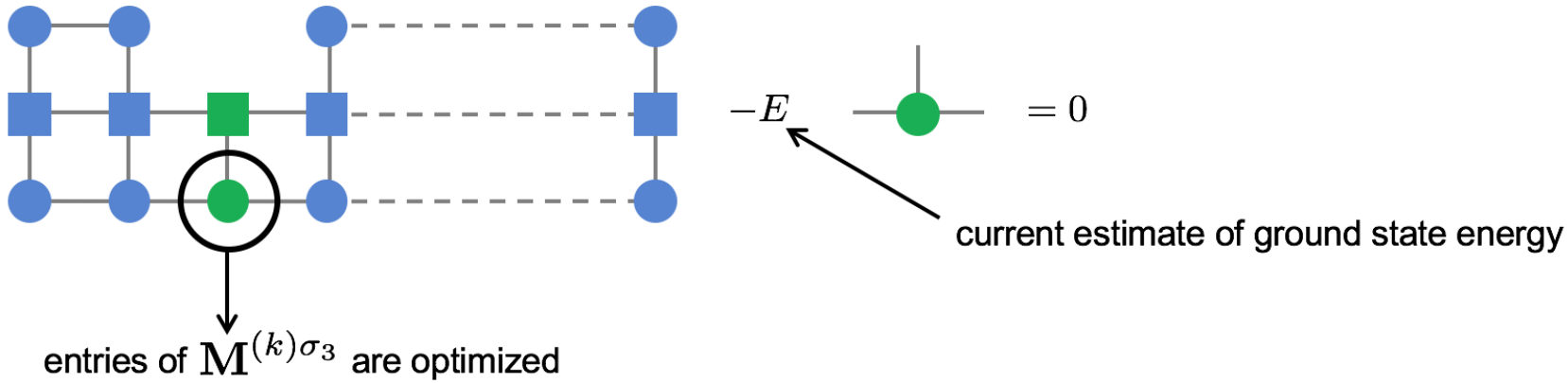
Find optimal approximation to $E^{(k)} = \frac{\langle \Psi^{(k)} | \hat{H} | \Psi^{(k)} \rangle}{\langle \Psi^{(k)} | \Psi^{(k)} \rangle}$

by optimizing the entries in $\mathbf{M}^{(k)\sigma_i}$.

Extreme sparsity requires:

- sparse, iterative eigensolvers that aim at the ground state (Jacobi-Davidson)
- in general an iterative procedure with decimation steps

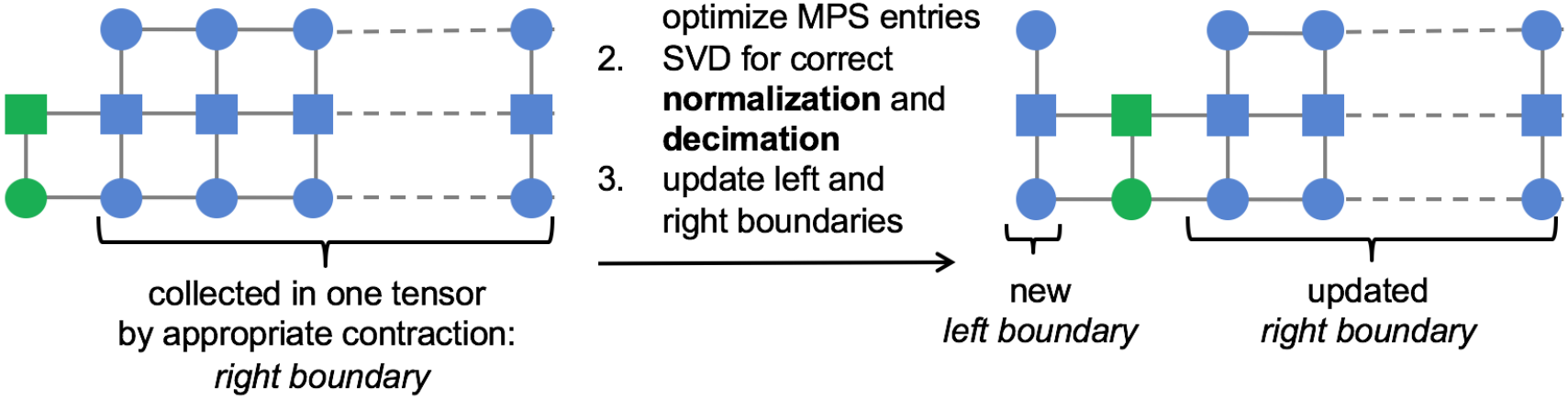
Graphical representation of the standard eigenvalue problem:

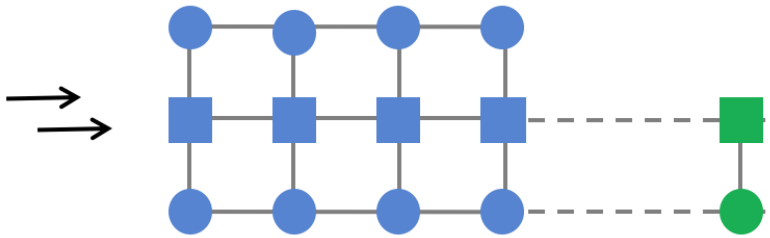


U. Schollwöck, *Ann. Phys.* (**2011**), *326*, 96.

DMRG – ground state search

Sketch of sweep algorithm:





revert **sweep** direction and continue back and forth until convergence

- decimation step **reduces scaling from exponential to polynomial**
- full-CI solution is approximated in a least-squares sense

U. Schollwöck, *Ann. Phys.* (**2011**), *326*, 96.

Does DMRG Work for Compact Molecules?

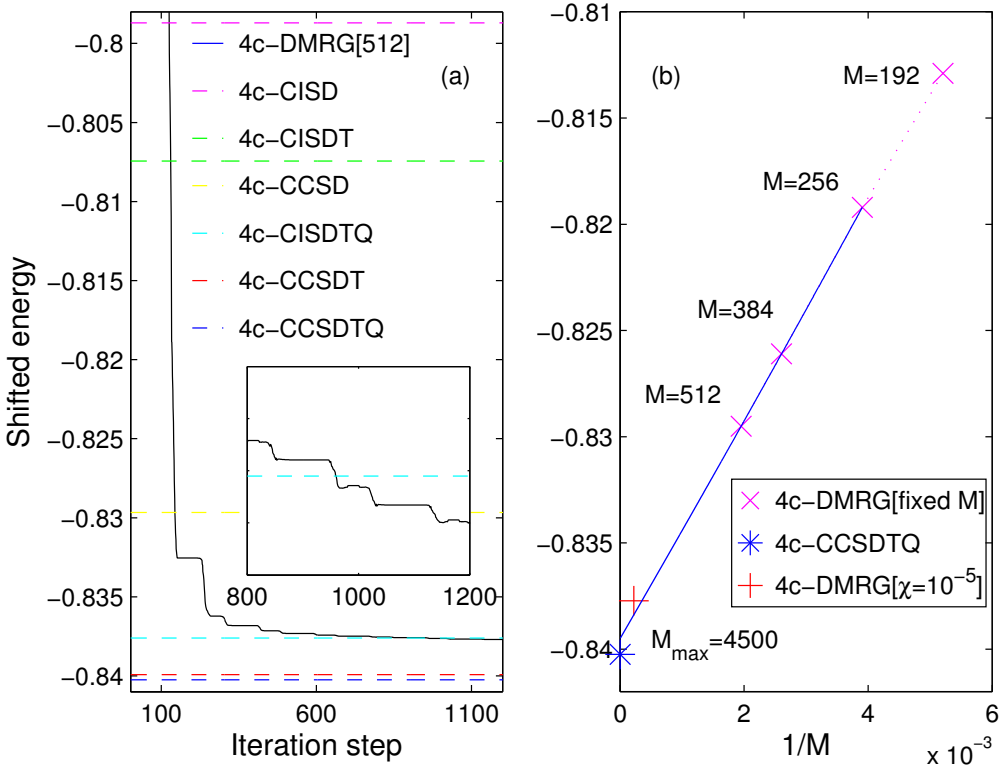
- Original 'opinion' in the DMRG community:
  Works only for pseudo-one-dimensional, non-compact systems!
- Test for a mononuclear transition metal system CAS(10,10): CoH

m	$E_{singlet}/\mathrm{E}_h$	$E_{triplet}/\mathrm{E}_h$	$\Delta E/\mathrm{kJmol}^{-1}$
64	−1381.952 054	−1381.995 106	**113.03**
76	−1381.952 063	−1381.995 109	113.02
91	−1381.952 070	−1381.995 110	113.00
109	−1381.952 073	−1381.995 110	112.99
CAS(10,10)	−1381.952 074	−1381.995 110	**112.99**
CASPT2(10,10)	−1382.189 527	−1382.241 333	130.57
DFT/BP86	−1383.504 019	−1383.585 212	213.1
DFT/B3LYP	−1383.202 267	−1383.279 574	203.0

original work to propose DMRG for compact, strongly correlated molecules:

K. Marti, I. Malkin Ondik, G. Moritz, M. Reiher, *J. Chem. Phys 128* (2008) 014104

'Fully-Relativistic' Four-Component DMRG: TlH



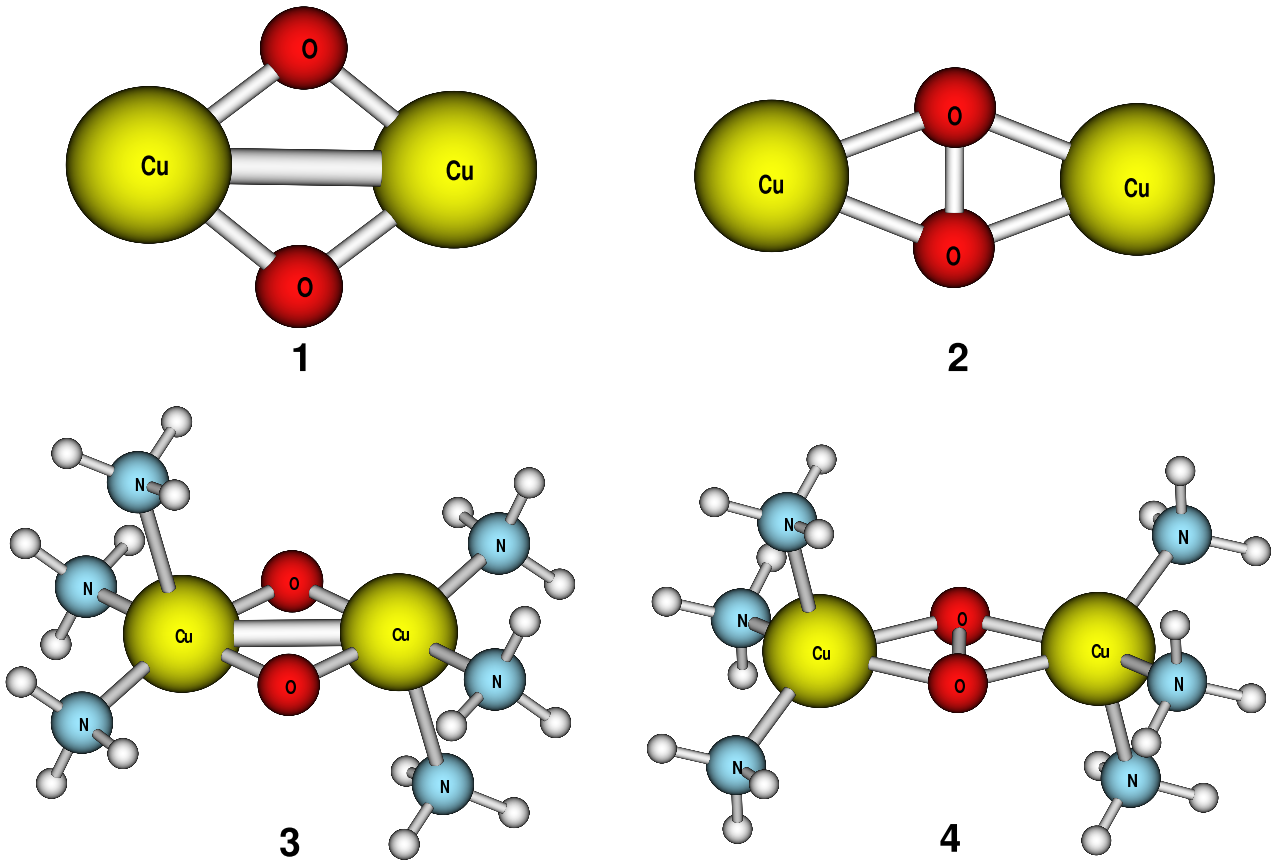
S. Knecht, Ö. Legeza, M. Reiher, *J. Chem. Phys 140* (2014) 041101

method	r_e Å	ω_e $\frac{1}{cm}$	$\omega_e x_e$ $\frac{1}{cm}$
4c-DMRG(14,94)[512]	1.873	1411	26.64
4c-CISD(14,94)	1.856	1462	23.11
4c-CISDTQ(14,94)	1.871	1405	20.11
4c-MP2(14,94)	1.828	1546	47.27
4c-CCSD(14,94)	1.871	1405	19.36
4c-CCSD(T)(14,94)	1.873	1400	23.52
4c-CCSDT(14,94)	1.873	1398	22.28
4c-CCSDT(Q)(14,94)	1.873	1397	21.01
4c-CCSDTQ(14,94)	1.873	1397	22.24
CCSD(T)[a]	1.876	1385	n/a
CCSD(T)[b]	1.877	1376	n/a
MRD-CI[c]	1.870	1420	n/a
SO-MCQDPT[d]	1.876	1391	29.42
experiment[e]	1.872	1390.7	22.7

[a] 4c-DC CCSD(T) [14 electrons], Visscher et al. 2001.
[b] 4c-DC-Gaunt CCSD(T) [36 electrons], Visscher et al. 2001.
[c] GRECP spin-orbit MRD-CI, Titov et al. 2000.
[d] model-core potential spin-orbit MCQDPT, Zeng et al. 2010.
[e] experimental data.

