Hylleraas

MRCC methods based on the bivariational principle and why the tensor-network people should care

Workshop II: Tensor Network States and Applications, IPAM@UCLA/Virtual, April 19–23 2021

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European Research Council
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The Research Council of Norway

BIVAQUM

UiO : University of Oslo

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Electronic-structure theory

- N-electron problem:

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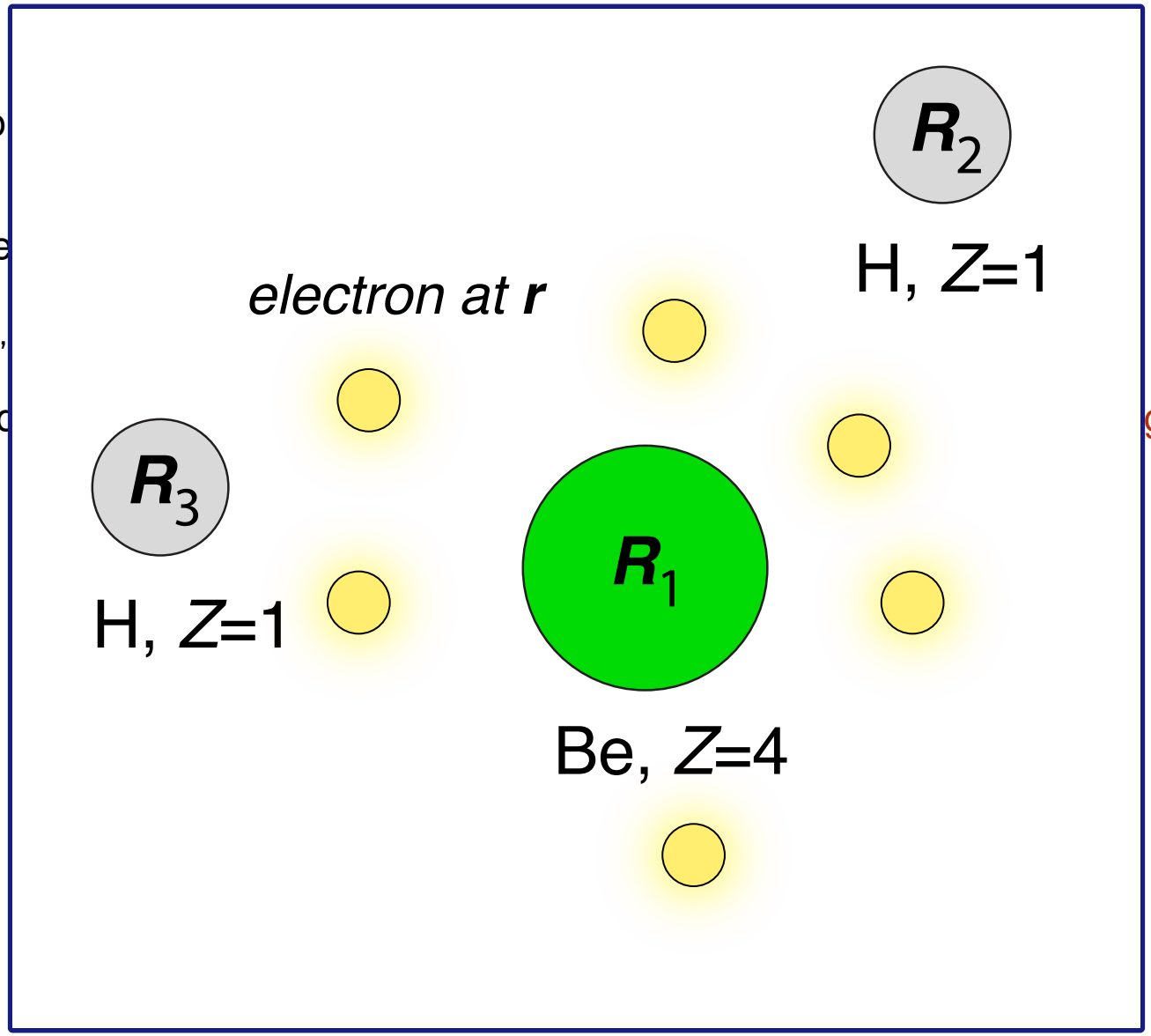

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- The most popular method is the coupled-cluster method (CC): A non-variational method!

