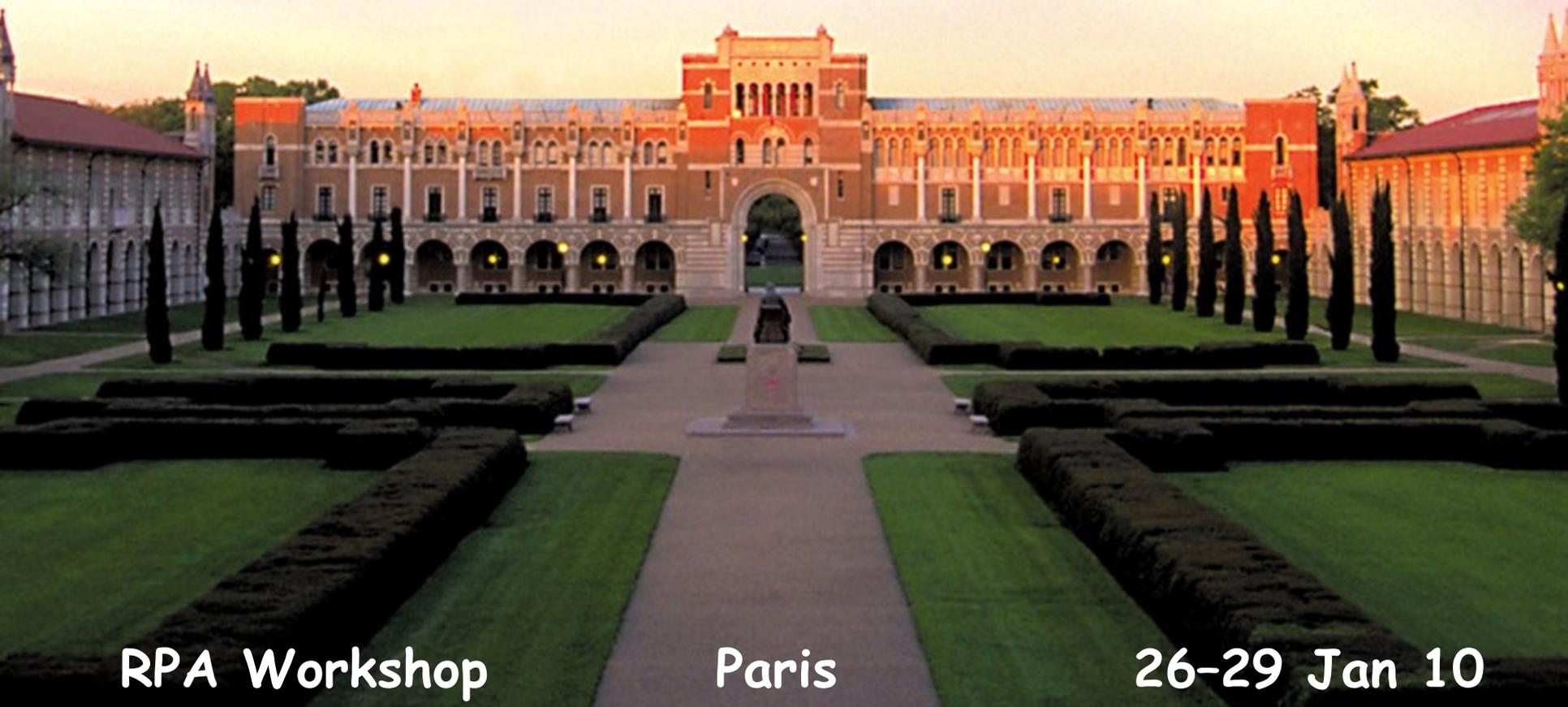


RPA and CC theory & some recent results including range separation

Gustavo E. Scuseria



RPA Workshop

Paris

26-29 Jan 10

Outline

- The connection between **RPA** and **coupled cluster (CC)** theory
- Range-separation: a powerful tool for mixing **wavefunction** and **density functional** theories
- Some recent results for **RPA ground-state correlations**
- A model for **strong correlations** based on **HFB**

Coupled Cluster (CC) Theory

- Arguably the **most successful** quantum chemistry theory
- Borrowed from **nuclear physics** (Coester-Kümmel) in the 60s by Cizek & Paldus
- Single-reference version **can treat metals** but **not strongly-correlated** systems (requires multi-reference [MR])
- **MRCC** theory has "issues" and has never taken off...
- **Size extensivity (CC)** is more important than **variational energy bound (CI)**. This was settled in mid to late 80s and changed the **QC** paradigm
- Of course, 2nd and **larger revolution** in **QC** was **DFT** in early 90s (hybrid functionals)

Coupled Cluster (CC) Theory

$|\Psi\rangle = e^T |\Phi\rangle$ Exponential (as opposed to Linear) T ansatz
 $T = T_1 + T_2 + T_3 + \dots$ Electronic structure: T_2 dominates!

