

Symmetry broken and restored mean-field theory

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outline

- ▶ motivation
- ▶ symmetry-projected Hartree–Fock (SPHF)
 - ▶ symmetry dilemma
 - ▶ projection operators
 - ▶ SPHF energy functional
 - ▶ variational optimization
 - ▶ evaluation of matrix elements
 - ▶ structure of intrinsic determinants
 - ▶ size extensivity
- ▶ beyond SPHF
 - ▶ configuration mixing
 - ▶ excited electronic states
 - ▶ cluster product states

Motivation

- ▶ Hartree–Fock provides a reasonable zeroth-order description of weakly correlated systems.
- ▶ Weak correlations can be accurately described by traditional quantum chemical methods with polynomial scaling.
- ▶ Strong correlations can only be accurately described by expensive methods (typically combinatorial scaling).

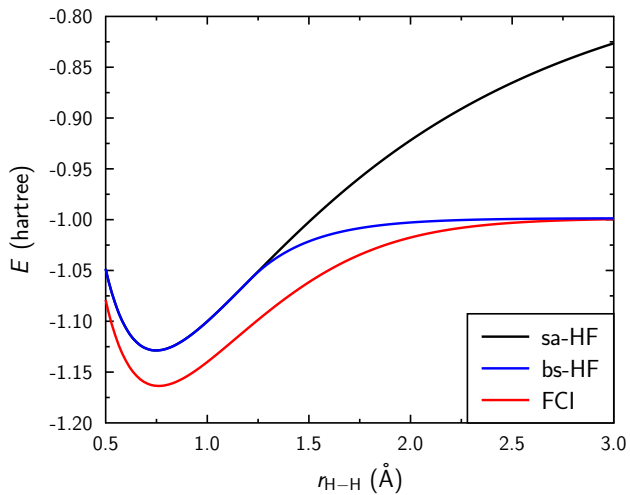
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We aim to provide an approach that can:

- ▶ Account for at least some of the strong correlations at a reduced computational cost (mean-field).
- ▶ Be systematically improved towards the exact answer.
- ▶ Provide a description of the full quantum mechanical character of the system (access ground *and* excited states).
- ▶ Be fully variational. (This seems to be inconsistent with being extensive.)

dissociation of H₂



cc-pVDZ basis set

strong correlation in molecular dissociations

This strong correlation in molecular dissociation curves is a fairly general phenomenon: it occurs when closed shell molecules dissociate into open-shell fragments.

In general, the correct treatment of breaking of q bonds requires

$$\approx \binom{q}{q/2}^2 \text{ configurations.}$$

broken symmetry HF

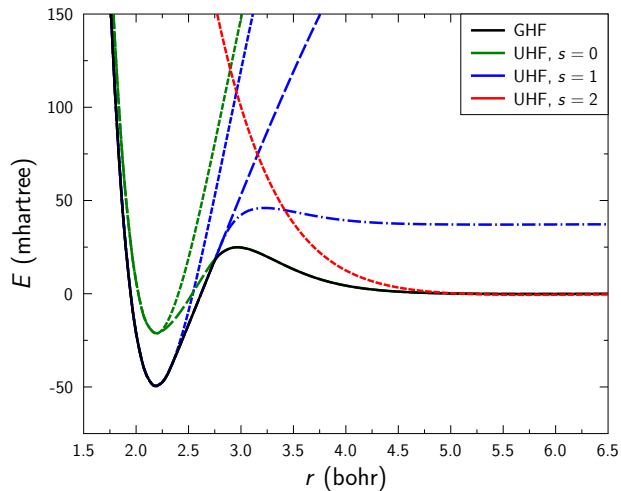
- ▶ Unrestricted HF (UHF) can *partially* capture some of the strong correlations by localizing the electrons.
- ▶ This is accomplished at a *mean-field* cost.
- ▶ Broken symmetry HF is **always size-consistent**.
- ▶ The UHF wavefunction is, to some extent, unphysical: good quantum numbers are lost. For instance, spin symmetry breaking leads to *spin contamination*.
- ▶ Correlated approaches based on UHF-type wavefunctions are not better than RHF-based ones.

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A **symmetry-adapted** formalism is needed in order to compare with experimental (spectroscopic) results. Broken symmetries are unphysical in finite systems.

dissociation of O₂



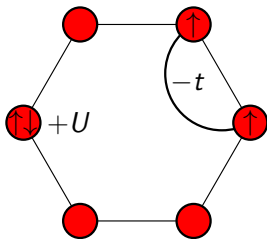
cc-pVDZ basis set

1D periodic Hubbard Hamiltonian

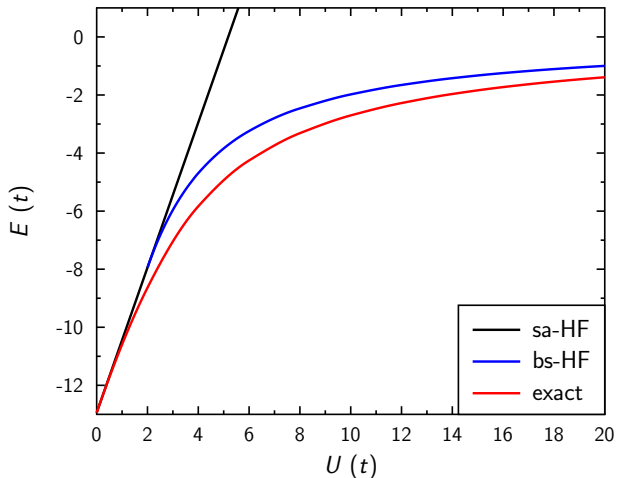
Describes a set of electrons in a lattice of L sites:

$$\hat{H} = -t \sum_j \sum_{\sigma=\uparrow,\downarrow} \left[a_{j+1\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{j+1\sigma} \right] + U \sum_j a_{j\uparrow}^\dagger a_{j\uparrow} a_{j\downarrow}^\dagger a_{j\downarrow}$$

