

Projection Methods Applied to Electronic Structure Theory

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Restoring Symmetries

CEA-Saclay

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Outline

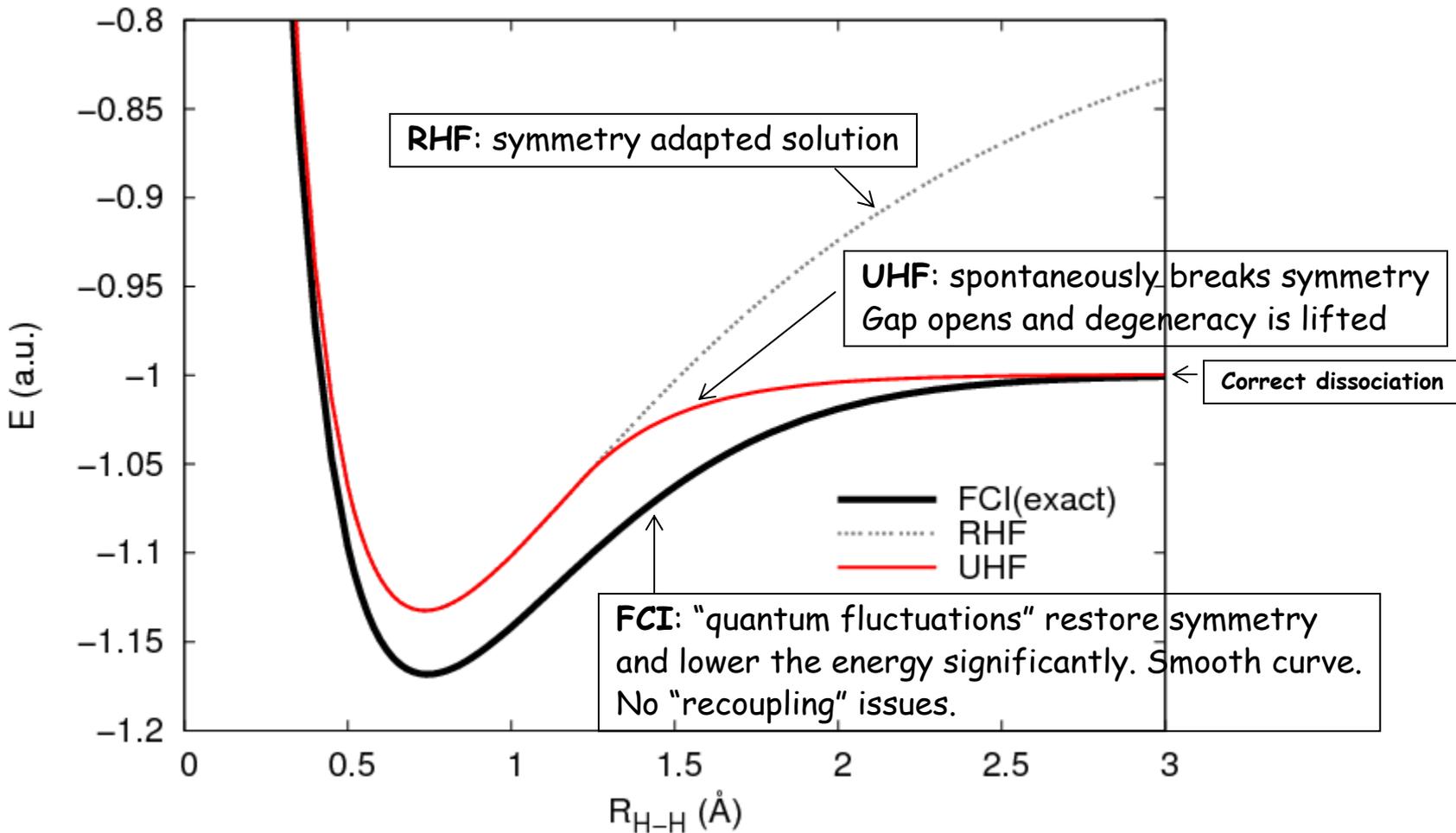
- **The Quantum Chemistry Perspective:**
 - Important Goal: Describing **static/strong correlation** "black-box" with mean-field computational cost.
 - All results presented here are for **molecules**.
 - Solids (**infinite systems**) are a different beast !
- **The Method:**
 - Symmetry breaking and restoration (Sheik & Ring) generalized from **number** to **triaxial spin** projection
 - Other discrete symmetries like **point group** and **complex conjugation** broken and restored
- **The Solution:**
 - **MR wavefunction** whose **energy** is a **DMFT**
 - Solvable by **diagonalization**
 - Old **projection problems** revisited with new vistas

What is static/strong correlation in finite electronic structure systems?

- It is all about **exact** and **near-degeneracies**
- A single-determinant **RHF** wavefunction (with **correct** symmetries) becomes a **very poor descriptor** of the electronic structure as the orbital energy gap closes
- Static correlation examples:
 - Closed-shell $H_2 \rightarrow H + H$ near dissociation:
 σ_g/σ_u MOs become **degenerate**
(**LEFT-RIGHT** correlation, a nonlocal effect; **entanglement**)
 - **Heavy atoms** due to **AO near degeneracies** (eg, Be atom)
(**ANGULAR** static correlation)
 - **Solid State Physics** "definition" of strong correlation:
 - When traditional Kohn-Sham **DFT** fails miserably
 - Correlations that are **not weak** and are not captured by **BS MF**

$H_2 \rightarrow H + H$: Prototype of left-right static correlation

At dissociation, the symmetry-correct RHF orbitals (σ_g and σ_u) become **degenerate**



UHF at dissociation : right energy but **wrong** wavefunction
(linear combination of a singlet and a triplet)

Angular Static Correlation

- Related to **near degeneracies** in atoms as opposed to molecular dissociation
- Prototype case:
4-electron series; **2s/2p** near-degeneracy:
Li⁻, Be, B⁺, C²⁺, N³⁺ ...
- When **$Z \rightarrow \infty$** , atomic levels with same **n** but different **L** become nearly-degenerate ("**angular**" degeneracy)
- Correlation energy diverges linearly as **-0.01173 Z**
- Crucially important in **3d, 4f, 5f** electrons

Dynamic Correlation

- “**Weak**” as opposed to “**strong (static)**” correlation
- Has **strong** basis set dependence because of electron-electron cusp (**static** correlation has **weak** basis set dependence)
- Ubiquitous in the $2e$ -series: **He**, **Li⁺**, **Be²⁺**...
- When $Z \rightarrow \infty$, correlation energy goes to a constant ($\sim 44 mE_H$) independent of Z
- Treatable by **perturbation** or **coupled-cluster** theories
- Essentially a solved problem albeit with $O(M^6)$ computational cost

How to deal with static correlation ?

- **Unrestricted formalism** yielding **spin-** and **space-symmetry breaking** has been the standard way of dealing with **static correlation** in a computationally inexpensive manner
- Symmetry breaking in **finite** systems is artifactual
There are **no phase transitions** in finite systems!
- Of course **CAS/FCI** captures static correlation but has **combinatorial cost**. Other methods like **DMRG** are $O(M^6)$
- **Exchange hole localization** in **DFT** incorporates **static correlation** but this introduces **self-interaction error**
- Downside of **breaking** symmetries is that the **correct** quantum numbers are **hard** to recover

Static Correlation Method

Wish List

- ✓ Should preserve **space** and **spin** symmetries (and other Hamiltonian symmetries like **N** and **K**)
- ✓ Should have low-computational cost (**mean-field**) instead of **CASSCF** or **FCI** combinatorial blowup
- ✓ Should be applicable to large systems where **FCI** is impractical
- ✓ Should **smoothly connect** the dissociation limit with the equilibrium region (no "phase transitions")
- ✗ Should be **size consistent** ($E_{AB} = E_A + E_B$ when $R_{AB} \rightarrow \infty$)

