Multideterminant wave functions
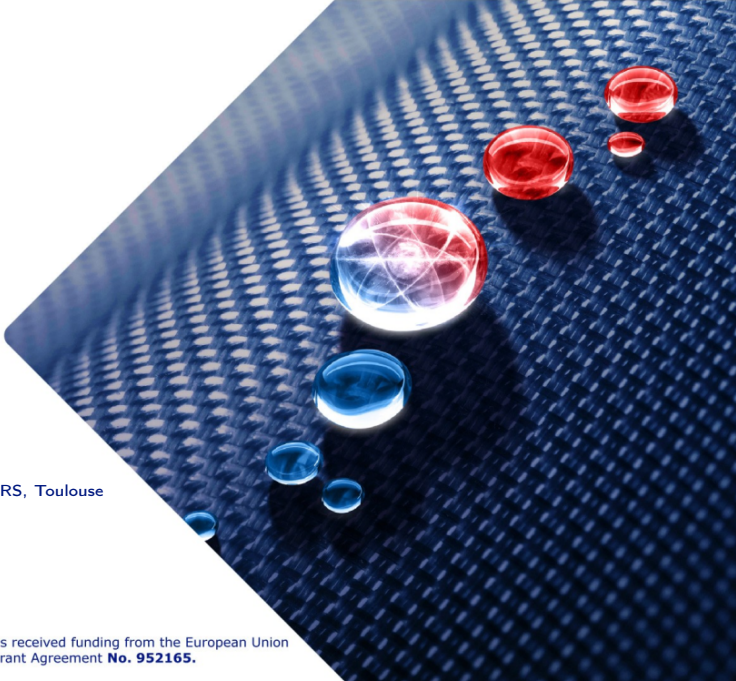
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18/06/2022

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Introduction

- Atomic orbitals (AOs): χ_k. *Non-orthogonal* set of one-electron functions.

$$\chi_k(\mathbf{r}) = \sum_l P_{kl}(\mathbf{r}) e^{-\gamma_{kl}|\mathbf{r}|^p}$$

P : Spherical harmonics or Polynomial. $p = 1$: Slater, $p = 2$: Gaussian

- Molecular orbitals (MOs): LCAO. *Orthonormal* set of one-electron functions.

$$\phi_i(\mathbf{r}) = \sum_k C_{ik} \chi_k(\mathbf{r})$$

- Many different types of MOs: Hartree-Fock, Kohn-Sham, localized, natural, . . .
- N-electron Wave function: Anti-symmetric product of MOs $\implies$ Slater determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \ldots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \ldots & \phi_N(\mathbf{r}_2) \\ \vdots & & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \ldots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

- MOs are linear combinations of AOs (LCAO)
- One can build as many MOs as AOs
- The space spanned by MOs is the same as the space spanned by AOs

- Hartree-Fock MOs are divided into occupied and virtual MOs
  - Occupied Hartree-Fock MOs: Orthonormal set of LCAOs which minimize the energy of a Slater determinant
  - Virtual Hartree-Fock MOs: The orthonormal complement of the Occupied MOs

The Slater determinant can be rewritten by separating ↑- and ↓-spin electrons:

$$\Psi(r_1, r_2, \ldots, r_{N_\uparrow}, r_{N_\uparrow+1}, \ldots, r_N) =$$

$$\begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \ldots & \phi_{N_\uparrow}(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \ldots & \phi_{N_\uparrow}(r_2) \\ \vdots & & \ddots & \vdots \\ \phi_1(r_{N_\uparrow}) & \phi_2(r_{N_\uparrow}) & \ldots & \phi_{N_\uparrow}(r_{N_\uparrow}) \end{vmatrix} \times \begin{vmatrix} \phi_1(r_{N_\uparrow+1}) & \phi_2(r_{N_\uparrow+1}) & \ldots & \phi_{N_\downarrow}(r_{N_\uparrow+1}) \\ \phi_1(r_{N_\uparrow+2}) & \phi_2(r_{N_\uparrow+2}) & \ldots & \phi_N(r_{N_\uparrow+2}) \\ \vdots & & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \ldots & \phi_{N_\downarrow}(r_N) \end{vmatrix}$$

$$= D_\uparrow(r_1, r_2, \ldots, r_{N_\uparrow}) \times D_\downarrow(r_{N_\uparrow+1}, \ldots, r_N)$$

$$\Psi^2 = (D_\uparrow \times D_\downarrow)^2$$
$$= D_\uparrow^2 \times D_\downarrow^2$$

- The N-electron density is the product of a density of $N_\uparrow$ $\uparrow$-spin electrons and a density of $N_\downarrow$ $\downarrow$-spin electrons.
- Mean-field approach: $\uparrow$-spin and $\downarrow$-spin electrons are statistically independent
- Although same-spin electrons are *not* statistically independent, the single-determinant model is said to be uncorrelated.

