Strong Correlations from Constrained Mean-Field Approaches

Gustavo E. Scuseria

RICE
Unconventional Wisdom
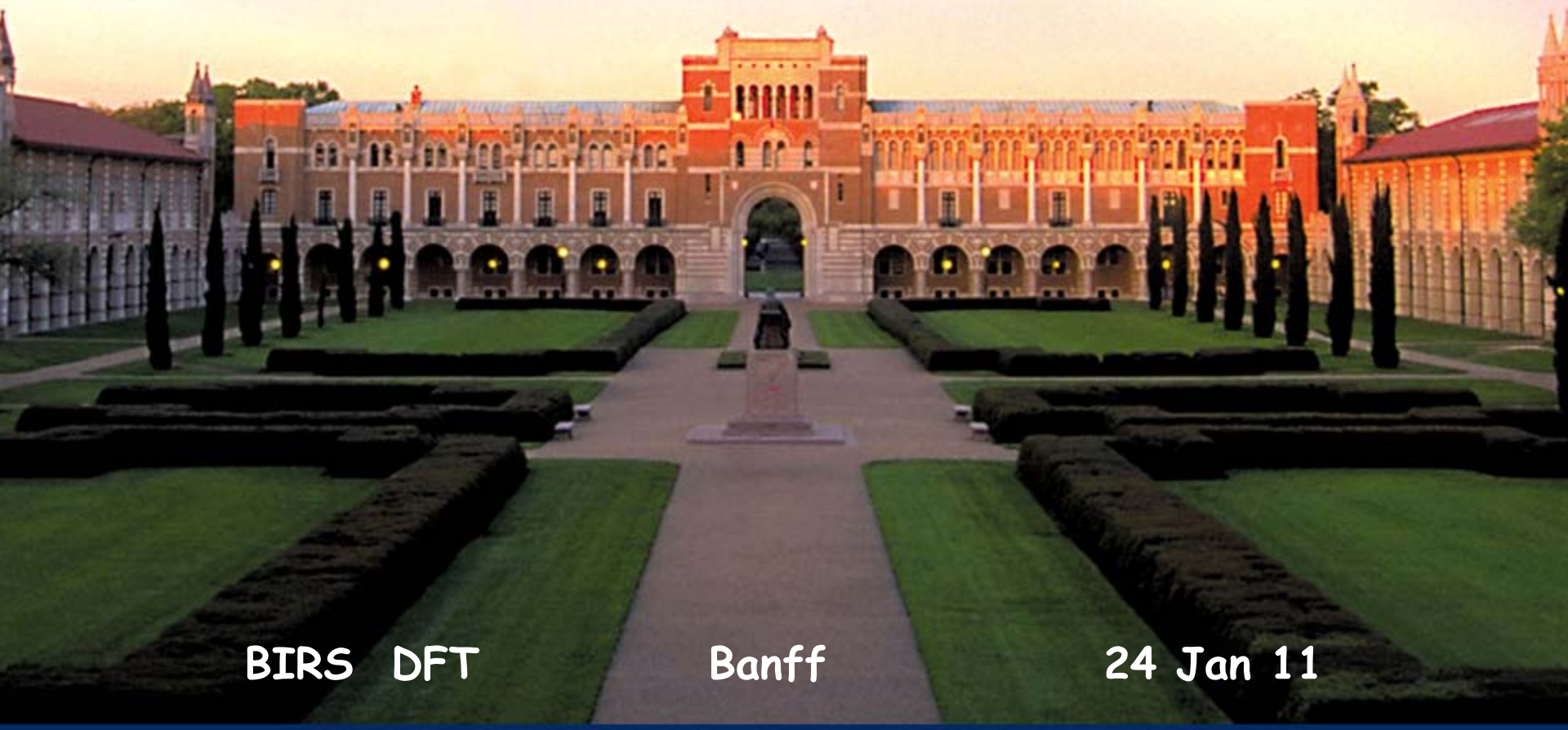
BIRS DFT   **Banff**   **24 Jan 11**

Outline

- **Themes**
  - What is **strong correlation** and how to describe it "black-box"
  - **Symmetry** breaking and restoration

- **Specific Topics**
  - **C**onstrained-**P**airing **M**ean-**F**ield **T**heory
    - **DMFT** for strong correlations
  - Spin-off
    - **ROHF** theory made simple
  - **C**onstrained Active Space Approaches
    - **C**UHF & **C**UMP2

What is Static/Strong Correlation?

- It is all about **near-degeneracies**

- A single-determinant **RHF** wavefunction (with **correct** symmetries) becomes a **very poor descriptor** of the electronic structure

- Static correlation examples:
  - Closed-shell **H_2 at dissociation:** σ_g/σ_u **MO** exact degeneracy
    (nonlocal, left-right correlation: the physics of **entanglement**)
  - **Heavy atoms** due to **AO** near degeneracies
    (transition metals, lanthanides, and actinides but even the Be atom)
  - **Diradicals** where unpaired spins localize and are entangled
  - Systems where **magnetic effects** are important
  - Large **DOS** at Fermi energy => **heavy fermions** in solid state

How to deal with strong correlation?

