

# Symmetry Breaking & Restoration

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# Introduction

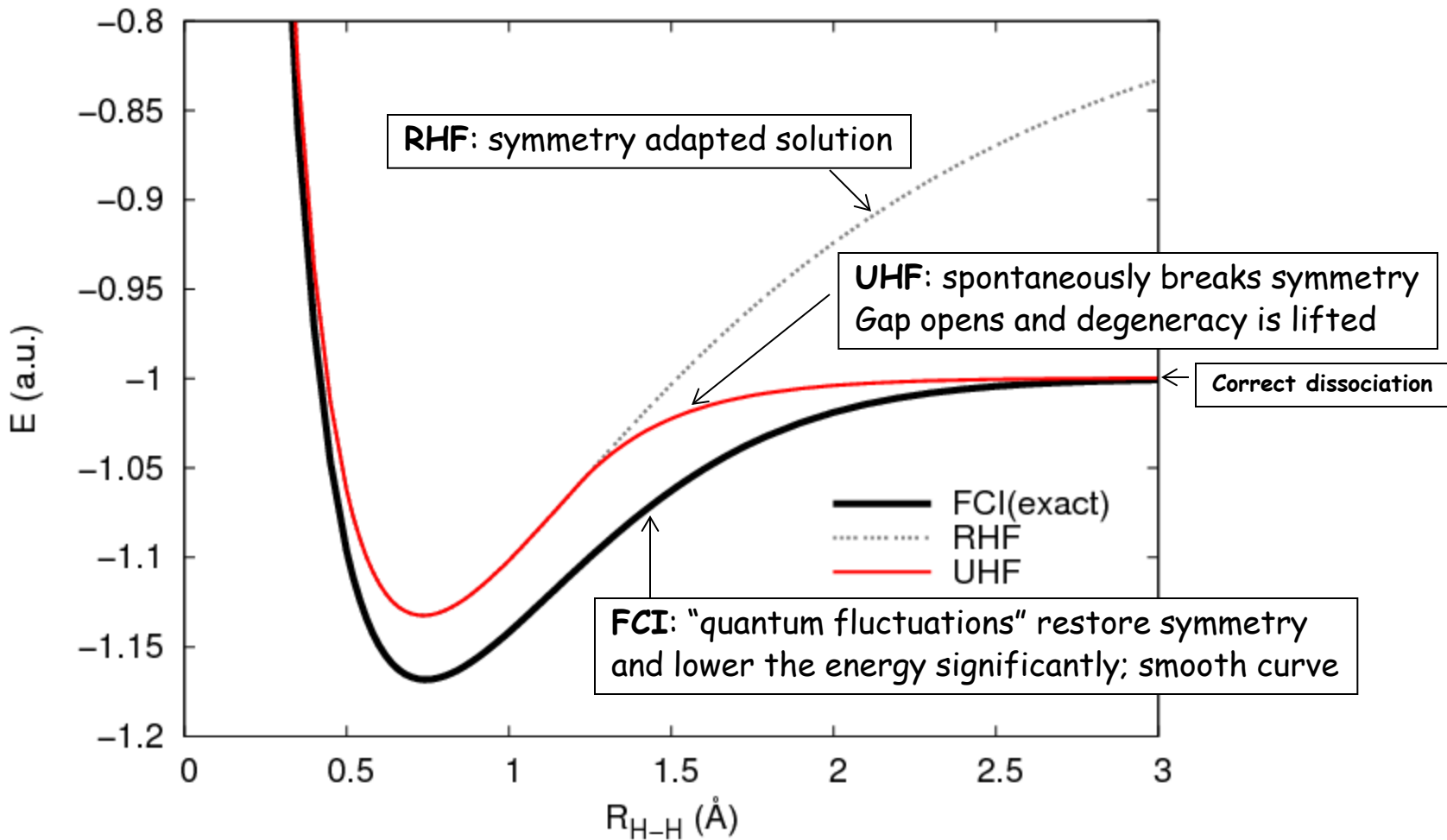
Symmetries, degeneracies,  
electron correlations,  
& quantum fluctuations