We have seen that electron correlation can be introduced with a Jastrow factor:

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = D_\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \times D_\downarrow(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N) \times \exp\left(J(\mathbf{r}_1, \ldots, \mathbf{r}_N)\right)$$

with

$$J(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i<j}^{N} \frac{a\,|\mathbf{r}_i - \mathbf{r}_j|}{1 + b\,|\mathbf{r}_i - \mathbf{r}_j|} + \ldots$$

J couples $\uparrow$-spin and $\downarrow$-spin electrons, so

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)^2 \neq p_\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \times p_\downarrow(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N)$$

and $\uparrow$-spin and $\downarrow$-spin electrons are correlated.

Correlation energy

$$E_{\text{cor}}[\Psi] = E[\Psi] - E_{\text{HF}}$$

- Ψ is an N-electron function
- It can be expressed as a linear combination of N-electron functions

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N_d} c_i\, D_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

- If the basis is infinitely large, the *exact* wave function can be obtained by finding the c_i which minimize the energy.

$$E(\Psi_1) \geq E(\Psi_m) \geq E(\Psi_{N_d}) \geq E(\Psi_\infty) = E_{\mathrm{exact}}$$

with $1 \leq m \leq N_d$.

A natural N-electron basis is the basis of all possible Slater determinants that can be built with a given set of M MOs:

$$\Psi = c_1 \begin{pmatrix} -\ - \\ -\ - \\ \uparrow\downarrow \end{pmatrix} + c_2 \begin{pmatrix} -\ - \\ \uparrow\ - \\ -\downarrow \end{pmatrix} + c_3 \begin{pmatrix} \uparrow\ - \\ -\ - \\ -\downarrow \end{pmatrix} + c_4 \begin{pmatrix} -\ - \\ -\downarrow \\ \uparrow\ - \end{pmatrix} +$$

$$c_5 \begin{pmatrix} -\ - \\ \uparrow\downarrow \\ -\ - \end{pmatrix} + c_6 \begin{pmatrix} \uparrow\ - \\ -\downarrow \\ -\ - \end{pmatrix} + c_7 \begin{pmatrix} -\downarrow \\ -\ - \\ \uparrow\ - \end{pmatrix} + c_8 \begin{pmatrix} -\downarrow \\ \uparrow\ - \\ -\ - \end{pmatrix} + c_9 \begin{pmatrix} \uparrow\downarrow \\ -\ - \\ -\ - \end{pmatrix}$$

Each basis function is antisymmetric $\Longrightarrow \Psi$ is antisymmetric

The size of the basis grows fast:

$$N_d = \left(\frac{M!}{N_\uparrow!(M - N_\uparrow)!} \right) \times \left(\frac{M!}{N_\downarrow!(M - N_\downarrow)!} \right)$$

Example: 18 electrons in 111 orbitals: $N_d = 2.5 \times 10^{25}$ determinants.

$$\begin{aligned} \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) &= c_1 \, D_{1\uparrow}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \, D_{1\downarrow}(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N) + \\ &\quad c_2 \, D_{2\uparrow}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \, D_{2\downarrow}(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N) \end{aligned}$$

$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)^2 \neq p_\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \times p_\downarrow(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N) \Longrightarrow$ electron correlation.

- The exact wave function is an eigenfunction of the spin operator $\hat{S}^2$
- Slater determinants are eigenfunctions of $\hat{S}_z$, but not of $\hat{S}^2$
- To obtain Ψ eigenfunction of $\hat{S}^2$, one needs to have in the determinant set all possible spin flips in open shells

$$
\begin{pmatrix} + \\ + \\ + \\ + \\ \text{\tiny⇅} \end{pmatrix} = a \begin{pmatrix} -\downarrow \\ -\downarrow \\ \uparrow- \\ \uparrow- \\ \uparrow\downarrow \end{pmatrix} + b \begin{pmatrix} \uparrow- \\ -\downarrow \\ -\downarrow \\ \uparrow- \\ \uparrow\downarrow \end{pmatrix} + c \begin{pmatrix} \uparrow- \\ -\downarrow \\ \uparrow- \\ -\downarrow \\ \uparrow\downarrow \end{pmatrix} + d \begin{pmatrix} \uparrow- \\ \uparrow- \\ -\downarrow \\ -\downarrow \\ \uparrow\downarrow \end{pmatrix} + e \begin{pmatrix} -\downarrow \\ \uparrow- \\ \uparrow- \\ -\downarrow \\ \uparrow\downarrow \end{pmatrix} + f \begin{pmatrix} -\downarrow \\ \uparrow- \\ -\downarrow \\ \uparrow- \\ \uparrow\downarrow \end{pmatrix}
$$