- Despite **80** years of Schrödinger equation, there is still no simple, black-bock, computationally efficient way of dealing with strong correlation

- The weak (dynamical) correlation problem has been solved, e.g., **CCSD(T)** with reasonable computational cost $N^6 \rightarrow O(N)$

- When strong correlation is pervasive, **CCSD(T)** does not yield high-quality results (e.g., **Cr_2**). Multi-reference treatment is needed. Combinatorial blowup limits **CASSCF** to ~**15e** in ~**15 orbs**, or **10^{10}** determinants

- Strong correlation is connected with the physics of localization and **DFT** falls dead too because of **self-interaction error**

- **Density Matrix Functional Theory (DMFT)** retains **nonlocal HF** exchange and has better chances to deal with strong correlation

Symmetry Breaking

- Spontaneous symmetry breaking in mean-field approaches is associated with the onset of strong correlation

- Treating these cases with exact diagonalization (**FCI** or **CASSCF**) yields a combinatorial blowup wall

- Thus, it is tempting (and hopefully rewarding) to use inexpensive mean-field approaches for treating strong correlation

- In wavefunction methods like **UHF**, the problem is **massive** spin contamination

- **Idea: break symmetry in an active space; control it elsewhere**

- **Restore symmetry** by **projection**: if contamination is small, projection techniques should work really well (**PAV**)

Theme: symmetry breaking & restoration

- **Ideally**: **V**ariation **a**fter **P**rojection (**VAP**)

- Unfortunately **VAP** is generally very involved; **PAV** is cheaper and easier

- **PAV** yields **approximate** variational coefficients but overcomes the combinatorial blowup of exact diagonalization

- Alternative view:
  - **CI** optimizes configurations coefficients
  - **MCSCF** or **CASSCF** optimizes conf coeffs and orbitals
  - Projected methods optimize orbitals and get non-variational **CI** coefficients by projection
  - **VAP** optimizes the **CI** coefficients. Key issue is whether this can be done in less than combinatorial complexity!

- **Question**: have we exhausted the exploration of symmetry breaking?

- **Answer**: NO !

- Most importantly particle number conservation has been overlooked

Theme: breaking electron number conservation

- **HFB** yields **HF** for Coulombic systems

- Our **Constrained-Pairing Mean-Field Theory (CPMFT)** induces symmetry breaking (fictitious attractive e-e interaction)

- Restores electron number conservation in the energy definition

- **CPMFT** is essentially a **DMFT** that breaks particle number conservation and restores it

- **CPMFT** yields excellent results if attractive pairing interactions are constrained to an __active__ space

CPMFT Energy Functional
(closed-shells)

$$E = 2 \Sigma\, h_{pq}\, P_{pq} + \Sigma\, [2(pq,rs)-(pr,qs)]\, P_{pq}P_{rs} - \Sigma\, (pr,qs)\, K_{pq}K_{rs}$$

where $K^2 = P - P^2$ $\qquad\qquad$ $P = P_\alpha = P_\beta$

- **Preserves** space and spin **symmetries**

- **Correctly dissociates** any polyatomic molecule into **ROHF** atoms (or fragments)

- **Smoothly connects** the dissociation limit (full entanglement) with the equilibrium region (where it yields **RHF** in the absence of static correlation)