The bivariational principle generalizes the Rayleigh–Ritz principle to (possibly) non-selfadjoint operators, but also generalizes the concept of variational methods

History

ANNALS OF PHYSICS **151**, 311–382 (1983)

Variational Principles and Linked-Cluster exp S Expansions for Static and Dynamic Many-Body Problems

JOUKO ARPONEN

Research Institute for Theoretical Physics, University of Helsinki, Helsinki, Finland

Received December 23, 1982

The exp S formalism for the ground state of a many-body system is derived from a variational principle. An energy functional is constructed using certain n-body linked-cluster amplitudes with respect to which the functional is required to be stationary. By using two different sets of amplitudes one either recovers the normal exp S method or obtains a new scheme called the extended exp S method. The same functional can be used also to obtain the average values of any operators as well as the linear response to static perturbations. The theory is extended to treat dynamical phenomena by introducing time dependence to the

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Essential ingredients

Bivariational formalism works with pairs of Hilbert spaces

$$\mathscr{H} \times \mathscr{H}^\dagger$$

- $\mathscr{H}$ — space of kets — complex separable Hilbert space

$$|\psi\rangle$$

- $\mathscr{H}^\dagger$ — space of bras — complex conjugate space/dual space

$$\langle\tilde{\psi}|$$

- So, dual pairing complex differentiable in both arguments

$$\partial_{\tilde{\psi}} \langle\tilde{\psi}|\psi\rangle = |\psi\rangle$$

$$\partial_{\psi} \langle\tilde{\psi}|\psi\rangle = \langle\tilde{\psi}|$$

- For simplicity, we always assume finite dimensions

The bivariational principle

$$\mathscr{E} : \mathscr{H} \times \mathscr{H}^{\dagger} \to \mathbb{C}$$

$$\mathscr{E}(\psi, \tilde{\psi}) = \frac{\langle \tilde{\psi} | H | \psi \rangle}{\langle \tilde{\psi} | \psi \rangle}$$

The bivariational principle

bivariate Rayleigh quotient / energy functional

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$$\partial \mathscr{E} = 0 \iff \langle \tilde{\psi} | \psi \rangle \neq 0,$$

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Note: H is not assumed selfadjoint, and $\mathscr{E}$ is not below bounded
$\implies$ tread carefully!

The single-reference CC method – Arponen formulation

- Standard Hartree–Fock partitioning:

$$H = F + W$$

[1] J. Arponen, *Ann. Phys,* **151** (1983), 311–382; T. Helgaker and P. Jørgensen, *Adv. Quant. Chem.* **19** (1988), 183–245

The single-reference CC method – Arponen formulation

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Best possible separable approximation

$$H = F + W$$

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The single-reference CC method – Arponen formulation

- Standard Hartree–Fock partitioning:

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- Diagonalize separable F:

$$F\,|\phi_\mu\rangle = \epsilon_\mu\,|\phi_\mu\rangle$$

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$$H = \text{Antisymmetrized tensor products, basis for } \mathscr{H}$$

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$$|\psi\rangle = e^T\,|\phi_0\rangle\,, \quad T \in \mathcal{T}$$

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Commutative algebra of cluster operators

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- Gives "extended" CC energy function

$$E_{\mathrm{ECC}}(T,\tilde{T}) = \langle\phi_0|e^{\tilde{T}}e^{-T}He^T|\phi_0\rangle$$

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$$\cancel{E_{\mathrm{ECC}}}\mathcal{L}(T,\Lambda) = \langle\phi_0|(I+\Lambda)e^{-T}He^T|\phi_0\rangle$$

- CC Lagrangian for standard SRCC theory.[1]
- Galerkin approximations are polynomially scaling and separable

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In bivariational methods, the bra and ket is parameterized with new bra and kets.

Bivariational approximations

- Introduce parameterization

$$V \times V^\dagger \to \mathscr{H} \times \mathscr{H}^\dagger$$
$$\begin{pmatrix} z \\ \tilde{z} \end{pmatrix} \mapsto \begin{pmatrix} \psi(z, \tilde{z}) \\ \tilde{\psi}(z, \tilde{z}) \end{pmatrix}$$

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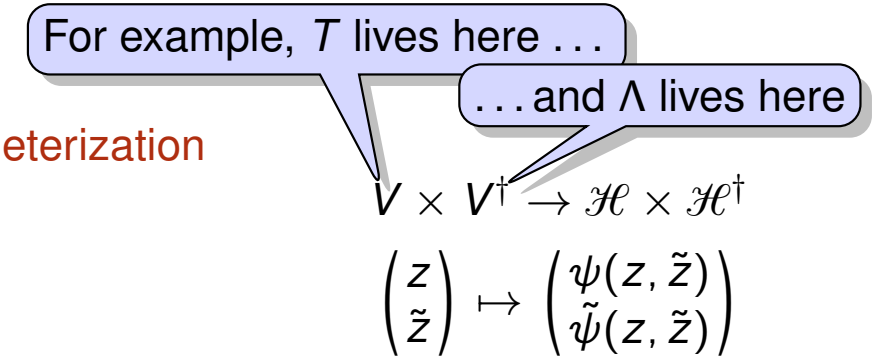