- Configuration state functions (CSF): Linear combinations of Slater determinants, which are eigenfunctions of S^2:

$$
\begin{pmatrix} + \\ + \\ + \\ + \\ \sharp \end{pmatrix} = A \times \frac{1}{2} \left[\begin{pmatrix} \uparrow\downarrow - \\ - \downarrow \\ - \downarrow \\ \uparrow - \\ \uparrow\downarrow \end{pmatrix} + \begin{pmatrix} - \downarrow \\ \uparrow - \\ \uparrow - \\ - \downarrow \\ \uparrow\downarrow \end{pmatrix} - \begin{pmatrix} \uparrow - \\ - \downarrow \\ \uparrow - \\ - \downarrow \\ \uparrow\downarrow \end{pmatrix} - \begin{pmatrix} - \downarrow \\ \uparrow - \\ - \downarrow \\ \uparrow - \\ \uparrow\downarrow \end{pmatrix} \right]
$$

$$
+ \quad B \times \frac{\sqrt{3}}{6} \left[-2 \begin{pmatrix} - \downarrow \\ - \downarrow \\ \uparrow - \\ \uparrow - \\ \uparrow\downarrow \end{pmatrix} + \begin{pmatrix} \uparrow - \\ - \downarrow \\ - \downarrow \\ \uparrow - \\ \uparrow\downarrow \end{pmatrix} + \begin{pmatrix} \uparrow - \\ - \downarrow \\ \uparrow - \\ - \downarrow \\ \uparrow\downarrow \end{pmatrix} - 2 \begin{pmatrix} \uparrow - \\ \uparrow - \\ - \downarrow \\ - \downarrow \\ \uparrow\downarrow \end{pmatrix} + \begin{pmatrix} - \downarrow \\ \uparrow - \\ \uparrow - \\ - \downarrow \\ \uparrow\downarrow \end{pmatrix} + \begin{pmatrix} - \downarrow \\ \uparrow - \\ - \downarrow \\ \uparrow - \\ \uparrow\downarrow \end{pmatrix} \right]
$$

- The CSF basis is smaller than the determinant basis: one selects only basis functions with the desired $\langle \hat{S}^2 \rangle$

Configuration interaction (CI)

- Ψ is a linear combination of Slater determinants (or CSFs)
- The energy is minimized by diagonalizing the Hamiltonian in the basis of Slater determinants

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

CI methods

Differ by the choice of the basis:

- Full configuration interaction (FCI): All possible Slater determinants. $\mathcal{O}(N!)$
- CI with Single and Double substitutions (CISD): No more than one or two MOs differ from the Hartree-Fock determinant. $\mathcal{O}(N_o^2 N_v^2)$
- Complete Active Space (CAS): Only a subset of m MOs can be substituted from the Hartree-Fock determinant. $\mathcal{O}(m!)$

- Dynamic : short-range effects due to the Coulomb hole. Hartree-Fock qualitatively correct, many small contributions.
- Static : near-degeneracies. Hartree-Fock qualitatively incorrect, few large contributions.

Examples

- CH_4, 6-31G: 38×10^6 determinants. Dynamic

$$E_{HF} \quad -40.1805 \text{ a.u}$$
$$E_{FCI} \quad -40.3011 \text{ a.u}$$

- Dissociated H_2, STO-6G: 2 determinants (1 CSF). Static

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \Big(\phi_1(1)\phi_1(2) - \phi_2(1)\phi_2(2) \Big)$$

$$E_{HF} \quad -0.5572 \text{ a.u} \quad \epsilon_1 = -0.08619 \text{ a.u}$$
$$E_{FCI} \quad -0.9421 \text{ a.u} \quad \epsilon_2 = -0.08619 \text{ a.u}$$

- **Dynamic**: Well described by a Jastrow factor
- **Static**: Well described by a linear combination of Slater determinants
- <u>Optimal representation</u>:

$$\Psi = \left(\sum_i c_i D_i \right) \exp{(J)}$$

- Interplay between static and dynamic correlation: c_i should be optimized in the presence of J

Size consistency: Strict separability. When two systems A and B are far enough to not interact:

$$E[\Psi_{A\ldots B}] = E[\Psi_A] + E[\Psi_B]$$

- If the MOs are localized on fragments A and B, determinants can be written as

$$|K^{A\ldots B}\rangle = |I^A J^B\rangle = |I^A\rangle \otimes |J^B\rangle$$

- FCI^{AB} is built as the tensor product of FCI^A and FCI^B

$$\Psi_{A\ldots B} = \sum_K c_K |K^{A\ldots B}\rangle = \left(\sum_I c_I^A |I^A\rangle\right) \otimes \left(\sum_J c_J^B |J^B\rangle\right)$$

CI is usually *not size-consistent*. Example: CISD

The CISD space for $A \ldots B$ is *not* the tensor product of the spaces of A and B

- $|I^A\rangle = \hat{T}_{ij}^{kl}|HF^A\rangle \quad |J^B\rangle = \hat{T}_{mn}^{pq}|HF^B\rangle$
- $|I^A J^B\rangle = \hat{T}_{ij}^{kl}\hat{T}_{mn}^{pq}|HF^A HF^B\rangle$
- $|K^{A \ldots B}\rangle = \hat{T}_{ijmn}^{klpq}|HF^{A \ldots B}\rangle$: quadruple excitation, missing in CISD space

The size-consistency error is positive:

$$E[\Psi_{CISD}^{A \ldots B}] \geq E[\Psi_{CISD}^A] + E[\Psi_{CISD}^B]$$

Size-consistent particular cases

$$\text{Hartree-Fock} \quad \text{FCI} \quad \text{CAS-SCF}$$

Configuration Interaction

- Define an orthonormal basis of N-electron functions: Slater determinants or CSFs $\{|I\rangle\}$
- Express the wave function on this basis: $\langle I|\Psi\rangle = c_I$

$$|\Psi\rangle = \sum_I c_I |I\rangle$$

- The energy is given by

$$E[\Psi] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

- The optimal c_I are obtained when $|\Psi\rangle$ is an eigenfunction of H, and E is the corresponding eigenvalue