The Cu_2O_2-Torture Track

- Standard CASSCF fails for large CASs relevant in polynuclear clusters
- Example: two different isomers of dinuclear copper clusters



C. J. Cramer, M. Włoch, P. Piecuch, C. Puzzarini, L. Gagliardi *J. Phys. Chem. A 110* (2006) 1991

Torture Track: $[Cu_2O_2]^{2+}$

Ref.,method	E_{bisoxo}	E_{peroxo}	ΔE
'Standard' methods			
A),CASSCF(16,14)	−541.50307	−541.50345	1
A),CASPT2(16,14)	−542.06208	−542.06435	6
A),bs-B3LYP	−544.19419	−544.27844	221
B),RASPT2(24,28)			120
Previously published DMRG energies			
C),DMRG(26,44)[800]	−541.46779	−541.49731	78
D),DMRG(26,44)[128]	−541.47308	−541.51470	109
E),DMRG(32,62)[2400]	−541.96839	−542.02514	149
F),DMRG(28,32)[2048]-SCF	−541.76659	−541.80719	107
F),DMRG(28,32)[2048]-SCF/CT			113
our latest DMRG results with QIT, without noise			
G), DMRG(26,44)[256/1024/10^{-5}]	−541.53853	−541.58114	112

A) C. J. Cramer *et al.*, *J. Phys. Chem. A 110* (2006) 1991; B) P. A. Malmqvist *et al.*, *J. Chem. Phys 128* (2008) 204109; C) K. Marti, *et al.*, *J. Chem. Phys 128* (2008) 014104; D) K. Marti, M. Reiher, *Z. Phys. Chem. 224* (20109 583; E) Y. Kurashige, T. Yanai, *J. Chem. Phys. 130* (2009) 234114; F) T. Yanai *et al.*, *J. Chem. Phys. 132* (2010) 024105; **G) G. Barcza** *et al.*, *Phys. Rev. A 83* **(2011) 012508**

Other Options: Tensor Network States (TNS)

$$\Psi_{el}^{\mathrm{TNS}} = \sum_{i_1 i_2 \ldots i_n} \prod_{i}^{n} \prod_{j \leq i} f_{ij}^{I[i]I[j]} \underbrace{|i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_n\rangle}_{|I\rangle} \tag{24}$$

- Idea: Rewrite CI coefficient tensor by reducing number of variational parameters (still obtain qualitatively correct wave function).

- **TNS originally proposed for simple** *Spin Hamiltonians*:
  - String-Bond States

N. Schuch, M. Wolf, F. Verstraete, J. I. Cirac, *Phys. Rev. Lett.* **2008** *100* 040501

  - Entangled-Plaquette States

F. Mezzacapo, N. Schuch, M. Boninsegni, J. I. Cirac **2009** arXiv:0905.3898v3

  - Correlator-Product States

H. J. Changlani, J. M. Kinder, C. J. Umrigar, G. K.-L. Chan, **2009** arXiv:0907.4646v1

Complete-Graph Tensor Network States (CG-TNS)

- First implementation of TNS for full quantum-chemical Hamiltonian
- Considering *all* pairs of parameters f_{ij}: CG-TNS
- Parameters optimized with Monte Carlo techniques
- First studied for methylene and ozone; S/T splitting in ozone:

	$\mathrm{E}_{\mathrm{S}=0}/E_h$	$\mathrm{E}_{\mathrm{S}=1}/E_h$	$\Delta\mathrm{E}/\mathrm{kcalmol}^{-1}$
HF	−224.282 841	−224.357 167	46.6
CASCI	−224.384 301	−224.416 172	20.0
CG-TNS	−224.381 648	−224.412 775	19.5

K. H. Marti, B. Bauer, M. Reiher, M. Troyer, F. Verstraete, New J. Phys. *12* **2010** 103008

Current Status of TNS in Chemistry

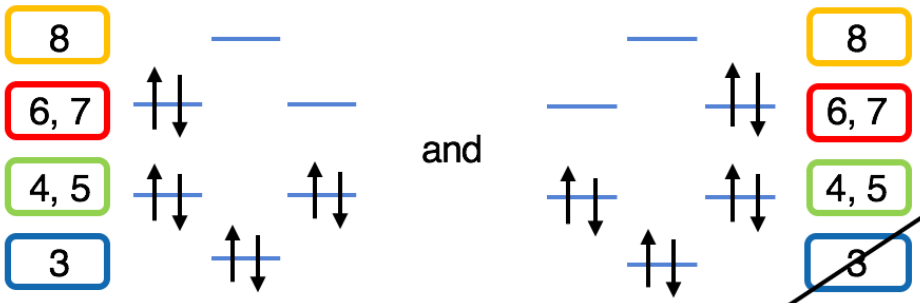
- tree tensor network states (TTNS; Legeza, Chan, ...)
- general problem: efficient optimization schemes required
- most promising solution: utilize principles of the DMRG algorithm (most efficiently exploited in an MPS/MPO framework)
- we extended CG-TNS to 3-site correlators (explosion of parameters!)

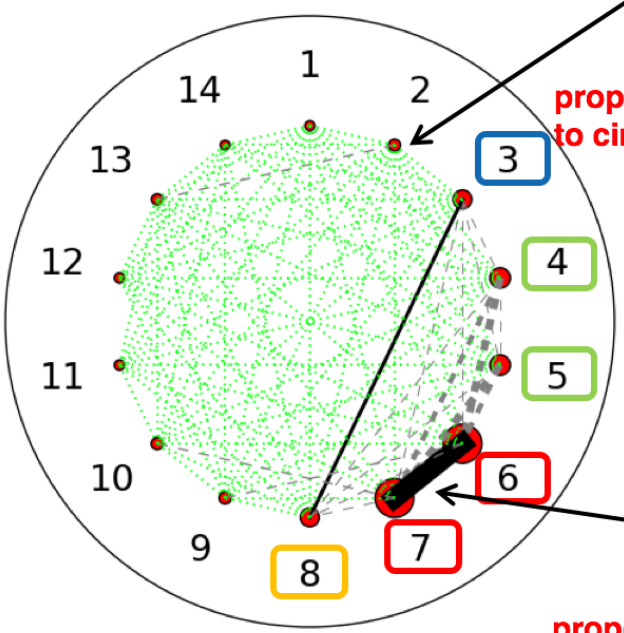
  A. Kovyrshin, M. Reiher, *NJP 18* (2016) 113001
- ... however, it can only be made accurate and efficient if entanglement-based correlator selection is introduced

  A. Kovyrshin, M. Reiher, *J. Chem. Phys. 147* (2017) 214111.
- unique features of (T)TNS: still to be demonstrated at an example that cannot be solved by standard approaches

Orbital Entanglement Relates to Electron Correlation

dioxygen $^1\Delta_g$





proportional to circle area

proportional to thickness of connecting lines

C.J. Stein, M. Reiher, *Chimia* **2017**, *4*, 170.
arXiv: 1702.00450

deviation from a pure state α (—, ↑, ↓, ↑↓) is measured by **single-orbital entropy**

$$s_i(1) = -\sum_{\alpha=1}^{4} w_{\alpha,i} \ln w_{\alpha,i}$$

$w_{\alpha,i}$: eigenvalue of the reduced one-orbital density matrix for orbital *i*

analogously for two orbitals: **two-orbital entropy**

$$s_{ij}(2) = -\sum_{\alpha=1}^{16} w_{\alpha,ij} \ln w_{\alpha,ij}$$

$w_{\alpha,ij}$: eigenvalue of the reduced two-orbital density matrix for orbitals *i, j*

mutual information

$$I_{ij} = \frac{1}{2}\left[s_i(1) + s_j(1) - s_{ij}(2)\right](1 - \delta_{ij})$$

How to cope with the active space selection problem ?

Can one choose the CAS in an automated way?

Exploit Two Advantages of DMRG for the CAS choice

- DMRG is iterative
- DMRG can handle large CAS sizes

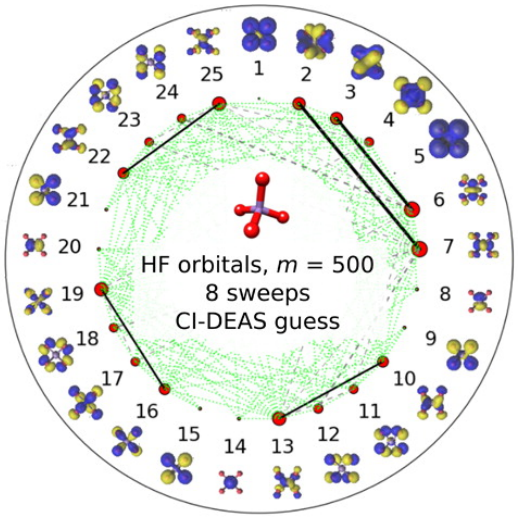
$\Longrightarrow$ ... toward an automated CAS determination

requires selection criterion ...

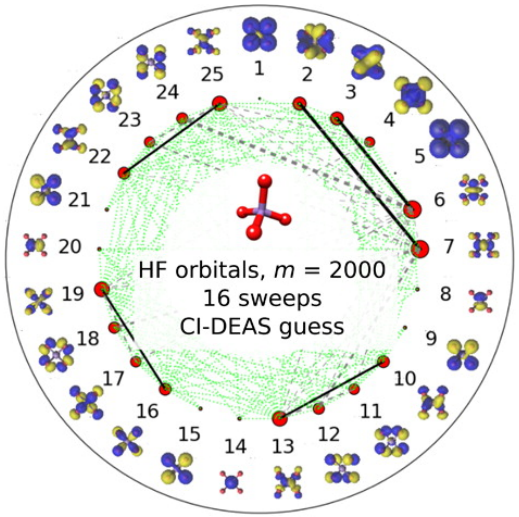
Automated CAS selection? Black-box CASSCF?

... reduce the human time by automatizing manual selection (if manual selection fails, the automated protocol will have a problem, too)

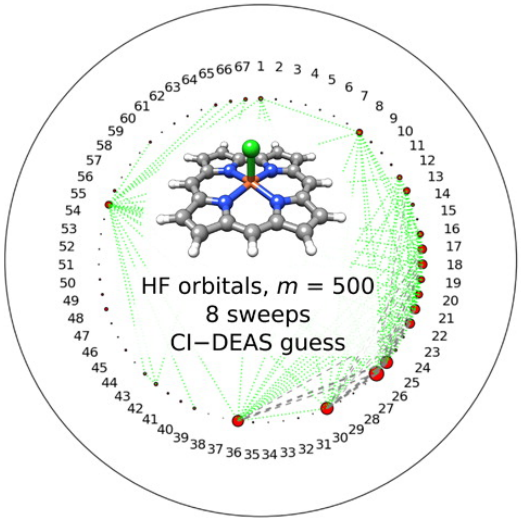
Partially converged entanglement information is sufficient