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E.g., CC Lagrangian $\mathcal{L}(T,\Lambda)$

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Fancy word for cluster operator truncation

Mathematical analysis of bivariational approximations

We first mention:

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- Separability (size-consistency) relatively easy to address

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The multireference problem is the breakdown of a "classical" picture in terms of independent particles

The multireference problem

When $|\phi_0\rangle$ is no longer a good approximation:

- W is no longer small relative to F

The multireference problem

When $|\phi_0\rangle$ is no longer a good approximation:

- W is no longer small relative to F
- We must correlate multiple unperturbed solutions:

$$|\psi\rangle = \Omega\,|\psi_0\rangle\,, \quad |\psi_0\rangle = \sum_{\text{a few } \mu} |\phi_\mu\rangle\, c_\mu \in \mathscr{H}_0$$

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Dynamic correlation

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The multireference problem

When $|\phi_0\rangle$ is no longer a good approximation:

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- MR a hard problem:
  - Optimal $\mathscr{H}_0$ is geometry dependent
  - Not straightforward to generalize the SRCC method
  - Exponential wall of scaling for model spaces

The BIVP is the correct setting for coupled-cluster type methods.

bivar-MRCC is the first MR method within this framework.

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About bivar-MRCC

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- Based on SRCC formalism

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bivar-MRCC bra and ket

Parameter space:

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bivar-MRCC bra and ket

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bivar-MRCC energy functional

$$E(T, \Lambda, C, D) = (d^T c)^{-1} \langle \tilde{\Phi}_0 | D(1 + \Lambda) e^{-T} H e^{T} C | \Phi_0 \rangle$$

- Exact under mild conditions on H, CAS

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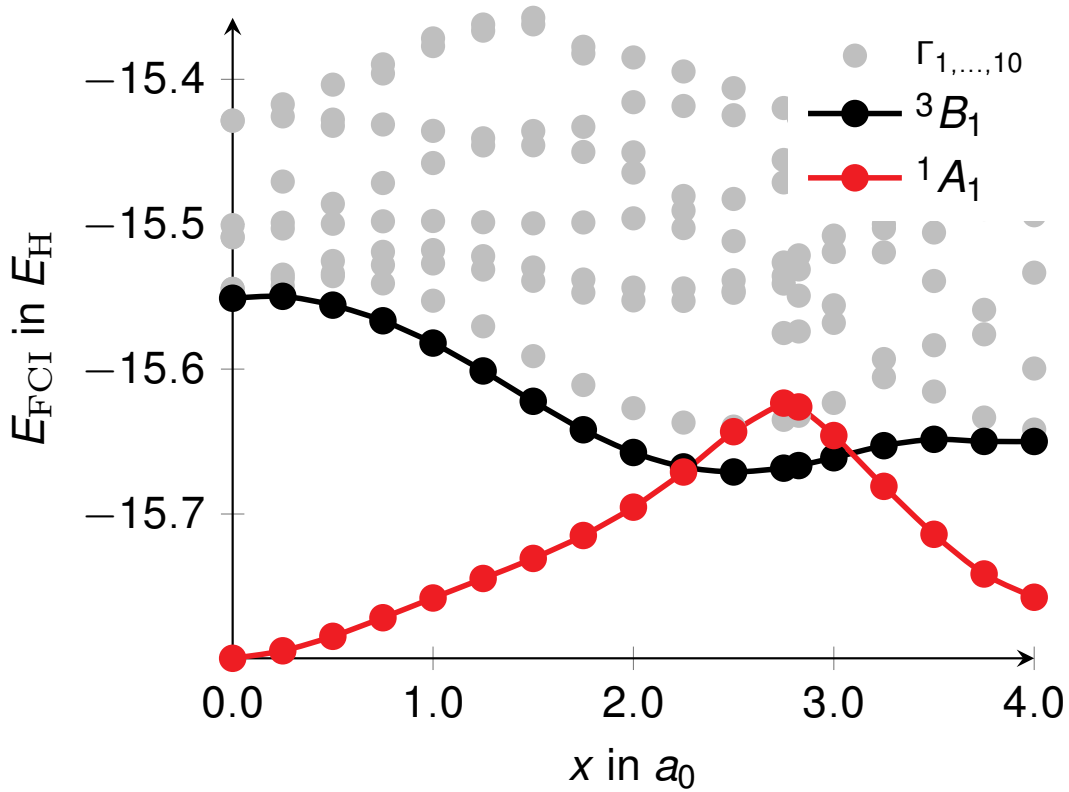
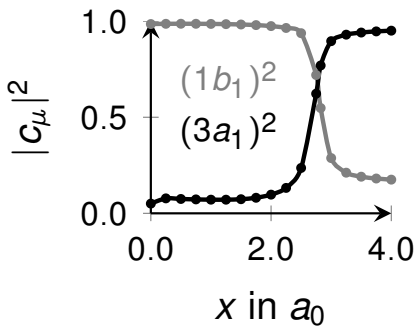
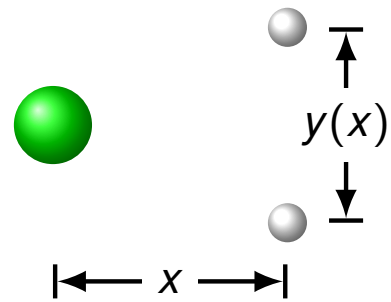
- Cost is $O(n_{\text{CAS}} \times n_{\text{SRCC}})$