In simplest form, **CCD**:

$$T_2 = \sum t_{ik}^{ab} a_a^\dagger a_b^\dagger a_i a_k$$

CCD equations:

$$E = \langle \Phi | e^{-T} H e^T | \Phi \rangle = \text{linear eqn in } T_2$$

$$0 = \langle \Phi | T_2^\dagger H e^T | \Phi \rangle = \text{quadratic algebraic eqn in } T_2$$

**The ground state correlation energy of the random phase approximation
from a ring coupled cluster doubles approach**

Gustavo E. Scuseria, Thomas M. Henderson, and Danny C. Sorensen

RPA problem for
excitations is:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \omega, \quad (1)$$

**RPA ground-state
correlation energy:**

difference in **ZPVE** between
two harmonic oscillators

$$E_c^{\text{RPA}} = \frac{1}{2} \text{Tr}(\omega - \mathbf{A}). \quad (2)$$

(1) is mathematically
equivalent to a
ring CCD equation

$$\mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = 0, \quad (3)$$

Energies are
mathematically identical
with **CC** amplitudes

$$E_c^{\text{rCCD}} = \frac{1}{2} \text{Tr}(\mathbf{B}\mathbf{T}) = \frac{1}{2} \text{Tr}(\omega - \mathbf{A}). \quad (4)$$

$$\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}, \quad (13a)$$

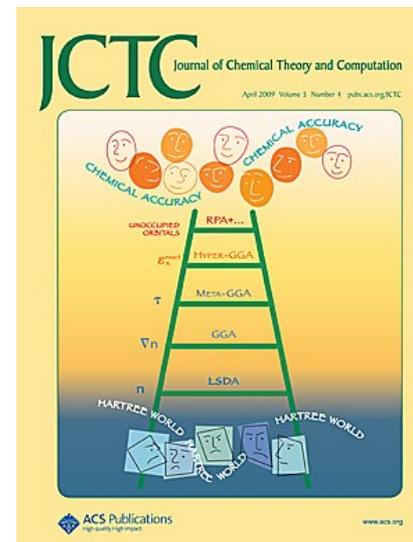
RPA for ground-state correlations

- **Q-Chem perspective** from the late 70s & early 80s:
 - Plagued by **triplet** instability problem
 - When no instabilities are present ($\sim \text{Re}$), E_c is **off** by a factor **2**
 - Ouch! Not good
- **Green's function & DFT** perspective:
 - Forget about **exchange**, just keep only the "**direct**" (Coulomb) part of the interaction!
- Perdew & Langreth (80s): **long-range RPA** correlation energy is ok, **short-range** is bad

A hierarchy of DFT approximations

The quest for accurate exchange-correlation potentials

- **LSDA** : functional of electron density
- **GGA**: adds gradient of electron density
- **meta-GGA**: adds kinetic energy density
- **hybrids**: add nonlocal HF-type exchange
(Generalized Kohn-Sham scheme)
- **This talk**: range-separated **hybrids**
+ long-range **RPA** correlation
+ strong static correlation via **"HFB"**



Hybrid Functional example

- **PBE** : Perdew, Burke, Ernzerhof, PRL (1996)
 - **GGA** (depends on e-density + gradient e-density)
 - No empirical parameters
- **PBEh** : add HF-type exchange

$$E(\text{PBEh}) = a E_x(\text{HF}) + (1-a) E_x(\text{PBE}) + E_c(\text{PBE})$$

$a = 0.25$ based on good theory

Uses nonlocal HF-type potential

(Generalized Kohn-Sham scheme)

Perdew, Ernzerhof & Burke (1997); Ernzerhof & Scuseria (1999);
Adamo & Barone (1999)

Range-separation

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}} \quad \omega \geq 0$$

short-range **long-range**

ω determines the splitting between **short-** and **long-range**

- **Andreas Savin (1985)** proposed to use
 - **DFT** for **short-range**
 - **Wavefunction theory** for **long-range**
- Keep the **best** of both worlds:
SR \rightarrow local **LR** \rightarrow nonlocal
- Rigorous **mathematical** support (ask Andreas!)