- $\langle I|J\rangle = \delta_{IJ}$, because MOs are orthonormal.
- $H_{IJ} = \langle I|\hat{H}|J\rangle$
- $\langle \Psi|\Psi\rangle = \sum_{IJ} c_I\, c_J\, \delta_{IJ} = \sum_I c_I^2 = 1$

$$E[\Psi] = \sum_{IJ} c_I\, c_J\, H_{IJ}$$

- When N_d is small $< 10^4$, direct diagonalization of H
- When N_d is large, Davidson's algorithm to extract the desired roots.
  Iterative computation of $|W\rangle = \sum_I w_I|I\rangle = \sum_I |I\rangle\langle I|H|\Psi\rangle$ (power method).

Thanks to $\langle I|J\rangle = \delta_{IJ}$:

- **Diagonal** terms:

$$H_{II} = \sum_i \langle i|\hat{h}|i\rangle + \sum_{ij} \langle ij||ij\rangle$$

- $|J\rangle = \hat{T}_p^r|I\rangle$: $|I\rangle$ and $|J\rangle$ differ by **one MO**:

$$H_{IJ} = \langle p|\hat{h}|r\rangle + \sum_i \langle pi||ri\rangle$$

- $|J\rangle = \hat{T}_{pq}^{rs}|I\rangle$: $|I\rangle$ and $|J\rangle$ differ by **two MOs**:

$$H_{IJ} = \langle pq||rs\rangle$$

- $|I\rangle$ and $|J\rangle$ differ by **more than two MOs**:

$$H_{IJ} = 0$$

There are:

- $\mathcal{O}(N^4)$ two-electron integrals
- N_d Slater determinants

Algorithms

- Integral-driven
    - Loop over integrals
    - Add the contributions to $|W\rangle$
- Determinant-driven
    - Loop over determinants
    - Usually, $N_d \ggg \mathcal{O}(N^4)$, so less efficient than determinant-driven

- Same symmetry:
  Obtained as different eigenvectors of H. Expanded on the same set of determinants:

$$\Psi^{(k)} = \sum_I c_I^{(k)} |I\rangle$$

- Lowest states of different symmetries:
  H is block-diagonal:
  - Pick only determinants of the desired symmetry
  - Obtain the ground state

  Expanded on different sets of determinants:

$$\Psi^{(k)} = \sum_I c_I^{(k)} |I^{(k)}\rangle$$

- All CI methods are approximations to FCI
- They differ by the choice of the Slater determinant basis

- CIS, CISD, CISDT, CISDTQ, ... : Number of differences *wrt* Hartree-Fock (dynamic)
- CAS, RAS, GAS, ... : CI in an active space (static)

- MR-CI : active space + CISD for each reference (static + dynamic)
- MP2, CAS-PT2, dynamic correlation is computed with perturbation theory: cheaper than CI

Selected Configuration Interaction

FCI: Exact solution of $\hat{H}\Psi = E\Psi$ in a complete basis of Slater determinants

- The determinant basis is derived from the one-electron basis set
- Only approximation : one-electron basis-set incompleteness
- Intractable : $\mathcal{O}(N!)$ scaling
- All the post-Hartree-Fock methods are *approximations* of the FCI within the same basis set

CrossMark

Pushing configuration-interaction to the limit: Towards massively parallel MCSCF calculations

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A new large-scale parallel multiconfigurational self-consistent field (MCSCF) implementation in the open-source NWChem computational chemistry code is presented. The generalized active space approach is used to partition large configuration interaction (CI) vectors and generate a sufficient number of batches that can be distributed to the available cores. Massively parallel CI calculations with large active spaces can be performed. The new parallel MCSCF implementation is tested for the chromium trimer and for an active space of 20 electrons in 20 orbitals, which can now routinely be performed. Unprecedented CI calculations with an active space of 22 electrons in 22 orbitals for the pentacene systems were performed and a single CI iteration calculation with an active space of 24 electrons in 24 orbitals for the chromium tetramer was possible. The chromium tetramer corresponds to a CI expansion of one trillion Slater determinants (914 058 513 424) and is the largest conventional CI calculation attempted up to date. *Published by AIP Publishing.*
https://doi.org/10.1063/1.4989858

- Each row $\langle I|$ of H has non-zeros when $|J\rangle$ differs by less than 3 MOs (Slater-Condon rules)
- Each row has at most $\mathcal{O}(N_o^2 N_v^2)$ non-zero elements
- H is symmetric, the same applies to columns
- Davidson's algorithm involves computing $\langle I|\hat{H}|\Psi\rangle$
- Sparse matrix-vector multiplication: $\mathcal{O}(N_d \times N_o^2 N_v^2)$

FCI has seen a breakthrough in 2007-2012

- DMRG[a]
- FCI-QMC : Stochastic solution of FCI equations.[b]
    - First row diatomics cc-pV5Z.[c]
- Selected Configuration Interaction
    - Scaling is still $\mathcal{O}(N!)$, but pre-factor is killed.
    - Much larger active spaces are possible today