Symmetry Breaking: Spontaneous vs. Deliberate

- Why does **spontaneous** symmetry breaking occur in HF?
- Schrodinger's equation is **linear** in Ψ : $H \Psi = E \Psi$
but HF is **cubic**: $F(|\Psi_i|^2) \Psi_i = \epsilon_i \Psi_i$
- New solutions appear that break symmetry and have lower energies. They are like **phase transitions** but they are not physical.
- “**Quantum fluctuations**” smoothen this “**phase transition**” in finite systems. The correct wavefunction is **multireference** in nature.
- When symmetries are not **spontaneously** broken, we can break them **deliberately** and then **restore** them

Symmetry Breaking & Restoration

- **When SSB occurs: Projection After Variation**
"Phase transitions" are enhanced rather than eliminated!
Not good.
- **Much better: Variation After Projection (DSB + opt)**
The reference wavefunction is deformed on purpose and then optimized with projection operators included
 $E = \langle 0 | P^\dagger H P | 0 \rangle, \quad \delta E = 0$
- Heavily traveled road in the 60s, mostly forgotten now !
- **New vista:** borrow the tools developed in the nuclear physics community and apply them in quantum chemistry

Projected Quasiparticle Theory

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J. Chem. Phys. in press

(available at [arXiv.org>cond-mat>str-e:1106.0956](https://arxiv.org/abs/cond-mat/1106.0956))

(I) Geminals and AGP

- **Geminal** = Two-particle wavefunction: $g(1,2)$
- **Antisymmetrized Geminal Power**: same geminal on every pair:
 $AGP = A [g(1,2) g(3,4) g(5,6) \dots]$
- **AGP** has the ability to smoothly connect **HF** with a fully entangled wavefunction depending on the geminal "**rank**" and occupations
- Write geminal in **NO** basis (geminal & 1pdm **NO** basis are the same)
 $g(1,2) = \sum_i w_i \Psi_i^*(1) \Psi_i(2)$; $w_i =$ geminal occ; $n_i =$ 1pdm occ
- If **rank** of g is N (electron number) $\rightarrow n_i = 1, 0 \rightarrow$ HF
- If **rank** of g is M (orbital basis) and $w_i = 1/M \rightarrow$ "extreme **AGP**"
a fully entangled wavefunction with all n_i equal
- **AGP** is the simplest wavefunction that spans the **disentangled** to **fully entangled** limits

(II) HFB theory in one slide

- Consider transformations mixing Fermion creation & annihilation operators

$$\beta_i^\dagger = \sum_{ij} (U_{ji} a_j^\dagger + V_{ji} a_j)$$

- The **quasiparticle** determinant $|HFB\rangle = \prod_{i=1, M/2} \beta_i^\dagger |vac\rangle$ dwells in **Fock** space and **breaks particle number symmetry**.
- The **U** and **V** matrices are the eigenvectors of the **HFB** Hamiltonian:

$$H = \begin{bmatrix} F & \Delta \\ -\Delta^* & -F^* \end{bmatrix} \quad \begin{array}{ll} F = F(\rho) & \text{Fock Hamiltonian} \\ \Delta = \Delta(\kappa) & \text{Pairing Hamiltonian} \end{array}$$

- The regular $\rho = VV^T$ and anomalous $\kappa = -U^*V^T$ density matrices form an idempotent quasiparticle density matrix **R**

$$R = \begin{bmatrix} \rho & \kappa \\ -\kappa^* & I - \rho^* \end{bmatrix} \quad \begin{array}{l} \rho_{ij} = \langle a_j^\dagger a_i \rangle \\ \kappa_{ij} = \langle a_j^\dagger a_i^\dagger \rangle \end{array}$$

- At **SCF** convergence $[H, R] = 0$
- HFB** theory ignored in q-chem because **HFB** \rightarrow **HF** for repulsive $1/r_{12} > 0$

(III) Projection Operators

Spin Projection Operators:

- Löwdin (1955)

$$P_S = \prod_{S' \neq S} [\hat{S}^2 - s'(s'+1)] / [s(s+1) - s'(s'+1)]$$

- Peierls & Yoccoz (1957), Percus & Rotenberg (1962), Villars (1966)

$$P_S = (s + \frac{1}{2}) \int d\beta \sin\beta d_s(\beta) e^{i\beta\hat{S}_y}$$

Number Projection Operator:

- Bayman (1960)

$$P_N = 1/2\pi \int d\varphi e^{i\varphi(\hat{N}-n)}$$

In all cases, $P = P^\dagger = P^2$

Integral representation of P totally ignored in q-chem !

Lowdin's version of spin-projection: totally ignored in nuc-phys !

(IV) BCS, HFB, PBCS, PHFB & AGP

- **BCS wavefunction:** $|\text{BCS}\rangle = \prod_{i=1, M} (u_i + v_i a_i^\dagger a_i^\dagger) |\text{vac}\rangle$
 - Contains determinants of different number of electrons (Fock space)
 - BCS is HFB in the Natural Orbital (NO) basis (where 1pdm is diagonal)
- **Pairing:** Ψ_i and Ψ_j are "paired" spin-orbitals:
 - "Singlet" pairing: spatial part of Ψ_i and Ψ_j is the same
 - "Unrestricted" pairing: spatial part is different but still α and β spin
 - "General" pairing: each orbital is a linear combination of α and β spins
 - Ψ orbitals can be **real** or **complex**
- **Number projected BCS:** use projector operator to remove all determinants that do not contain the correct number of electrons
- **AGP** = number-PHFB or number-PBCS
- **AGP** is **exact** for one electron pair (He atom, H_2)
- All previous variational **AGP** calculations are singlet-paired
- Heavily explored in the 80s... **but abandoned in q-chem**
- **AGP** evaluation **had** steep cost: combinatorial to $\mathcal{O}(M^5)$

PHFB Basics (I)

- Given a **symmetry** $A = A^\dagger$ and $[H, A] = 0$
- Build a **unitary operator** $U = e^{i\varphi \hat{A}}$ where $\varphi \in \mathbb{R}$
- Given a “**deformed**” broken symmetry reference state $|HFB\rangle$
- U creates a **manifold of states**: $|\varphi\rangle = U |HFB\rangle = e^{i\varphi \hat{A}} |HFB\rangle$

that are all **degenerate in energy** (“**Goldstone manifold**”)

$$\langle \varphi | H | \varphi \rangle = \langle HFB | e^{-i\varphi \hat{A}} H e^{i\varphi \hat{A}} |HFB\rangle = \langle HFB | H |HFB\rangle$$

but interact among themselves $\langle HFB | H e^{i\varphi \hat{A}} |HFB\rangle \neq 0$
they are **non-orthogonal coherent states**

- Build a **projection operator** $P_A = 1/2\pi \int d\varphi e^{i\varphi(\hat{A}-a)}$
and extract the component with desired eigenvalue a

PHFB Basics (II)

- Use the variational theorem to minimize the energy E (variation-after-projection) while discretizing P over a gauge grid $\{\varphi\}$

$$E = \frac{\langle \text{HFB} | P^\dagger H P | \text{HFB} \rangle}{\langle \text{HFB} | P^\dagger P | \text{HFB} \rangle} = \frac{\langle \text{HFB} | H P | \text{HFB} \rangle}{\langle \text{HFB} | P | \text{HFB} \rangle} = \int d\varphi C(\varphi) \langle \text{HFB} | H | \text{HFB}(\varphi) \rangle$$

P here is $P_N P_S \dots$ etc. all Hermitean, idempotent & commuting

- Key result:** the energy E above is a **density matrix functional !**

$$E = \text{Tr } h \gamma + \frac{1}{2} \text{Tr } v \Gamma \quad \gamma \text{ is 1pdm} \quad \Gamma \text{ is 2pdm}$$

$$\Gamma = \int d\varphi C(\varphi) [\rho(\varphi) \wedge \rho(\varphi) + \kappa(\varphi) \kappa(\varphi)]$$

$$\gamma = \text{Tr } \Gamma$$

$$[\text{Recall: } \Gamma_{\text{CPMFT}} = \rho \wedge \rho - \kappa \kappa]$$

Note factorization of **2pdm** over the gauge grid

PHFB Bullets

- The **PHFB energy** can be written as a functional of the **HFB** unprojected quasiparticle **density matrices** $\rho(\varphi)$ and $\kappa(\varphi)$
- **PHFB** is the regular **HFB** energy functional but it includes an integration over the gauge grid
- The energy minimization yields an eigenvalue problem with an effective 1e Hamiltonian (**HFB**-style, twice the **HF** size). Orbitals and geminal coefficients are optimized simultaneously. Fully variational.
- **For number-projection, the result of this minimization is an **AGP** wavefunction obtained with mean-field (HF) computational cost**
- Only **~6-10** points per symmetry are needed in the quadrature
 - **Excellent** agreement with previous **AGP** energies
 - **5-6 grid points** are enough for μE_h accuracy