LC- ω PBE : a long-range hybrid

Vydrov & Scuseria, JCP 125, 234109 (2006)

$$E(\text{LC-}\omega\text{PBE}) = E_x(\omega\text{PBE,SR}) + E_x(\omega\text{HF,LR}) + E_c(\text{PBE})$$

100% PBE exchange in SR

100% HF exchange in LR

Only one parameter: ω

$$\omega = 0.40 \text{ (fitted)}$$

No range-separation for correlation
(we will add RPA ground state correlation later)

LC-wPBE: Mean Absolute Errors (Molecules)

Functional	Atomic E (mH)	G2/148 (kcal/mol)	HTBH38 (kcal/mol)
LDA	68.0	83.3	18.9
PBE	7.6	16.9	9.7
PBEh	6.3	4.9	4.6
LC-wPBE	3.4	3.7	1.3

Excellent HTBH38 activation barriers
and G2 heats of formation

Vydrov & Scuseria, JCP 125, 234109 (2006)

One missing ingredient:

van der Waals

important for biological applications

RPA as ring-CCD for correlation

- Using the **CC** connection we can range-separate **DFT**+ **RPA** like **DFT** + **WF** (wavefunction method)
- **Ansatz:**
$$E_{xc} = E_{xc}(\text{SR-DFT}) + E_x(\text{LR-HF}) + E_c(\text{LR-RPA})$$
- Alternative approach: Toulouse et al. (PRL 2009)

The ground state correlation energy of the random phase approximation
from a ring coupled cluster doubles approach

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$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle ib|aj\rangle, \quad (7a)$$

$$B_{ia,jb} = \langle ij|ab\rangle. \quad (7b)$$

“Single-bar” integrals define *direct* RPA (dRPA)
No instability issues!

Two-electron integrals
are positive definite

$$\langle ib|aj\rangle = \langle ij|ab\rangle = u_{ia}^A u_{jb}^A, \quad (18a)$$

In *direct ring-CCD*
T are negative definite

$$-t_{ij}^{ab} = \theta_{ia}^A \theta_{jb}^A, \quad (18b)$$

RPA correlation can be evaluated very efficiently:

$$t_{ij}^{ab} = \frac{1}{\Delta\epsilon_{ij}^{ab}} (u_{ia}^A u_{jb}^A - u_{ia}^A u_{kc}^A \theta_{kc}^B \theta_{jb}^B - \theta_{ia}^A \theta_{kc}^A u_{kc}^B u_{jb}^B + \theta_{ia}^A \theta_{kc}^A u_{kc}^B u_{ld}^B \theta_{ld}^C \theta_{jb}^C) \quad (19)$$

Why not MP2 ?

- **MP2** = **2nd order** perturbation theory
= **1st** term of **RPA** equations
- **Problems:**
 - **MP2** cannot treat metals (diverges)
 - **RPA** remains finite for metals
 - **MP2** is **OK** for van der waals (but not as good as **RPA**)
- **RPA** resolves the **conundrum*** of **molecules** versus **solids**
 - **Molecules**: LR-HFx is **good**; **LR-RPA** adds vdw
 - **Small band gap solids**: LR-HFx is **pathological**
LR-RPA fixes it!

(**HSE** neglects both LR-HF and LR-RPA)

Some RPA results

- Adding range-separated **RPA** correlation to **LC-wPBE...** not ready yet...
- No range-separated **PBE** correlation (coming soon)
- Instead, use **LC-wLDA**

Long-range-corrected hybrids including random phase approximation correlation

Benjamin G. Janesko, Thomas M. Henderson, and Gustavo E. Scuseria

Approximation tested is based on **LSDA**

$$E_{xc} = E_{xc}^{SR-LSDA} + E_x^{LR-HF} + c_{RPA} E_c^{LR-RPA}. \quad (6)$$

LC-wLDA + dRPA

SR-LDA correlation from Gori-Giorgi et al.

dRPA orbitals from LC-wLDA

Two parameters: w and c_{RPA}

Two models tested:

1. For $c_{RPA} = 1.00 \rightarrow w$ (opt) = 0.70
2. Both optimized: $w = 1.20$, $c_{RPA} = 1.50$

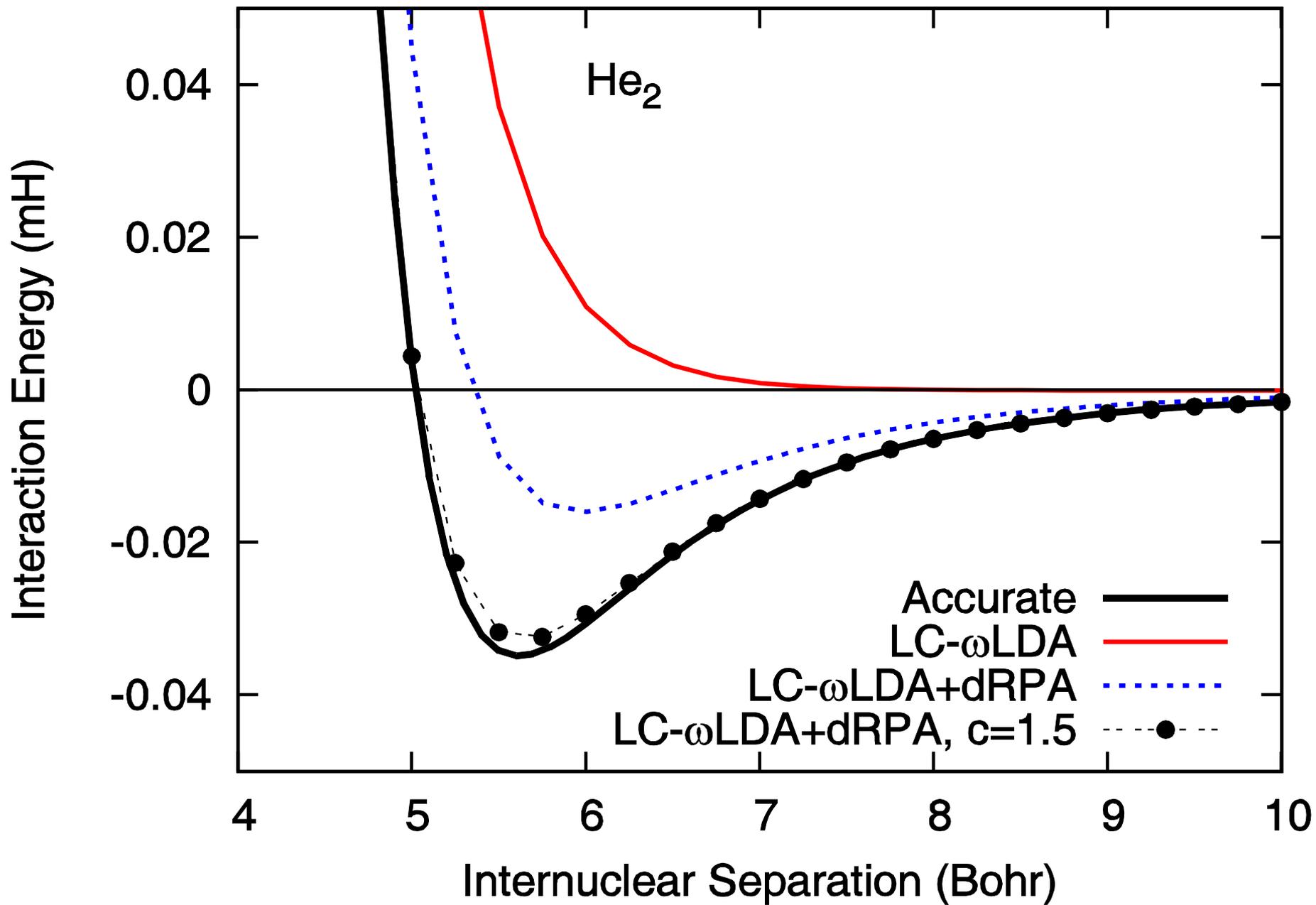