- Cleanly separates **static** & **dynamic** correlation

- Has low computational cost **(mean-field)** instead of **CASSCF** combinatorial blowup
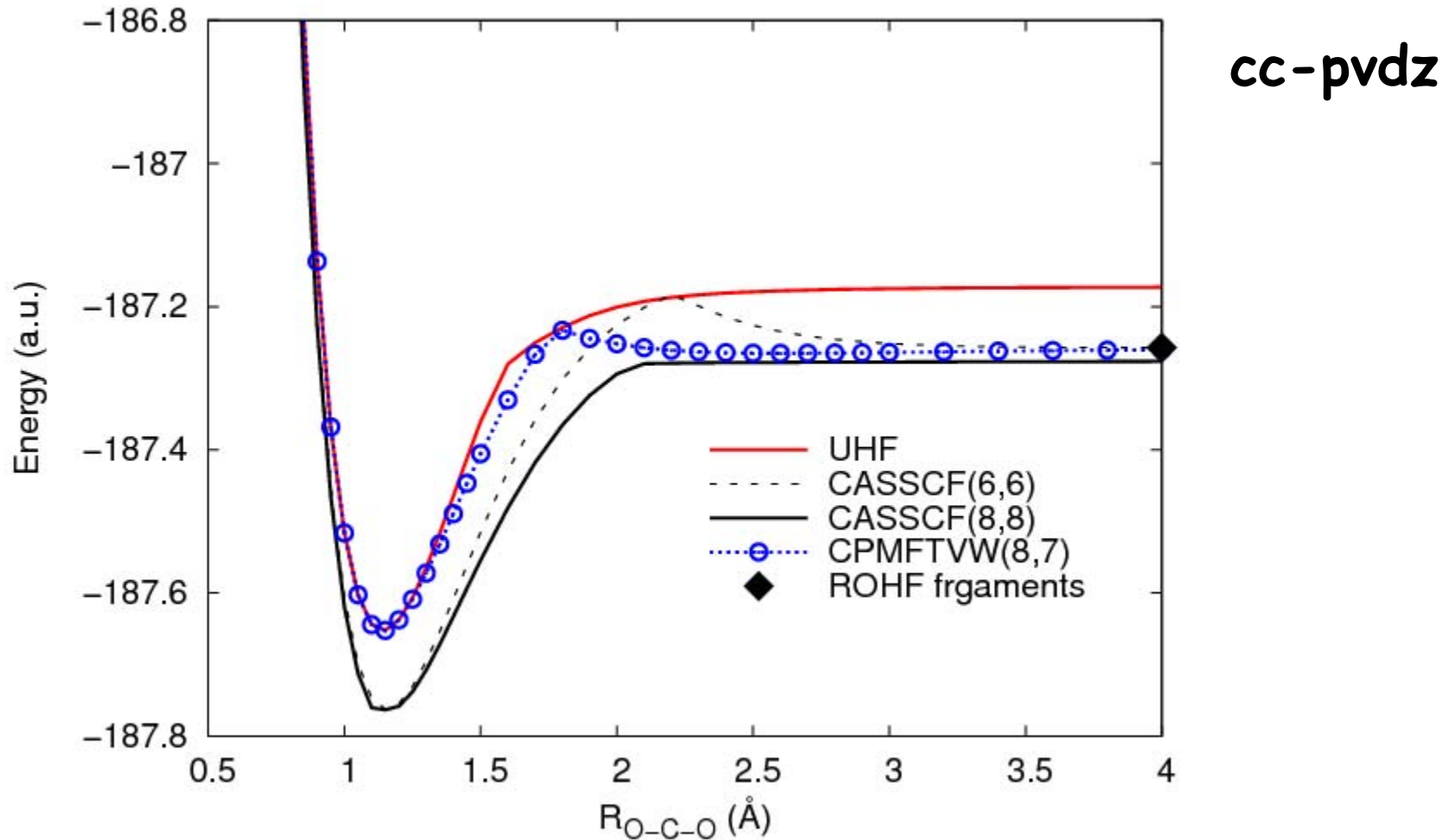
H₂ cc-pV5Z