Application: Complicated potential curve of BeH_2, FCI results





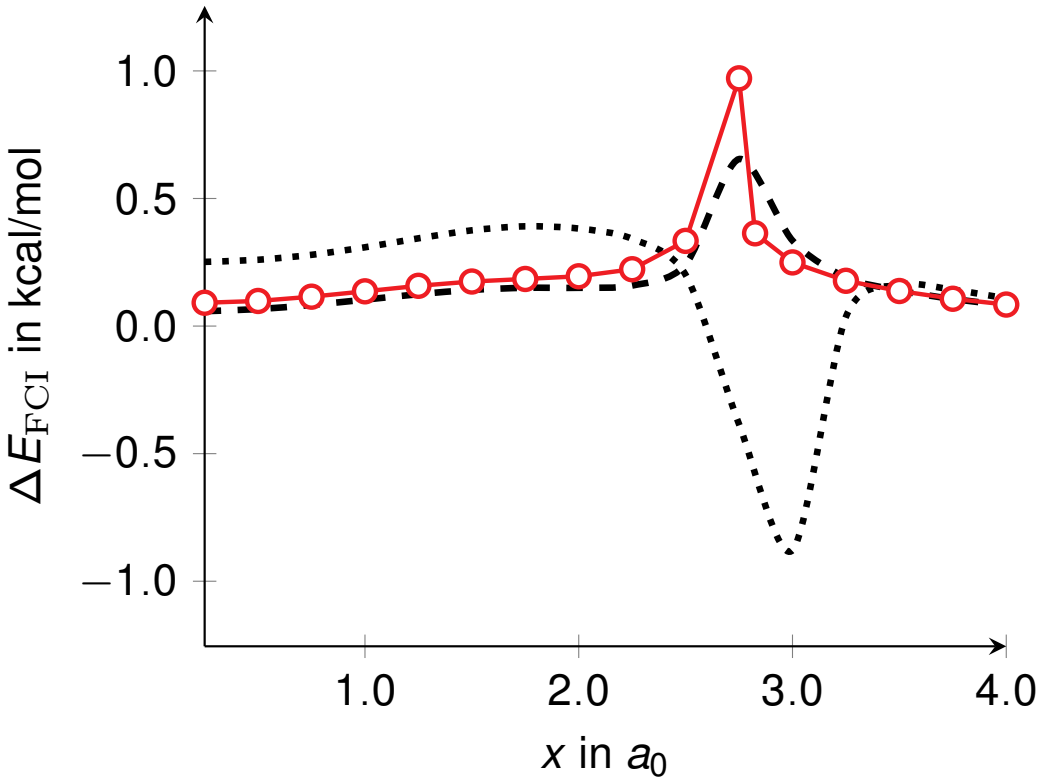


- Standard test bench for novel methods[7]
- DZ-type basis (10s3p/3s2p and 4s/2s)

[7] G.D. Purvis *et al. IJQC* **23**, 835 (1983).