LC-wLDA + dRPA model chemistry

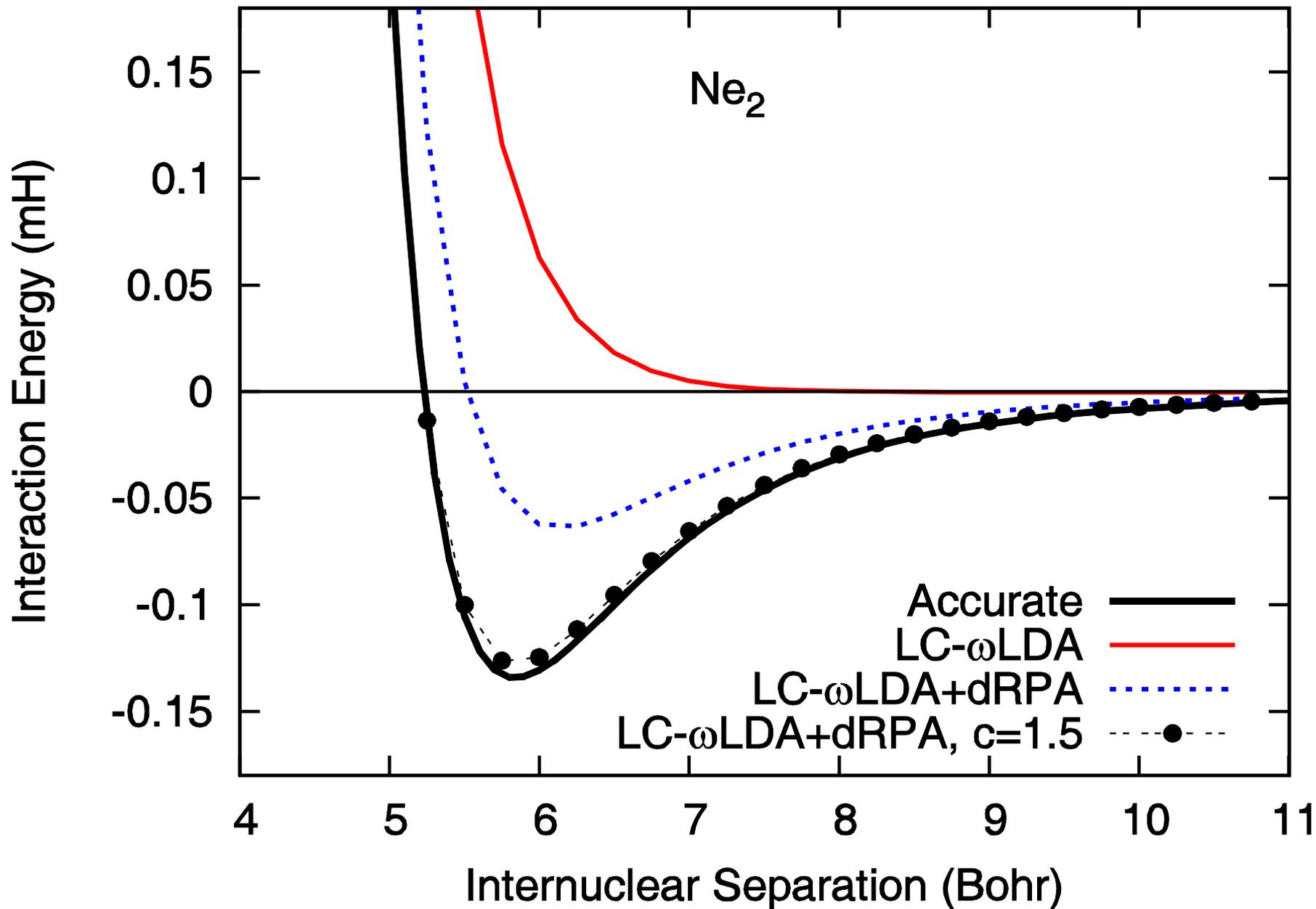
Mean Absolute Errors (kcal/mol)