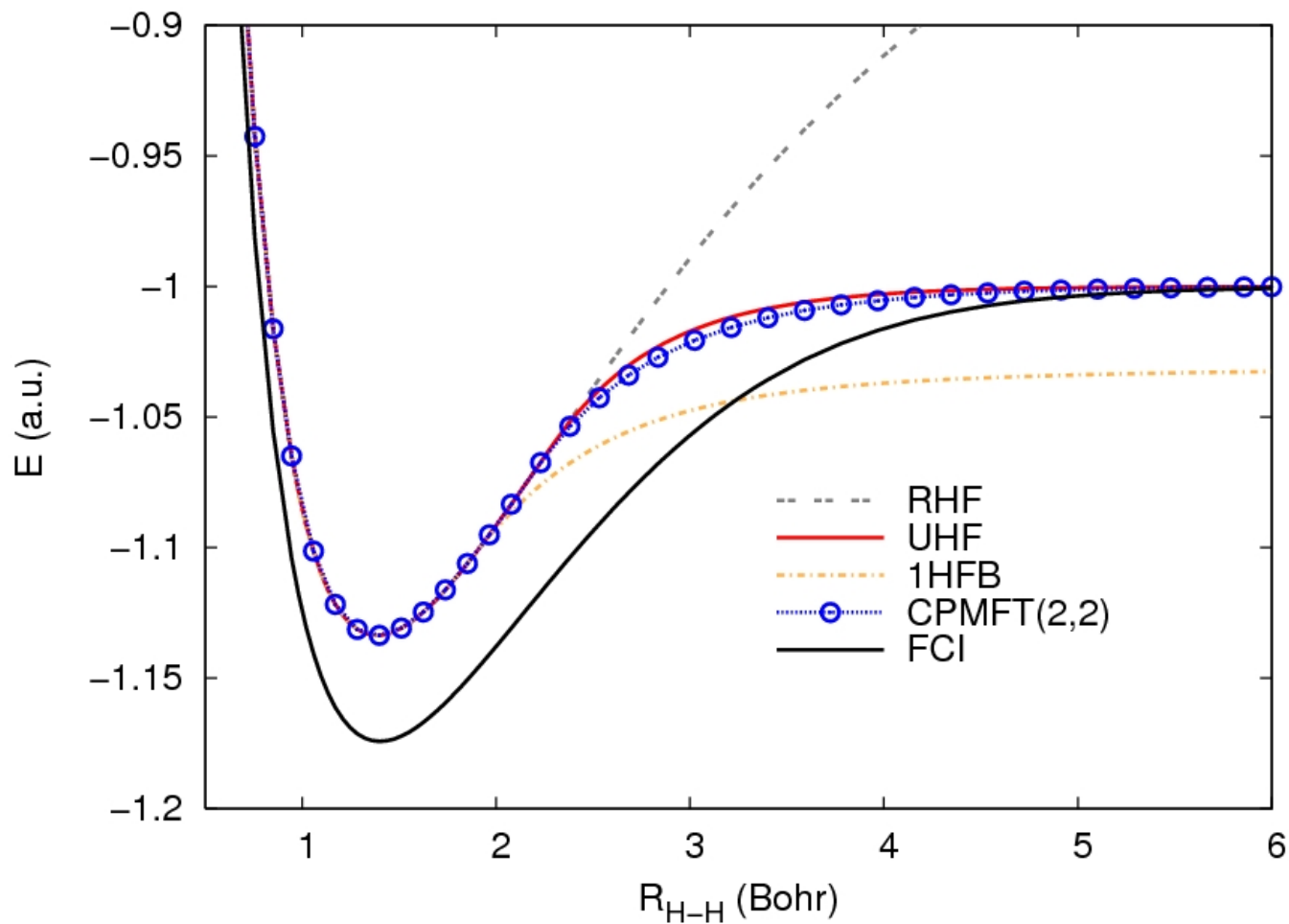
N₂ 6-311++G**
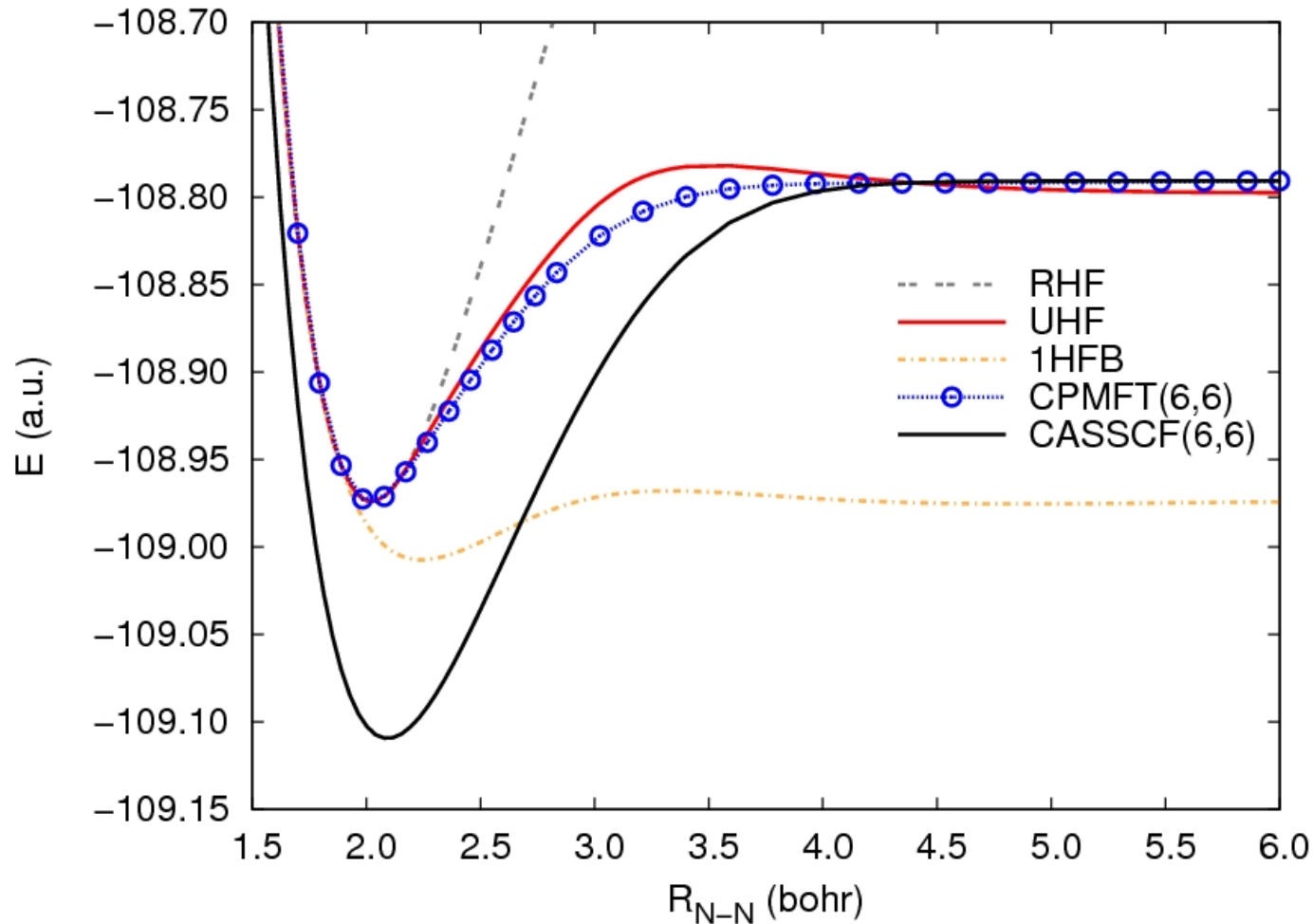
CPMFT results are similar but not identical to **UHF**
CPMFT preserves symmetry in the density matrix