- ▶ periodic boundary conditions are used:
sites j and $j + L$ are equivalent
- ▶ kinetic energy due to hopping to nearest-neighbor sites
- ▶ on-site repulsion for opposite-spin electrons



1D periodic Hubbard Hamiltonian



$L = 10$ Hubbard chain results at half-filling ($N = L$)

Symmetry-projected Hartree–Fock

Löwdin's symmetry dilemma

If the Hamiltonian \hat{H} has a given symmetry $\hat{\Lambda}$,

$$[\hat{H}, \hat{\Lambda}] = 0,$$

then exact solutions $|\Psi\rangle$ are **symmetry adapted**:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \quad \hat{\Lambda}|\Psi\rangle = \lambda|\Psi\rangle.$$

For approximate wavefunctions $|\Phi\rangle$ this need not be true. The imposition of symmetry constraints can only raise the energy.

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Symmetry dilemma:

- ▶ A **symmetry-adapted** solution $|\Phi\rangle$ possesses good quantum numbers, but it has higher energy.
- ▶ A **broken-symmetry** solution $|\Phi'\rangle$ is lower in energy, but the good quantum numbers are gone.

a way around the dilemma?

Consider the ansatz

$$|\Psi^j\rangle = \hat{P}^j|\Phi\rangle.$$

$|\Phi\rangle$ is a **broken-symmetry** Slater determinant

\hat{P}^j is a projection operator that recovers the j -th quantum number

This symmetry-projected HF ansatz, proposed by Löwdin [Phys. Rev. **97**, 1509 (1955)], gets around the dilemma:

- ▶ Quantum numbers are restored.
- ▶ Correlations due to symmetry breaking can still be recovered.

broken symmetries and deformed states

Let $U(\alpha)$ be a unitary operator such that

$$\hat{H} = U^\dagger(\alpha) \hat{H} U(\alpha).$$

Then $U(\alpha)$ represents an invariance of the Hamiltonian.
Here, α may be a continuous or discrete label.

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If $|\Phi\rangle$ is a **broken-symmetry** state, then all states of the form

$$|\Phi(\alpha)\rangle \equiv U(\alpha)|\Phi\rangle$$

are **degenerate**. That is,

$$\langle\Phi(\alpha)|\hat{H}|\Phi(\alpha)\rangle = \langle\Phi|\hat{H}|\Phi\rangle.$$

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Peierls and Yoccoz [Proc. Phys. Soc. A **70**, 381 (1957)] realized that diagonalizing the Hamiltonian in this subspace achieves:

- ▶ The degeneracy is lifted.
- ▶ Symmetries are restored.

on the form of projection operators

For generally non-Abelian groups (such as spin), we use projection-like operators

$$\hat{P}_{mk}^j = \sum |j; m\rangle \langle j; k|.$$

They trivially satisfy

$$\hat{P}_{k'm'}^{j'} \hat{P}_{mk}^j = \hat{P}_{k'k}^j \delta_{jj'} \delta_{m'm}$$

$$(\hat{P}_{mk}^j)^\dagger = \hat{P}_{km}^j$$

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Projection operators are written as integrals (or sums) over **unitary** operators, e.g.:

$$\hat{P}_{mk}^s = \frac{2s+1}{8\pi^2} \int d\Omega D_{mk}^{s*}(\Omega) \hat{R}(\Omega),$$

where $\Omega = (\alpha, \beta, \gamma)$. $\hat{R}(\Omega)$ is the standard spin-rotation operator:

$$\hat{R}(\Omega) = \exp(-i\alpha\hat{S}_z) \exp(-i\beta\hat{S}_y) \exp(-i\gamma\hat{S}_z).$$

detour: Löwdin spin-projection

The **spin-projected** ansatz was popular in quantum chemistry. It was difficult to handle due to the form of the spin projection operator:

$$\hat{P}^s = \prod_{l \neq s} \frac{\hat{S}^2 - l(l+1)}{s(s+1) - l(l+1)}.$$

Note that this is a **many-body** operator, as opposed to the one-body exponential shown before.

projected Hartree–Fock ansatz

We write our symmetry projected ansatz as:

$$|\Psi_m^j\rangle = \sum_k f_k \hat{P}_{mk}^j |\Phi\rangle,$$

where $|\Phi\rangle$ is a Slater determinant. Here, $\{f\}$ is a set of linear variational coefficients.

The linear combination guarantees independence with respect to the orientation of the deformed determinant.

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The projection operator is generically written as

$$\hat{P}_{mk}^j = \frac{h}{L} \int_L d\vartheta w_{mk}^{j*}(\vartheta) \hat{R}(\vartheta),$$

where $\hat{R}(\vartheta)$ is a **unitary, one-body** rotation operator.

projected HF optimization

In **standard HF**, we make the ansatz $|\Psi\rangle = |\Phi\rangle$. The energy is given by

$$E_{\text{HF}}[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}.$$

In **symmetry-projected HF**, we make the ansatz $|\Psi_m^j\rangle = \sum_k f_k \hat{P}_{mk}^j |\Phi\rangle$.
The energy is given by

$$E_{\text{PHF}}[\{f\}, \Phi] = \frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{km}^j \hat{H} \hat{P}_{mk'}^j | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{km}^j \hat{P}_{mk'}^j | \Phi \rangle} = \frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{H} \hat{P}_{kk'}^j | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{kk'}^j | \Phi \rangle}.$$

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Two choices:

- ▶ **projection-after-variation** (PAV): Minimize $E_{\text{HF}}[\Phi]$ and then perform a single-shot evaluation of $E_{\text{PHF}}[\{f\}, \Phi]$.
- ▶ **variation-after-projection** (VAP): Minimize $E_{\text{PHF}}[\{f\}, \Phi]$.