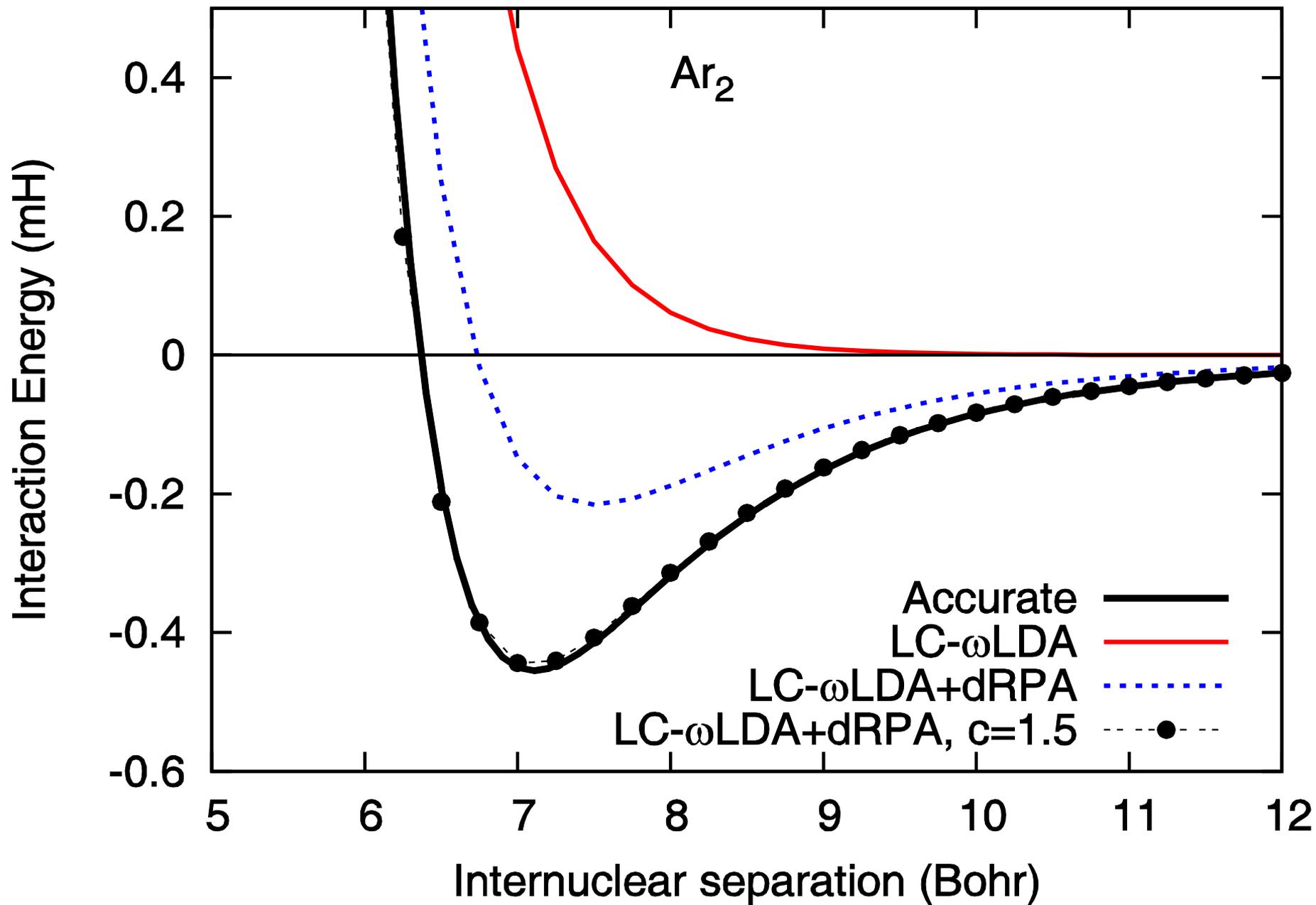
Method	w(opt)	AE6	G2	BH6	HT	NHT
LC-wPBE	0.4	5.5	4.2	1.2	1.3	2.0
LC-wLDA	0.5	5.8	7.0	2.3	3.0	4.4
LC-wLDA + dRPA	0.7	5.6	6.2	1.8	2.3	3.5
LC-wLDA + C dRPA	1.2	4.0	4.4	1.2	1.6	3.5

C=1.5

6-311+G(2d,2p)







LC-wLDA + dRPA

“Biological” noncovalent interactions

Mean Absolute Errors (kcal/mol)

Method	HB6	CT7	DI6	WI9	MARE
MP2	0.44	0.29	0.06	0.05	13
CCSD(T)	0.38	0.47	0.29	0.05	12
LC-wLDA + dRPA	0.33	1.41	0.72	0.24	34
LC-wLDA + C dRPA	0.49	0.35	0.06	0.02	8

$w=1.2$ $C=1.5$

aug-cc-pVTZ basis

CCSD(T)/CBS, MARE=0

HB: Hydrogen Bonds

CT: Charge Transfer Complexes

DI: Dipole-Dipole Complexes

WI: Weak Interactions

Janesko, Henderson, Scuseria, JCP (2009)

Why $C=1.5$? (for $w=1.2$)

Correction for:

1. Basis set effects?

1. Beyond-RPA correlation?

1. Orbitals?

1. Large w ?

Answer:

3 and 4

The role of the reference state in long-range RPA,
B. G. Janesko and G. E. Scuseria, *J. Chem. Phys.* **131**, 154106 (2009)

A short story about RPA

Scuseria, Henderson, and Sorensen,
JCP **129**, 231101 (2008)

$$\langle ij|ab\rangle + (\varepsilon_c - \varepsilon_k)\delta_{ac}\delta_{ik}t_{kj}^{cb} + \langle ic|ak\rangle t_{kj}^{cb}$$