CO_2 : a very challenging test

cc-pvdz

UHF fails to describe strong correlation

Connection to UHF formalism

CPMFT paper IV:

T. Tsuchimochi, T. M. Henderson, G. E. Scuseria, and A. Savin

J. Chem. Phys. 133, 134108 (2010)

UHF, DMFT, and CPMFT

- In terms of a charge P and spin density M

$$P = \tfrac{1}{2}(P_\alpha + P_\beta) \qquad M = \tfrac{1}{2}(P_\alpha - P_\beta)$$

and a closed-shell energy term:

$$E_{CS} = \Sigma_{ij}\, 2h_{ij}\, P_{ij} + \Sigma_{ijkl}\, [2(ij,kl)-(ik,jl)]\, P_{ij}\, P_{kl}$$

the **UHF** energy expression is a **DMFT**:

$$E_{UHF} = E_{CS}[P] - \Sigma_{ijkl}\, (ik,jl)\, M_{ij}\, M_{kl}$$

- This has the same form as **CPMFT**

$$E_{CPMFT} = E_{CS}[P] - \Sigma_{ijkl}\, (ik,jl)\, K_{ij}\, K_{kl}$$

- Except that $K = +\mathrm{sqrt}\,[P - P^2]$ is not M !

CPMFT Summary

- A very efficient low-cost (mean-field) computational model for dealing with strong correlations within a **DMFT** framework

- The **1pdm** <u>is</u> **N**-representable

- The **2pdm** (Γ) <u>is not</u> **N**-representable

- **E ~ Tr [H Γ]** and the wavefunction is gone…

- Results are different from **UHF**, **PUHF, and variants**

- **CPMFT** inspired some interesting spin-off **wavefunction work** that I will discuss next:
  - **ROHF** theory made simple
  - **Constraining symmetry breaking** to an active space

ROHF theory made simple

T. Tsuchimochi & G. E. Scuseria

Problems with ROHF

- **Roothaan's** formalism defines the wavefunction and densities (both charge and spin) but orbitals and orbital energies are ambiguous and depend on the choice of "coupling parameters"

- This is unsatisfactory for **post-ROHF** methods (correlation and excited states) as the results depend on these choices

- Long controversy in the literature for **~50 years**
  No Koopmans' theorem in regular (Roothaan's) **ROHF** !

- **Unphysical:** why do we have the same orbitals and orbital energies for alpha and beta electrons if the potentials that they see are different? ➔ **the MOs should be different**

- **UHF** is not the answer because of spin contamination

Attempts to fix ROHF

- Handy's **SUHF** (**S**pin-projected **UHF**) uses a single Lagrange multiplier λ to constrain: λ **[Ŝ² –s(s+1)] = 0**
  - Unfortunately λ is infinity! ➔ not a practical scheme

- Our solution: **C**onstrained **UHF** (**CUHF**)
  - Using the **UHF** energy formula as a function of **P** and **M**, we constrain **M** using (occ x vir) Lagrange multipliers
  - In "**core**" space: **M=0**; in "**open-shell**" space **M=correct**
  - "**Spaces**" are only defined in the **NO** basis
  - Solution for Lagrange multipliers is analytical

- **It works!** Crisp and quick convergence to **ROHF** energy and densities… **Alpha** orbitals and orbital energies are different from **beta**. **CUHF** carries no spin-contamination.

Errors (eV) on IPs ($-\varepsilon_{HOMO}$)
(24 high-spin open-shell systems)

	ROHF (MD)	ROHF (PGB)	CUHF	UHF
ME	-7.38	0.57	0.54	0.68
MAE	7.38	0.64	0.61	0.71

CUHF gives good results and has no spin contamination

CUHF can predict both IPs & EAs

Valence and Rydberg excited states (eV) via quick & dirty TD-HF

	$\langle S^2 \rangle - s(s+1)$	State		CUHF	UHF	Exp.
BeF	0.001	V	$^2\Pi$	**4.19**	4.20	4.14
		R	$^2\Sigma^+$	**6.33**	6.34	6.16
CH_3	0.012	R	$^2A'_1$	**6.23**	6.54	5.73
		R	$^2A''_2$	**7.34**	7.73	7.44
CO^+	0.141	V	$^2\Pi$	**4.84**	6.93	3.26
		V	$^2\Sigma^+$	**9.81**	11.10	5.82
CN	0.406	V	$^2\Pi$	**0.95**	4.13	1.32
		V	$^2\Sigma^+$	**2.01**	5.42	3.22
MAE				**0.77**	1.44	0.00