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OpenMolcas: From Source Code to Insight

Morgane Vacher, Ali Alavi, Celestino Angeli, Jochen Autschbach, Jie J. Bao, Sergey I. Bokarev, Nikolay A. Bogdanov, Rebecca K. Carlson, Liviu F. Chibotaru, Joel Creutzberg, Nike Dattani, Mickaël G. Delcey, Sijia Dong, Andreas Dreuw, Leon Freitag, Luis Manuel Frutos, Laura Gagliardi, Frédéric Gendron, Angelo Giussani, Leticia Gonzalez, Gilbert Grell, Meiyuan Guo, Chad E. Hoyer, Marcus Johansson, Sebastian Keller, Stefan knecht, Goran Kovačević, Erik Källman, Giovanni Li Manni, Marcus Lundberg, Yingjin Ma, Sebastian Mai, João Pedro Malhado, Per Åke Malmqvist, Philipp Marquetand, Stefanie A. Mewes, Jesper Norell, Massimo Olivucci, Markus Oppel, Quan Manh Phung, Kristine Pierloot, Felix Plasser, Markus Reiher, Andrew M. Sand, Igor Schapiro, Prachi Sharma, Christopher J. Stein, Lasse Kragh Sørensen, Donald G. Truhlar, Mihkel Ugandi, Liviu Ungur, Alessio Valentini, Steven Vancoillie, Valera Veryazov, Oskar Weser, Per-Olof Widmark, Sebastian Wouters, J. Patrick Zobel, Roland Lindh

CATEGORIES

- Computational Chemistry and Modeling
- Theory - Computational
- Chemoinformatics - Computational Chemistry
- Spectroscopy (Physical Chem.)
- Physical and Chemical Properties

KEYWORD(S)

Multiconfigurational methods

Molecular dynamics

Wave function analysis   Spectroscopy

Basis sets

In this article we describe the OpenMolcas environment and invite the computational chemistry community to collaborate. The open-source project already includes a large number of new developments realized during the transition from the commercial MOLCAS product to the open-source platform. The paper initially describes the technical details of the new software development platform. This is followed by brief presentations of many new methods, implementations, and features of the OpenMolcas program suite. These developments include novel wave function methods such as stochastic complete active space self-consistent field, density matrix renormalization group (DMRG) methods, and hybrid multiconfigurational wave function and density functional theory models. Some of these implementations include an array of additional options and functionalities. The paper proceeds and describes developments related to explorations of potential energy surfaces. Here we present methods for the optimization of conical intersections, the simulation of adiabatic and nonadiabatic molecular dynamics and interfaces to tools for semiclassical and quantum mechanical nuclear dynamics.
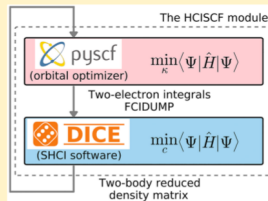
LICENCE

Cheap and Near Exact CASSCF with Large Active Spaces

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ABSTRACT: We use the recently developed Heat-bath Configuration Interaction (HCI) algorithm as an efficient active space solver to perform multiconfiguration self-consistent field calculations (HCISCF) with large active spaces. We give a detailed derivation of the theory and show that difficulties associated with non-variationality of the HCI procedure can be overcome by making use of the Lagrangian formulation to calculate the HCI relaxed two-body reduced density matrix. HCISCF is then used to study the electronic structure of butadiene, pentacene, and Fe—porphyrin. One of the most striking results of our work is that the converged active space orbitals obtained from HCISCF are relatively insensitive to the accuracy of the HCI calculation. This allows us to obtain nearly converged CASSCF energies with an estimated error of less than 1 mHa using the orbitals obtained from the HCISCF procedure in which the integral transformation is the dominant cost. For example, an HCISCF calculation on the Fe—porphyrin model complex with an active space of (44e, 44o) took only 412 s per iteration on a single node containing 28 cores, out of which 185 s was spent in the HCI calculation and the remaining 227 s was used mainly for integral transformation. Finally, we also show that active space orbitals can be optimized using HCISCF to substantially speed up the convergence of the HCI energy to the Full CI limit because HCI is not invariant to unitary transformations within the active space.

The HCISCF module

pyscf (orbital optimizer) $\min_\kappa \langle \Psi | \hat{H} | \Psi \rangle$

Two-electron integrals
FCIDUMP

DICE (SHCI software) $\min_c \langle \Psi | \hat{H} | \Psi \rangle$

Two-body reduced density matrix

- Select determinants on-the-fly
  - with perturbation theory (CIPSI[1])
  - or based only on the matrix elements of $\hat{H}$ (SHCI[2])
- Target spaces : Full-CI, MR-CISD, large CAS, . . .
- Use PT2 to estimate the missing part

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[2] A.A. Holmes, C.J. Umrigar, and S. Sharma, J. Chem. Phys. 147, 164111 (2017)

Start with $\mathcal{D}_0 = \{|\mathrm{HF}\rangle\}$ and $|\Psi_0\rangle = |\mathrm{HF}\rangle$.