# The Electronic Structure Problem

- We know how to solve the time-independent Schrodinger equation with computational cost that grows exponentially with system size => **"full CI"** or **"exact diagonalization"**. This is useful only for small systems.
- **Our goal** is to find quantitatively accurate polynomial cost approximations to these solutions.
- **Mean-field theory = Hartree-Fock** has low computational cost and is a good starting point when correlations are **"dynamic"**.
- **In finite systems** if correlations are **dynamic**, single-reference **Coupled Cluster** theory gets the right answer for the right reason with polynomial computational cost. This is a solved problem.
- In the presence of exact or near-degeneracies, **"static"** correlations appear => **HF** is no longer good and **SR-CC** theory falls apart.
- A black-box treatment of **static** correlations with mean-field computational cost would be good => **our first objective**

# $H_2 \rightarrow H + H$ : Prototype of static correlation

At dissociation, the symmetry-correct RHF orbitals ( $\sigma_g$  and  $\sigma_u$ ) become **degenerate**



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

# Symmetries

- Symmetries play a crucial role in our theory:  $[H, \Omega] = 0$
- There are many different symmetries in electronic structure:
  - Number, spin, complex conjugation  $\mathbf{K}$ , point group (rotations, inversions, mirror planes), lattice translation, time reversal...
- Some symmetries are represented by continuous groups, e.g., **number** with  $U(1)$  and **spin**  $SU(2) \approx SO(3)$ .
- Other symmetries ( $\mathbf{K}$ ,  $\mathbf{PG}$ ,  $\mathbf{LM}$ ) have discrete spectra.
- Unitary symmetries ( $\Omega = \Omega^\dagger$ ) have good quantum numbers.
- Antiunitary symmetries do not carry quantum numbers (e.g.,  $\mathbf{K}$ )

# Symmetries and Degeneracies

- If two operators commute  $[H, \Omega] = 0$ , they share a common set of eigenfunctions: we can use symmetry labels for  $H$  eigenfunctions
- In the presence of **degeneracies**, eigenfunctions of  $H$  may be chosen to **violate symmetries** (e.g., breaking spherical symmetry in an atom) but this **does not lower the energy**.
- In infinite systems (thermodynamic limit), symmetries can break spontaneously because of **degeneracies**, e.g.,
$$E_J = \lim_{M \rightarrow \infty} \frac{J(J+1)}{2M}$$
- In the thermodynamic limit (TDL), symmetries break so that long-range order can appear. **Symmetry restoration does not lower the energy**.
- This form of symmetry breaking is known as a **phase transition**. From a **time dependent QM** perspective, the broken symmetry state is trapped in a well with infinite fluctuation time.



# Symmetry Breaking

- Symmetry breaking also occurs because of **approximations**; this is Lowdin's "symmetry dilemma" in **Hartree-Fock** theory.
- **Spontaneous Symmetry Breaking (SSB) in HF** lowers the energy by sacrificing good quantum numbers; it pinpoints the appearance of near degeneracies; it is artifactual because there are no phase transitions in finite systems (full **CI** has good quantum numbers).
- In this sense, **HF** is a theory that predicts its own failure.
- **Key concept: Goldstone manifold**: the set of degenerate determinants  $\{\Phi_i\}$  associated with **symmetry breaking**.
- In **finite** systems symmetry restoration ("quantum fluctuations" from diagonalizing  $\langle \Phi_i | H | \Phi_j \rangle$ ) **will lower** the energy because  $\langle \Phi_i | H | \Phi_j \rangle \sim \langle \Phi_i | \Phi_j \rangle \neq 0$
- If the symmetry manifold becomes **non-interacting**, symmetry restoration **will not lower** the energy. This happens in the **infinite TDL**.

# Summary

Symmetry breaking can be **legitimate** or **artifactual**.

If **artifactual**, symmetry restoration will lower the energy.

If **legitimate**, symmetry restoration will not lower the energy.