More PHFB details

- Model is exact (**FCI**) for 1e and 2e systems
- No **DFT** dirty laundry: no minima at fractional charges, no **self-interaction error**
- We break and restore all molecular symmetries:
number, **spin** (S^2 and S_3), **complex conjugation**, **spatial**
- Details vary as a function of symmetry
- Note that **SO(3)** is isomorphic to **SU(2)**
- The model can accommodate **UHF and GHF-type orbitals** either **real or complex** and we can optimize these wavefunctions fully variationally

Complex Conjugation restoration

- The exact eigenfunctions $|\Psi\rangle$ of a **real** Hamiltonian H in a **real** N -particle Hilbert space $\{|\alpha\rangle\}$ *can be chosen to be real*
 - Note, however, that an arbitrary phase factor can be introduced

$$|\Psi'\rangle = e^{i\varphi}|\Psi\rangle$$

that does not change expectation values of observables

- A mean-field wavefunction *does not need to be real*
- We form a broken-symmetry state $|\Phi\rangle$ where each quasi-particle orbital is complex and has its own phase

Complex Conjugation restoration

- Restoration of *complex conjugation symmetry* can be achieved by solving the eigenvalue problem

$$\mathbf{HC} = \mathbf{SCE}$$

in the basis of **non-orthogonal** states $\{|\Phi\rangle, K|\Phi\rangle\}$

- The two states $\{|\theta\rangle, |\theta'\rangle\}$ that one gets out of the eigenvalue problem are eigenfunctions of K :

$$\hat{K}|\theta\rangle = e^{ix}|\theta\rangle$$

$$\hat{K}|\theta'\rangle = -e^{ix}|\theta'\rangle$$

Projected Hartree-Fock (PHF)

- Spin projection (VAP) : an OLD problem in q-chem
- Spin projection is VERY important to describe the dissociation of molecules into separate fragments:
 - Broken-symmetry states display “phase transitions” that are smoothed-out with spin projection (VAP)
 - In the absence of spin-orbit coupling or magnetic interactions, S and M_S are good quantum numbers:

$$\hat{S}^2|\Psi\rangle = S(S+1)|\Psi\rangle$$

$$\hat{S}_z|\Psi\rangle = M_S|\Psi\rangle$$

Projected Hartree-Fock (PHF)

- The energy expression used in PHF is akin to the PHFB one:

$$E = \frac{\langle \Phi | \hat{P}^\dagger \hat{H} \hat{P} | \Phi \rangle}{\langle \Phi | \hat{P}^\dagger \hat{P} | \Phi \rangle} = \frac{\langle \Phi | \hat{H} \hat{P} | \Phi \rangle}{\langle \Phi | \hat{P} | \Phi \rangle}$$

$|\Phi\rangle$ is restricted to be a HF Slater determinant in Hilbert(N)

- The required matrix elements are simple to evaluate:
(Blaziot and Ripka)
 - $P|\Phi\rangle$ is related to $|\Phi\rangle$ by a Thouless transformation
 - A canonical transformation can be defined such that
 - $P|\Phi\rangle$ is a right vacuum
 - $\langle\Phi|$ is a left vacuum
 - Wick's theorem can be applied

Projected Hartree-Fock (PHF)

Overlap matrix elements:

$$\langle \Phi | \hat{R}(\varphi) | \Phi \rangle = \det_N (\mathbf{C}^\dagger \mathbf{R}(\varphi) \mathbf{C})$$

\mathbf{C} - orbital coefficients

\det_N - NxN determinant

Note that:

- **There is no phase problem!**
- It is numerically robust as it is always an NxN determinant.

Projected Hartree-Fock Bogoliubov (PHFB)

Overlap matrix elements:

$$\langle \Phi | \hat{R}(\varphi) | \Phi \rangle = \pm \sqrt{\frac{\det_M (\mathbf{I} - \mathbf{Z}^* \mathbf{Z}_\varphi)}{\det_M (\mathbf{I} - \mathbf{Z}^* \mathbf{Z})}}$$

$$\mathbf{Z} = \mathbf{V}^* (\mathbf{U}^*)^{-1}$$

$$\mathbf{Z}_\varphi = \mathbf{R}(\varphi) \mathbf{Z} [\mathbf{R}(\varphi)]^\dagger$$

\mathbf{U}, \mathbf{V} – quasiparticle orbital coefficients

\det_M – MxM determinant

Note that:

- **Phase issue!** (extensively discussed)
- Numerically difficult when

$$\frac{v_k}{u_k} \ll 1, \quad \frac{v_k}{u_k} \gg 1$$

which prevents the use of large basis sets ($M \gg N$)

Acronym Soup

Acronyms are composed of two parts:

Symmetry

N: number

S: spin

K: complex conjugation

C_i: inversion (spatial)

QP determinant deformation

R: restricted (closed-shell)

U: unrestricted (spin-polarized)

G: general (non-collinear)

complex orbitals

Examples:

NRHFB is singlet-paired number-PBCS (= **AGP**)

NUHFB is number-projected spin-polarized **UAGP**

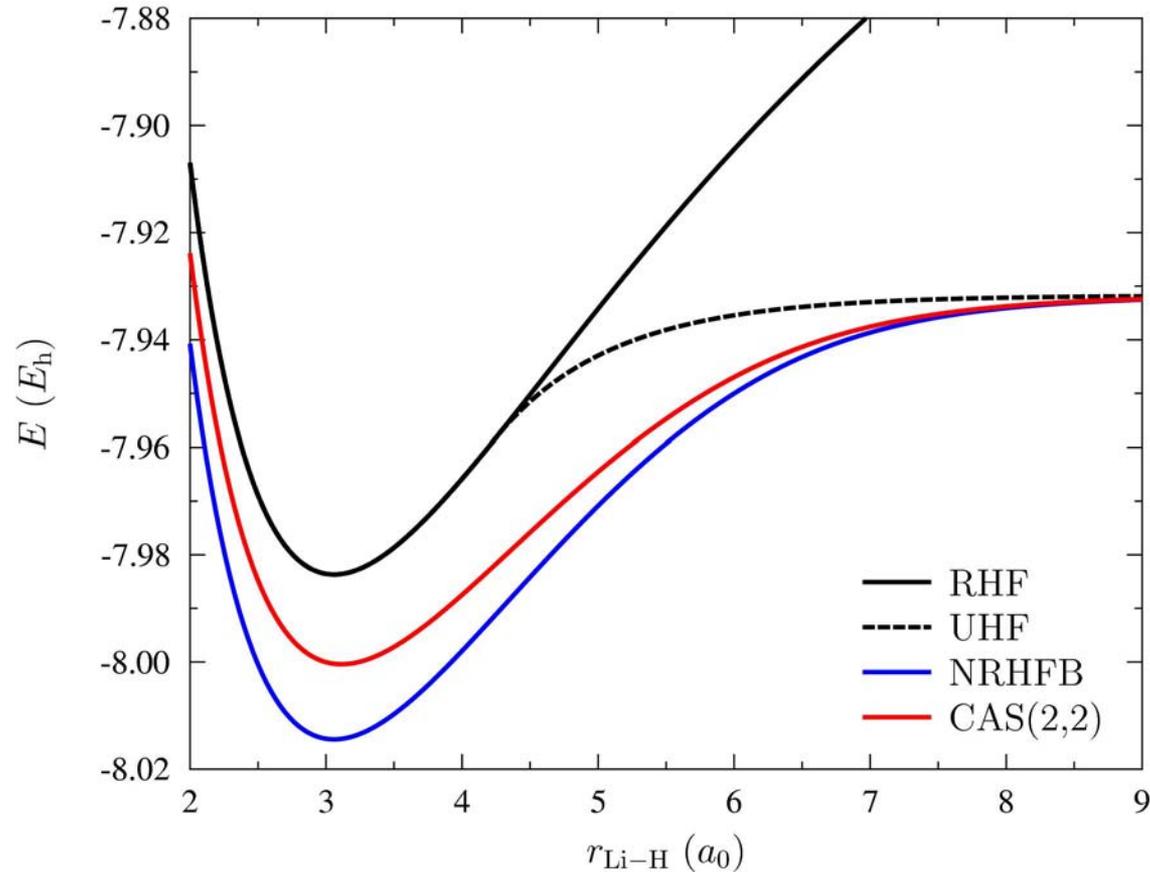
SNUHFB is **NUHFB** + spin projection (collinear spin)