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1. $\forall |i\rangle \in \{\hat{T}_{\mathrm{SD}}|\Psi_n\rangle\} \setminus \{\mathcal{D}_n\}$, compute $e_i = \frac{\langle i|\mathcal{H}|\Psi_n\rangle^2}{E(\Psi_n) - \langle i|\mathcal{H}|i\rangle}$

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2. if $|e_i| > \epsilon_n$, select $|i\rangle$

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3. Estimated energy : $E(\Psi_n) + E_{\text{PT2}}(\Psi_n) = E(\Psi_n) + \sum_i e_i$

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4. $\mathcal{D}_{n+1} = \mathcal{D}_n \cup \{\cup_{i(\text{selected})}|i\rangle\}$

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5. Minimize $E(\Psi_{n+1})$ (Davidson),
   $\Psi_{n+1} = \Psi_n + \sum_{i(\mathrm{selected})} c_i|i\rangle$

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4. $\mathcal{D}_{n+1} = \mathcal{D}_n \cup \{\cup_{i(\mathrm{selected})}|i\rangle\}$

5. Minimize $E(\Psi_{n+1})$ (Davidson),
   $\Psi_{n+1} = \Psi_n + \sum_{i(\mathrm{selected})} c_i|i\rangle$

6. Choose $\epsilon_{n+1} < \epsilon_n$

Start with $\mathcal{D}_0 = \{|\mathrm{HF}\rangle\}$ and $|\Psi_0\rangle = |\mathrm{HF}\rangle$.

1. $\forall |i\rangle \in \{\hat{T}_{\mathrm{SD}}|\Psi_n\rangle\} \setminus \{\mathcal{D}_n\}$, compute $e_i = \frac{\langle i|\mathcal{H}|\Psi_n\rangle^2}{E(\Psi_n) - \langle i|\mathcal{H}|i\rangle}$

2. if $|e_i| > \epsilon_n$, select $|i\rangle$

3. Estimated energy : $E(\Psi_n) + E_{\mathrm{PT2}}(\Psi_n) = E(\Psi_n) + \sum_i e_i$

4. $\mathcal{D}_{n+1} = \mathcal{D}_n \cup \{\cup_{i(\mathrm{selected})}|i\rangle\}$

5. Minimize $E(\Psi_{n+1})$ (Davidson),
   $\Psi_{n+1} = \Psi_n + \sum_{i(\mathrm{selected})} c_i|i\rangle$

6. Choose $\epsilon_{n+1} < \epsilon_n$

7. Iterate

aug-cc-pVDZ
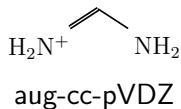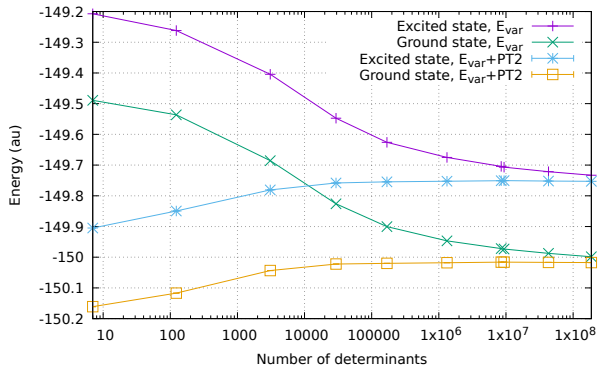
- When $N_d = N_{\text{FCI}}$, $E_{\text{PT2}} = 0$, CI is solved *exactly*.
- Every CI problem can be solved by iterative perturbative selection
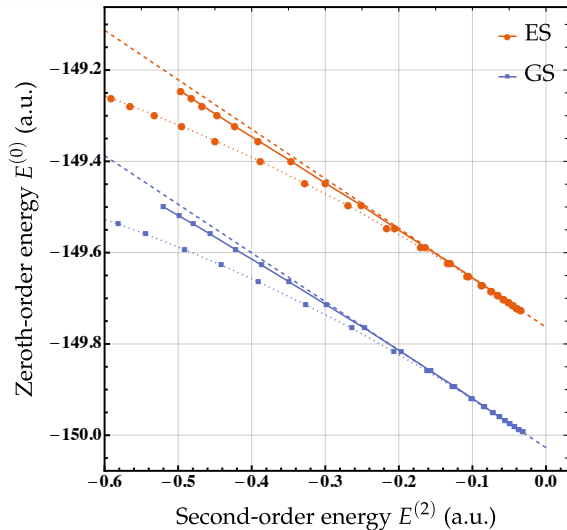
exFCI : Extrapolate $E = f(E_{PT2})$ at $E_{PT2} = 0$, estimates the complete CI solution.