Hylleraas

Application: BeH_2, comparison to other MRCC methods



ic-MRCCSD(2,2)
Mk-MRCCSD(2,2)
bivar-MRCCSD(2,2)FOIS

∗ F. A. Evangelista, *J. Chem. Phys.* 134, 224102 (2011)

- Comparable accuracy, within desired “chemical accuracy” range

Hylleraas

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Tensor methods and the BIVP

- Many high-dimensional real-world problems are non-selfadjoint
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- TNS/BIVP approach to static correlation

Tensor-network states in the bivariational world

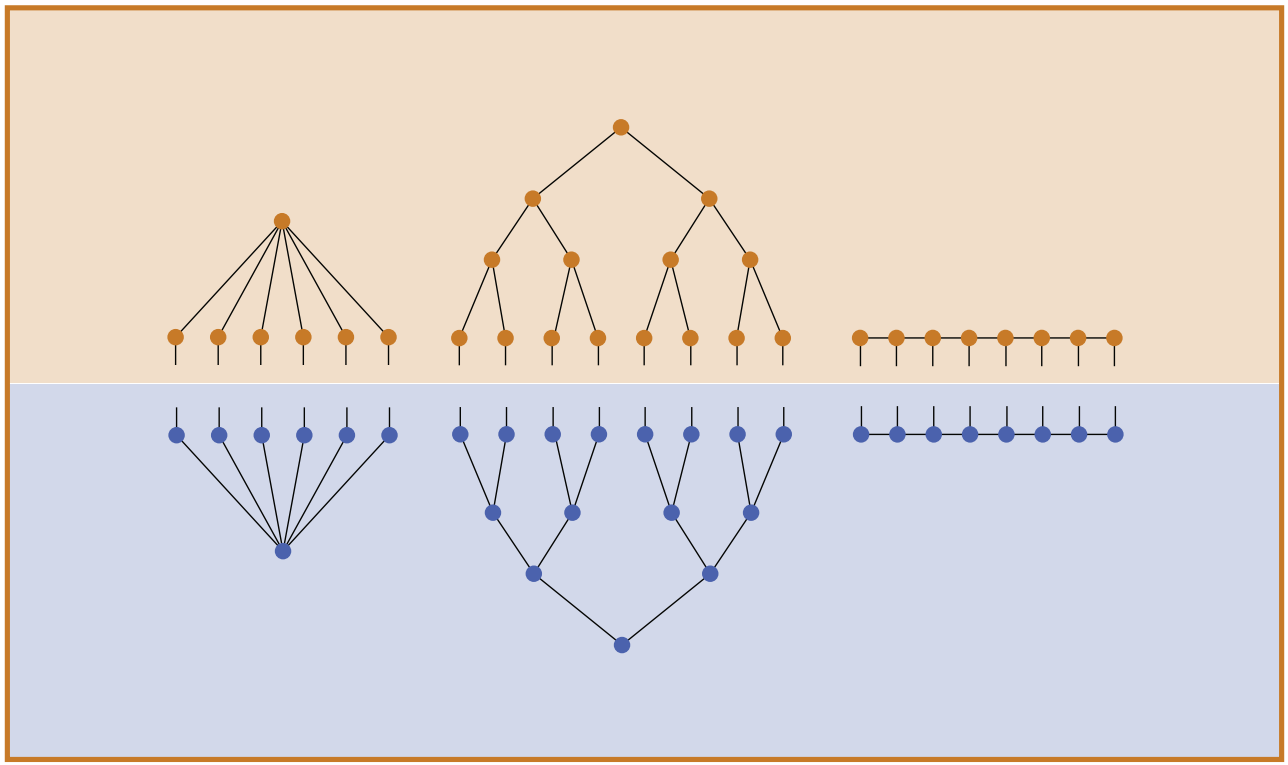


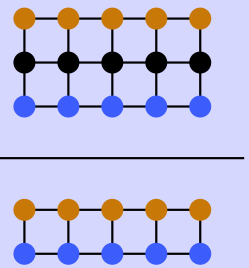
Figure: The Upside-Down

Ideas for bivariational optimization with TNS

Matrix-product state

$$|\psi\rangle \in \mathrm{MPS}, \quad \langle\tilde{\psi}| \in \mathrm{MPS}^{\dagger}$$

$$\mathcal{E}(\psi, \tilde{\psi}) = \frac{\langle\tilde{\psi}|H|\psi\rangle}{\langle\tilde{\psi}|\psi\rangle} =$$



[8] G. K.-L. Chan and T. van Voorhis, *JCP* **122** 204101 (2005)

[9] S. Holtz, T. Rohwedder, and R. Schneider, *SISC* **34**, A683 (2012)

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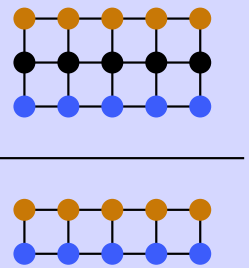

- Basic idea: ψ and $\tilde{\psi}$ independent variables. Generalize standard algorithms accordingly.