SNGHFB is the triaxial (noncollinear) spin projection

KSNGHFB adds complex conjugation to **SNGHFB**

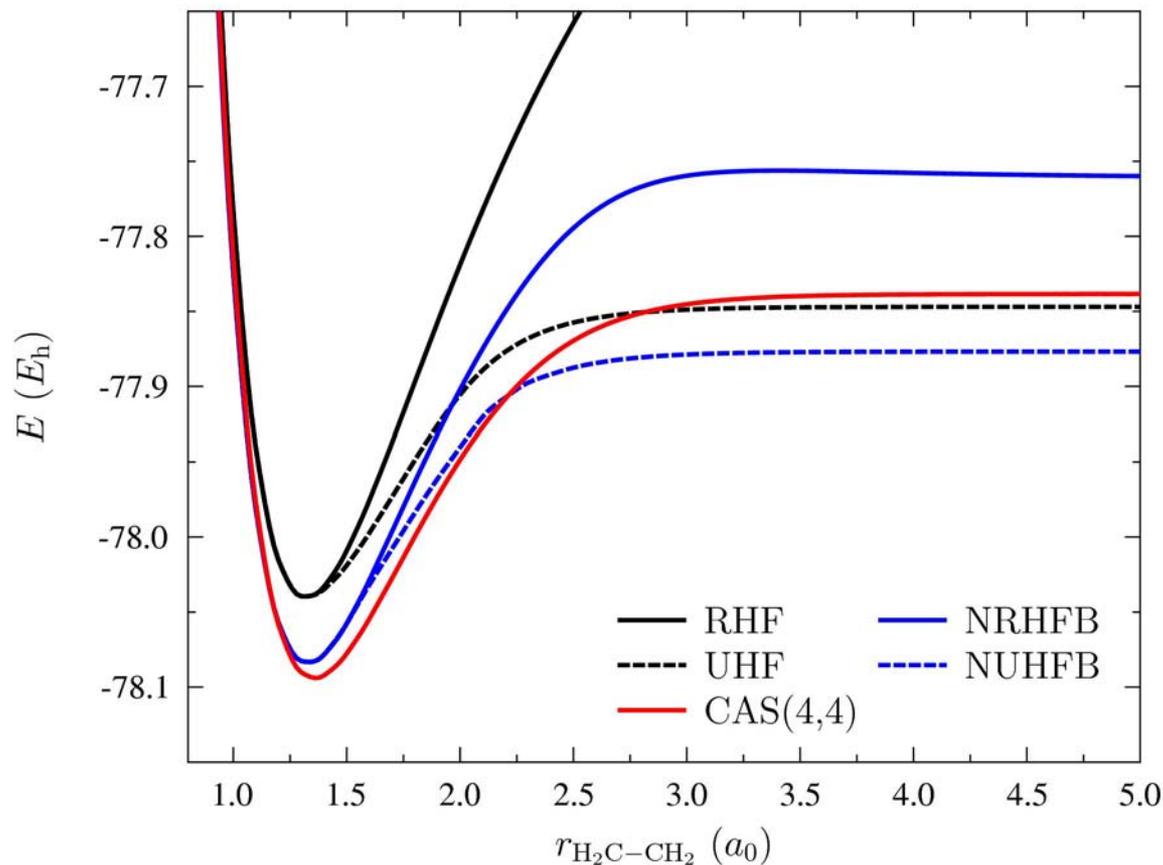
Same thing without "B" at acronym end for **PHF** instead of **PHFB**

LiH: single-bond dissociation



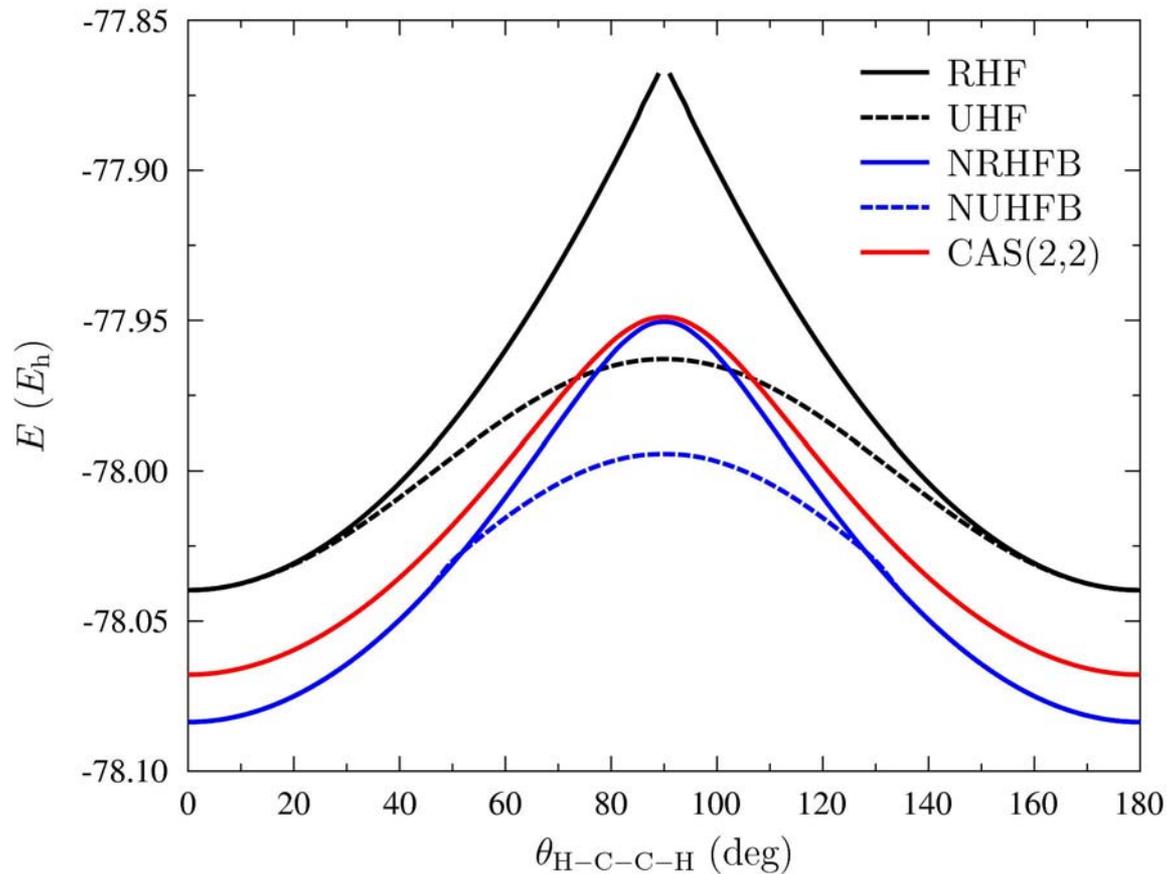
NRHFB: singlet-paired PBCS = regular AGP