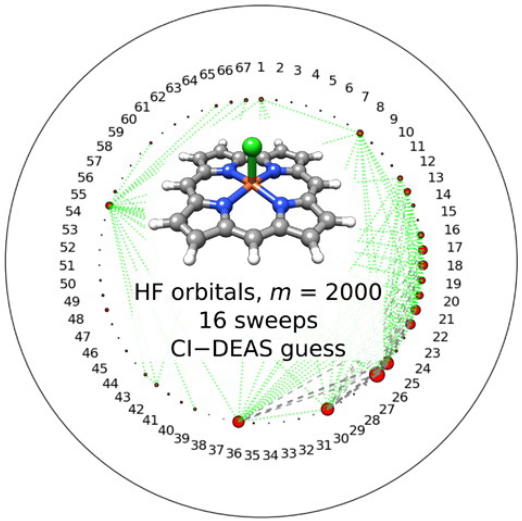
E = -1449.290301 E_H



E = -1449.302426 E_H



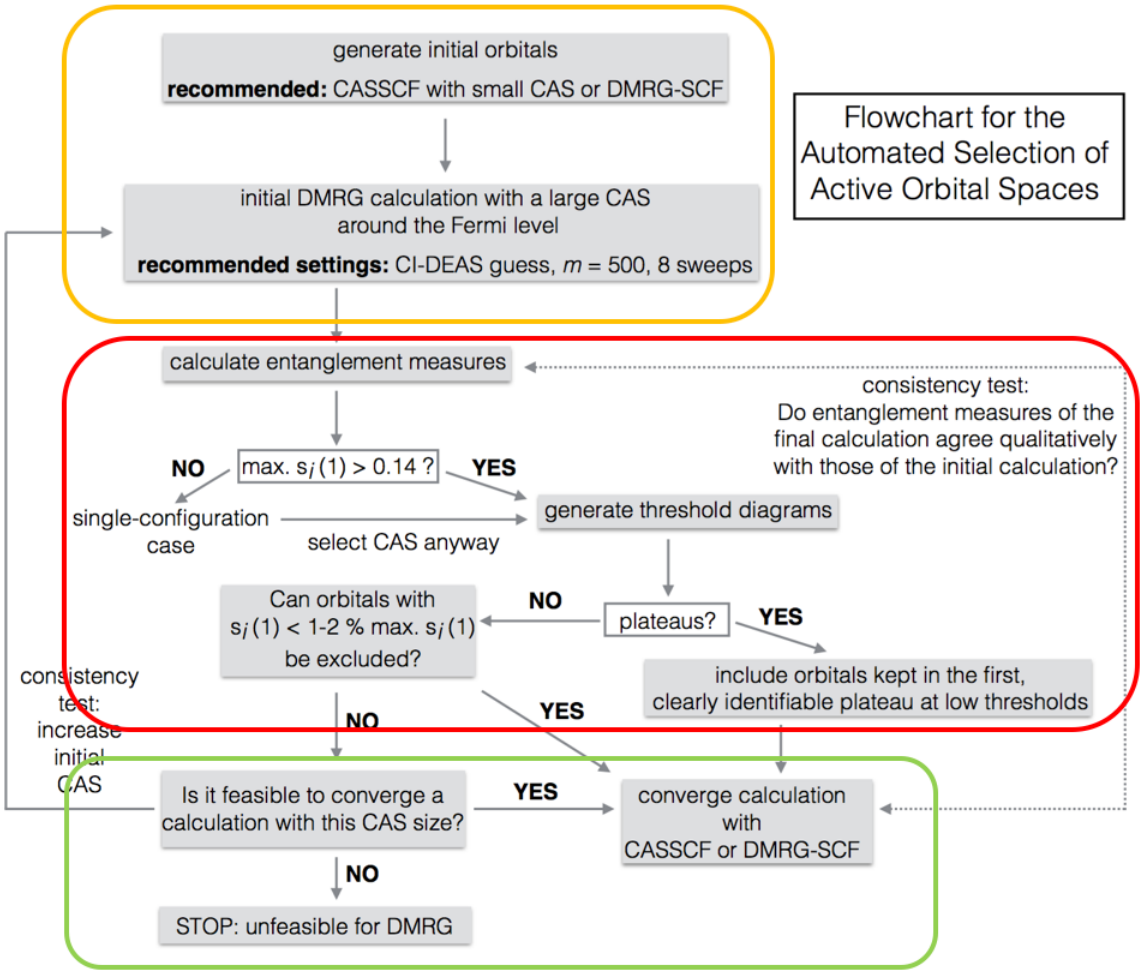
E = -2665.877397 E_H



E = -2665.878045 E_H

C. J. Stein, M. Reiher, J. Chem. Theory Comput, **2016**, 12, 1760–1771.

Automated Orbital Selection Algorithm



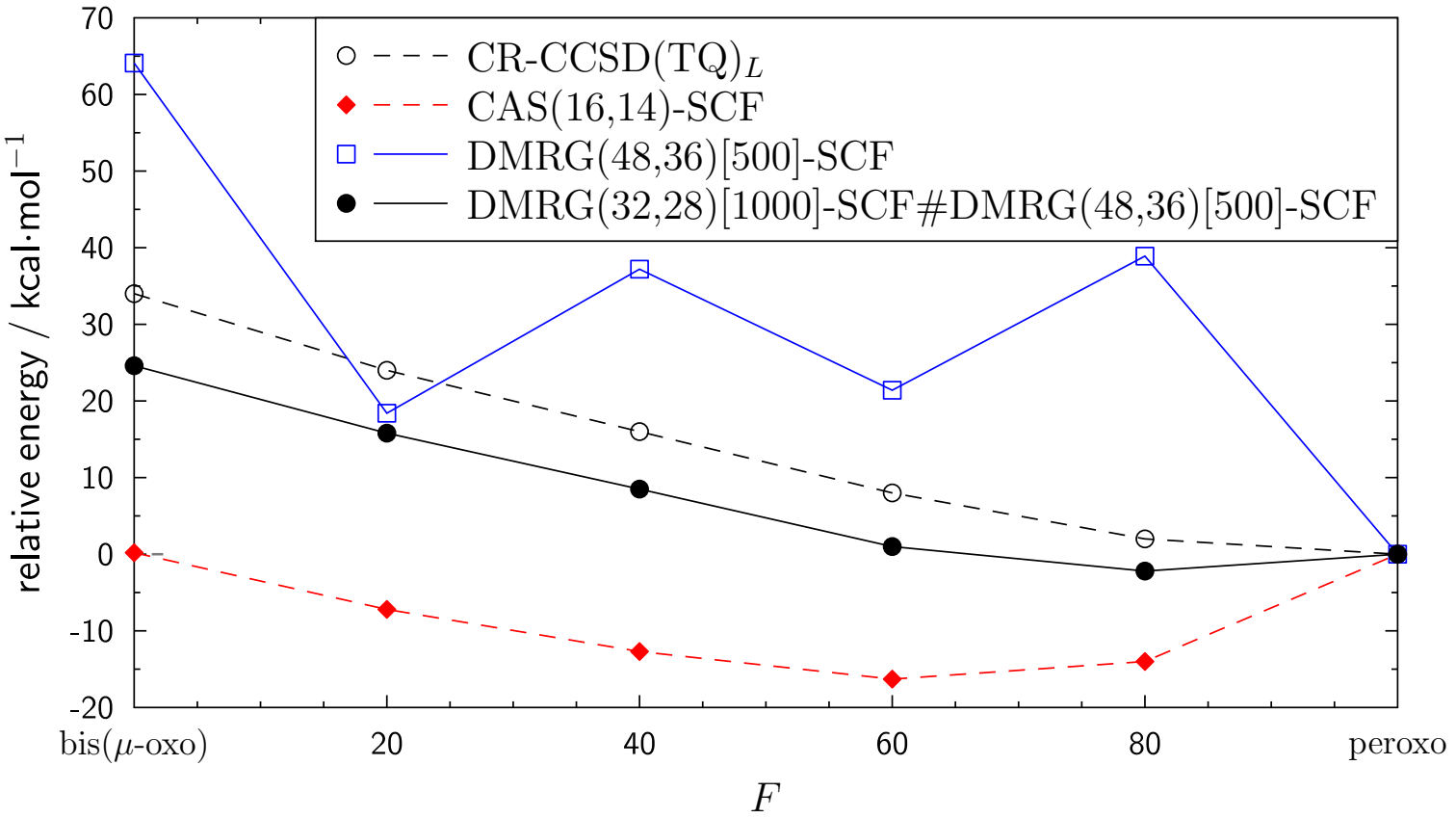
Flowchart for the Automated Selection of Active Orbital Spaces

recipe

1. **partially converged DMRG calculation** with a large number of active orbitals
2. **identify "important" orbitals**
3. **converge the calculation** with only "important" orbitals

Stein, C. J., Reiher, M. *JCTC*, **2016**, *12*, 1760.

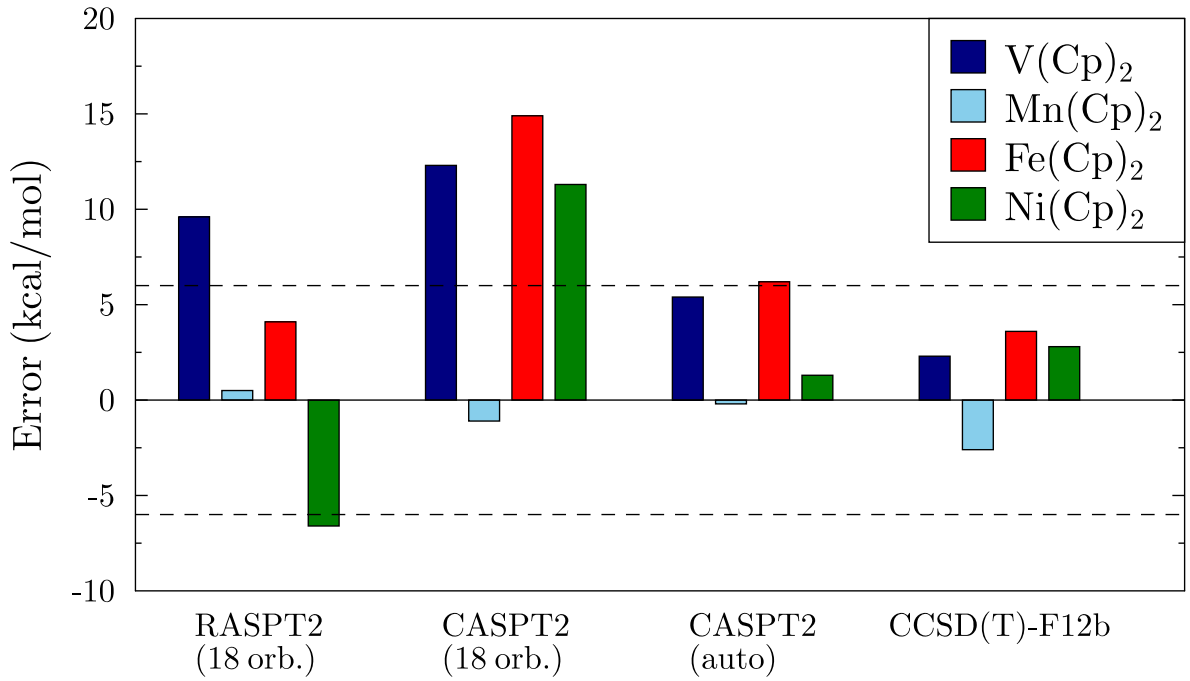
The $Cu_2O_2^{2+}$ Torture Track



- Coupled cluster and CASSCF data from C. J. Cramer *et al.*, *JPC A* (**2006**), 110, 1991.
- discrepancy to coupled-cluster result can be explained by (still) missing dynamical correlation C. J. Stein, M. Reiher, J. Chem. Theory Comput, **2016**, 12, 1760–1771.

Need dynamic correlation for quantitative reference data!

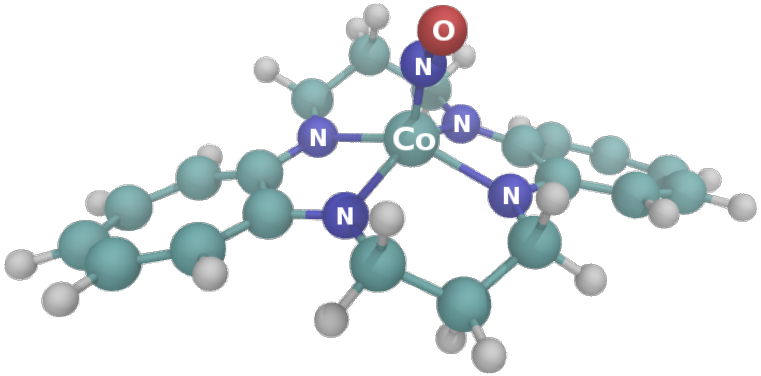
Metallocene Double Dissociation Energies



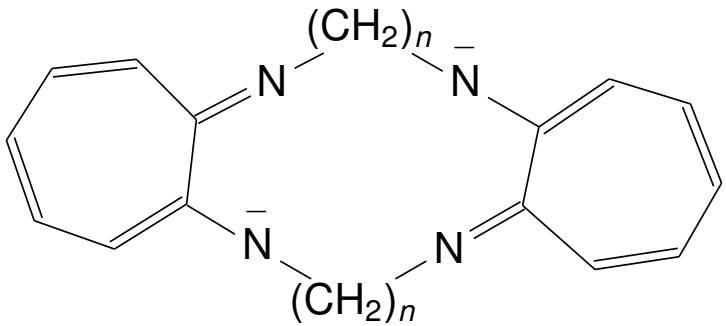
- Double dissociation energies are around 600 kcal/mol!

C. J. Stein, V. von Burg, M. Reiher, J. Chem. Theory Comput, *12* **2016**, 3764.

Spin states of a cobalt tropocoronand complex



[Co(TC-3,3)(NO)]



TC-n,n

[Co(TC-n,n)(NO)]

- $n = 4$-6 – diamagnetic
- $n = 3$ – paramagnetic or diamagnetic?

Before Ref. 5: paramagnetic

Ref. 5: diamagnetic (from DFT and new experimental results)

calls for an additional investigation!

L. Freitag, S. Knecht, C. Angeli, M. Reiher, JCTC *13* **2017**, 451.)

[5] Hopmann et al., Inorg. Chem. 2015, 54, 7362

[Co(TC-3,3)(NO)] – spin state energetics

CD-DMRG-NEVPT2[512] (22,22)/ANO-RCC-VTZP (1147 basis functions)

S_0-T_1 gap of [Co(TC-3,3)(NO)] in eV:

SC-NEVPT2	DMRG-SCF	OLYP[5]	PW91[5]	B3LYP-D3[5]
1.52	1.67	1.03	1.09	0.45

- SC-NEVPT2 confirms the singlet ground state prediction of DFT
- DFT energies significantly lower – OLYP and PW91 energies closest
- SC-NEVPT2 not far off from DMRG-SCF
  - dynamic correlation well covered in large (22,22) active space?

L. Freitag, S. Knecht, C. Angeli, M. Reiher, JCTC (2016) *13* **2017**, 451.

[5] Hopmann et al., Inorg. Chem. 2015, 54, 7362

K. Bourzac, C&EN, 2017, 95 (43), pp 27-31, October 30, 2017

So, what are the problems that might be solved?

Depends on the quantum algorithms that allow for exponential or high-order polynomial speed-up ...

Density matrices are not easily accessible

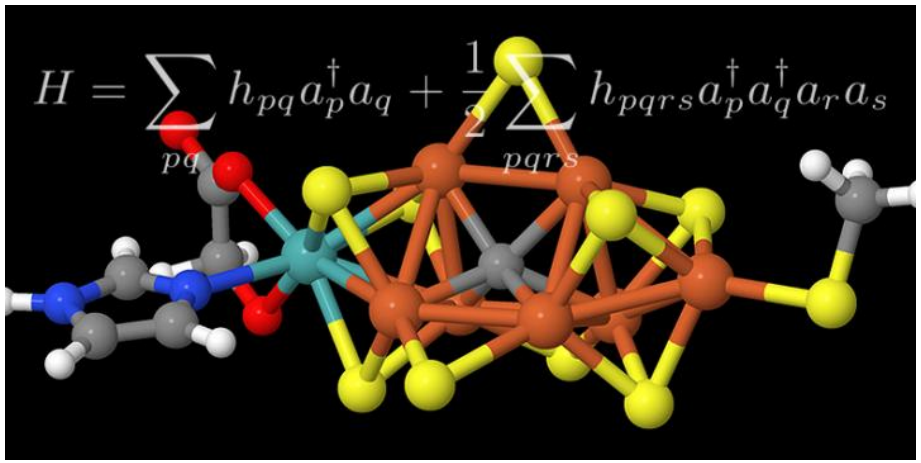
$\rightarrow$ focus on energies for the time being
(specifically, trotterization on universal quantum computer)

$\Rightarrow$ study reaction mechanisms and questions of molecular design
(provided that molecular structures can be obtained from somewhere - usually DFT optimizations)

Elucidating reaction mechanisms on quantum computers

In 2014, Matthias Troyer stepped into my office: Are there applications of moderately sized quantum computers (say, 200 logical qubits for state representation) in chemistry? $\rightarrow$ static electron correlation

My choice was the iron-sulfur active site of nitrogenase:



Rigorous resource estimates (excluding state preparation):
For this model structure of the resting state, we obtained integrals to parametrize the second-quantized Coulomb Hamiltonian for some electronic states in a Hartree-Fock orbital basis.

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, PNAS 114 (2017) 7555-7560.

Elucidation of Nitrogenase's mode of action

from air accessible to plants, the mechanism of nitrogen fixation at FeMoco is not known. Experiments have not yet been able to provide sufficient details on the chemical mechanism, and theoretical attempts are hampered by intrinsic methodological limitations of traditional quantum chemical methods.