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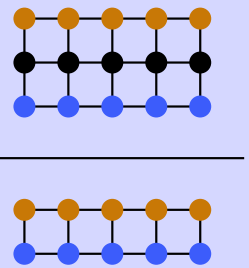

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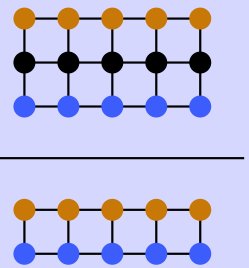

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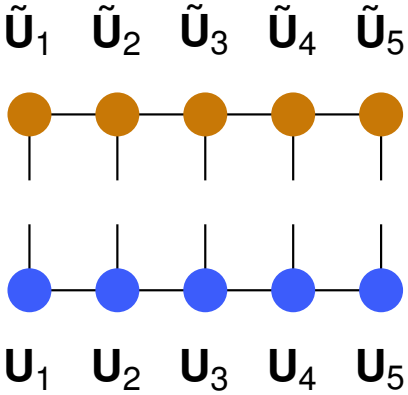
bivar-ALS sketch



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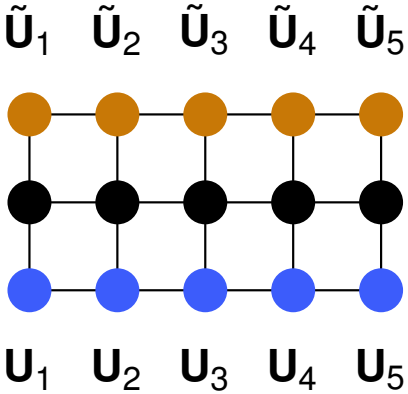

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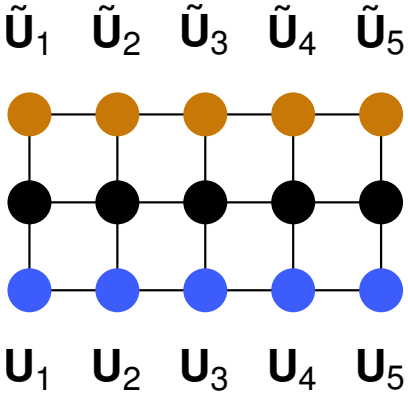

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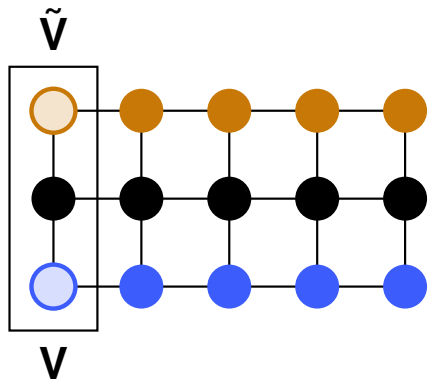

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Inserts $\mathbf{V}$ at location i in ψ etc.

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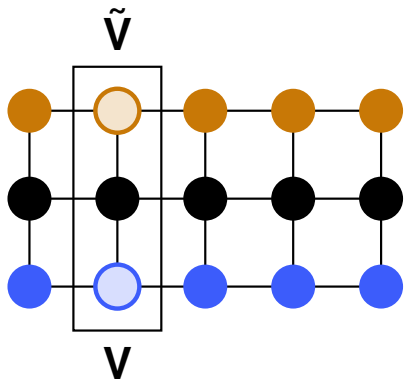

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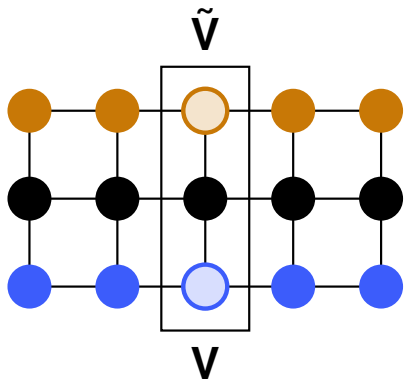

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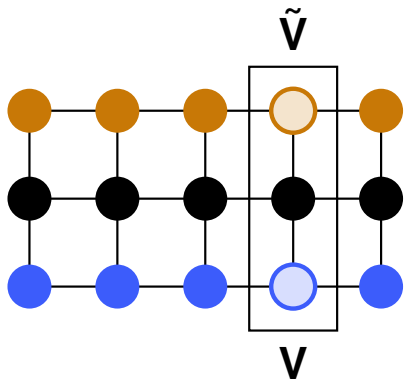