# Symmetry Breaking & Correlations

=> **My classification of electron correlations:**

- **Dynamic:** HF is a good approximation and single-reference coupled-cluster theory rules.
- **Static or non-dynamic:** Near degeneracies in finite systems; HF is pretty bad.
- **Strong:** **Collective** excitations plays a key role. **SR-CC** theory needs huge  $T_n$ . All occupations are small (it looks like weakly correlated) but entropy is maximum (all states are equally occupied).
- In **finite** systems, phase fluctuations (overlap related) lower the energy (unless the Goldstone manifold is orthogonal signaling a legitimate broken symmetry).
- In **infinite** systems **phase fluctuations** disappear and only **amplitude fluctuations** (RPA) remain.

# Dealing with static correlation cheaply

- **Unrestricted formalism** yielding **broken-symmetry Slater determinants** has been the standard way of dealing with **static correlation** in a computationally inexpensive manner.
- But symmetry breaking that lowers the energy (symmetry dilemma) is artifactual.
- Symmetries should be restored.

# Static Correlation Method Wish List

- ✓ Should preserve **all** Hamiltonian symmetries
- ✓ Should have low-computational cost (**mean-field**) instead of **exact diagonalization** combinatorial blowup
- ✓ No artifactual phase transitions
- ✗ Should be **size consistent** ( $E_{AB} = E_A + E_B$  when  $R_{AB} \rightarrow \infty$ ) and **size extensive** ( $E_{\text{corr}} \sim$  number of electrons)

# Symmetry Restoration

- Spontaneous Symmetry Breaking (SSB) in HF flags method's own failure. In **finite systems**: quantum fluctuations are important; the correct wavefunction is multi-determinant in nature.
- **When SSB occurs we can do Projection After Variation**  
"Phase transitions" are enhanced rather than eliminated! **Not good.**
- **Much better is to do Variation After Projection**  
When symmetries are not spontaneously broken, we can break them deliberately and then restore them  $\Rightarrow E \sim \langle 0 | P^\dagger H P | 0 \rangle$  and  $\delta E = 0$
- Heavily traveled **QC** road in the **60/70s** but mostly abandoned. Kept alive in nuclear many body theory!
- Our work: we deliberately break and restore symmetries
  - Continuous: **Number**  $U(1)$  and **Spin** ( $S^2$  and  $S_z$ )  $SO(3)$
  - Discrete: **Complex Conjugation** (K), **Point Group** (PG)
  - Discrete in lattices: **Linear Momentum** (LM), (LM + PG = Space Group)

# Projected Quasiparticle Theory

G. E. Scuseria, C. A. Jimenez-Hoyos,  
T. M. Henderson, K. Samanta & J. K. Ellis  
*J. Chem. Phys.* 135, 124108 (2011)

PHFB : Projected Hartree-Fock-Bogoliubov

Number, Tri-axial spin, Complex Conjugation, and Point Group

Symmetry Breaking & Restoration  
using Variation After Projection

# PQT Outline

- **Number  $U(1)$  and tri-axial spin  $SO(3)$**  have continuous group representations. We discretize the projection operators and make sure that they are converged.
- **Point group symmetry** is discrete and leads to a non-orthogonal **CI** problem. But we know the **CI** coefficients from the desired symmetry of the solution, so we simply build the "eigenvector".  
No **CI** needed.
- **Complex conjugation** is a non-orthogonal **2x2 CI** problem.
- **Non-orthogonal CI** problems can be linearly dependent (we are working in an overcomplete space). **Solution**: remove linear dependencies.