Quantum Chemical Methods for Mechanistic Studies

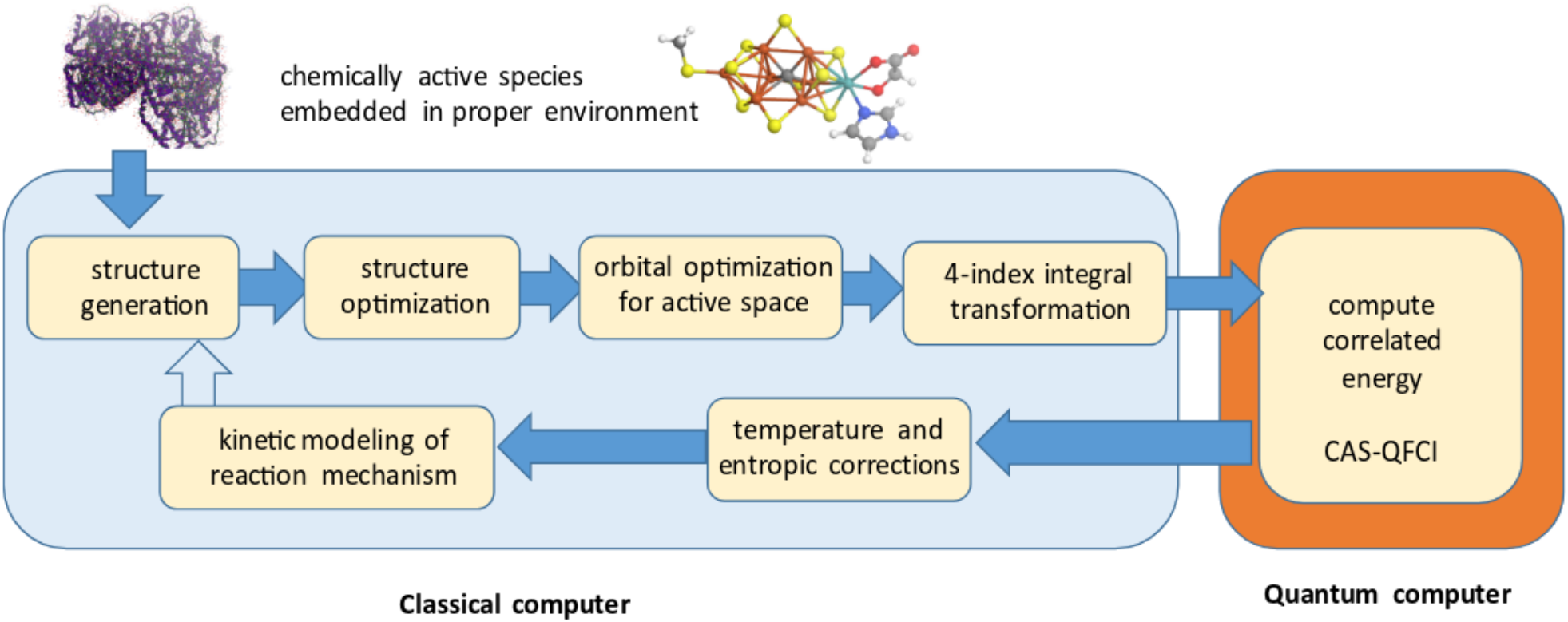
At the heart of any chemical process is its mechanism, the elucidation of which requires the identification of all relevant stable intermediates and transition states. In general, a multitude of charge and spin states need to be explicitly calculated in search of the relevant ones that make the whole chemical process viable. Such a mechanistic exploration can lead to thousands of elementary reaction steps (25) whose reaction energies must be reliably calculated. In the case of nitrogenase, numerous protonated intermediates of dinitrogen-coordinating FeMoco and subsequently reduced intermediates in different charge and spin states are feasible and must be assessed with respect to their relative energy. Especially, kinetic modeling poses tight limits on the accuracy of activation energies entering the argument of exponentials in rate expressions.

For nitrogenase, an electrostatic quantum mechanical/molecular mechanical (QM/MM) model (26) that captures the embedding of FeMoco into the protein pocket of nitrogenase can properly account for the protein environment. Accordingly, we consider a structural model for the active site of nitrogenase (Fig. 1, *Right*) carrying only models of the anchoring groups of the protein, which represents a suitable QM part in such calculations. To study this bare model is no limitation, as it does not at all affect our feasibility analysis (because electrostatic QM/MM embedding will not change the number of orbitals considered for the wave function construction). We carried out (full) molecular structure optimizations with DFT methods of this FeMoco model in different charge and spin states to avoid basing our analysis on a single electronic structure. Although our FeMoco model is taken from the resting state, binding of a small molecule such as dinitrogen, dihydrogen, diazene, or ammonia will not decisively change the complexity of its electronic structure.

The Born–Oppenheimer approximation assigns an electronic energy to every molecular structure. The accurate calculation of this energy is the pivotal challenge, here considered by quantum computing. Characteristic molecular structures are optimized to provide local minimum structures indicating stable intermediates and first-order saddle points representing transition structures. The electronic energy differences for elementary steps that connect two minima through a transition structure enter expressions for rate constants by virtue of Eyring's absolute

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, PNAS 114 (2017) 7555-7560.

QComputing replaces the exact diagonalization step



M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, PNAS 114 (2017) 7555-7560.

Be aware of competitors in classical computing!

Exact Diagonalization Methods in Chemistry. If the frontier orbital region around the Fermi level of a given molecular structure is dense, as is the case in π-conjugated molecules or open-shell transition metal complexes (such as FeMoco), then so-called strong static electron correlation plays a decisive role already in the ground state. Static electron correlations are even more pronounced for electronically excited states relevant in photophysical and photochemical processes such as light harvesting for clean energy applications. Such situations require multiconfigurational methods of which the complete-active-space self-consistent-field (CASSCF) approach has been established as a well-defined model that also serves as the basis for more advanced approaches (29). CAS-type approaches require the selection of orbitals for the CAS, usually from those around the Fermi energy, which can be automatized (30–33). Although CAS-type methods well account for static electron correlation, the remaining dynamic correlation is decisive for quantitative results. A remaining major drawback of exact-diagonalization schemes therefore is to include the contribution of all neglected virtual orbitals.

CASSCF is traditionally implemented as an exact diagonalization method, which limits its applicability to 18 electrons in 18 (spatial) orbitals, because of the steep scaling of many-electron basis states with the number of electrons and orbitals (34). The polynomially scaling density matrix renormalization group (DMRG) algorithm (35) can push this limit to about 100 spatial orbitals; this, however, also comes at the cost of an iterative procedure whose convergence for strongly correlated molecules is, due to the matrix product state representation of the electronic wave function, neither easy to achieve nor guaranteed.

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, PNAS 114 (2017) 7555-7560.

Quantitative data requires dynamic correlation!

Ways Quantum Computers Will Help Solve These Problems. Molecular structure optimizations are commonly found with standard DFT approaches. DFT-optimized molecular structures are, in general, reliable, even if the corresponding energies are affected by large uncontrollable errors. The latter problem can be solved by a quantum computer that implements a multiconfigurational wave function model to access truly large active orbital spaces. The orbitals for this model do not necessarily need to be optimized, as natural orbitals can be taken from an unrestricted Hartree–Fock (36) or small-CAS CASSCF calculation. The missing dynamic correlation can then be implemented in a "perturb-then-diagonalize" fashion before the quantum computations start or in a "diagonalize-then-perturb" fashion, where the quantum computer is used to compute the higher-order reduced density matrices required. The former approach, i.e., built-in dynamic electron correlation, is considerably more advantageous, as no wave function-derived quantities need to be calculated. One option for this approach is, for example, to consider dynamic correlation through DFT that avoids any double counting effects by virtue of range separation, as has already been successfully studied for CASSCF and DMRG (37, 38). Fig. 2 presents a flowchart that describes the steps of a quantum computer-assisted chemical mechanism exploration. Moreover, the quantum computer results can be used for the validation and improvement of parametrized approaches such as DFT to improve on the latter for the massive prescreening of structures and energies.

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, PNAS 114 (2017) 7555-7560.

Recall ...

We set out to study possible applications of quantum computing on moderately sized machines
(still requiring thousands/millions physical qubits for error correction)

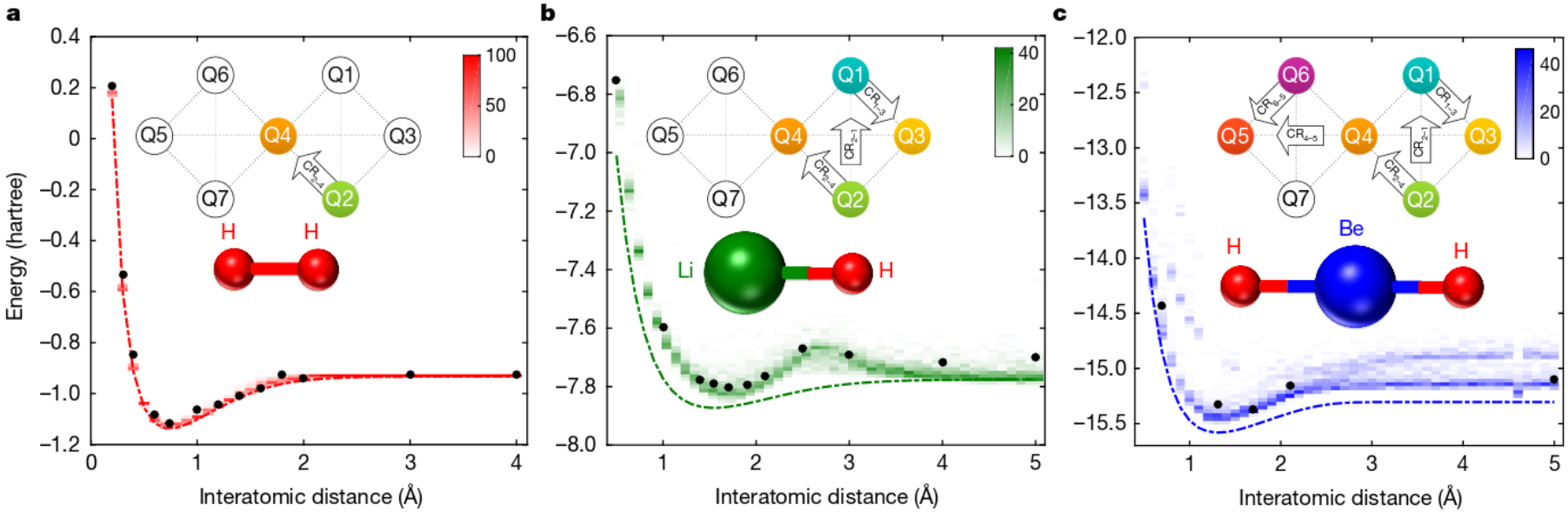
This choice introduces a distinction between static and dynamic correlation ...

$\rightarrow$ and is therefore the cause of all trouble

$\Rightarrow$ **If we would have a quantum computer with, say, a few thousands logical qubits than that could be a game changer in chemistry.**

Let's have a look at current state of experimentation

Take the IBM experiment published in 2017 in Nature as an example ...



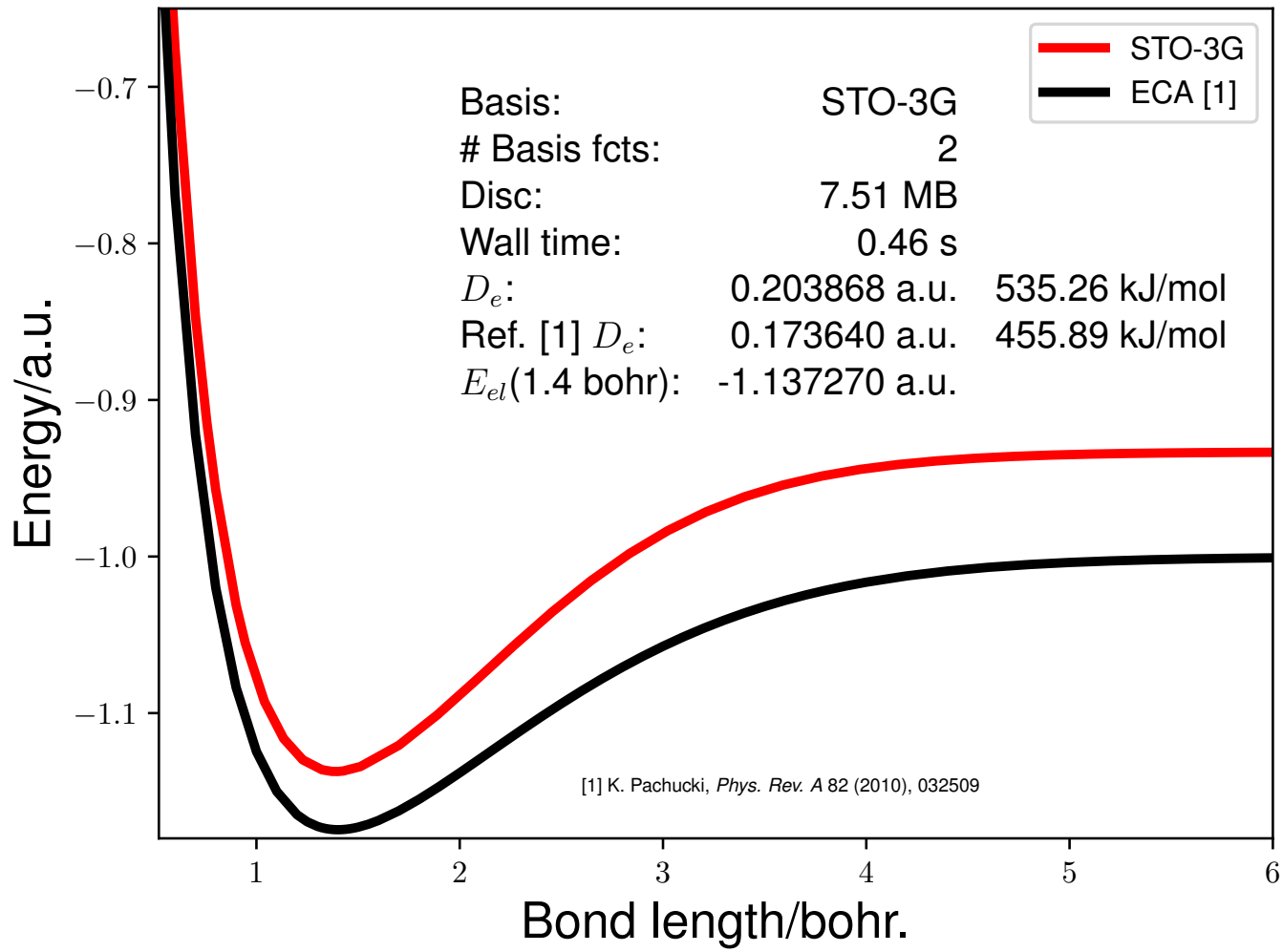
A. Kandala, A. Mezzacapo, K. Temme, M. Takita, M. Brink, J. M. Chow, J. M. Gambetta, Nature 549 (2017) 242-246.