Ethylene double-bond dissociation

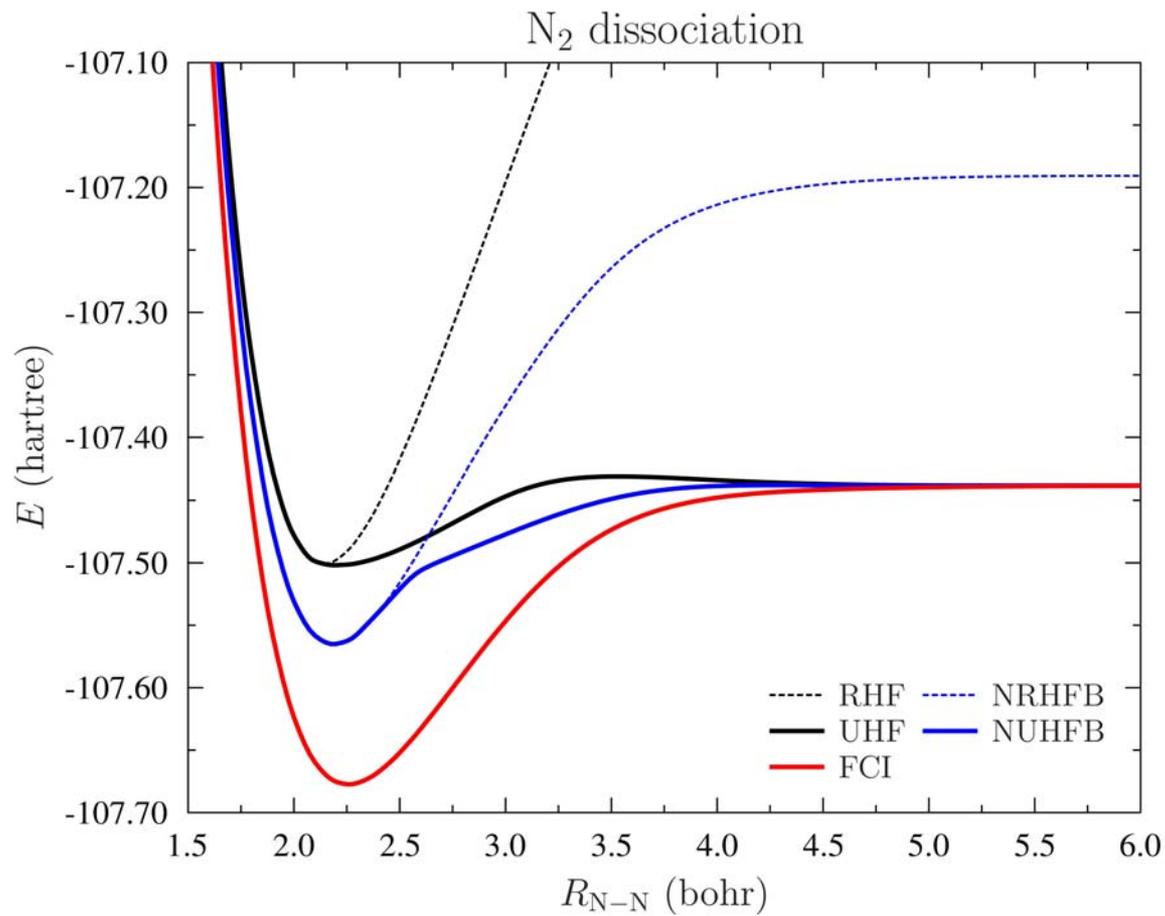


NUHFB: broken symmetry without spin restoration = **UAGP**

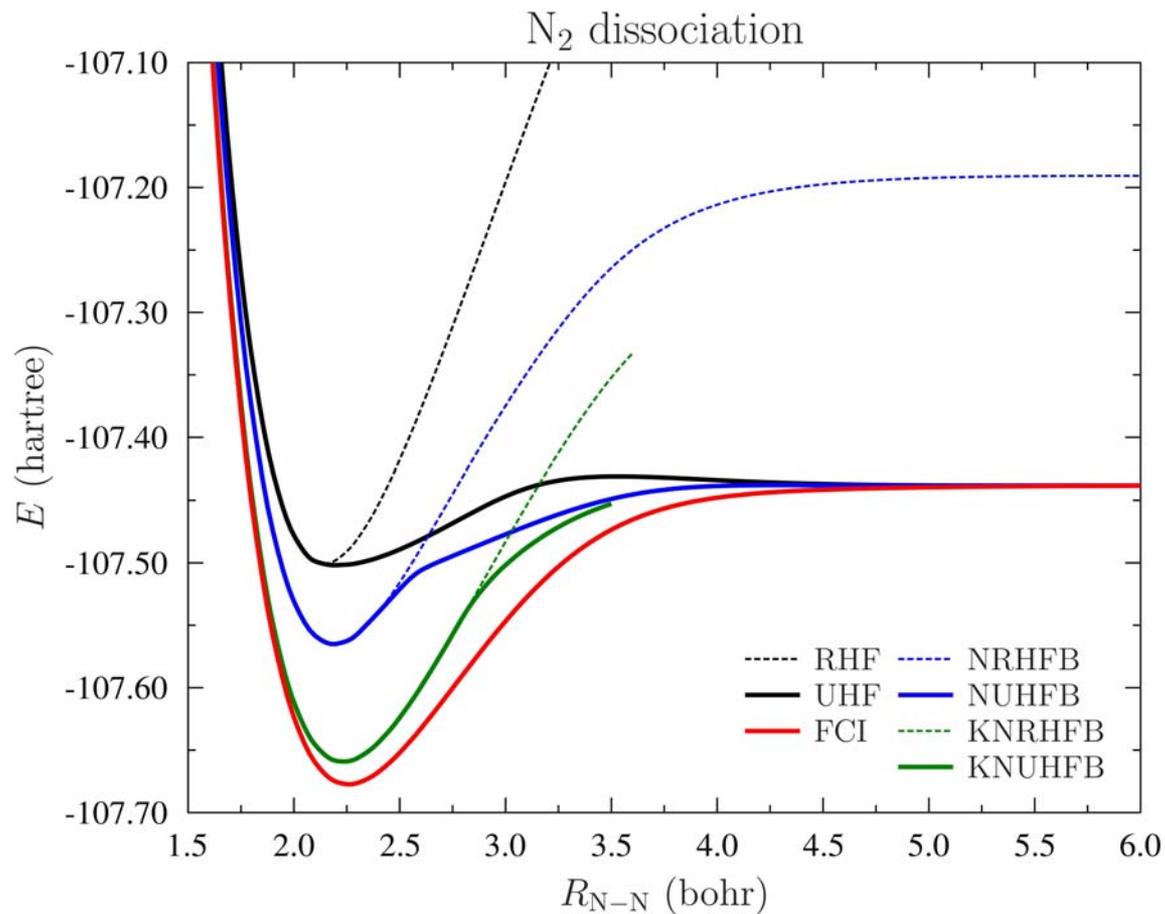
Ethylene rotational barrier



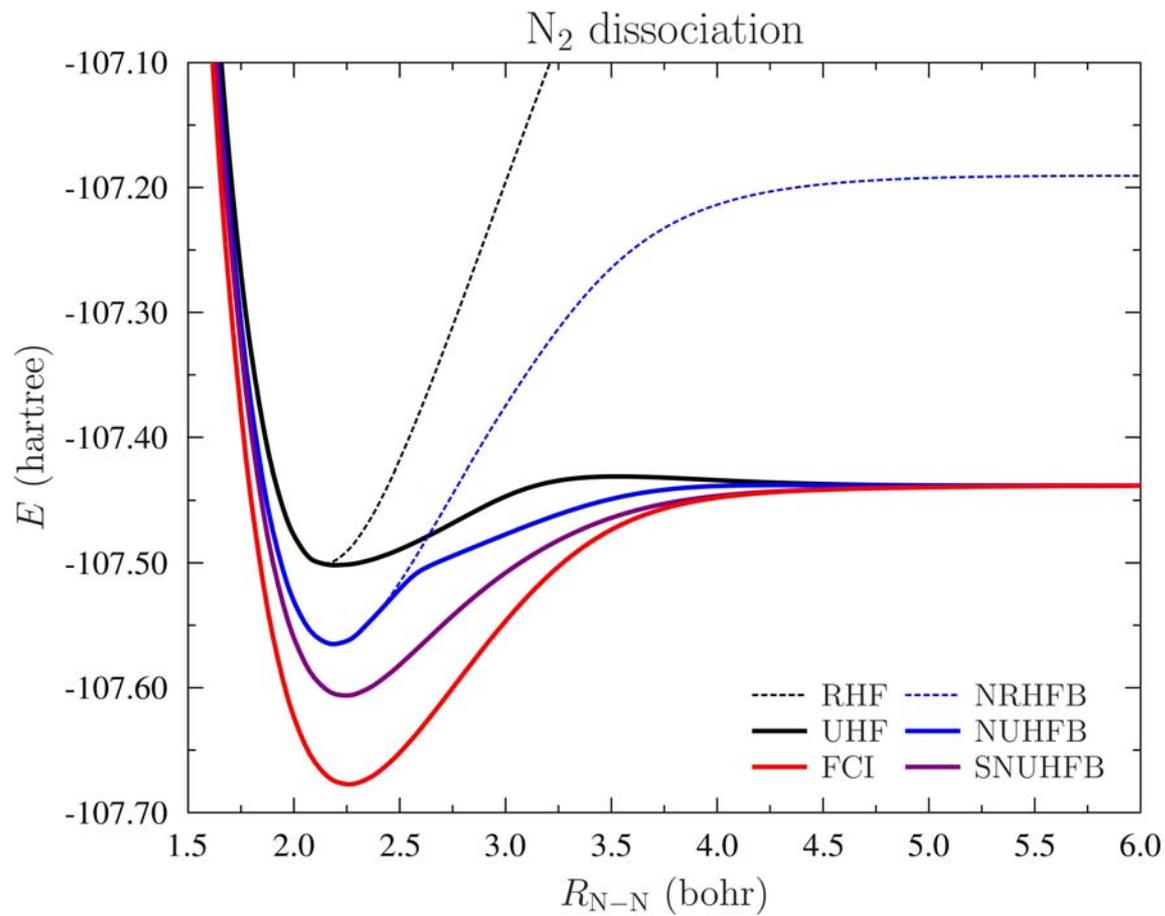