# 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  $|HFB\rangle = \prod_i \beta_i^\dagger |vac\rangle$  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 QChem because **HFB**  $\rightarrow$  **HF** for repulsive  $1/r_{12}$
- But **PHFB** is not the same as **HFB**



# PHFB Basics (I)

- Given a **symmetry operator**  $N=N^\dagger$  and  $[H,N] = 0$
- Build a **unitary operator**  $U = e^{i\varphi N}$  where  $\varphi \in \mathbb{R}$
- Consider a **broken symmetry determinant**  $|HFB\rangle$  and the **overcomplete manifold** of non-orthogonal **determinants** obtained from rotations:  $|\varphi\rangle = U |HFB\rangle = e^{i\varphi N} |HFB\rangle$
- They are all **degenerate in energy** (**Goldstone manifold**)  
 $\langle \varphi | H | \varphi \rangle = \langle HFB | e^{-i\varphi N} H e^{i\varphi N} |HFB\rangle = \langle HFB | H |HFB\rangle$   
**but** interact among themselves  
 $\langle HFB | e^{i\varphi N} |HFB\rangle = \langle HFB | HFB(\varphi) \rangle = \text{Sqrt} [ \det (S_{0\varphi}) ]$   
 $\langle HFB | H e^{i\varphi N} |HFB\rangle \neq 0$
- Build a **projection operator**  $P = 1/2\pi \int d\varphi e^{i\varphi(N-n)}$   
to extract from  $|HFB\rangle$  the component with desired eigenvalue  $n$

# PHFB Basics (II)

- Use the variational theorem to minimize the energy  $E$  (variation-after-projection)

$$E = \frac{\langle \text{HFB} | P^\dagger H P | \text{HFB} \rangle}{\langle \text{HFB} | P^\dagger P | \text{HFB} \rangle} = \frac{\langle \text{HFB} | H P | \text{HFB} \rangle}{\langle \text{HFB} | P | \text{HFB} \rangle} = \frac{1}{2\pi} \int d\varphi C(\varphi) \langle \text{HFB} | H | \text{HFB}(\varphi) \rangle$$

$P$  is Hermitean, idempotent & commutes with  $H$

$C(\varphi) = e^{-i\varphi n}$  ( $n$  is the desired electron number) is an analytic weight function determined by the symmetry group [ $U(1)$  for number]

- Discretize  $P$  over a gauge grid  $\{\varphi\}$
- **Key result:** the PHFB energy  $E$  above is a **density matrix functional** of the unprojected density matrices  $\rho_{ij}(\varphi)$  and  $\kappa_{ij}(\varphi)$
- Only **unknown** are the **orbitals**

# PQT in one slide

$$|PQT\rangle = P_N P_S \dots P_\Omega P_K |HFB\rangle$$

High-quality **MR wavefunction**.  
Factorizable representation  
of its 2-matrix.

Deformed state.  
All symmetries broken.  
Very simple structure:  
single determinant

Projection operators. Simple structure.  
Discretized over modest size grid (N,S).

**PQT energy is a 1-QRDM functional that  
can be optimized with mean-field cost**

# Projected Hartree-Fock Theory

C. A. Jimenez-Hoyos, T. M. Henderson,  
T. Tsuchimochi & G. E. Scuseria  
J. Chem. Phys. 136, 164109 (2012)

PHF : same as PHFB, without number projection

- Same philosophy just a different set of equations
- Historical significance (our SUHF  $\equiv$  Löwdin & Mayer's EHF)

# Spin Projection

**Lowdin's approach:** a two-body projection operator

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

Leads to a complicated set of equations (Mayer, AQC 1980).

**An alternative approach:**  $SO(3)$  rotational invariance

$$\hat{R}(\Omega) = e^{i\alpha \hat{S}_z} e^{i\beta \hat{S}_y} e^{i\gamma \hat{S}_z}$$

We impose that the wavefunction is invariant with respect to spin vector rotations via three one-body rotations like:

$$\hat{P}_{mm}^s = \frac{2s+1}{2} \int_0^\pi d\beta \sin \beta d_{mm}^s(\beta) e^{i\beta \hat{S}_y}$$

This leads to a much simpler set of equations.