“direct ring-CCD”

$$+ t_{ik}^{ac}(\varepsilon_c - \varepsilon_k)\delta_{bc}\delta_{jk} + t_{kj}^{cb}\langle ic|ak\rangle$$

$$+ t_{ik}^{ac}\langle kl|cd\rangle t_{lj}^{db} = 0$$



$$B + AT + TA + TBT = 0 \quad \text{“Riccati Equation”}$$

A short story about dRPA

direct RPA correlation energy:

$$E_{\text{corr}} = \frac{1}{2} \sum_{ijab} \langle ij|ab \rangle t_{ij}^{ab} \equiv \frac{1}{2} \text{Tr}(\mathbf{BT})$$

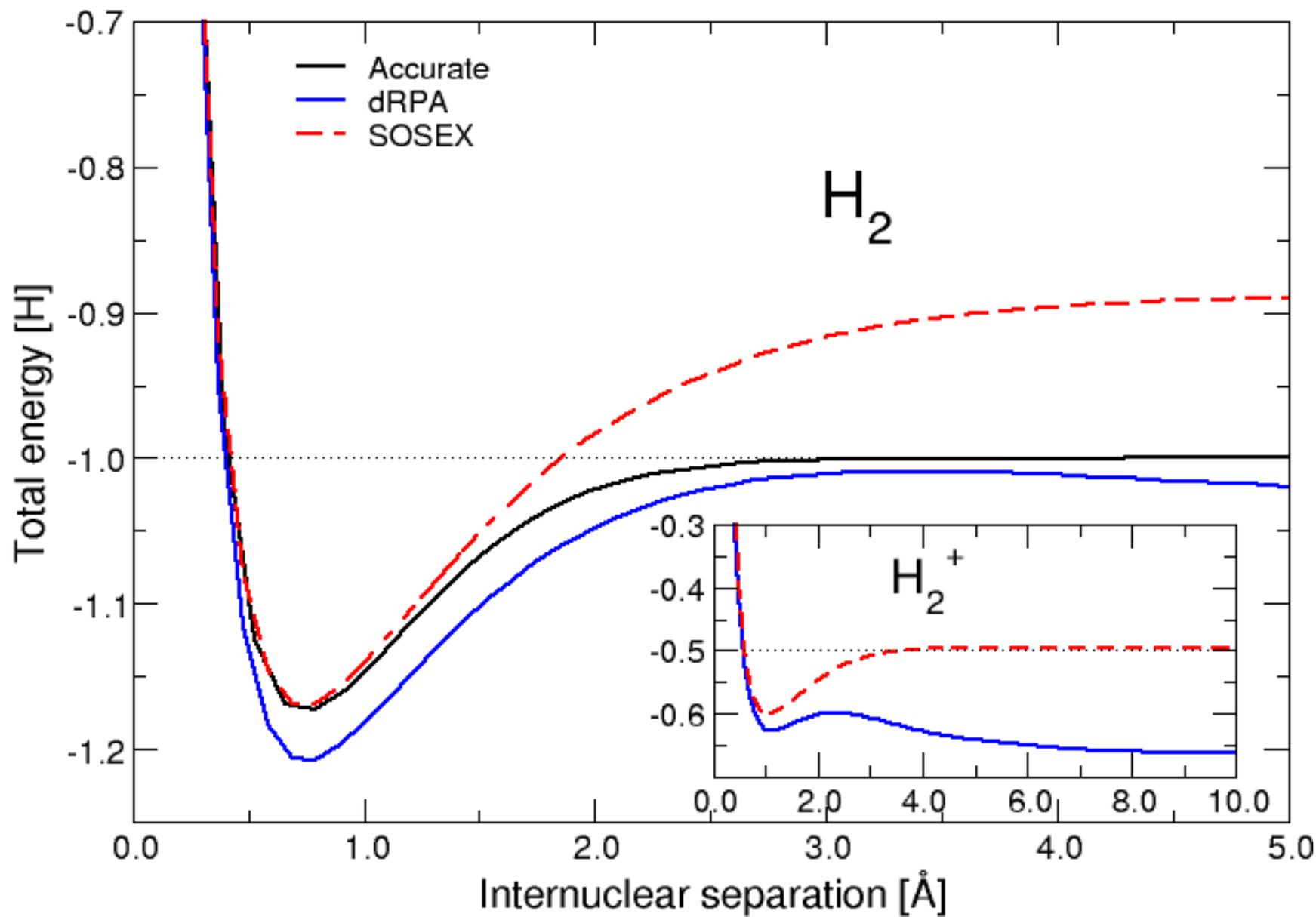
$$\begin{aligned} \Phi_{\text{dRPA}} &= \exp(\hat{T}_2) |\Psi_0^{\text{HF(PBE)}}\rangle \\ &= (1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \dots) |\Psi_0^{\text{HF(PBE)}}\rangle \end{aligned}$$