Note smoothness of **NRHFB** (=AGP) compared to **CAS**



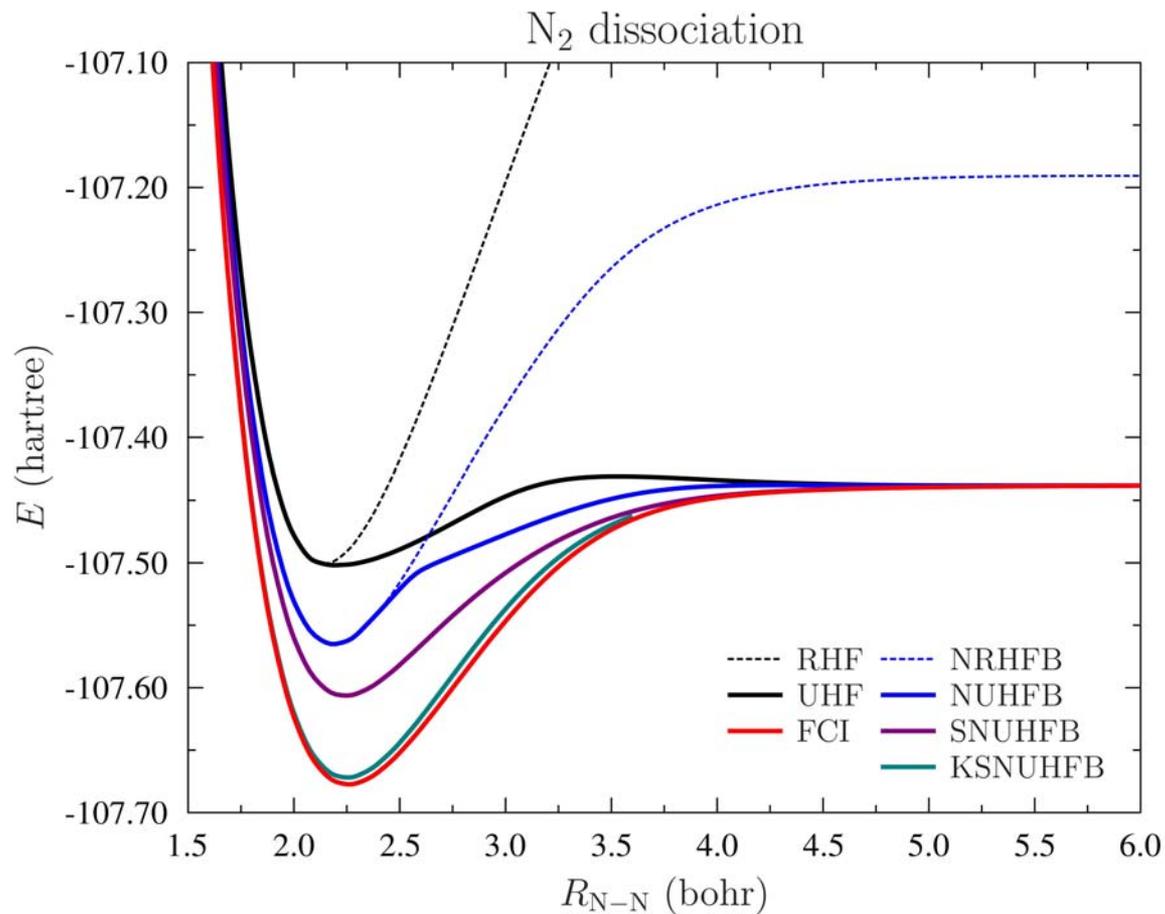
NUHFB: AGP with unrestricted orbitals



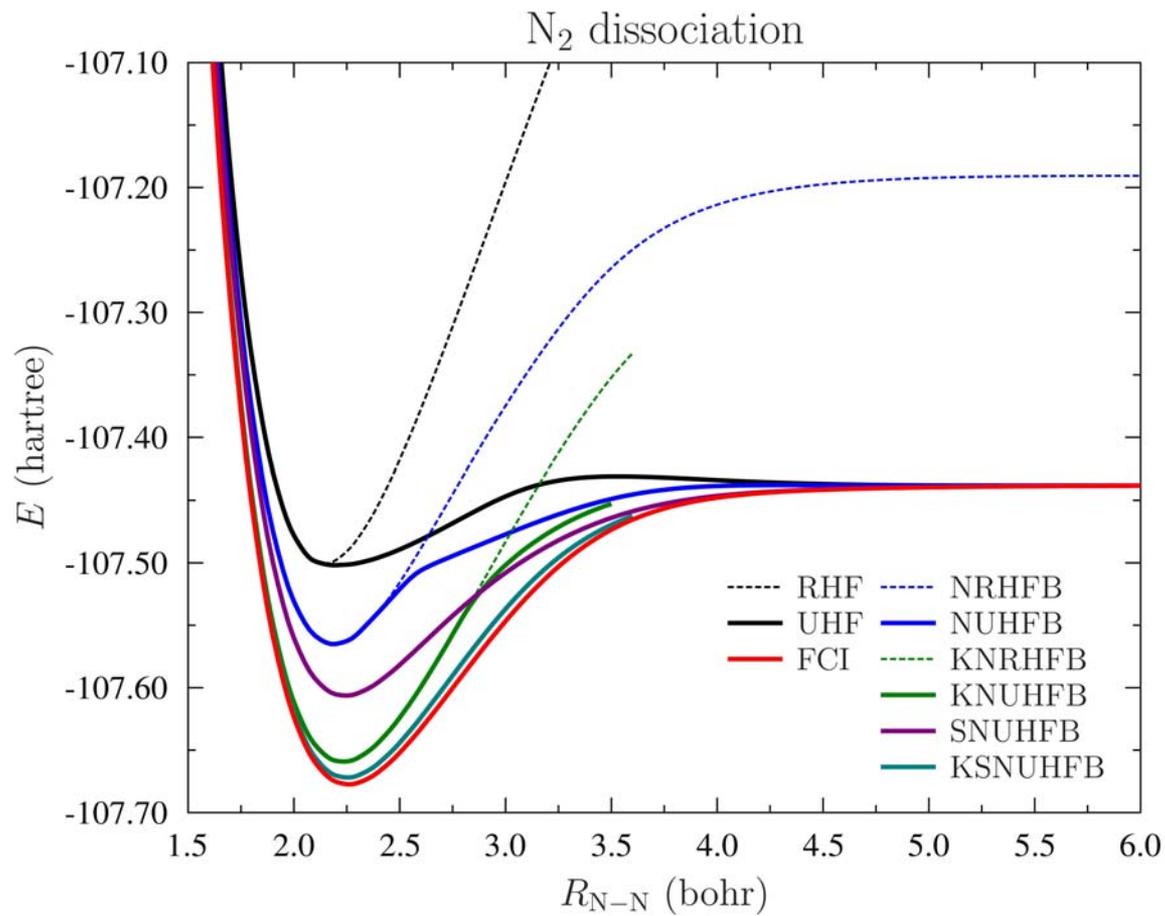
KNRHFB & **KNUHFB**: examples of complex conjugation restoration