# Benchmark Results

# Acronym Soup

Acronyms are composed of two parts:

## Symmetry

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**N**: number

**S**: spin

**K**: complex conjugation

**C<sub>i</sub>**: point group

## Reference determinant

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**R**: restricted (closed-shell)

**U**: unrestricted (spin-polarized)

**G**: general (non-collinear)

**G** orbitals are complex

## Examples:

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**NRHFB** is number-projection with closed-shell orbitals

**NUHFB** is number-projection with spin-polarized orbitals

**SNUHFB** adds spin projection (collinear spin)

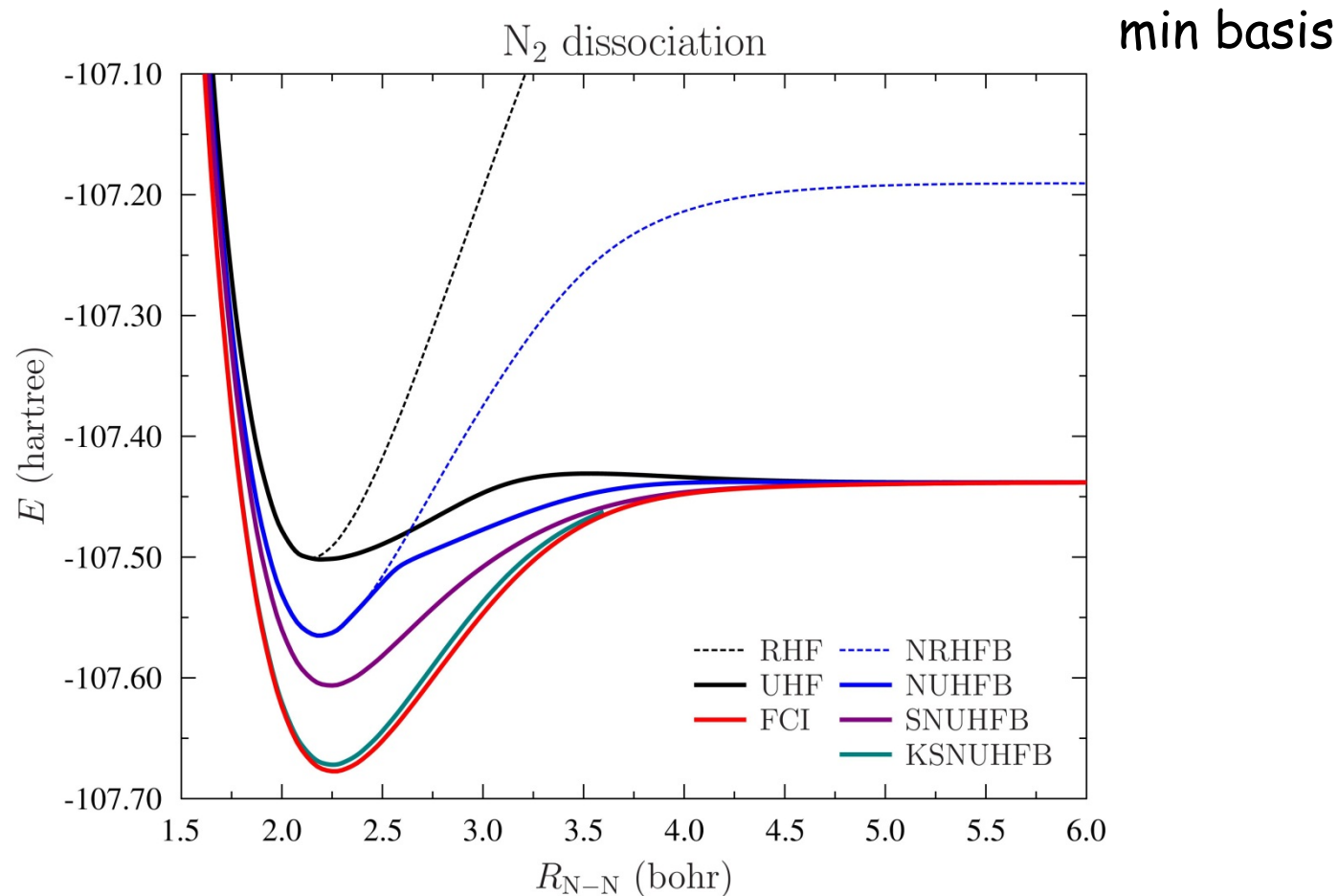
**SNGHFB** adds triaxial (noncollinear) spin projection