improved data available on arXiv: arXiv:1805.04492

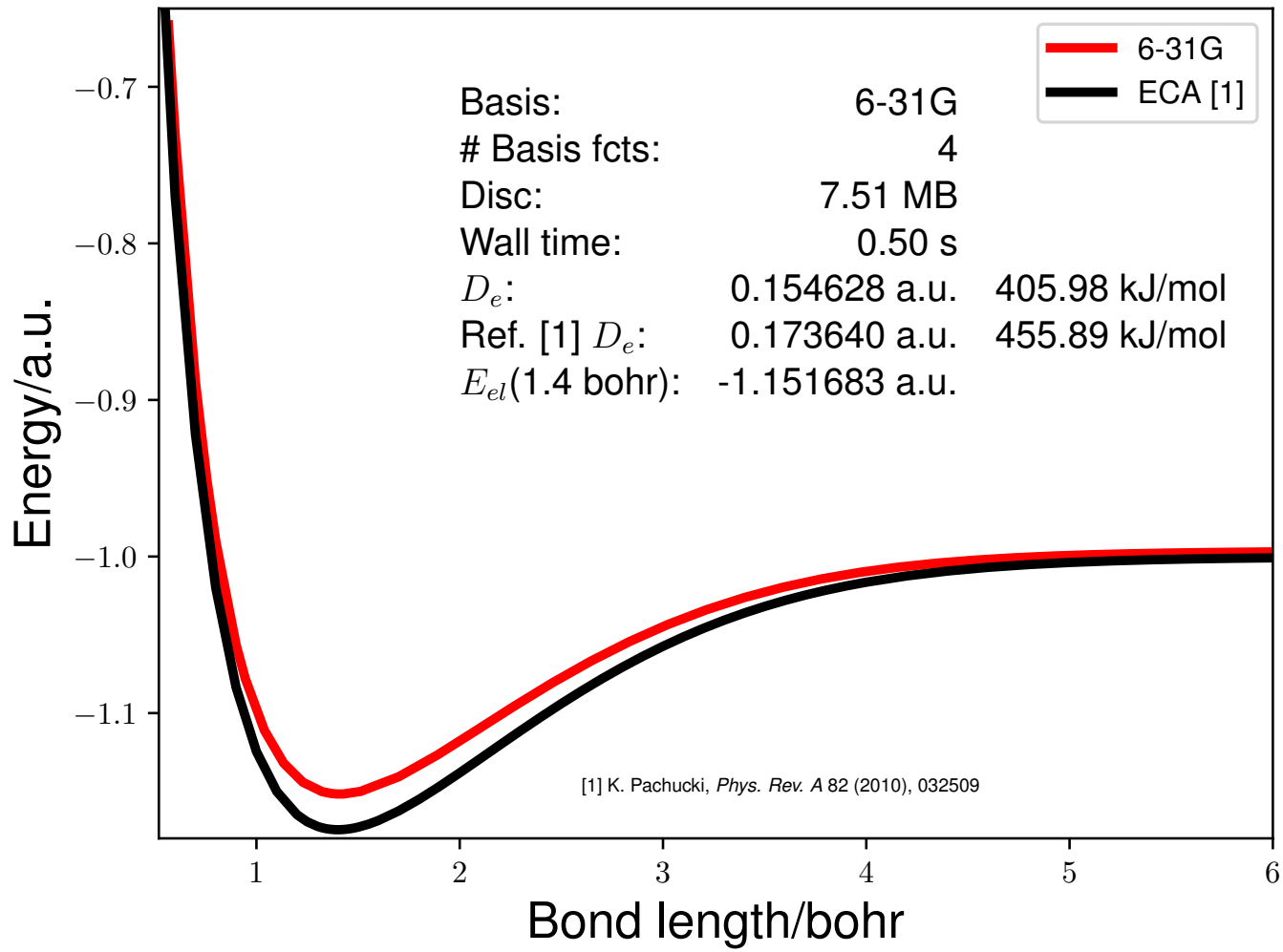
see also:

Quantum Chemistry Calculations on a Trapped-Ion Quantum Simulator, by C. Hempel et al., Phys. Rev. X 8 (2018) 031022

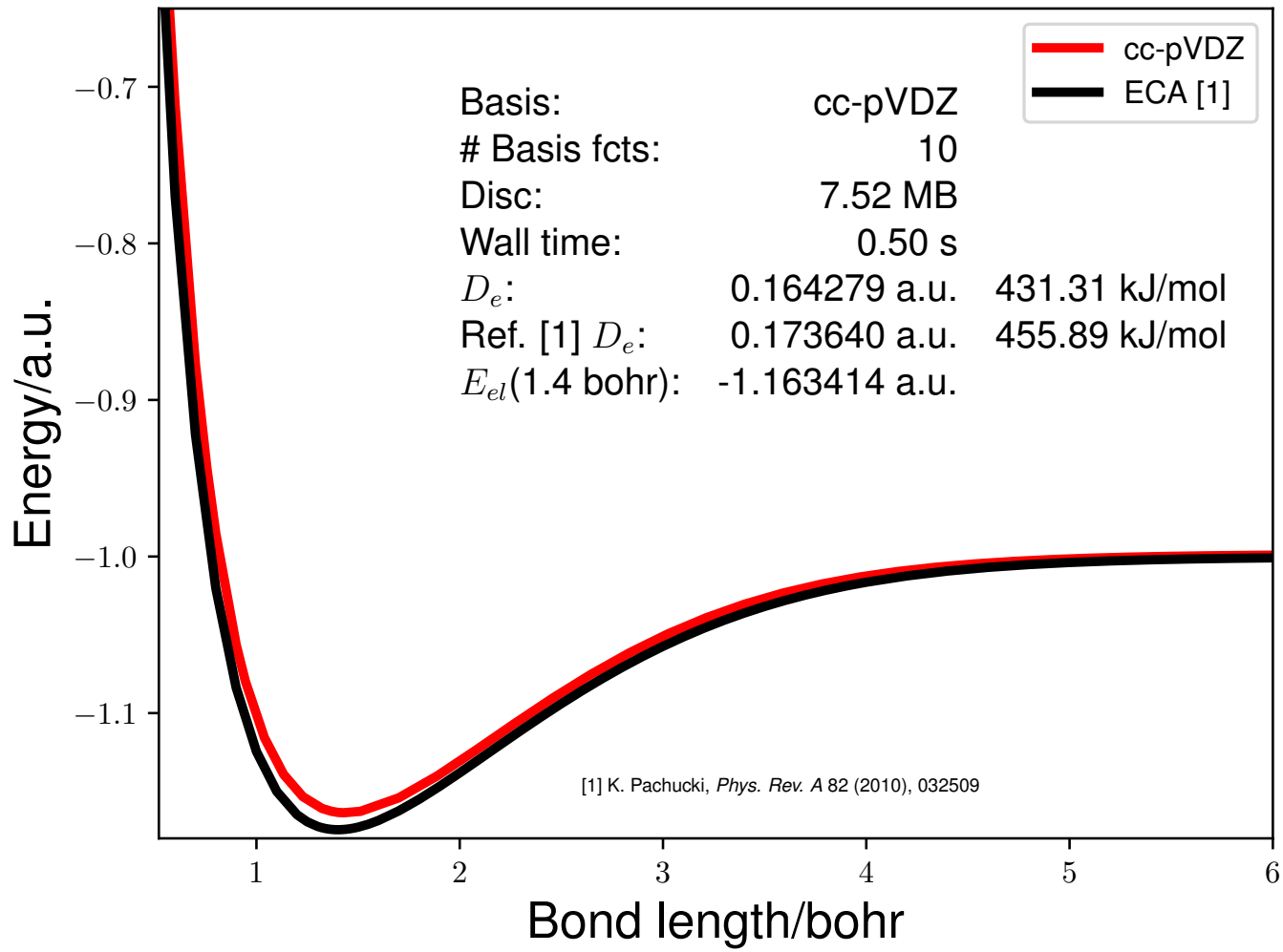
H_2 curve classical computing: minimal basis



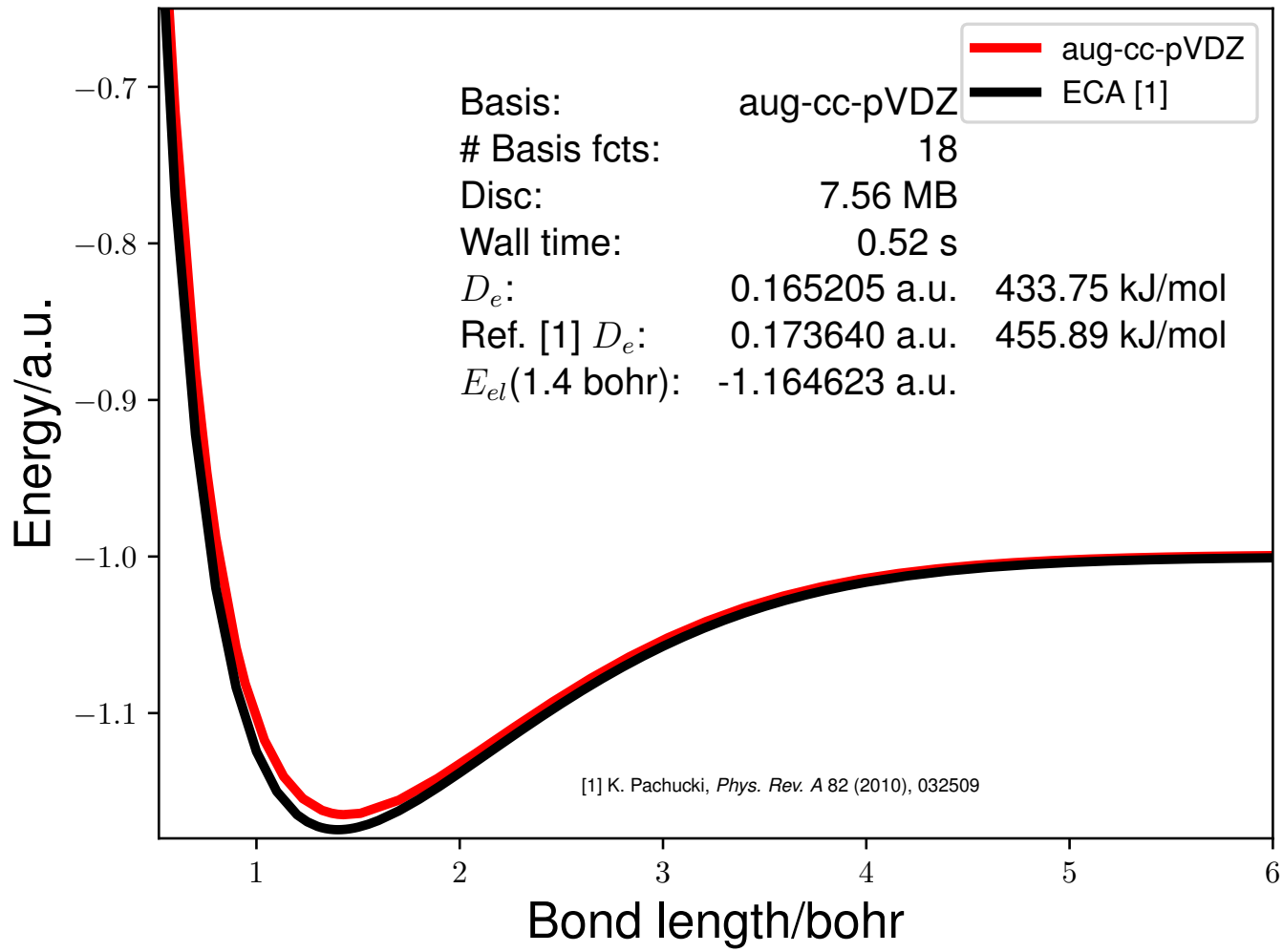
H_2 curve classical computing: small double-ζ



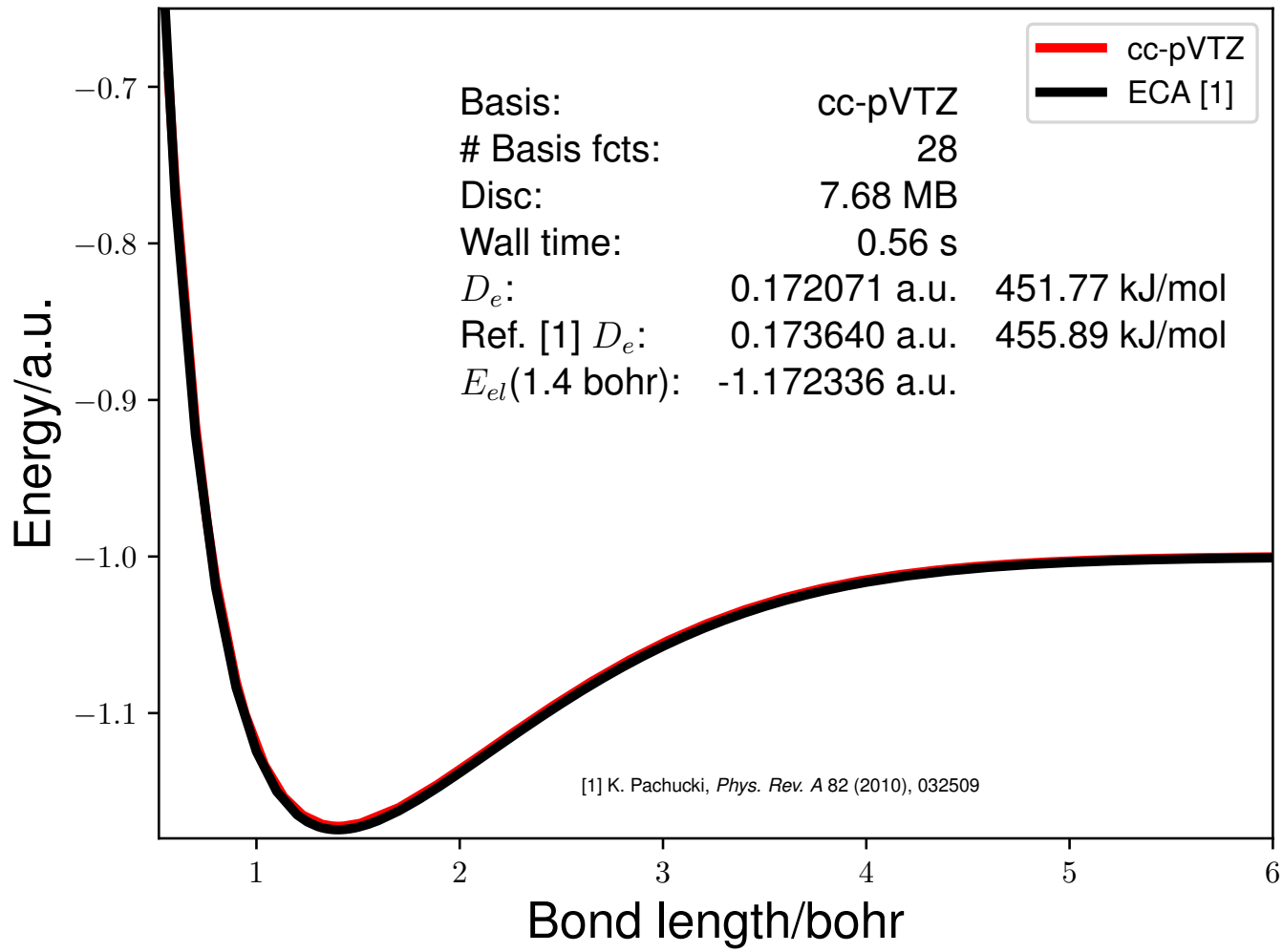
H_2 curve classical computing: larger double-ζ