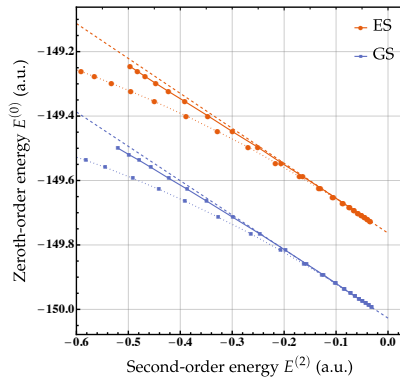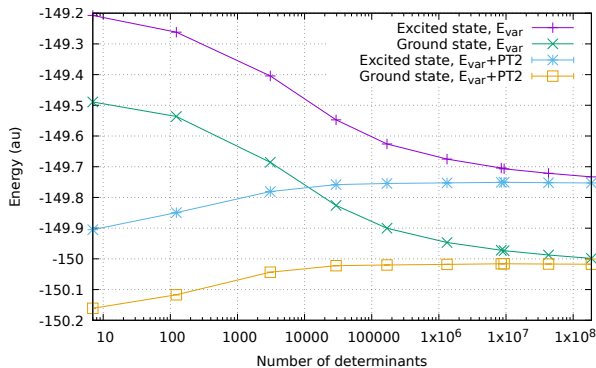**The error of $E_{\text{FCI}} \sim E + E_{\text{PT2}}$ is proportional to E_{PT2}**

$$E_{\text{FCI}} = E + (1 + \alpha)\, E_{\text{PT2}}$$

For 2 states

$$\begin{aligned}
E_{\text{FCI}}^{(1)} &= E^{(1)} + (1 + \alpha^{(1)})\, E_{\text{PT2}}^{(1)} \\
E_{\text{FCI}}^{(2)} &= E^{(2)} + (1 + \alpha^{(2)})\, E_{\text{PT2}}^{(2)}
\end{aligned}$$

If $\alpha^{(1)} = \alpha^{(2)}$ and $E_{\text{PT2}}^{(1)} = E_{\text{PT2}}^{(2)}$

$$E_{\text{FCI}}^{(2)} - E_{\text{FCI}}^{(1)} = E^{(2)} - E^{(1)}$$

- $-(1 + \alpha)$ is the slope of the extrapolation curve
- $\alpha^{(1)} \sim \alpha^{(2)}$ can be obtained using state-average orbitals

Multideterminant QMC

- In a CI calculation:

$$|\Psi\rangle = \sum_I c_I |I\rangle$$

- In QMC:

$$
\begin{aligned}
\Psi(r_1, \ldots, r_N) &= \left(\sum_k c_k D_k(r_1, \ldots, r_N) \right) e^{J(r_1, \ldots, r_N)} \\
&= \sum_k c_k \left(D_K(r_1, \ldots, r_N) e^{J(r_1, \ldots, r_N)} \right)
\end{aligned}
$$

Computationally expensive

- We need to evaluate *all* the Slater determinants at each MC step
- Compacting the wave function is desirable

1 Build the Slater Matrix $A_{ij} = \phi_j(r_i)$:

$$A = \begin{bmatrix} \phi_1(r_1) & \phi_2(r_1) & \ldots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \ldots & \phi_N(r_2) \\ \vdots & & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \ldots & \phi_N(r_N) \end{bmatrix}$$

2 LU factorization (`dgetrf`) : $A = P\,L\,U$, costs $\mathcal{O}(N^3)$

3 $\det A = \prod_i U_{ii}$

$$\frac{\nabla_i(\det A)}{\det A} = \sum_j \nabla_i \phi_j(\mathsf{r}_i).A_{ji}^{-1}$$

$$\frac{\Delta_i(\det A)}{\det A} = \sum_j \Delta_i \phi_j(\mathsf{r}_i).A_{ji}^{-1}$$

Inverse of A (`dgetri`) : costs $\mathcal{O}(N^3)$

A and A^{-1} are known, u and v are column vectors,

$$\left(A + uv^\dagger\right)^{-1} = A^{-1} - \frac{A^{-1}uv^\dagger A^{-1}}{1 + v^\dagger A^{-1}u}.$$

Costs $\mathcal{O}(N^2)$.

Single orbital change:

$$u = \begin{bmatrix} \phi_k(r_1) - \phi_l(r_1) \\ \vdots \\ \phi_k(r_N) - \phi_l(r_N) \end{bmatrix}, v = \begin{bmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{bmatrix},$$

$$\Psi(r) = \sum_{k}^{N_d} c_k D_k = \sum_{i}^{N_{d\uparrow}} \sum_{j}^{N_{d\downarrow}} C_{ij} \, D_{i\uparrow}(r_\uparrow) \, D_{j\downarrow}(r_\downarrow)$$

- $D_\uparrow(r_\uparrow)$: vector of $N_{d\uparrow}$ elements
- $D_\downarrow(r_\downarrow)$: vector of $N_{d\downarrow}$ elements
- C : $N_{d\uparrow} \times N_{d\downarrow}$ matrix. The matrix contains N_d non-zero elements

C is constant in a QMC calculation $\implies$ preprocessing.