Spin Symmetry Breaking
in a
Constrained Active Space:
CUHF & CUMP2

T. Tsuchimochi & G. E. Scuseria

Controlled Symmetry Breaking

virtual — $M = 0$

active — allow $M \neq 0$

core — $M = 0$

RHF   UHF   CUHF
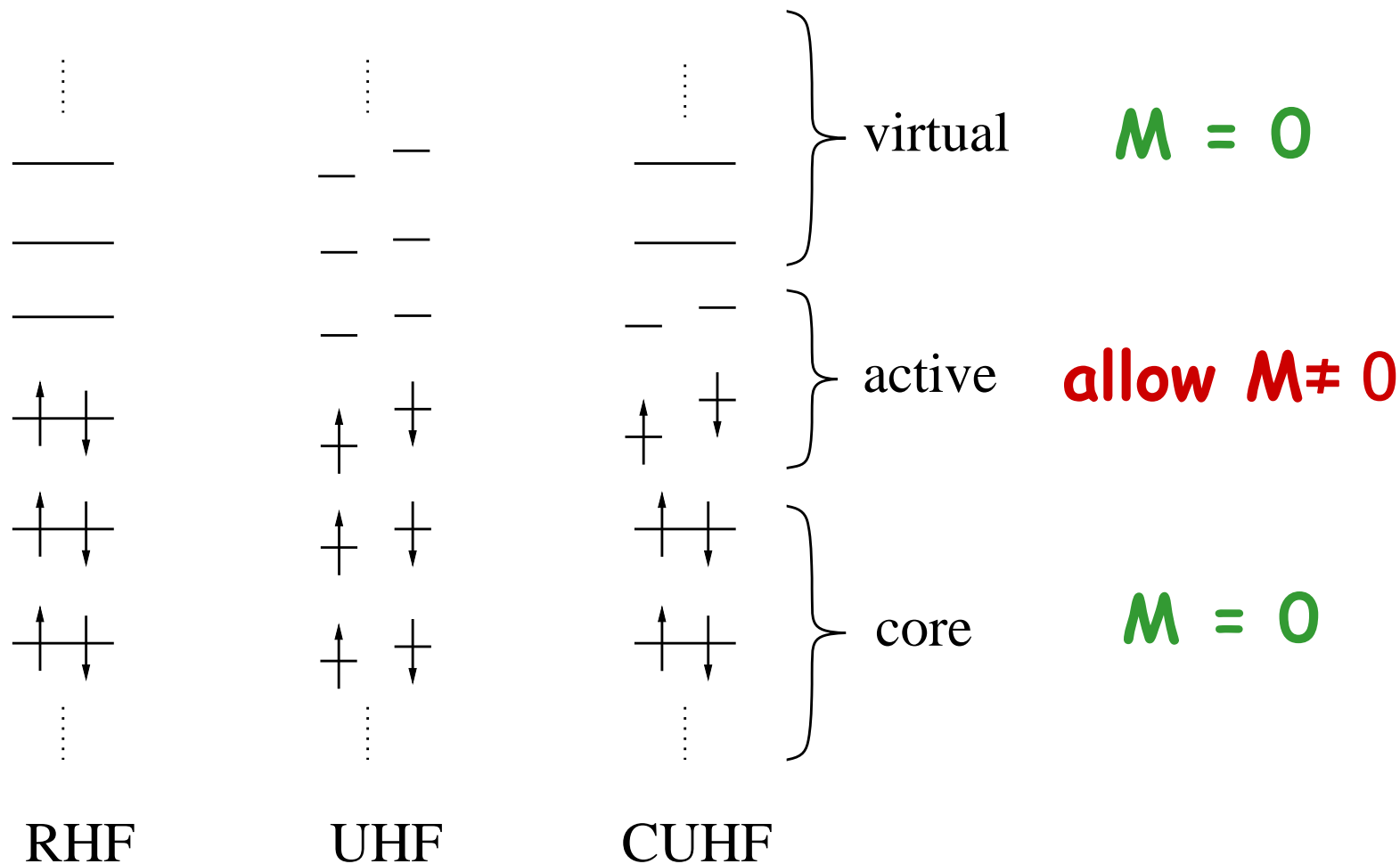
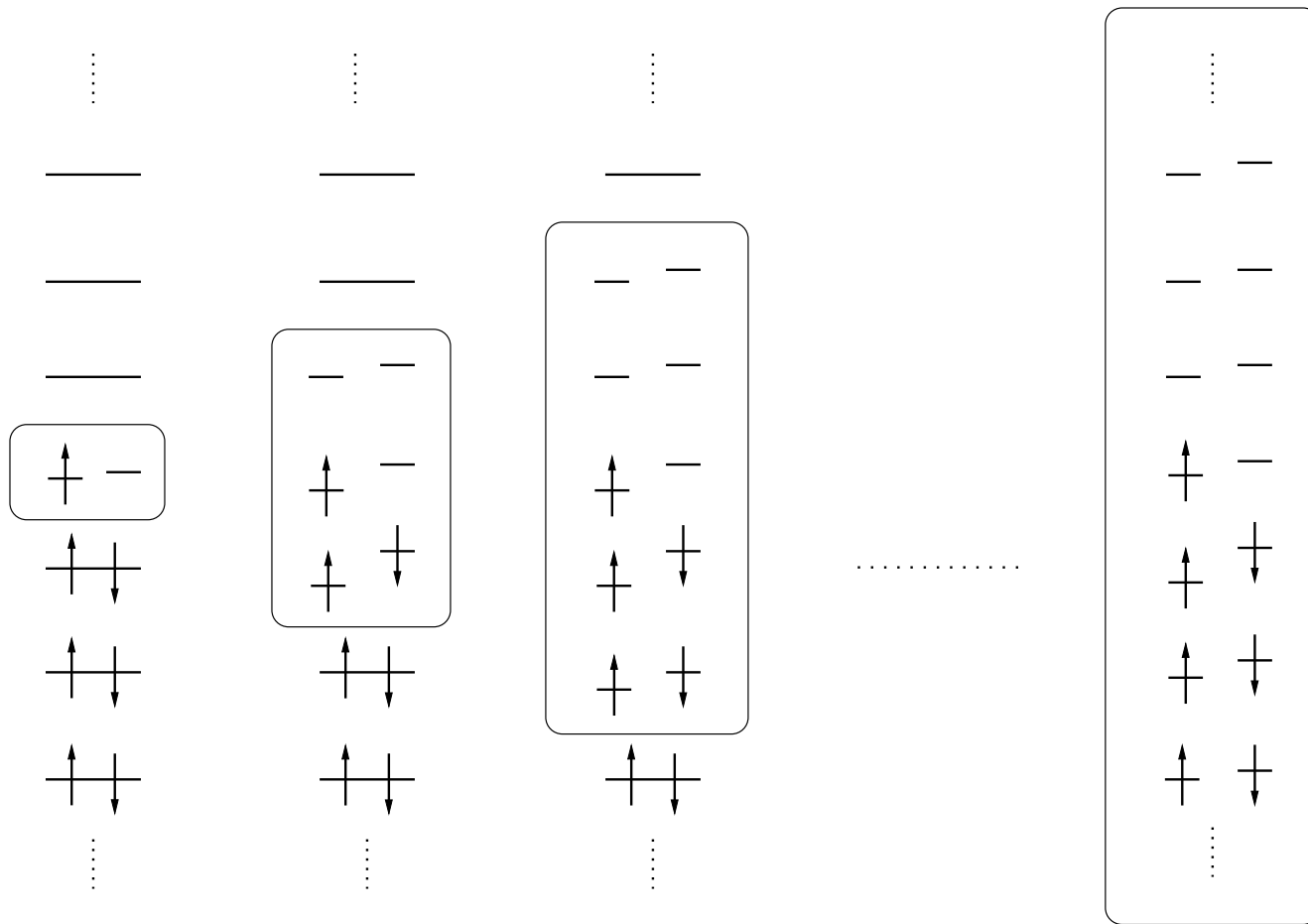M is the spin-density