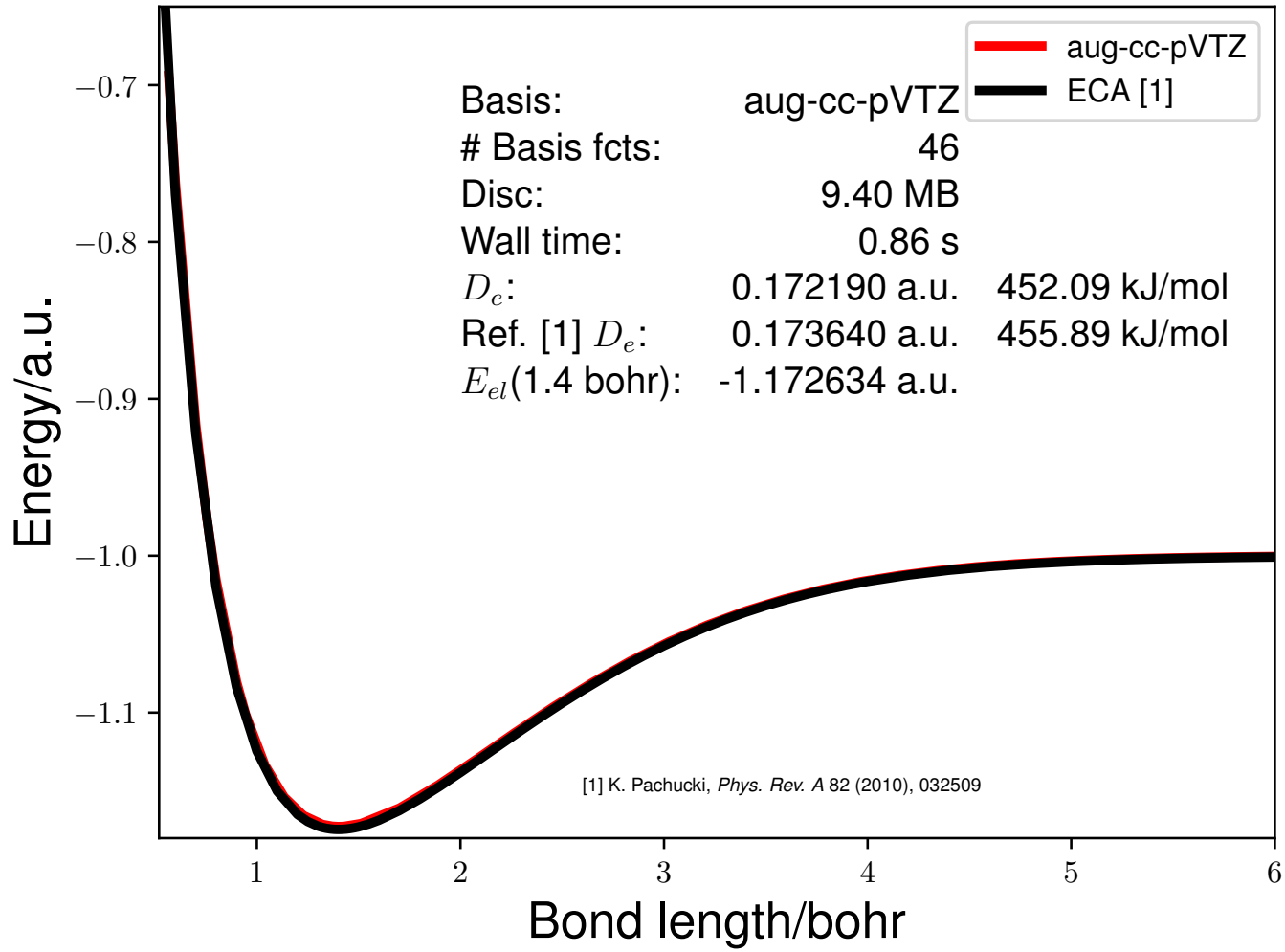
H_2 curve classical computing: even larger bases



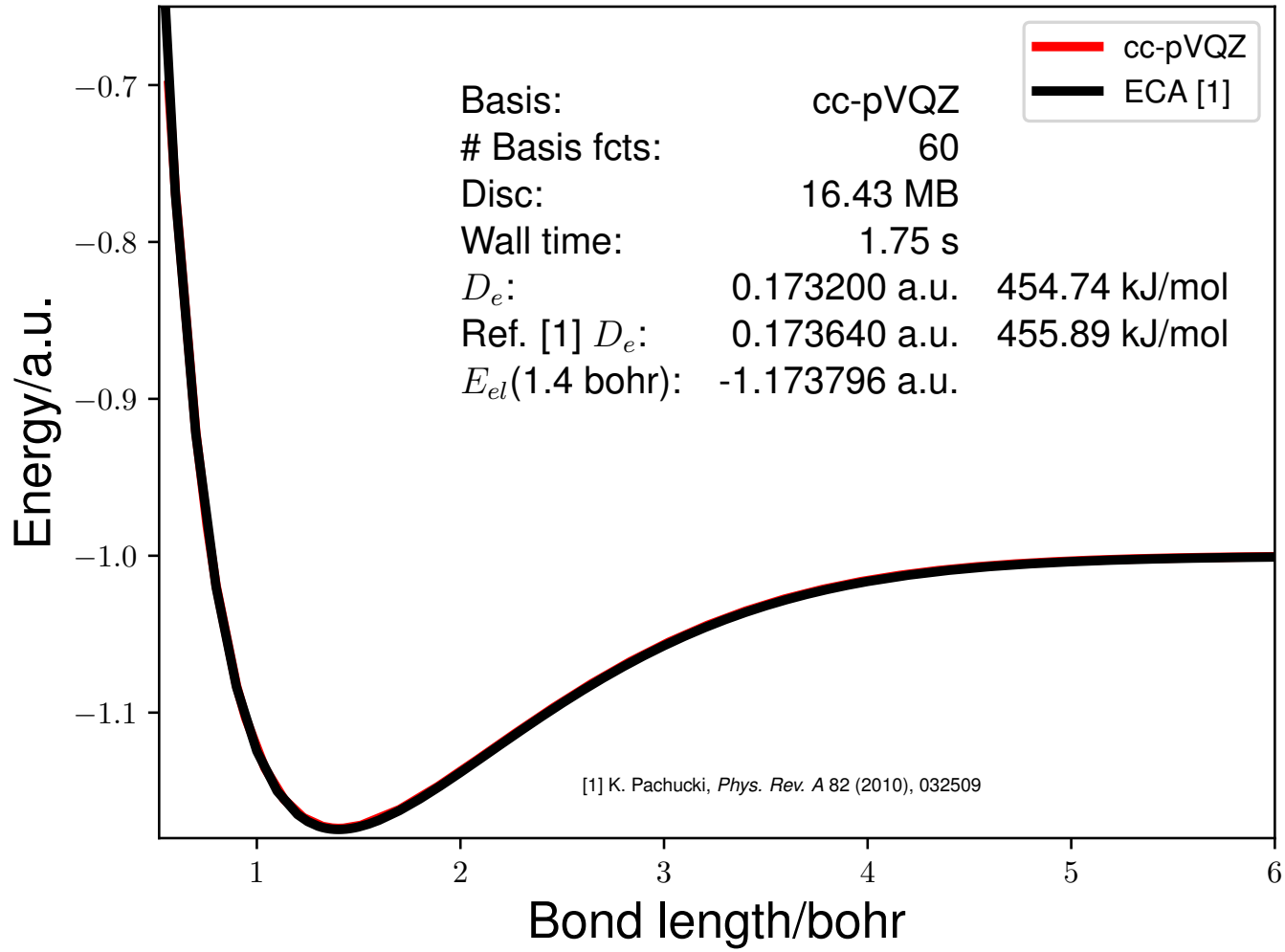
H_2 curve classical computing: even larger bases



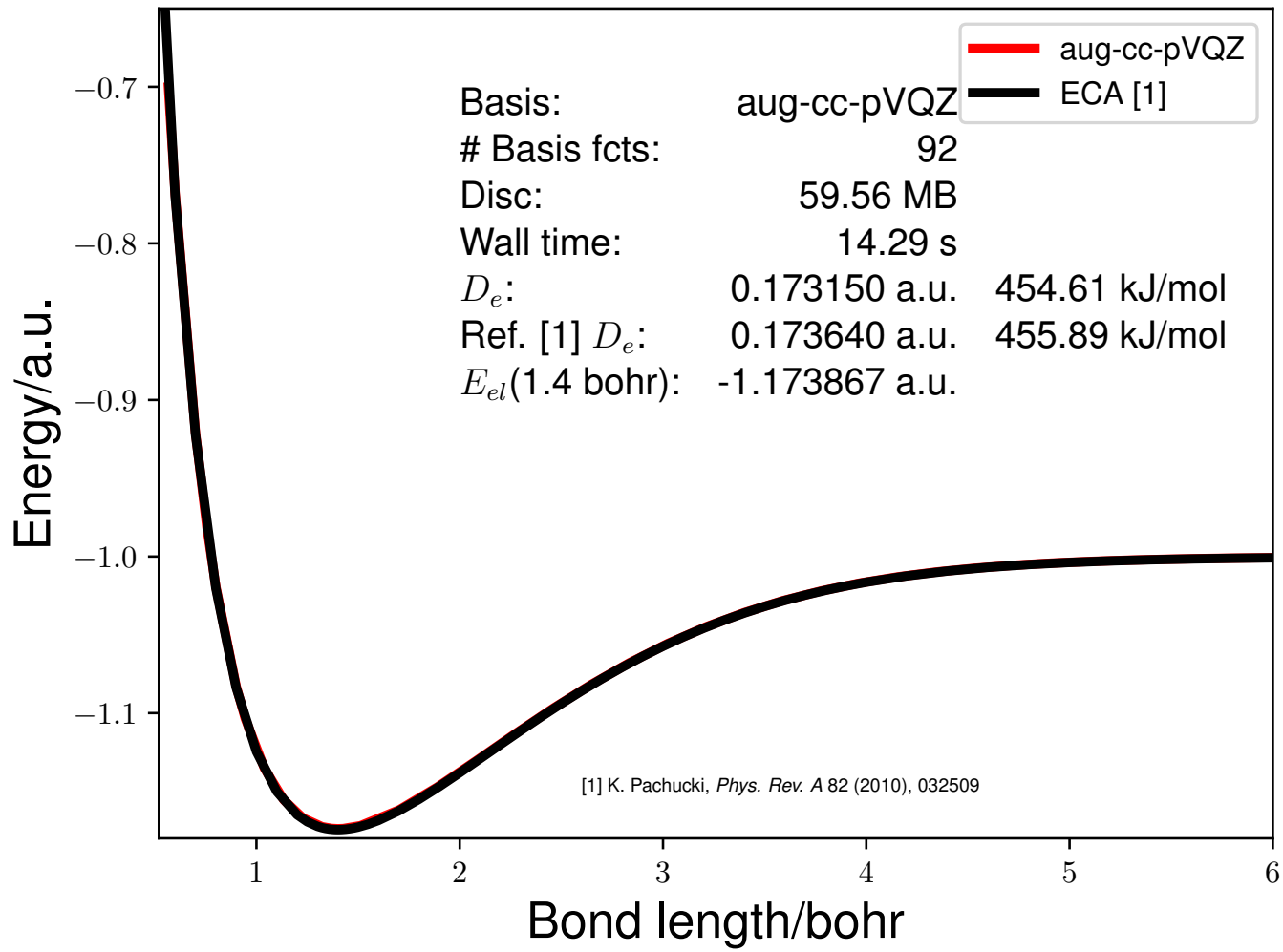
H_2 curve classical computing: even larger bases



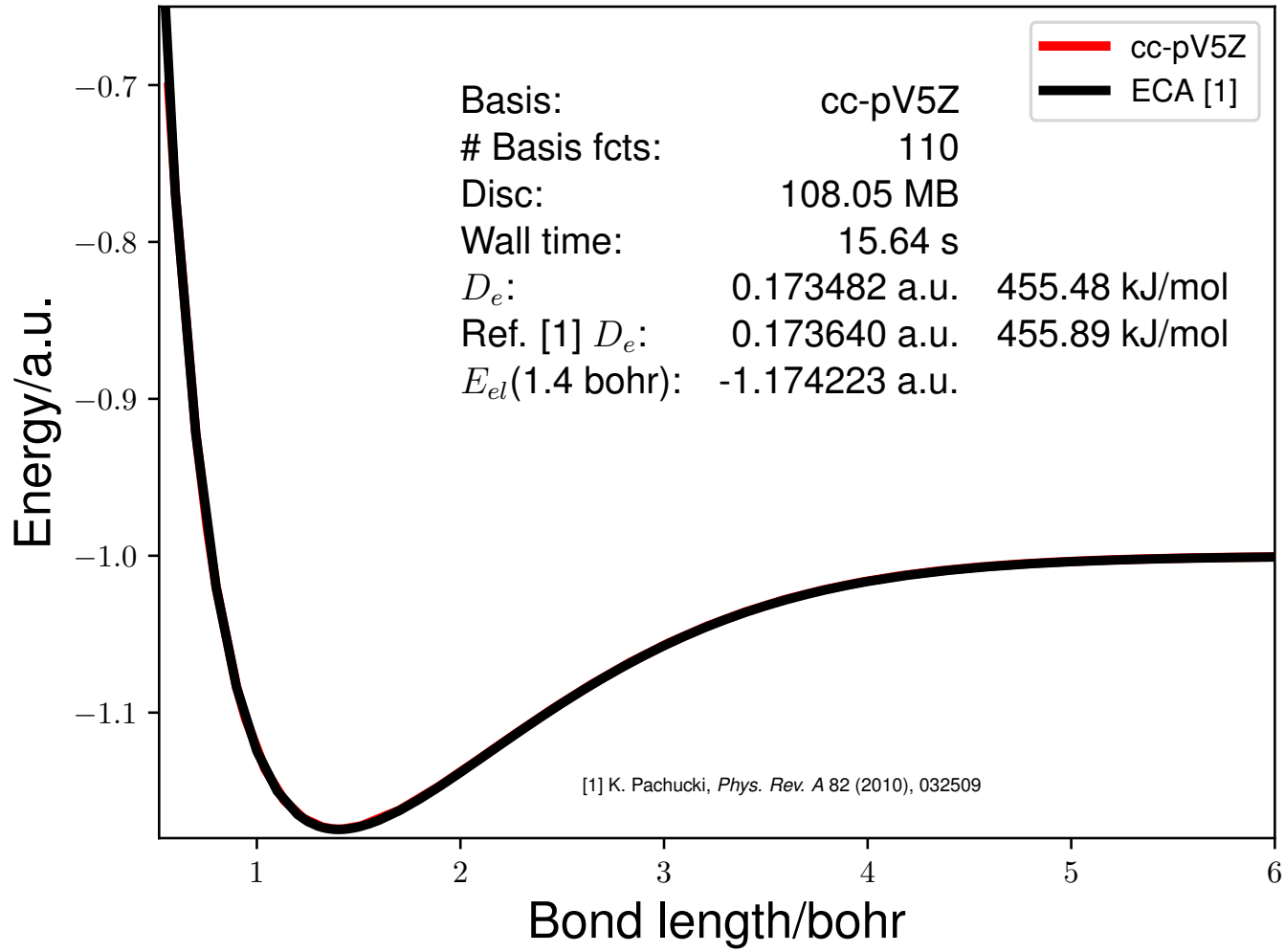
H_2 curve classical computing: even larger bases