quick detour: notation

type of reference determinant $|\Phi\rangle$ (suffix)

$$\begin{aligned} \text{restricted HF (RHF)} \quad \langle \mathbf{r} | \chi_{2i-1} \rangle &= u_i(\mathbf{r}) | \uparrow \rangle \\ &\langle \mathbf{r} | \chi_{2i} \rangle = u_i(\mathbf{r}) | \downarrow \rangle \end{aligned}$$

$$\begin{aligned} \text{unrestricted HF (UHF)} \quad \langle \mathbf{r} | \chi_{2i-1} \rangle &= u_i(\mathbf{r}) | \uparrow \rangle \\ &\langle \mathbf{r} | \chi_{2i} \rangle = v_i(\mathbf{r}) | \downarrow \rangle \end{aligned}$$

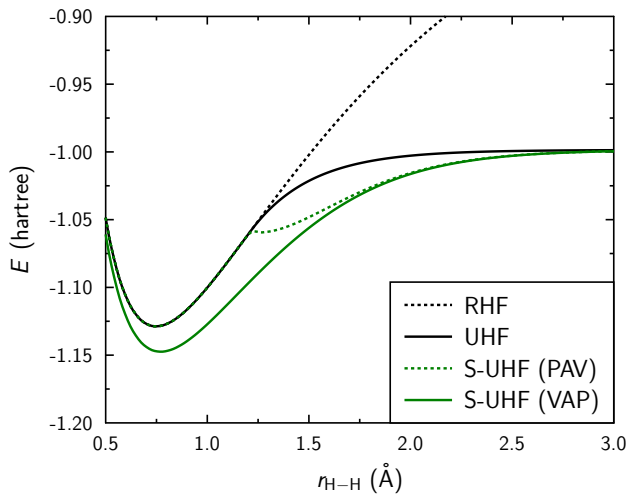
$$\text{generalized HF (GHF)} \quad \langle \mathbf{r} | \chi_j \rangle = u_j(\mathbf{r}) | \uparrow \rangle + v_j(\mathbf{r}) | \downarrow \rangle$$

type of symmetry projection (prefix)

S	spin projection
K	complex conjugation projection
$C_s, C_{2v}, D_{2h}, \dots$	spatial symmetry projection

D_{2h} S-GHF: spin + D_{2h} projection based on a GHF reference

dissociation profile of H₂



cc-pVDZ basis set

projected HF optimization

In a VAP approach, we minimize the energy functional

$$E_{\text{PHF}}[\{f\}, \Phi] = \frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{H} \hat{P}_{kk'}^j | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{kk'}^j | \Phi \rangle}$$

with respect to the variational coefficients $\{f\}$ and $|\Phi\rangle$.

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with respect to the variational coefficients $\{f\}$ and $|\Phi\rangle$.

- ▶ The variation with respect to $\{f\}$ leads to a generalized eigenvalue problem that can be solved on each iteration.
- ▶ We parametrize the determinant $|\Phi\rangle$ using Thouless' theorem:
Any Slater determinant $|\Phi\rangle$ can be expressed as a Thouless rotation from a non-orthogonal reference determinant $|\Phi_0\rangle$:

$$|\Phi\rangle = \exp(\hat{Z})|\Phi_0\rangle,$$
$$\hat{Z} = \sum_{ai} Z_{ai} c_a^\dagger c_i.$$

The Z matrix is unique and its elements become the variational parameters.

projected HF optimization

A necessary and sufficient condition for a stationary point in the PHF optimization is that the local gradient vanishes:

$$\frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi_i^a | (\hat{H} - E^j) \hat{P}_{kk'}^j | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{kk'}^j | \Phi \rangle} = 0 \quad \forall \quad a, i,$$

where

$$|\Phi_i^a\rangle = c_a^\dagger c_i |\Phi\rangle.$$

This is a [generalized Brillouin condition](#) that implies the orthogonality of the optimized state with respect to symmetry-projected particle-hole configurations.

detour: evaluation of matrix elements

The projection operator was generically written as

$$\hat{P}_{mk}^j = \frac{h}{L} \int_L d\vartheta w_{mk}^{j*}(\vartheta) \hat{R}(\vartheta),$$

The energy functional was written as

$$E_{\text{PHF}}[\{f\}, \Phi] = \frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{H} \hat{P}_{kk'}^j | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{kk'}^j | \Phi \rangle}$$

The Hamiltonian and norm matrix elements can be evaluated as

$$\begin{aligned} \langle \Phi | \hat{H} \hat{P}_{kk'}^j | \Phi \rangle &= \frac{h}{L} \int_L d\vartheta w_{kk'}^{j*}(\vartheta) \langle \Phi | \hat{H} \hat{R}(\vartheta) | \Phi \rangle \\ \langle \Phi | \hat{P}_{kk'}^j | \Phi \rangle &= \frac{h}{L} \int_L d\vartheta w_{kk'}^{j*}(\vartheta) \langle \Phi | \hat{R}(\vartheta) | \Phi \rangle \end{aligned}$$

Note that the evaluation of these matrix elements is embarrassingly parallel.

evaluation of matrix elements

The norm matrix elements,

$$\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle,$$

can be evaluated in the same way as the overlap between two non-orthogonal Slater determinants.

$$\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle = \det \mathbf{M}_{\vartheta}$$

$$\mathbf{M}_{\vartheta} = \mathbf{C}^{\dagger} \mathbf{R}_{\vartheta} \mathbf{C},$$

where \mathbf{C} is the $M \times N$ matrix of occupied orbitals in $|\Phi\rangle$ and \mathbf{R}_{ϑ} is the matrix representation of the operator $\hat{R}(\vartheta)$.