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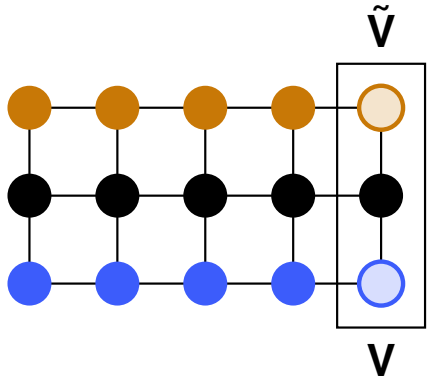

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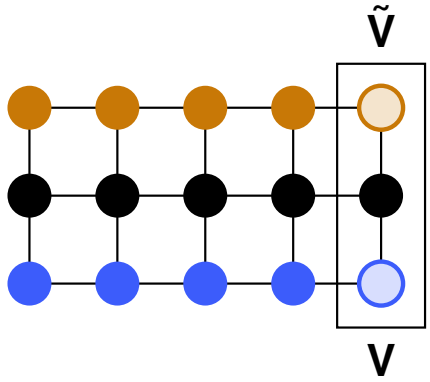

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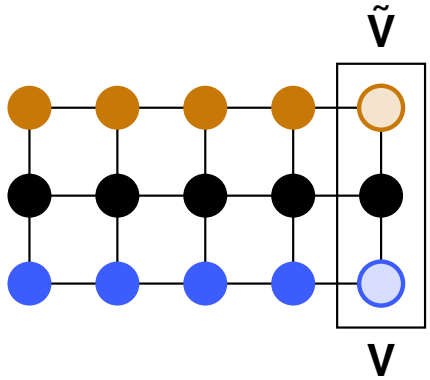
- Should be applicable to a wide range of objective functions $J(\tilde{\psi}, \psi)$:
  - non-selfadjoint eigenvalue problems, linear systems, ...

bivar-ALS sketch



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- Should be applicable to a wide range of objective functions $J(\tilde{\psi}, \psi)$:
  - non-selfadjoint eigenvalue problems, linear systems, ...
- Error analysis feasible based on monotonicity of some suitably modified ∇J

TNS and static correlation

- MPS/DMRG emerging competitive method for the electronic Schrödinger equation[10]
  - Good at resolving static correlation
  - Less good for dynamic correlation

[10] S. White and R.L. Martin, *J. Chem. Phys.* **110** (1999), 4127; G.K.-L. Chan and M. Head-Gordon, *JCP* **116** (2002), 4462; S. Wouthers and D. Van Neck, *Eur. Phys. J. D* **68** (2014), 272; many others

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- **Idea:** Hybrid methods that combine CC for dynamic correlation with TNS for static correlation

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- What is new: The BIVP allows self-consistency of static and dynamic correlation

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TNS and bivar-MRCC (sketch)

1. Introduce variational approximation on CAS/model space:

$$\mathscr{M} \subset \mathscr{H}_{\text{CAS}} \text{ smooth submanifold, e.g., rank-fixed MPS}$$

$$\hat{E} : \mathscr{M} \times \mathscr{M}^{\dagger} \times \mathscr{T}_{\text{ext}} \times \mathscr{T}_{\text{ext}}^{\dagger} \to \mathbb{C}$$

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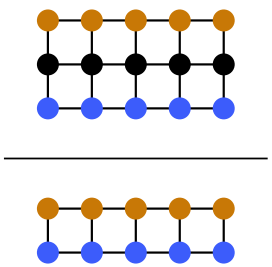

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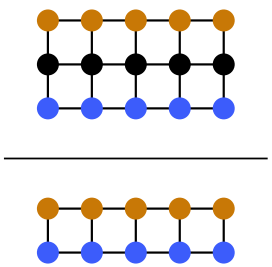


3. Stationary conditions:
   - Left/right eigenvalue problem for $K(T, \Lambda)$
   - bivar-MRCC T and Λ equations
   - Strategy: bivar-(M)ALS replaces linear eigenvalue solver

What could go wrong?

- $K(T, \Lambda)$ very expensive!
  - Up to 4-body operators
- Complex eigenvalues
- MPS may give qualitatively wrong model vector, even if energy is good
- Is the extra effort worth it?