H_2 curve classical computing: even larger bases



H_2 curve classical computing: even larger bases



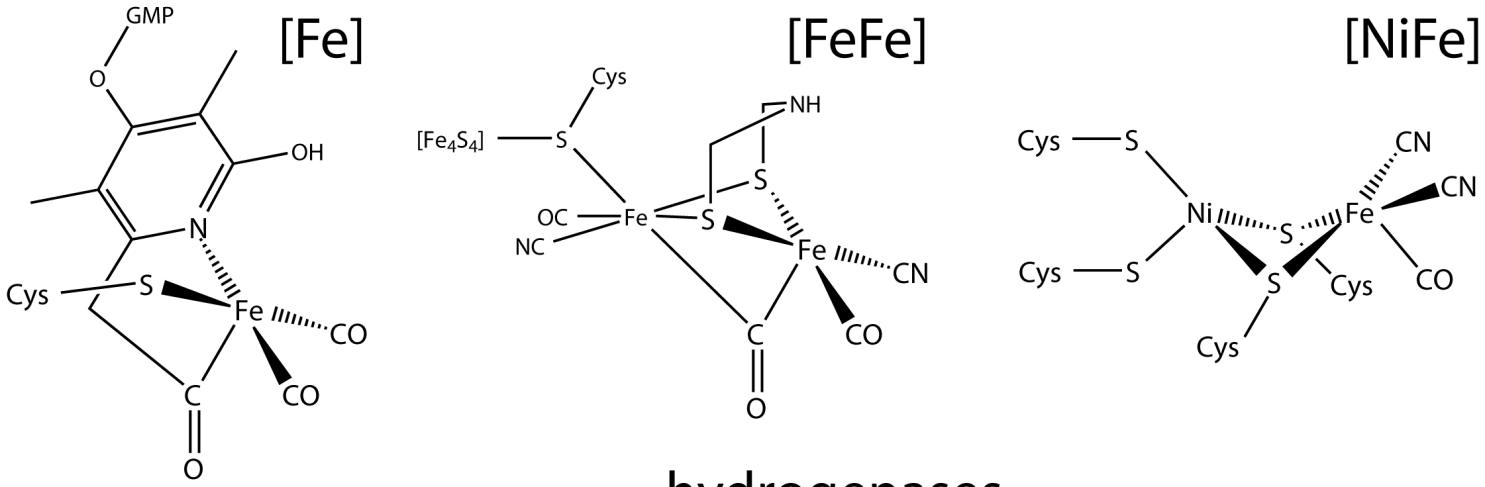
Let's get back to the question of what it actually takes to solve a chemical problem ...

... and let's not again bring up the Nitrogenase problem, which I took as an example already at this Microsoft Workshop in 2012:

https://www.microsoft.com/en-us/research/video/quantum-computation-for-quantum-chemistry-status-challenges-and-prospects-session-1

Another Real-World Example: Hydrogenases

- Catalyze the reversible oxidation of H_2, $H_2 \rightleftharpoons 2\ H^+ + 2\ e^-$.
- Three unrelated classes are known $\rightarrow$ convergent evolution.
- Common theme: Catalysis at Fe centers.



hydrogenases

P.M. Vignais, B. Billoud, *Chem. Rev.*, **2007**, *107*, 4206–4272.
K.A. Vincent, A. Parkin and F.A. Armstrong, *Chem. Rev.*, **2007**, *107*, 4366–4413.
A.L.D. Lacey, V.M. Fernandez, M. Rousset, R. Cammack, *Chem. Rev.* **2007**, *107*, 4304–4330.
W. Lubitz, H. Ogata, O. Rüdiger, E. Reijerse, *Chem. Rev.* **2014** *114*, 4081–4148.

- Intensive efforts to employ them in H_2-based clean-energy projects

  by Armstrong, Fontecilla-Camps, Friedrich, Ghirardi, Happe, Leger, Lenz, Lubitz, ...

- Most crucial obstacle: O_2 inhibition !

Focus on: Fe-only Hydrogenases

- [Fe] hydrogenases occur only in methanogenic archaea.

  $\rightarrow$ reduction of CO_2 to CH_4 with H_2.

- [FeFe] hydrogenases in anaerobic bacteria and unicellular algae.

  $\rightarrow$ formation of H_2, protons act as electron end-acceptor.

  $\rightarrow$ [FeFe] hydrogenases most efficient H_2 producers!

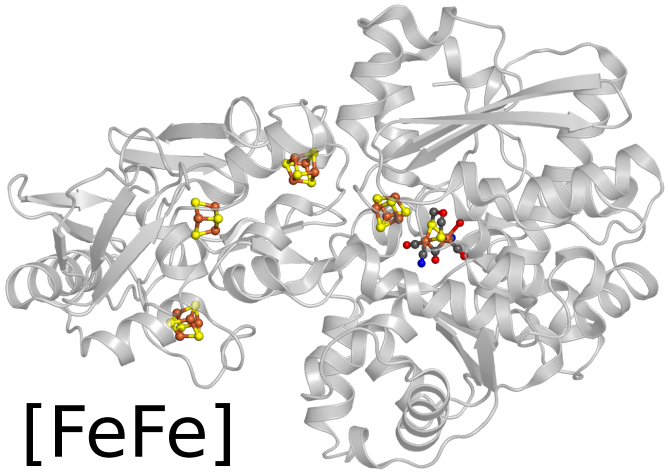
R.K. Thauer et al., *Annu. Rev. Biochem.*, **2010**, *79*, 507–536.

P.M. Vignais, B. Billoud, *Chem. Rev.*, **2007**, *107*, 4206–4272.

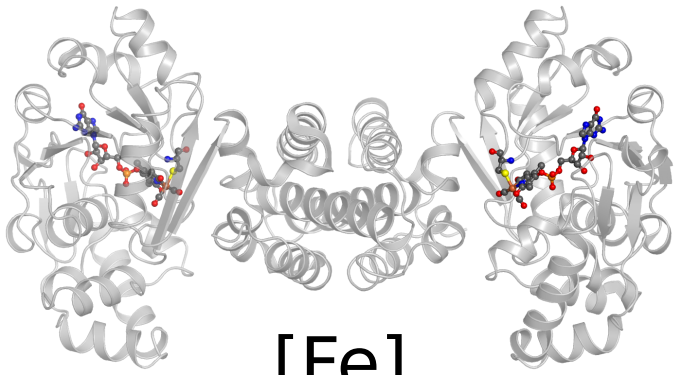
Structural characterization

[FeFe] hydrogenase structurally characterized from *Desulfovibrio* and *Clostridium* species.

[Fe] crystal structure revealed unusual coordination of central Fe atom.



[FeFe]



[Fe]

S. Shima et al., *Science*, **2008**, *321*, 572–575.
T. Hiromoto et al., *Angew. Chem. Int. Ed.*, **2009**, *48*, 6457–6460.
J.W. Peters et al., *Science*, **1998**, *282*, 1853–1858.
Y. Nicolet et al., *Structure Fold. Des.*, **1999**, *7*, 13–23.

DFT: mechanism of [FeFe] hydrogenases (selection)

Investigations into the catalytic cycle with a $[2Fe]_H$ model:

- H.-J. Fan, M.B. Hall, *J. Am. Chem. Soc.* **2001**, *123*, 3828–3829
- Z.-P. Liu, P. Hu, *J. Chem. Phys.* **2002**, *117*, 8177-8180
- G. Zampella, C. Greco, P. Fantucci, L. De Gioia, *Inorg. Chem.* **2006**, *45*, 4109–4118
- L. Yu, C. Greco, M. Bruschi, U. Ryde, L. De Gioia, M. Reiher, *Inorg. Chem.* **2011**, *50*, 3888–3900

$\Rightarrow$ Omitting the hydrogen bridges to the cyanides can change energetics

Thermodynamics of the μ-H vs. terminal-H species:

- M. Bruschi, C. Greco, M. Kaukonen, P. Fantucci, U. Ryde, L. De Gioia, *Angew. Chem. Int. Ed.* **2009**, *48*, 3503–3506

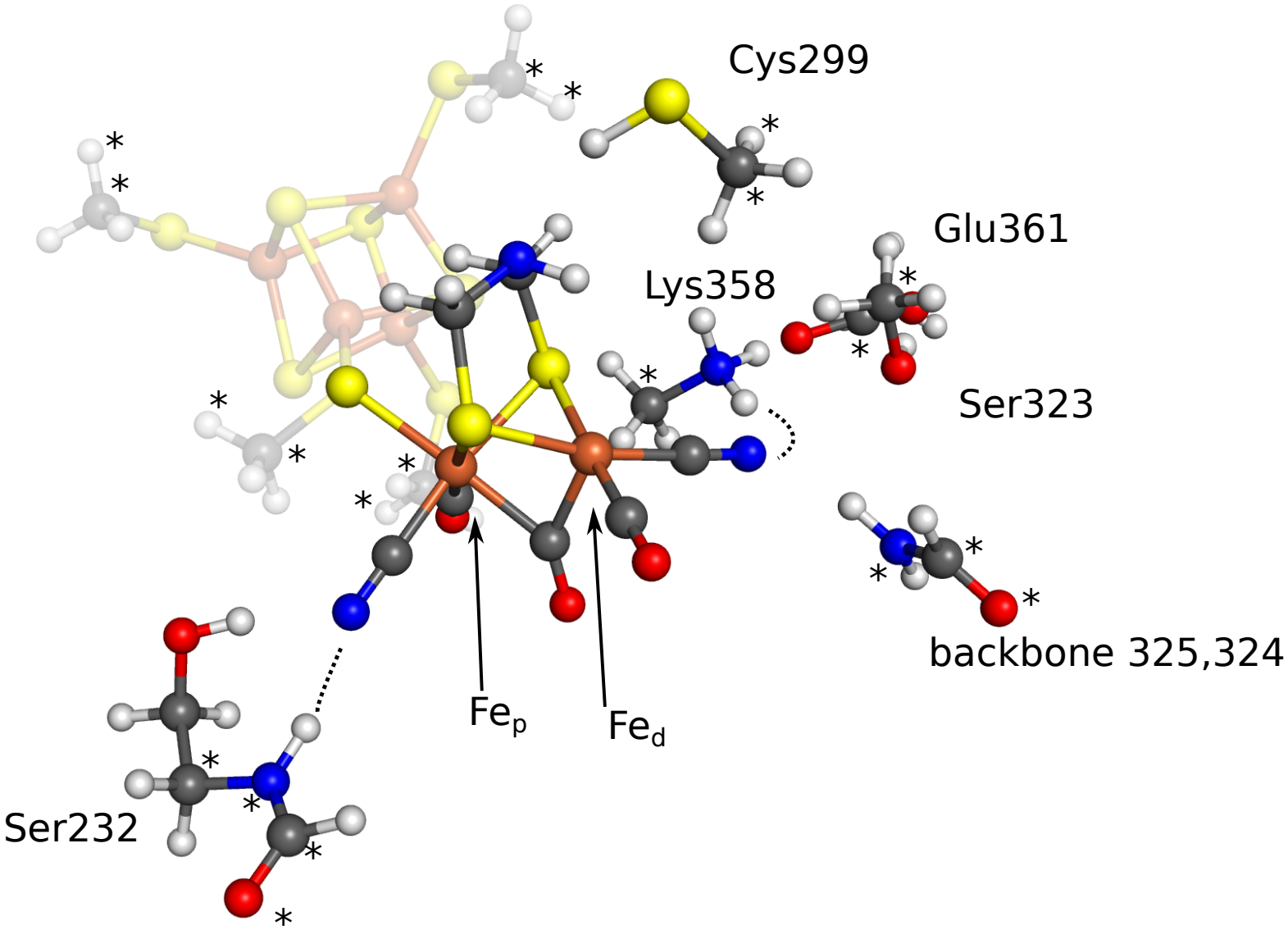
$\Rightarrow$ Relative stability of μ-H and terminal-H species only slightly affected by environment. Kinetic hindrance?