Hamiltonian matrix elements

The Hamiltonian matrix elements,

$$\langle \Phi | H \hat{R}(\vartheta) | \Phi \rangle$$

can be evaluated using a generalized Wick's theorem.

$$\langle \Phi | H \hat{R}(\vartheta) | \Phi \rangle = \sum_{ik} h_{ik} (\rho_{\vartheta})_{ki} + \frac{1}{2} \sum_{ijkl} \langle ij || kl \rangle (\rho_{\vartheta})_{ki} (\rho_{\vartheta})_{lj}$$

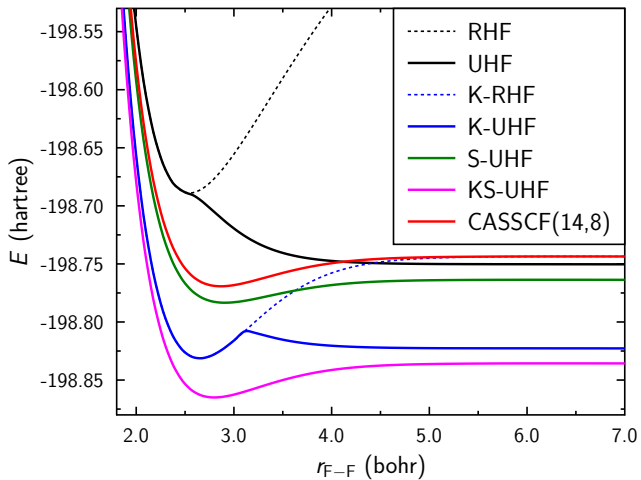
Here, the transition density matrices

$$(\rho_{\vartheta})_{kl} = \frac{\langle \Phi | a_l^{\dagger} a_k \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle}$$

can be evaluated as

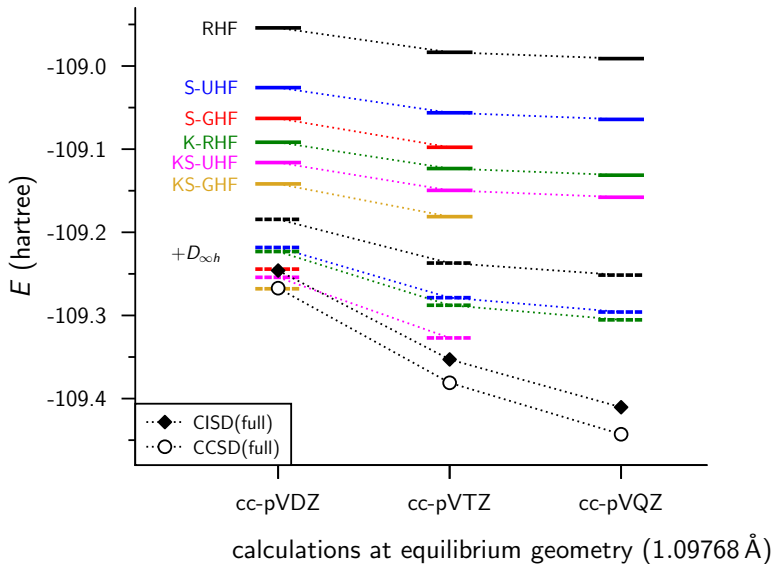
$$\rho_{\vartheta} = \mathbf{R}_{\vartheta} \mathbf{C} \mathbf{M}_{\vartheta}^{-1} \mathbf{C}^{\dagger}.$$

dissociation of F_2



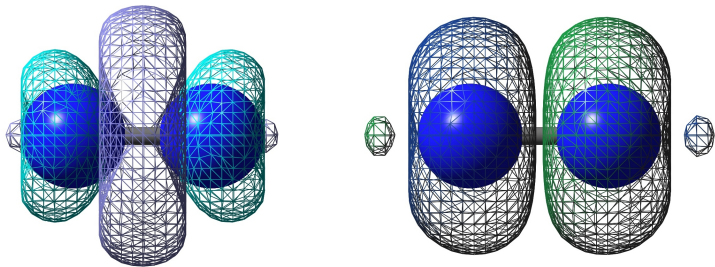
cc-pVDZ basis set

N₂ energy



structure of the underlying determinants

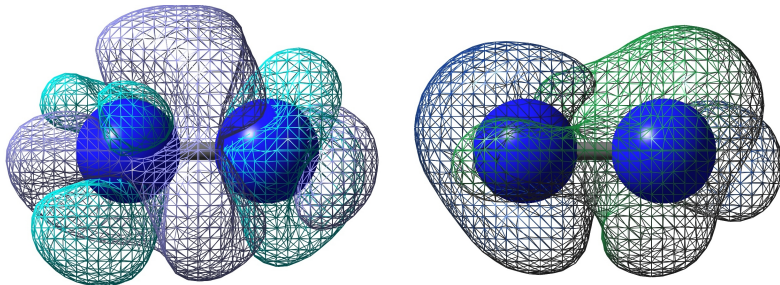
S-UHF calculation for N_2 (cc-pVDZ basis, equilibrium distance)



- ▶ **left:** electron density difference with respect to RHF (isosurface: 0.004 a.u.)
- ▶ **right:** spin density of underlying determinant (isosurface: 0.020 a.u.)

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$D_{\infty h}$ S-UHF calculation for N_2 (cc-pVDZ basis, equilibrium distance)



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symmetry-projected HF recap

A symmetry-projected HF ansatz has several great features:

- ▶ Good quantum numbers are preserved.
- ▶ Correlations due to symmetry breaking are accounted for.
- ▶ The wavefunction is fully determined by a single determinant; one can still relate to a single-particle-like picture.

Using symmetry-projected HF wavefunctions is straightforward:

- ▶ The cost is mean field (with an $\mathcal{O}(N_{\text{grid}})$ prefactor).
- ▶ Analytic energy gradients have been derived and implemented.
- ▶ Density matrices (of arbitrary order) can be easily computed.