**KSNGHFB** adds complex conjugation

**PHF** (no number projection): same acronyms as above without "B"

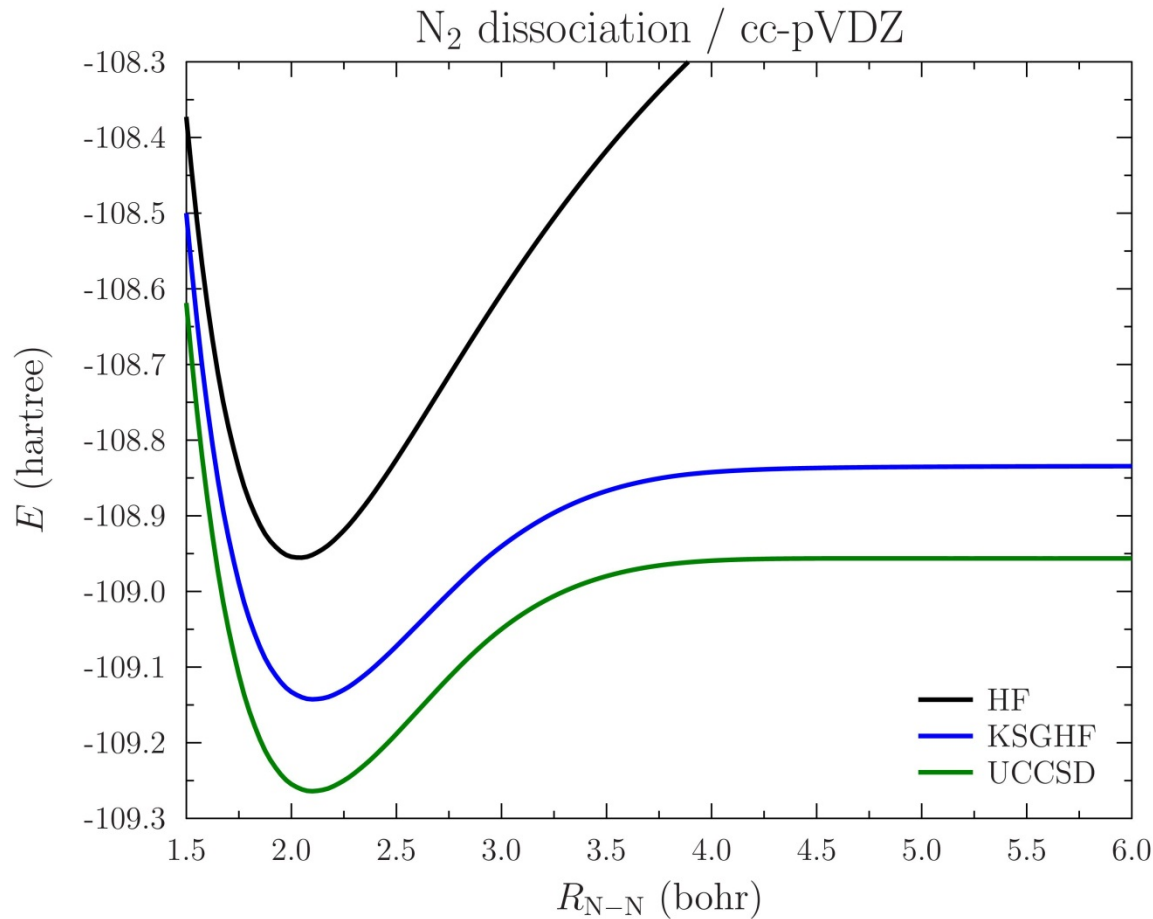


# N<sub>2</sub>: triple-bond dissociation



**KSNUHFB ~ FCI quality**

# N<sub>2</sub>: triple-bond dissociation



polarized basis

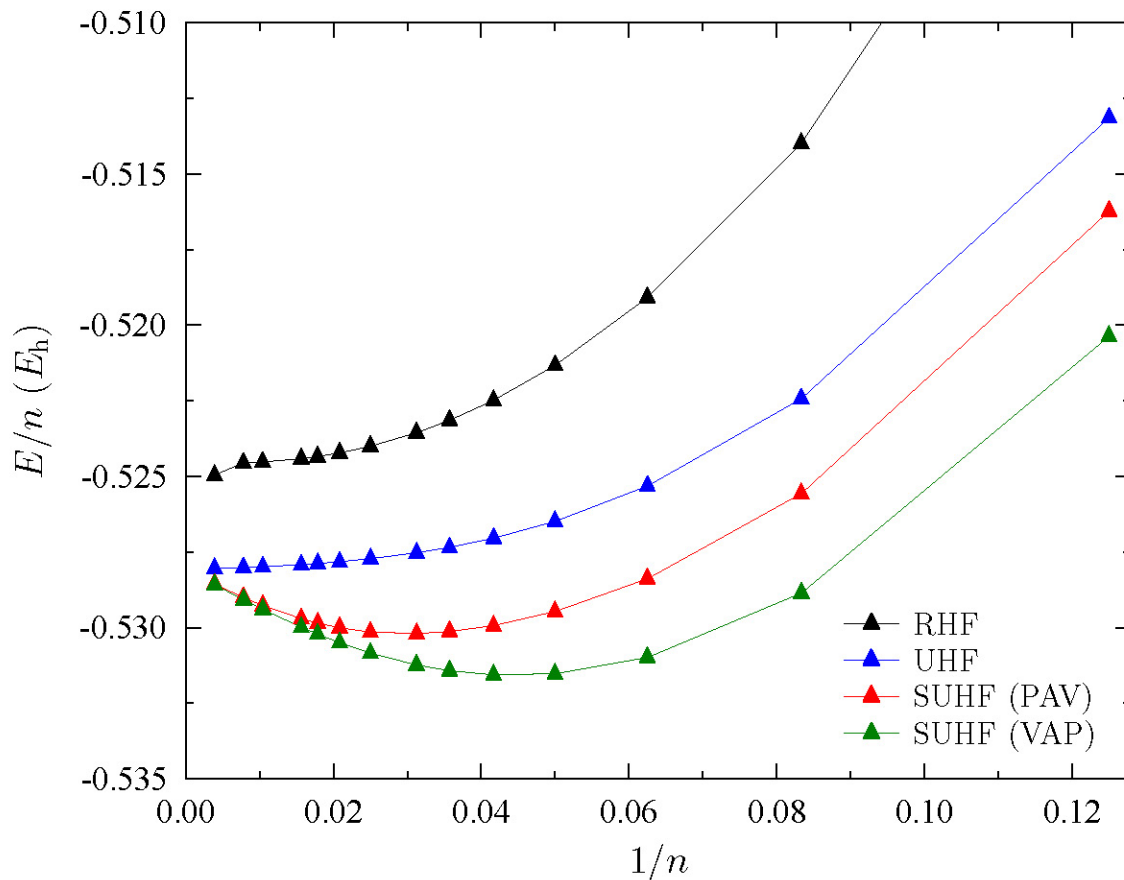
Residual correlations are large !

# Infinite Systems

bad news... ?

# The curse of the thermodynamic limit

Equidistant H atom rings @ 1.80 Bohr with minimum basis



In TDL spin projection (SUHF) yield zero correlation (per e) beyond UHF

# Summary

- **Variation after Projection Symmetry Restoration**
  - Energy is a one-body density matrix functional
  - Small number of variational parameters
  - Compact representation of the wavefunction
- **Computational Cost:** mean-field,  $N_g^*HF$
- **Fundamental ingredient:** we work with non-orthogonal Slater determinants (symmetry coherent states)
- **More work is needed** to address **“residual”** correlations and better balance static & dynamic correlations
- **More work is needed** to address the challenge of strong correlation for **infinite systems** (thermodynamic limit)

# Acknowledgements

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