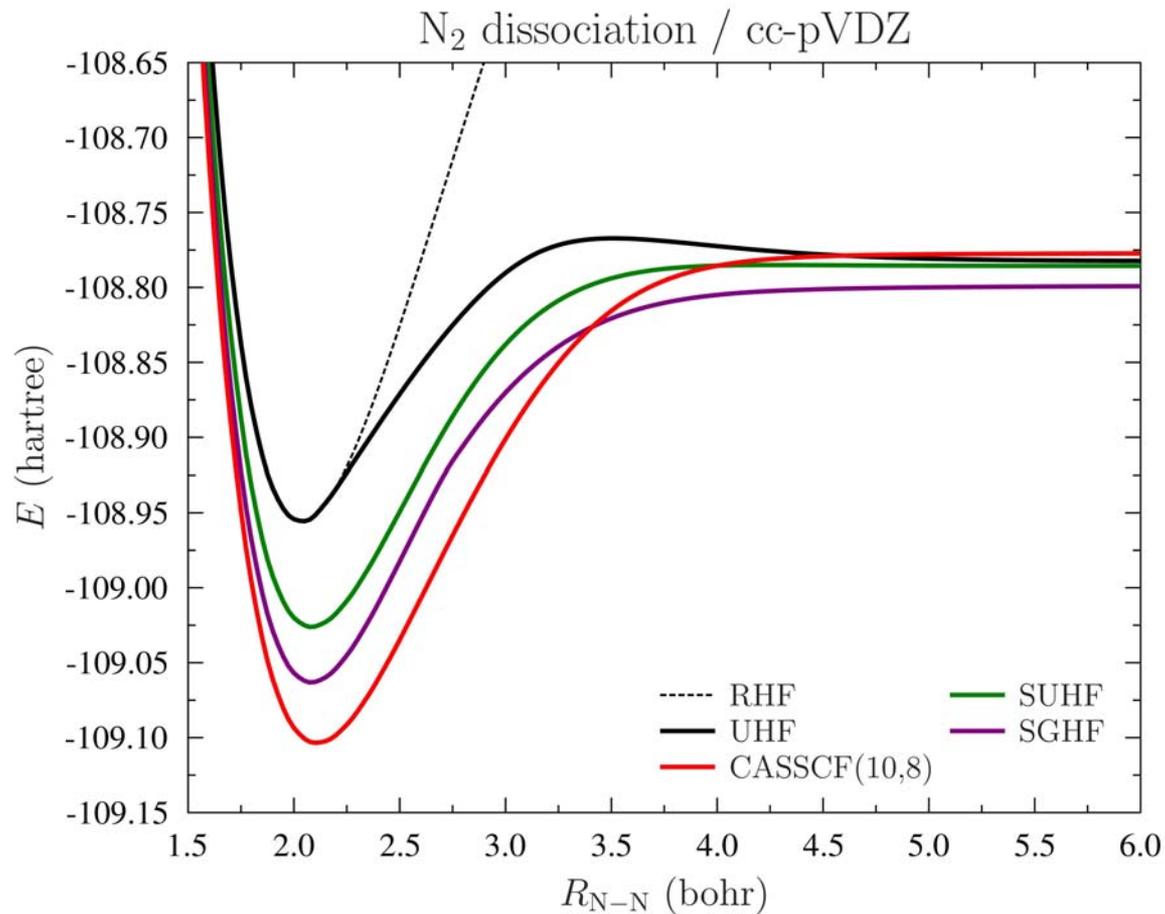
SNUHFB: example of collinear spin projection



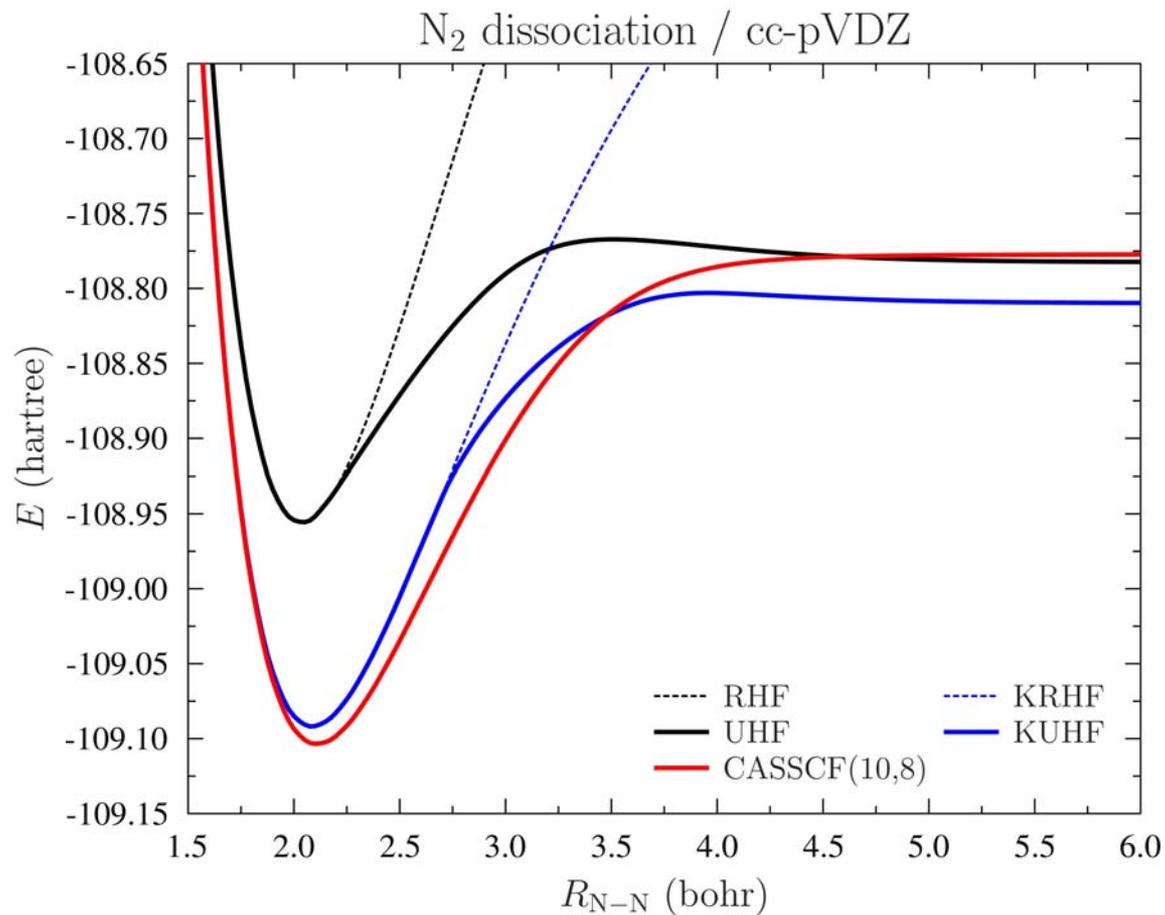
KSNUHFB: all symmetries broken & restored ~ **FCI** quality