Incorporating dynamical correlation is not straightforward.

size consistency in PHF

PHF is **not size-consistent**. That is,

$$E[\text{N}_2](r \rightarrow \infty) - 2 E[\text{N}] > 0.$$

For KSUHF, the size inconsistency error is ≈ 17 kcal/mol.

Size inconsistent methods cannot be blindly used in association / dissociation reactions.

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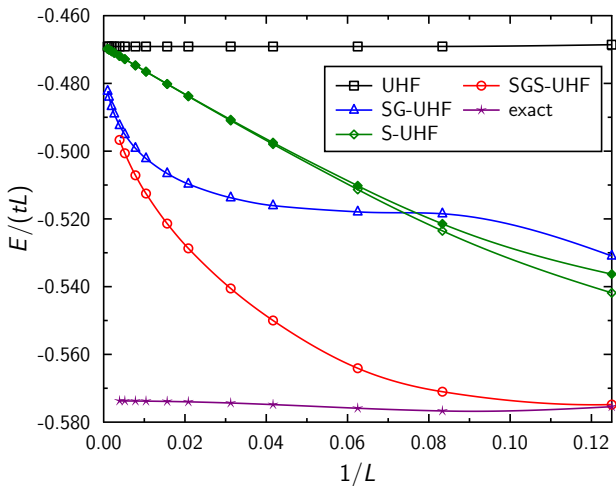
This is because the ansatz is not *factorizable* into fragments:

$$\hat{P}|\Phi_{AB}\rangle \neq \hat{P}|\Phi_A\rangle \otimes \hat{P}|\Phi_B\rangle$$

even though

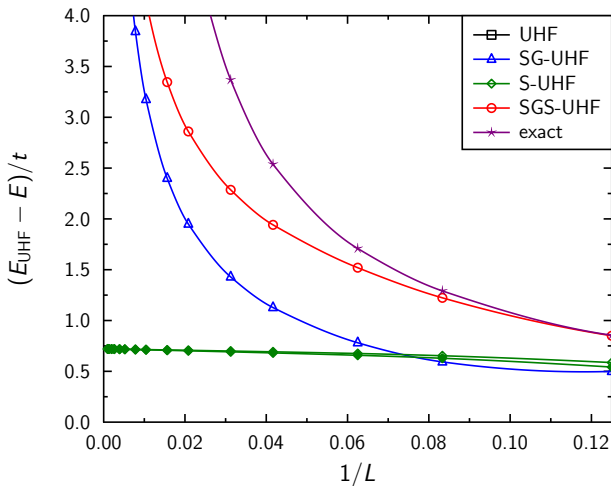
$$|\Phi_{AB}\rangle = |\Phi_A\rangle \otimes |\Phi_B\rangle.$$

size extensivity in PHF



Hubbard chain calculations; $U = 4t$ at half-filling ($N = L$)
exact results from solution to Lieb-Wu equations

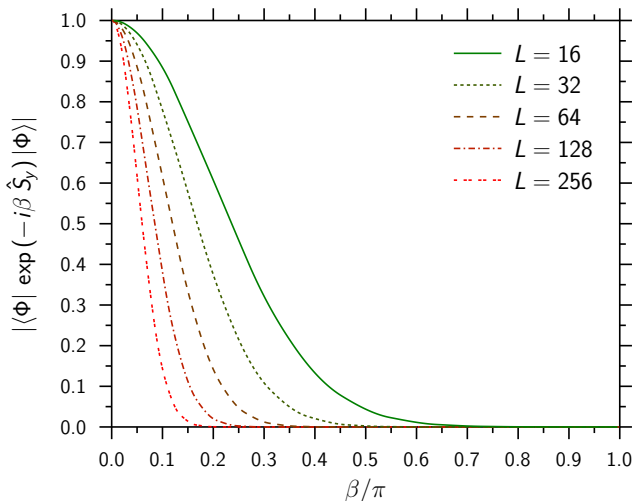
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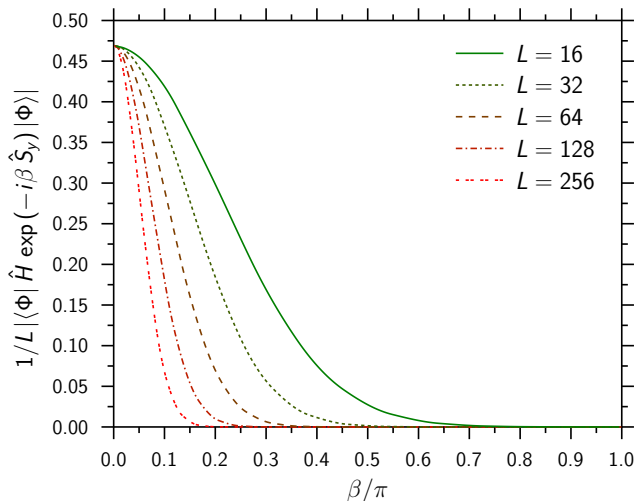
For large L , rotated determinants become orthogonal to reference one.



S-UHF calculations; $U = 4t$ at half-filling ($N = L$)

size extensivity in PHF

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S-UHF calculations; $U = 4t$ at half-filling ($N = L$)

beyond SPHF: configuration mixing

exact diagonalization

A full configuration interaction ansatz can be written as

$$|\psi^{j,m}\rangle = \sum_k \hat{P}_{mk} \left(f_{0;k} |\Phi\rangle + \sum_{ia,k} f_{ia;k} |\Phi_i^a\rangle + \sum_{ijab,k} f_{ia,jb;k} |\Phi_{ij}^{ab}\rangle + \dots \right)$$

Note, however, that

- ▶ The Hamiltonian is **dense**.
- ▶ One has to deal with the presence of an overlap matrix, which leads to a generalized eigenvalue problem.
- ▶ Each matrix element is expensive to evaluate: $\mathcal{O}(M^3 N_{\text{grid}})$.