At every MC step, we need to evaluate:

$$
\begin{aligned}
\Psi &= (D_\uparrow^\dagger (C) D_\downarrow) \\
\nabla_i \Psi &= \nabla_i D_\uparrow^\dagger . (C D_\downarrow) \text{ or } (D_\uparrow^\dagger C) . \nabla_i D_\downarrow \\
\Delta_i \Psi &= \Delta_i D_\uparrow^\dagger . (C D_\downarrow) \text{ or } (D_\uparrow^\dagger C) . \Delta_i D_\downarrow \\
V_{\text{pseudo}}^{\text{non}-\text{loc}} \Psi &= V_{\text{pseudo}}^{\text{non}-\text{loc}} D_\uparrow^\dagger . (C D_\downarrow) \text{ or } (D_\uparrow^\dagger C) . V_{\text{pseudo}}^{\text{non}-\text{loc}} D_\downarrow
\end{aligned}
$$

($\uparrow$ electrons and $\downarrow$ electrons)

$\mathcal{O}(N_{d\uparrow} \times N_{\textbf{elec}\uparrow}^2)$

$$D_\uparrow \text{ and } D_\downarrow, \quad \nabla D_\uparrow \text{ and } \nabla D_\downarrow, \quad \Delta D_\uparrow \text{ and } \Delta D_\downarrow$$

$\mathcal{O}(N_d)$, **tiny prefactor**

- Sparse vector-matrix product $D_\uparrow{}^\dagger.C$: N_d operations, returns a $N_{d\downarrow}$ vector

$\mathcal{O}(N_{\textbf{elec}\downarrow} \times N_{d\uparrow})$

- Dot product with $D_\downarrow$: $N_{d\downarrow}$ operations, produces a scalar
- Matrix product with $\nabla D_\downarrow$: $3N_{\text{elec}\downarrow} \times N_{d\downarrow}$ operations, produces a $3N_{\text{elec}\downarrow}$ vector
- Matrix product with $\Delta D_\downarrow$: $N_{\text{elec}\downarrow} \times N_{d\downarrow}$ operations, produces a $N_{\text{elec}\downarrow}$ vector
- Matrix product with $V_{\text{pseudo}}^{\text{non}-\text{loc}} D_\downarrow$: $N_{\text{elec}\downarrow} \times N_{d\downarrow}$ operations, produces a $N_{\text{elec}\downarrow}$ vector

Use large CIPSI wave functions as trial wave functions for DMC[3]:

H_2O

- best estimate of the exact energy
- $\sim 10^6$ Slater determinants

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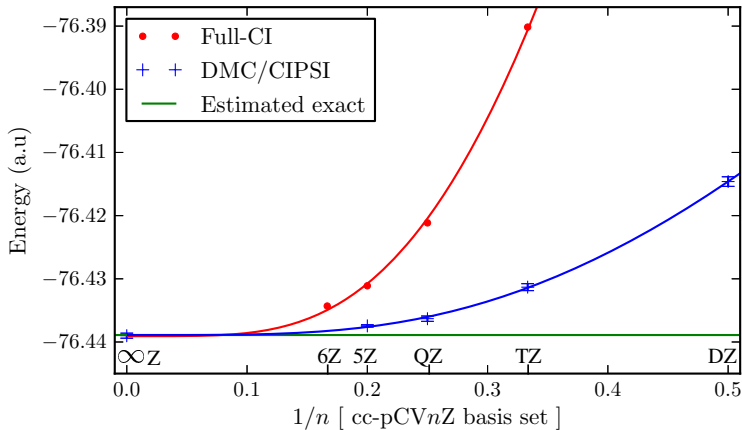
[3]Caffarel et al, (2016), J. Chem. Phys., 144:15(151103)

- Adding a Jastrow factor on top of a CI wave function:
  - The N-electron basis is no more orthonormal

  $$\langle D_I \, e^J | D_K \, e^J \rangle \neq \delta_{IK}$$

  - Double-counting of correlation
    - Dynamic correlation from the determinants
    - Dynamic correlation from the Jastrow
  - The CI coefficients are no more optimal

- Re-optimizing the CI coefficients in the presence of the Jastrow:
  - Increases large coefficients
  - Reduces small coefficients

- Solving H.C $= E$ S.C is difficult:
  - Statistical errors in matrix elements of H and S
  - Determinants with tiny CI coefficients have a negligible contribution to Ψ^2
  - The error on $\langle K|\hat{H}|L\rangle$ is often larger than the expectation value when c_K is small.

- Nodal surfaces (DMC energies) are determined by the determinant expansion.
- Accurate energy differences need balanced qualities between the states

Two different strategies:

1. Stochastic optimization
   - Use a deterministic method which gives a qualitatively good description (minimal CAS-SCF)
   - Reoptimize all the parameters: MOs, CI, Jastrow
2. Deterministic optimization
   - Use a deterministic method which gives a reasonable ΔE (MR-CI, CIPSI)
   - Run a DMC without modifying the wave function.

	Pros	Cons
Deterministic optimization	Very good quality control Smooth potential energy surfaces	Very large expansions Limited to small systems
Stochastic optimization	Compact wave functions Can be applied to large systems	Noisy optimization Harder to get balanced energies

Good strategy: The best of both worlds

- Small CIPSI expansions in FCI space : $\implies$ compact
- Enforcing constant $E_{textPT2}$ for selecting determinants $\implies \Delta E \sim \Delta E_{\text{FCI}}$ consistent quality for both states
- Optimize a Jastrow factor in QMC
- Re-optimize all parameters in QMC