Constrained UHF:
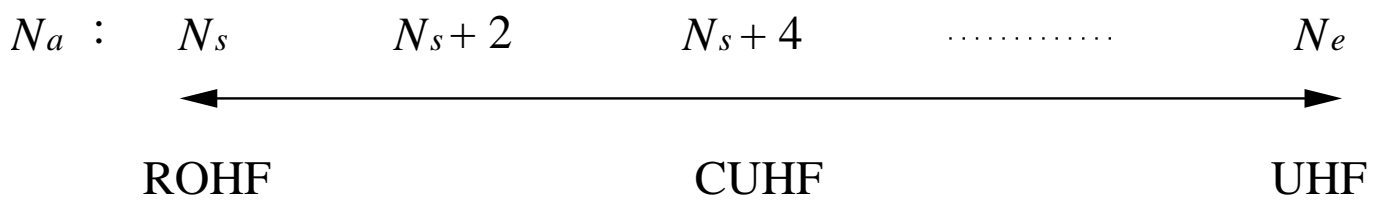## Controlled symmetry breaking for open-shells

Dimension of active space where M≠0 is variable

CUHF mathematically controls M=0 where desired

N_a : N_s N_s+2 N_s+4 .... N_e

ROHF   CUHF   UHF

Details: JCP in press

A Cacophony of Methods:

- **Some old:** UHF, UMP2, PUHF, PUMP2

- **Some new:** CUHF, CUMP2, PCUHF, PCUMP2

- "**P**" is Lowdin's spin projection operator technique eliminating the first contaminant

- **PUMP2** is Schlegel's flavor of projected **UMP2** (2nd order **PT**)

- All of the new methods are mathematically defined rigorously in our **JCP (2011)** paper in press.