QM/MM calculations on catalytic intermediates:

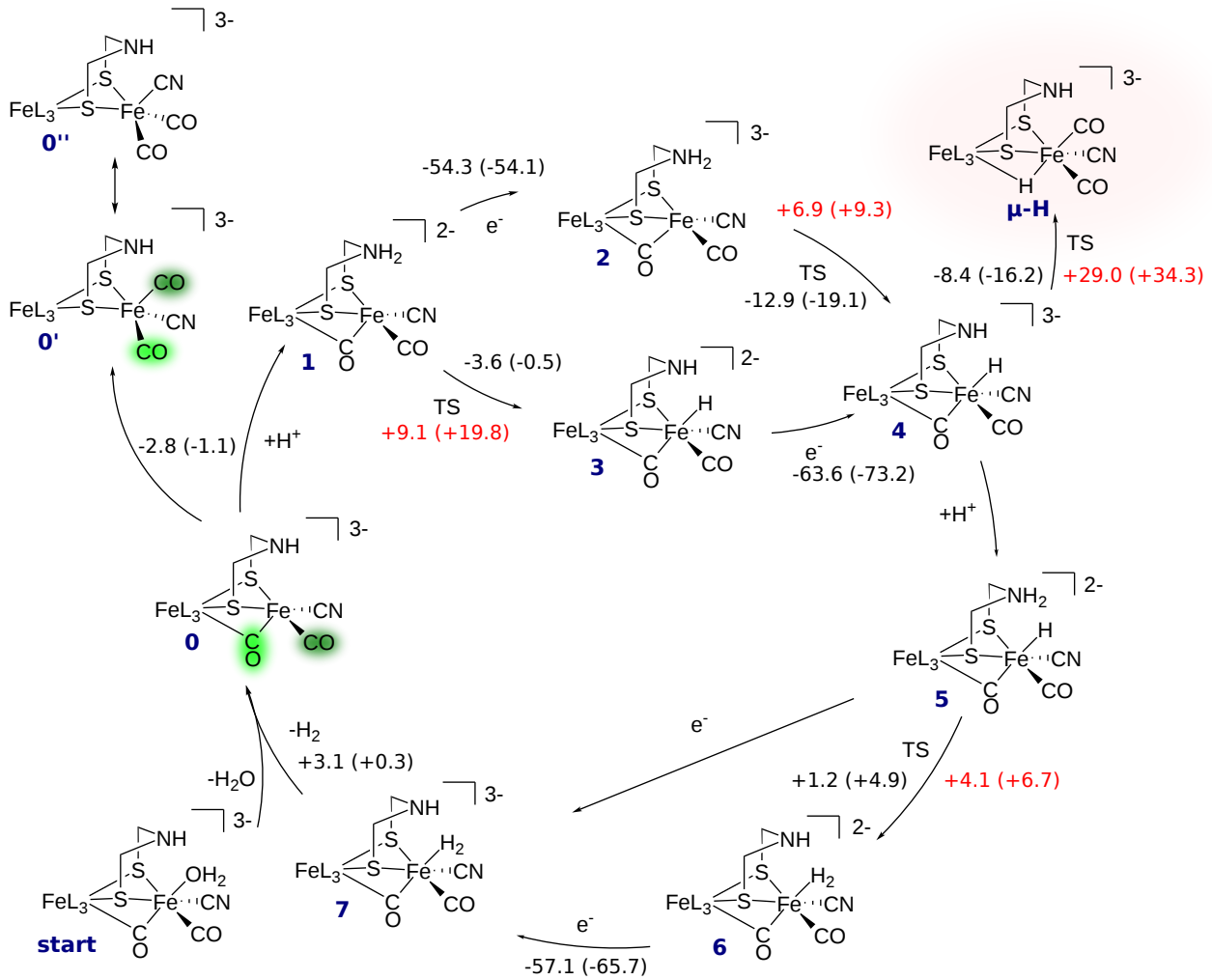
- C. Greco, M. Bruschi, L. De Gioia, U. Ryde, *Inorg. Chem.* **2007**, *46*, 5911–5921
- C. Greco, M. Bruschi, P. Fantucci, U. Ryde, L. De Gioia, *ChemPhysChem* **2011**, *132*, 3376–3382

$\Rightarrow$ Influence and interplay of cubanes on spin distribution and charges discussed in detail

Catalytic mechanism studied for large [FeFe] model



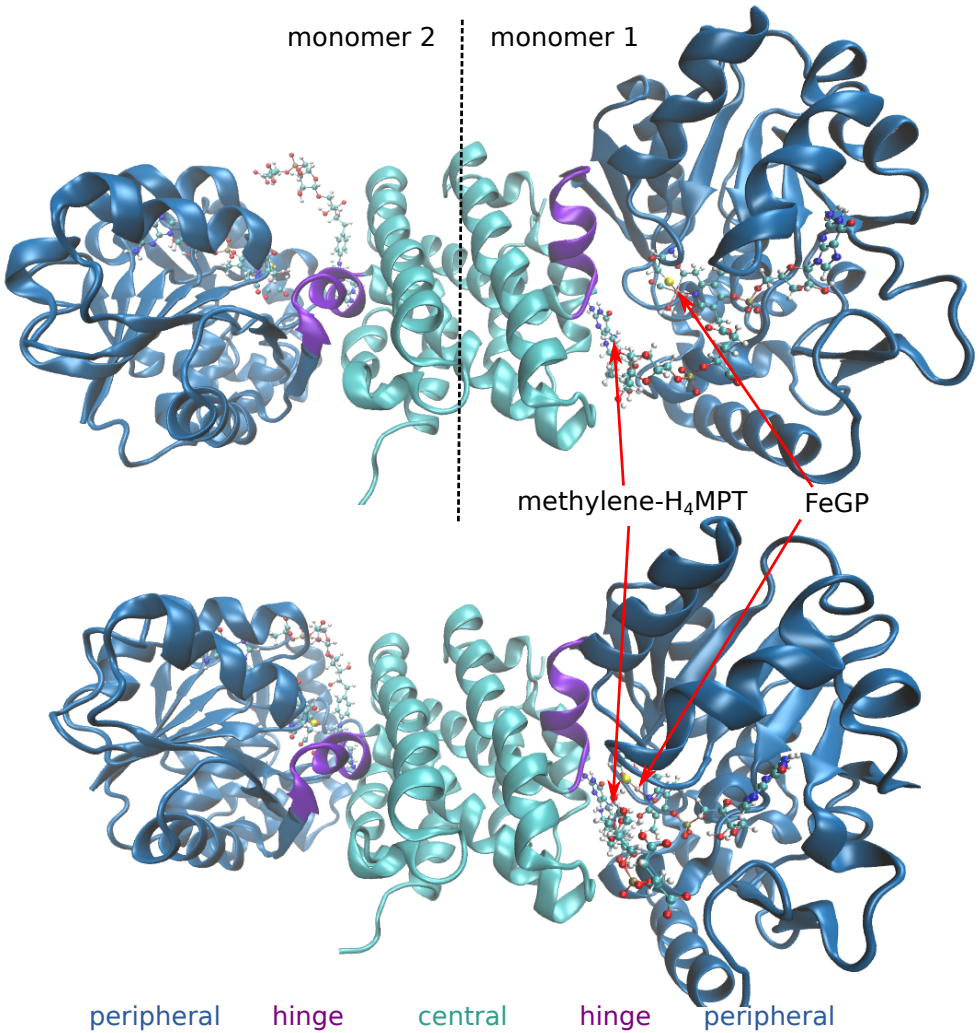
Catalytic mechanism studied for a large [FeFe] model



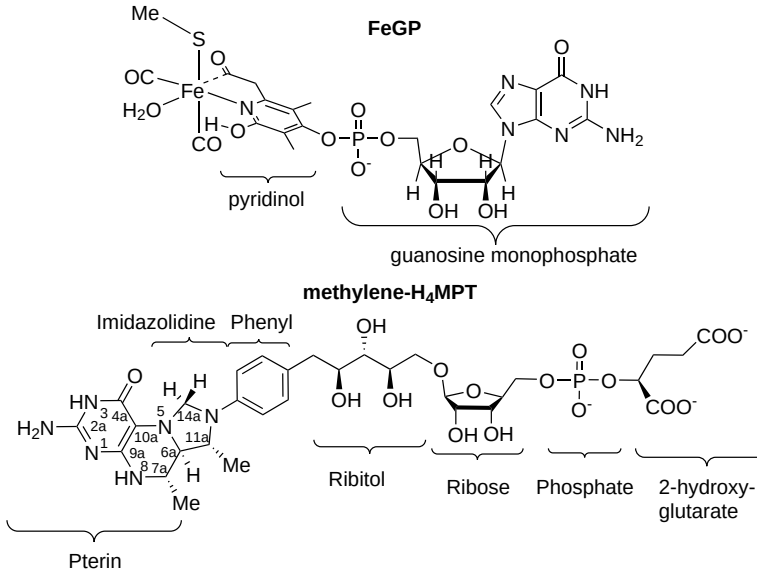
(all energies in kcal/mol)

A.R. Finkelmann, M.T. Stiebritz, M. Reiher, *Chem. Sci.* **2014**, *5*, 215–221

Structure of [Fe] Hydrogenase

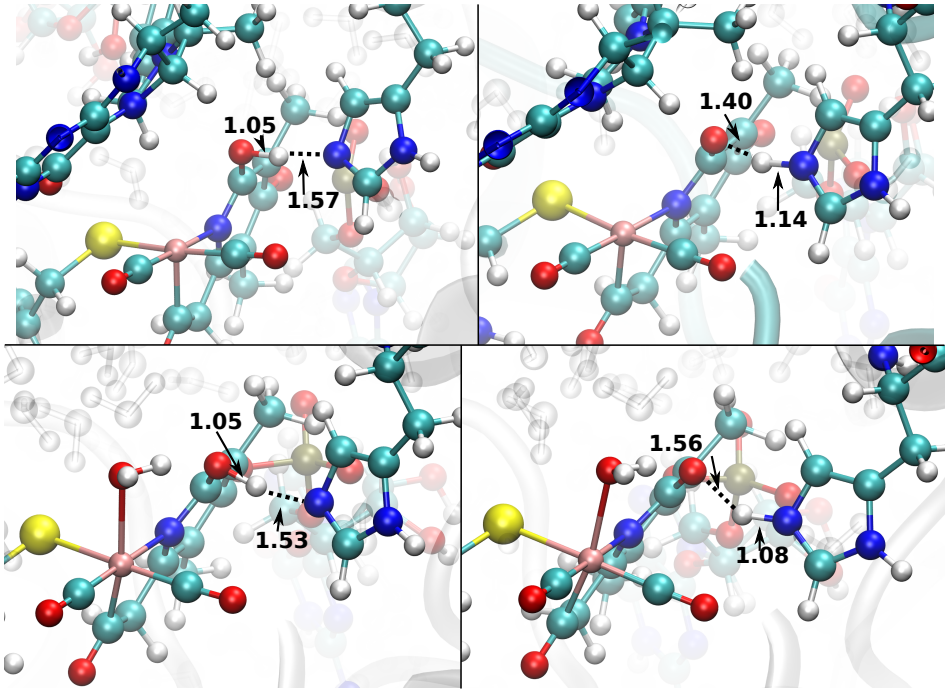


- $100/95\,\mathrm{ns}$ MD for *open* / *closed* conformation
- QM/MM calculations on representative snapshots



Protonation state of the pyridinol ligand

- In both conformations a hydrogen bond between His14 and the OH group of the hydroxyl ligand is formed frequently



- Deprotonation of the pyridinol endothermic by only $+2.3\,\mathrm{kcal/mol}$ in the *closed* conformation and thermoneutral in the *open* conformation

$\Rightarrow$ Deprotonated form exists in significant amounts

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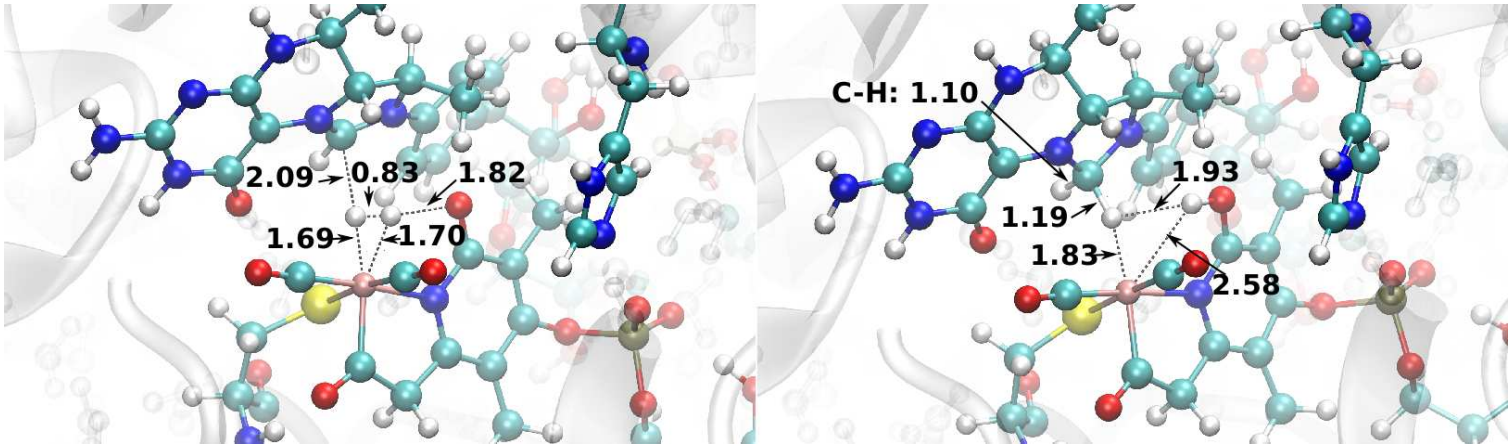
Hydrogen cleavage

- Hydrogen coordinated to the deprotonated form can rapidly be cleaved (barrier estimated to be below $1\,\mathrm{kcal/mol}$)



- H_2 cleavage exothermic by $-18.7\,\mathrm{kcal/mol}$
- No stable hydride species can be optimized!

$\Rightarrow$ This mechanism complies with the criteria stated before

- If the pyridinol is not deprotonated, H_2 can still be cleaved *via* the thiolate. This reaction is, however, less favored.

A. R. Finkelmann, H. M. Senn, M. Reiher, *Chem. Sci.*, *5* **2014** 4474–4482.

To actually solve a chemical problem will require many calculations ...

A single quantum computation will not contribute anything to chemistry.

A parallel quantum computer will be necessary.

Parallelizing the quantum computation of the energy landscape will be crucial to providing answers within a timeframe of several days instead of several years. Bounding the number of repetitions of phase estimation needed to prepare the ground state from an initial ansatz remains an open problem (see *SI Appendix*), and parallelism may often be needed to allow us to tolerate low success probability. Quantum computers therefore must be designed with a scalable architecture in mind and also built with the realization that constructing a single quantum computer is insufficient to solve such tasks. Instead, we should aim to have quantum computers that can be built en masse, because clusters of quantum computers will be needed to scan over the many structures that need to be examined to identify and estimate all important reaction rates (25).

Finally, chemical reactions that involve strongly correlated species that are hard to describe by traditional multiconfiguration approaches are not just limited to nitrogen fixation: They are ubiquitous. They range from C–H bond activating catalysts; to those for hydrogen and oxygen production, carbon dioxide fixation, and transformation; to industrially useful compounds; to photochemical processes. Given the economic and societal impact of chemical processes ranging from fertilizer production to polymerization catalysis and clean energy processes, the importance of a versatile, reliable, and fast quantum chemical approach powered by quantum computing can hardly be overemphasized.

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, PNAS 114 (2017) 7555-7560.