Moreover, **truncated CI expansions** have been abandoned for the most part in quantum chemistry in favor of CC theory because they are **not extensive**.

configuration mixing

Recall that the symmetry-projected HF ansatz is given by

$$|\Psi^{j,m}\rangle = \sum_k \hat{P}_{mk}^j f_k |\Phi\rangle$$

where $|\Phi\rangle$ is a Slater determinant.

We can prepare a more general ansatz by superposition of several [symmetry-projected configurations](#)

$$|\Psi^{j,m}\rangle = \sum_k \hat{P}_{mk}^j \sum_i f_{ik} |\Phi_i\rangle.$$

In general, we shall let the different broken-symmetry determinants to be non-orthogonal: $\langle \Phi_i | \Phi_j \rangle \neq 0$.

configuration mixing

$$|\Psi^{j,m}\rangle = \sum_k \hat{P}_{mk}^j \sum_i f_{ik} |\Phi_i\rangle$$

There are two-extreme approaches for optimizing this wavefunction with respect to the set of Slater determinants $\{|\Phi_i\rangle\}$:

- ▶ **resonating HF** (RES): all are optimized at the same time

Pros: The ansatz is fully optimized.

Cons: Expensive; hard to converge.

H. Fukutome, Prog. Theor. Phys. **80**, 417 (1988)

- ▶ **few-determinant** (FED): only the last-added one is optimized

Pros: Cheaper; convergence is typically easier.

Cons: The ansatz is not fully optimized.

K. W. Schmid, *et al.*, Nucl. Phys. A **499**, 63 (1989)

FED approach in detail

Suppose we have the symmetry-projected HF state at hand

$$|\Psi_1^{j,m}\rangle = \sum_k \hat{P}_{mk}^j f_k |\Phi_1\rangle.$$

We now consider the ansatz

$$|\Psi_2^{j,m}\rangle = \sum_k \hat{P}_{mk}^j \left\{ f_{1k} |\Phi_1\rangle + f_{2k} |\Phi_2\rangle \right\}.$$

The energy functional

$$E^j [\{f\}, \Phi_2] = \frac{\langle \Psi_2^{j,m} | \hat{H} | \Psi_2^{j,m} \rangle}{\langle \Psi_2^{j,m} | \Psi_2^{j,m} \rangle}$$

is minimized with respect to **all** $\{f\}$ and $|\Phi_2\rangle$.

- ▶ $|\Phi_1\rangle$ is kept fixed throughout the optimization

FED approach in detail

In general, we can have an $n - 1$ expansion and look for the n -th most correlating configuration:

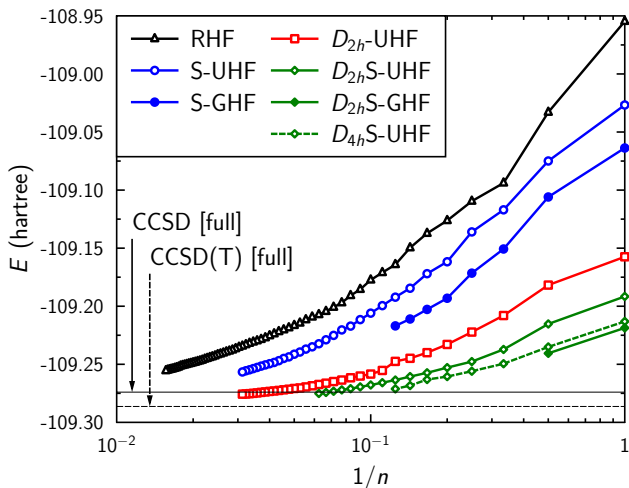
$$|\Psi_n^{j,m}\rangle = \sum_k \hat{P}_{mk}^j \sum_{i=1}^n f_{ik} |\Phi_i\rangle.$$

Because the optimization is carried out variationally, one can prove that

$$E_1 - E_2 \geq E_2 - E_3 \geq \dots \geq E_{n-1} - E_n.$$

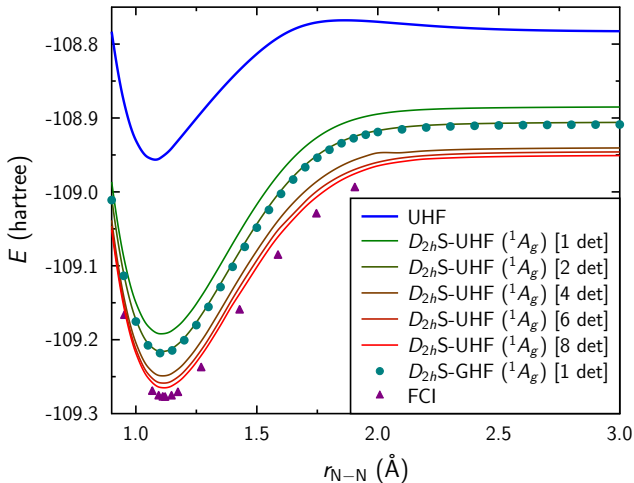
That is, each added determinant will bring less correlation than the previous one.

ground state energy of N_2



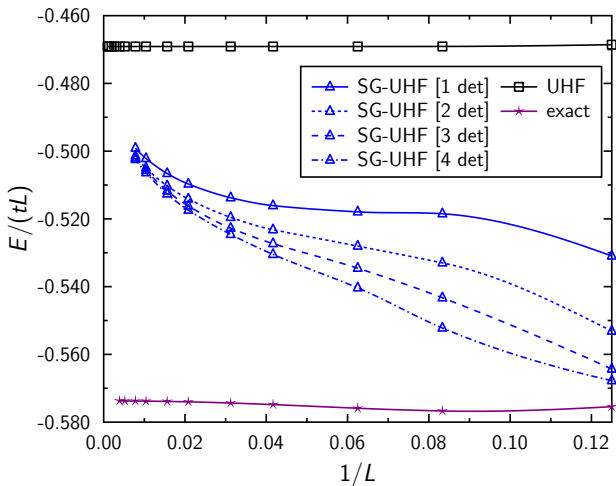
Cartesian cc-pVDZ basis set; equilibrium geometry (1.09768 Å)

dissociation profile of N_2



Cartesian cc-pVDZ basis set
FCI results from Larsen, H.; et al. J. Chem. Phys. **113**, 6677 (2000).

size extensivity in FED-PHF



Hubbard chain calculations; $U = 4t$ at half-filling ($N = L$)
exact results from solution to Lieb-Wu equations

**beyond SPHF:
excited electronic states**

excited states

The symmetry-projected HF ansatz is given by

$$|\psi^{j,m}\rangle = \sum_k \hat{P}_{mk}^j f_k |\Phi\rangle$$

where $|\Phi\rangle$ is a Slater determinant.