- A few results:
  - Singlet-triplet energy splitting in **TMM**: $C(CH_2)_3$
    (this is a "normal" case for **U** and **PU** methods)
  - Singlet-triplet energy splittings in **benzynes**
    (pathological case for **U** and **PU**)

TMM: tri-methylene-methane

$^3A_2'$

$^1A_1$
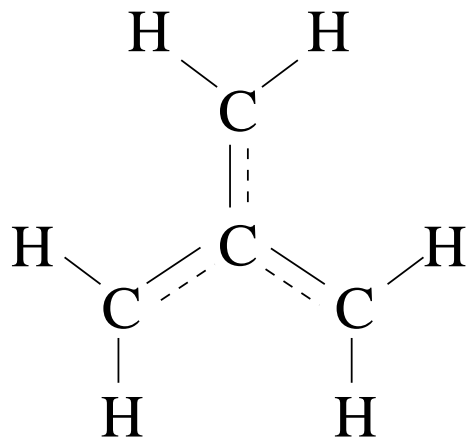
Triplet state has delocalized bonds
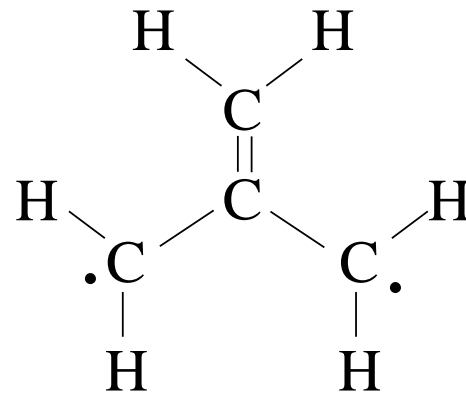
Singlet state is diradical in nature

TMM: wavefunction singlet-triplet splittings

	$^3A'_2$ $\langle S^2 \rangle$	$^1A_1$ $\langle S^2 \rangle$	ΔE_{st} (kcal/mol)
UHF	2.22	1.11	42.9
UMP2			26.6
PUHF	2.01	0.87	11.2
PUMP2			0.5
CUHF	2.00	1.00	14.9
CUMP2			35.5
PCUHF	2.00	0.00	10.5
PCUMP2			20.8
CAS(2,2)	2.00	0.00	9.8
CASPT2			23.0
Exp.			17.7

cc-pvtz basis

TMM: DFT singlet-triplet splittings

	$^3A'_2$ $\langle S^2 \rangle$	$^1A_1$ $\langle S^2 \rangle$	ΔE_{st} (kcal/mol)
UB3LYP	2.03	1.01	22.0
UHSE	2.04	1.01	24.6
ULCωPBE	2.08	1.01	29.6
CUB3LYP	2.00	1.00	17.5
CUHSE	2.00	1.00	18.8
CULCωPBE	2.00	1.00	19.0
Exp.			17.7

cc-pvtz basis

Benzynes:
wavefunction singlet-triplet splittings

	ortho	meta	para	MAE
UHF	-29.6	20.5	-31.1	25.7
UMP2	-24.4	-38.2	25.6	20.1
PUHF	-127.5	49.7	-292.9	149.7
PUMP2	-123.5	-30.0	-274.2	121.9
CUHF	-14.2	12.8	0.2	20.3
CUMP2	-34.4	-26.3	-2.1	3.6
PCUHF	-24.5	12.8	-0.5	16.6
PCUMP2	-37.8	-26.3	-1.6	2.6
CAS(2,2)	-29.0	8.5	-0.6	13.7
Exp.	-38.0	-20.6	3.5	0

All splittings in kcal/mol   **cc-pvtz basis**

Benzynes:
DFT singlet-triplet splittings

	ortho	meta	para	MAE
UB3LYP	-31.7	-13.0	-4.9	5.1
UHSE	-27.8	-15.6	-4.4	5.4
ULCωPBE	-27.8	-15.4	-3.4	5.2
CUB3LYP	-33.3	-16.3	-4.3	3.3
CUHSE	-29.7	-18.3	-3.5	3.5
CULCωPBE	-27.7	-18.7	-1.6	4.7
Exp.	-38.0	-20.6	3.5	0

All splittings in kcal/mol   cc-pvtz basis

Spin Contamination in benzynes: $\langle S^2 \rangle$

	Ortho		Meta		Para	
	$^3B_2$	$^1A_1$	$^3B_2$	$^1A_1$	$^3B_{1u}$	^1A_g
UHF	2.42	1.35	2.76	0.00	2.41	1.76
PUHF	2.09	3.55	2.35	0.00	2.09	5.22
CUHF	2.00	0.62	2.00	0.00	2.00	0.99
PCUHF	2.00	0.00	2.00	0.00	2.00	0.00
UB3LYP	2.01	0.00	2.02	0.00	2.01	0.94
UHSE	2.01	0.00	2.03	0.00	2.01	0.97
ULCwPBE	2.01	0.17	2.06	0.00	2.01	1.03
CUB3LYP	2.00	0.00	2.00	0.00	2.00	0.92
CUHSE	2.00	0.00	2.00	0.00	2.00	0.94
CULCwPBE	2.00	0.05	2.00	0.00	2.00	0.97

Last Thoughts

- **Spontaneous symmetry breaking** is intimately connected with the appearance of **strong correlation**

- **Allowing symmetry breaking** is not a bad idea if one can control the damage to good quantum numbers and somehow restore them

- **Constraining symmetry breaking** to an active space seems like a good idea

- **Projection after variation** as here done is successful if symmetry violations are small

Acknowledgements

- **Group**: Takashi Tsuchimochi, Tom Henderson, Jason Ellis, Carlos Jimenez-Hoyos