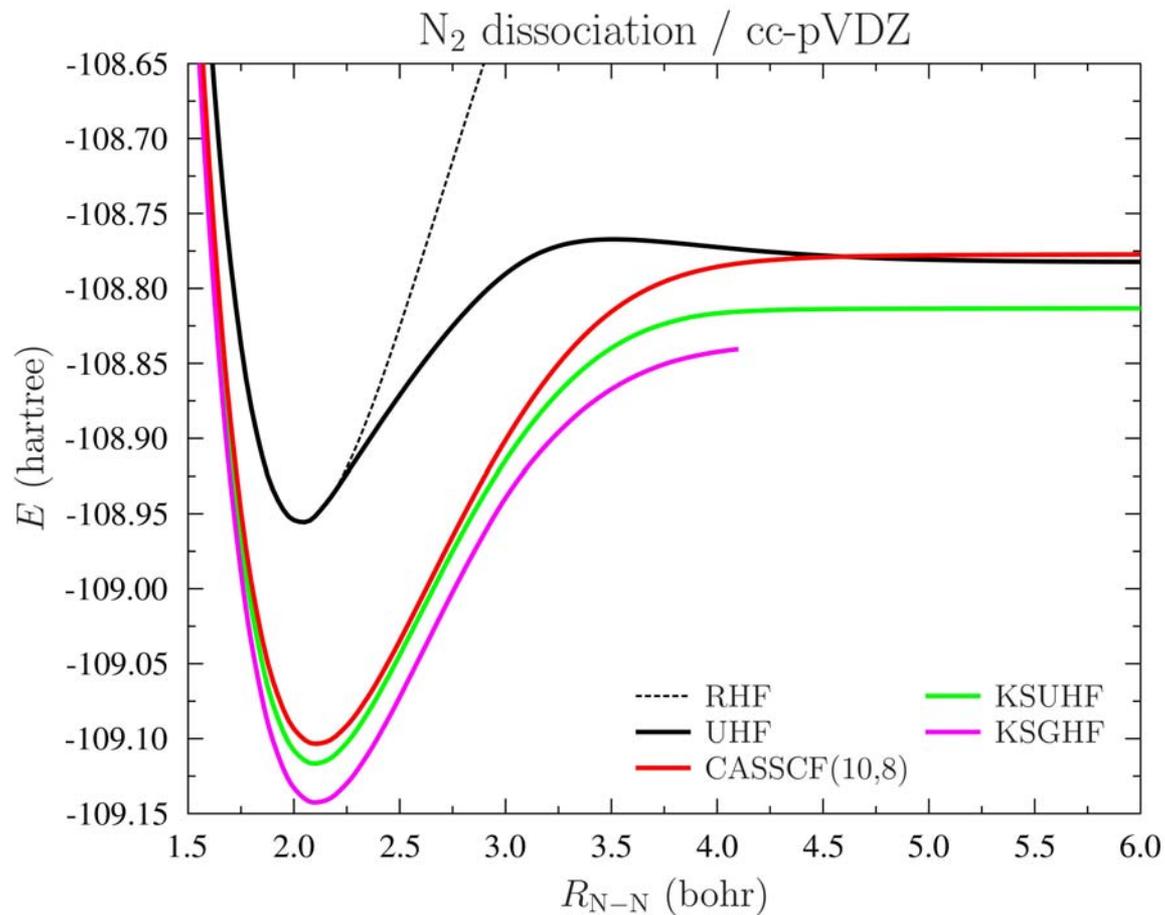
All curves together



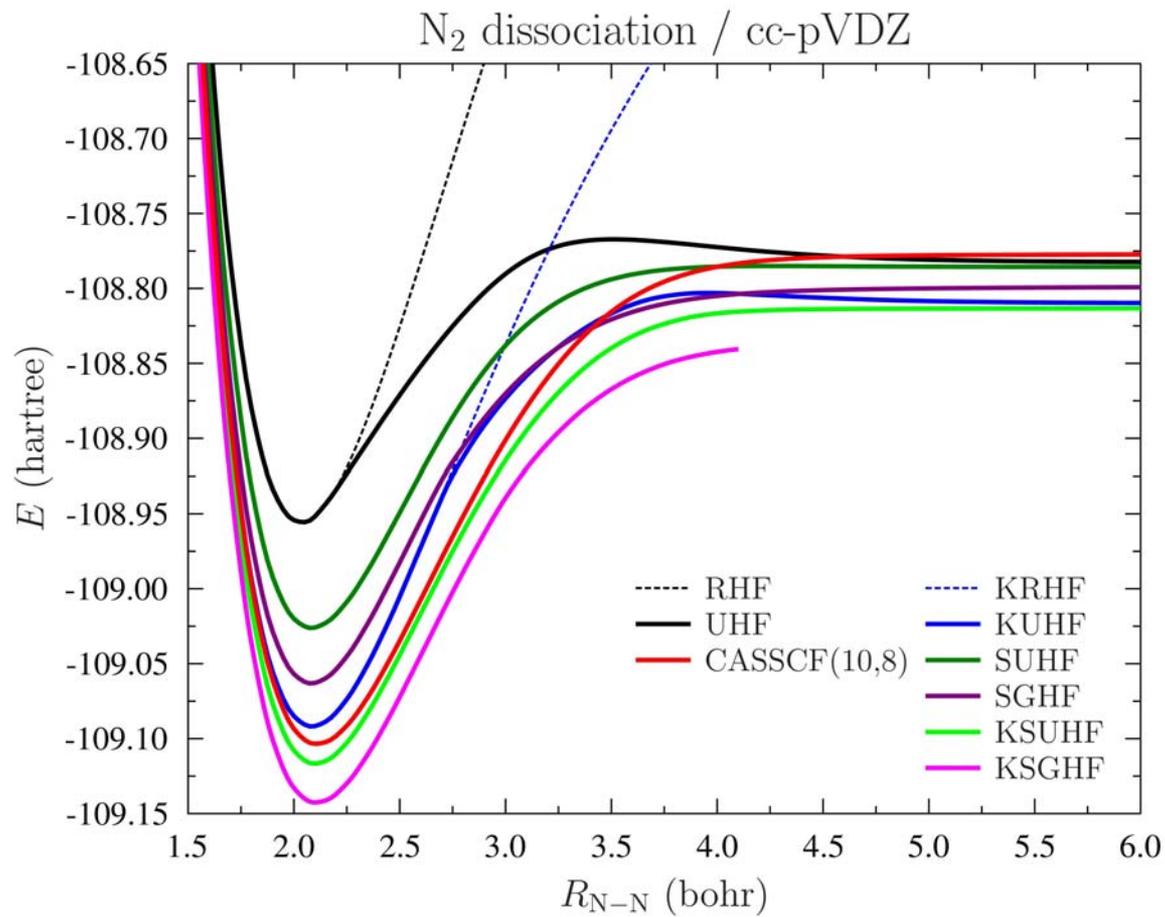
SUHF & **SGHF**: collinear and noncollinear spin restoration



KRHF & **KUHF**: complex conjugation symmetry restoration



KSUHF & **KSGHF**: add **K** to **S**



All curves together

Summary

- **Projection Problem:**

Variational solution to $\langle 0 | P^\dagger H P | 0 \rangle$, where:

- P are projection operators (spin, number, etc.)
- $|0\rangle$ is a symmetry broken Slater determinant

- **Solution:**

- Energy is a density matrix functional
- Projectors are discretized over a manifold of degenerate non-orthogonal Slater determinants
- Solved via diagonalization

- **Computational Cost:** mean-field, $N_g^* HF$

- **Optimization Problems Solved:**

- Coleman's **AGP** optimization ("Coulson's challenge")
- Löwdin & Mayer's **EHF** method (abandoned in late 70s)
- Goddard's **GF** method (proposed in 1968)

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