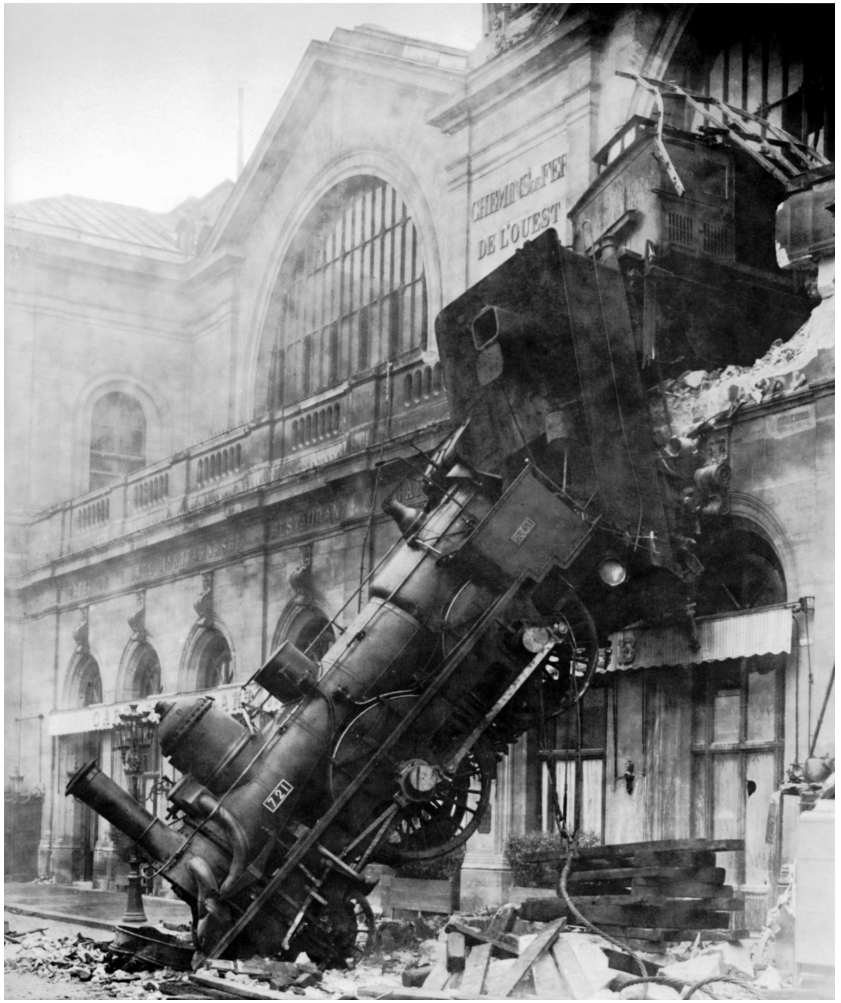


Table of Contents

Take-home messages, Part 1

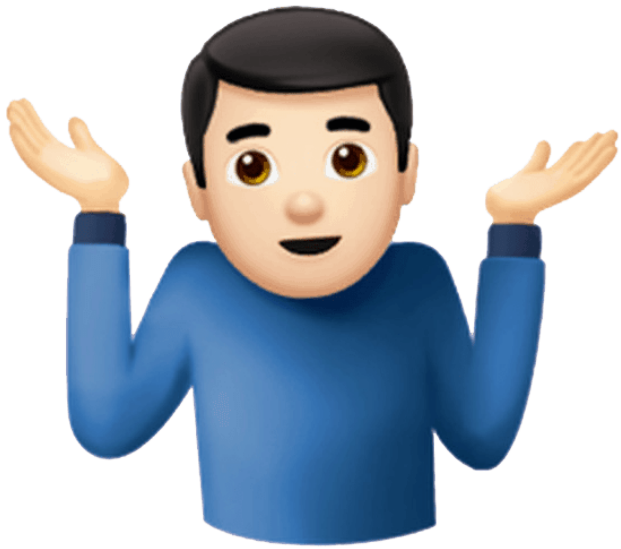
- The bivariational principle is the proper mathematical setting for CC type methods
- The bivar-MRCC method was discussed
- bivar-MRCC is just as good as established MR methods on the systems tested
- May have the potential to become a tool for quantum chemists

Take-home messages, Part 2

- The BIVP indicates bivariational versions of common optimization techniques for TNSs
  - Framework that includes NH-DMRG, imaginary-time propagation, (M)ALS, . . .
- Hybrid methods with TNS for static correlation exemplified with bivar-MRCC
- Work in progress

So, should the TNS people care?

- Non-selfadjoint problems could always get some more attention
- The BIVP approach and the bivar-(M)ALS algorithms may be fruitful
- Structure of hybrid MR methods fertile ground for analysis



Thank you!

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Hylleraas