An excited state wavefunction must be **orthogonal** with respect to the ground state.

excited states

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An excited state wavefunction must be **orthogonal** with respect to the ground state.

Two approaches to optimize excited states:

- ▶ Use the same ansatz as in PHF; enforce orthogonality with respect to the ground state via a Lagrange multiplier.
- ▶ Use an ansatz that is explicitly orthogonal to the ground state.

excited VAMP strategy

We write the symmetry-projected ground state as

$$|\Psi_0^{j,m}\rangle \equiv |\psi_0^{j,m}\rangle = \sum_k \hat{P}_{mk}^j f_k^0 |\Phi_0\rangle.$$

In the **excited VAMP** strategy of Schmid, *et al.* [Nucl. Phys. A **452**, 493 (1986)], the ansatz for the first excited state is

$$|\Psi_1^{j,m}\rangle = (1 - \hat{S}_1)|\psi_1^{j,m}\rangle = (1 - \hat{S}_1) \sum_k \hat{P}_{mk}^j f_k^1 |\Phi_1\rangle,$$

$$\hat{S}_1 = \frac{|\psi_0^{j,m}\rangle \langle \psi_0^{j,m}|}{\langle \psi_0^{j,m} | \psi_0^{j,m} \rangle}.$$

- ▶ $|\Phi_1\rangle$ is a Slater determinant; $\{f^1\}$ are variational coefficients.
- ▶ The ansatz is explicitly orthogonal to the symmetry-projected ground state (with the same symmetry).

excited VAMP strategy

The ansatz for the n -th excited state is given by

$$|\Psi_n^{j,m}\rangle = (1 - \hat{S}_n)|\psi_n^{j,m}\rangle = (1 - \hat{S}_n) \sum_k \hat{P}_{mk}^j f_k^n |\Phi_n\rangle,$$

$$\hat{S}_n = \sum_{r,s=0}^{n-1} |\psi_r^{j,m}\rangle A_{rs}^{-1} \langle \psi_s^{j,m}|$$

$$A_{rs} = \langle \psi_r^{j,m} | \psi_s^{j,m} \rangle$$

The energy functional becomes

$$E^j[\Phi_n, \{f^n\}] = \frac{\langle \psi_n^{j,m} | (1 - \hat{S}_n) \hat{H} (1 - \hat{S}_n) | \psi_n^{j,m} \rangle}{\langle \psi_n^{j,m} | (1 - \hat{S}_n) | \psi_n^{j,m} \rangle}.$$

- ▶ The variation with respect to $\{f^n\}$ leads to an eigenvalue problem.
- ▶ $|\Phi_n\rangle$ optimized with a Thouless parametrization: $|\Phi_n\rangle \rightarrow \exp(\hat{Z})|\Phi_0\rangle$

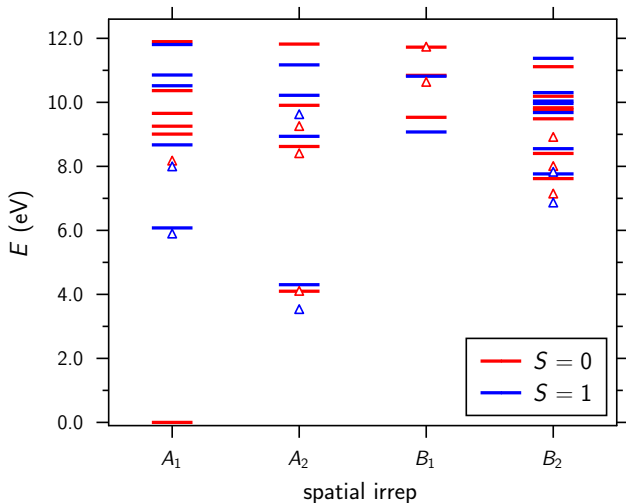
excited VAMP strategy

Even though the states $\{|\psi_l^{j,m}\rangle \mid l = 0, 1, \dots, n\}$ obtained by the excited VAMP strategy are orthogonal, they can **interact through the Hamiltonian**.

We perform a final diagonalization of the Hamiltonian among such states, or alternatively, among the $|\psi_l^{j,m}\rangle$ configurations.

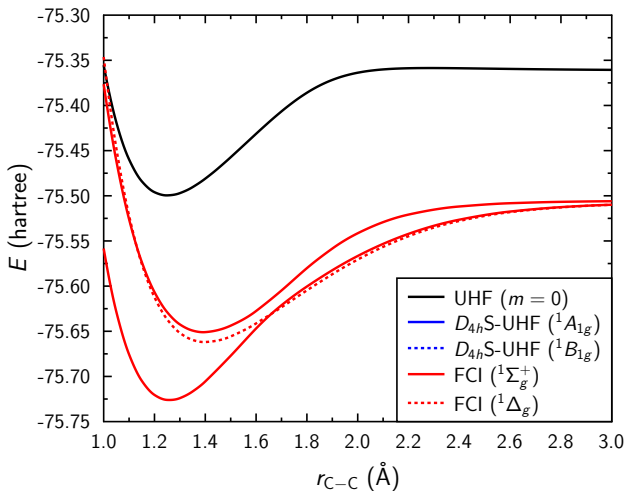
In this way, one may account for further correlations in the ground state wavefunction.

vertical excitation spectrum of formaldehyde ($\text{H}_2\text{C}=\text{O}$)



experimental excitation energies shown as triangles
 $\text{C}_{2v}\text{S-UHF} / 6\text{-}311(2+,2+)\text{G(d,p)}; \text{MP2} / 6\text{-}31\text{G(d)}$ geometry

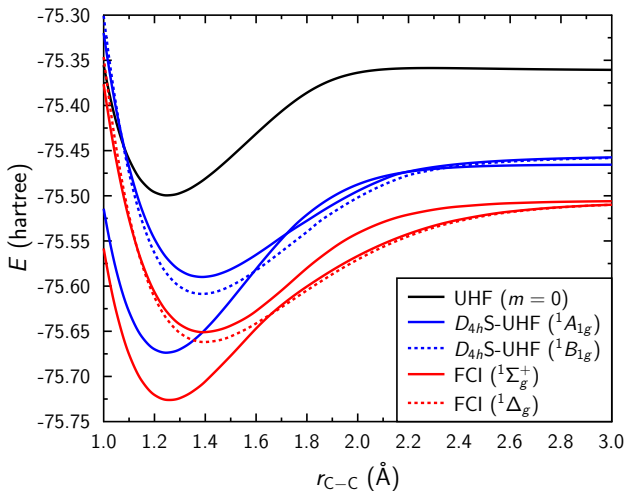
dissociation profile of C_2



6-31G(d) basis set

FCI results from J. Chem. Phys. **121**, 9211 (2004)

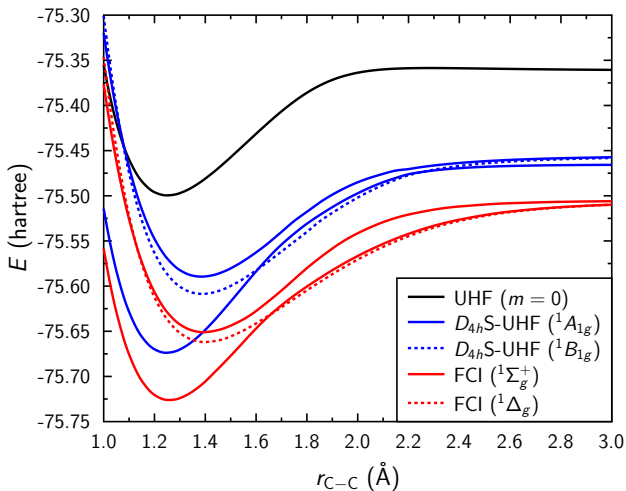
dissociation profile of C_2



6-31G(d) basis set

FCI results from J. Chem. Phys. **121**, 9211 (2004)

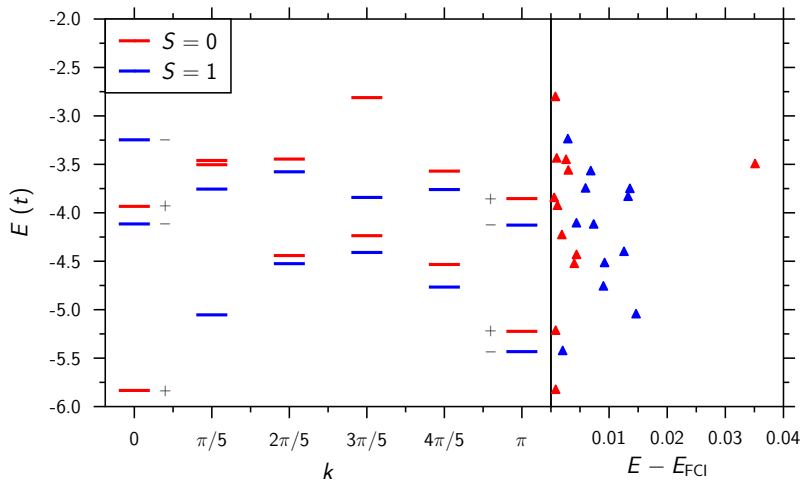
dissociation profile of C_2



6-31G(d) basis set

FCI results from J. Chem. Phys. **121**, 9211 (2004)

spectrum of an $L = 10$ 1D periodic Hubbard chain



SG,S-GHF calculations; $U = 4t$ at half-filling ($N = L$)
exact results obtained with in-house code

correlations in excited states

The excited VAMP strategy can be easily combined with the FED approach in order to account for further correlations.

Each state is written as a linear combination of symmetry-projected configurations:

$$|\psi_I^{j,m}\rangle = \sum_k \hat{P}_{mk}^j \sum_{i=1}^{n_I} f_{I,k}^i |\Phi_I^i\rangle.$$

conclusions

- ▶ A symmetry-projected HF ansatz has several key advantages:
 1. Good quantum numbers are preserved.
 2. Correlations due to symmetry breaking are accounted for.
 3. The wavefunction is fully determined by a single determinant.

- ▶ The single-configuration PHF approach is neither **size-consistent** nor **size-extensive**.

conclusions

- ▶ Further correlations in the ground state can be accounted by a symmetry-projected **configuration mixing** approach (FED or RES).
A few configurations are enough to obtain near-FCI results in simple molecular systems.
- ▶ For increasingly larger systems, more configurations are needed to maintain the quality of the wavefunction.
- ▶ Excited states of the same symmetry as the ground-state can be obtained using an **excited VAMP** strategy.
This approach can be combined with FED (or RES) to obtain high-quality results for both ground and excited states.
- ▶ Each state is described by a (short) expansion in terms of symmetry-projected configurations. This allows one to easily grasp the physics in the wavefunctions.

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