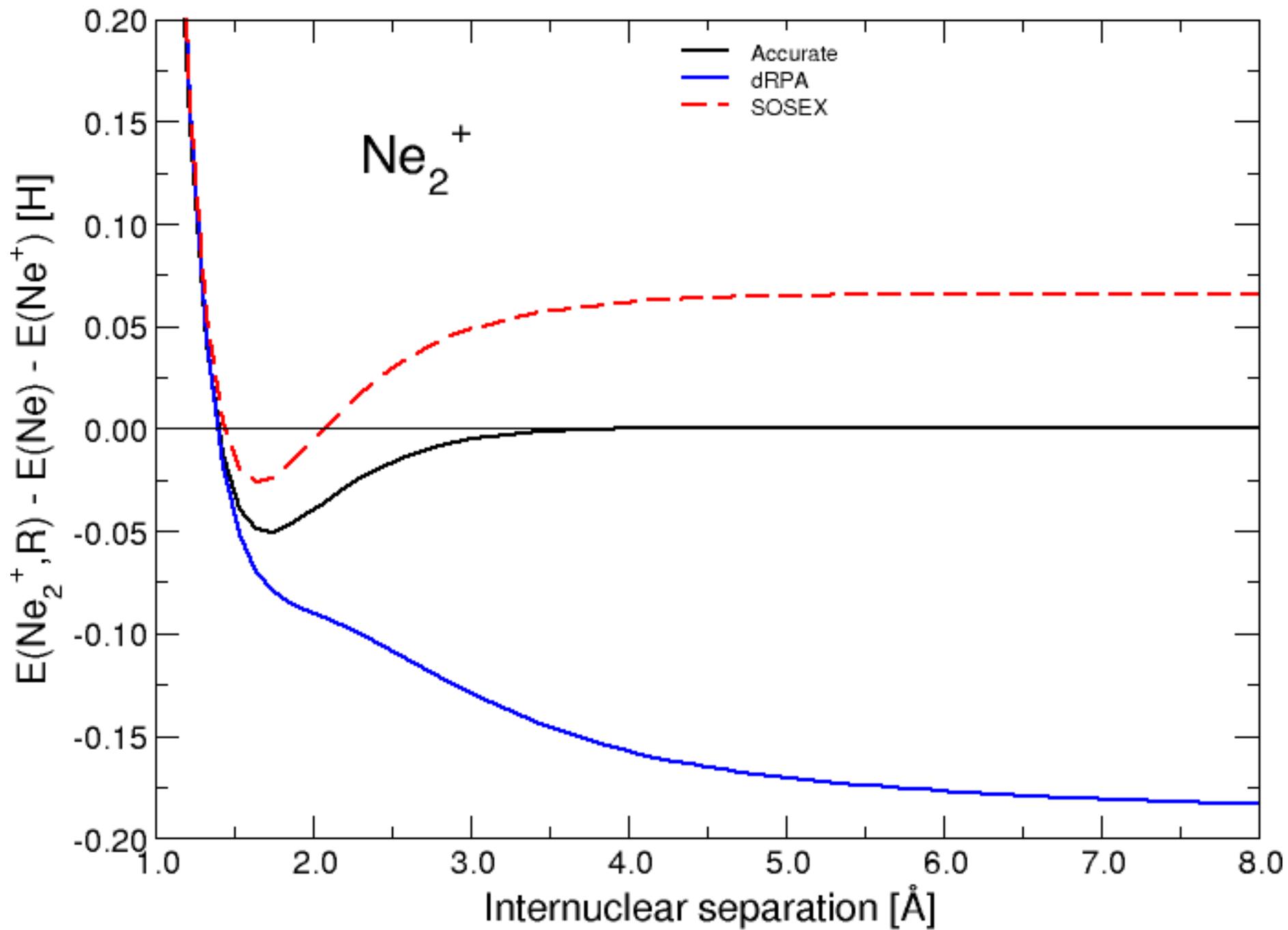
Definition of SOSEX

(David Freeman, Phys Rev 1977)

$$\begin{aligned} E_{\text{corr}} &= \frac{1}{2} \sum_{ijab} (\langle ij|ab\rangle - \langle ij|ba\rangle) t_{ij}^{ab} \\ &= \frac{1}{2} \text{Tr}(\mathbf{B}_{\text{as}}\mathbf{T}), \quad \text{with} \quad \mathbf{B}_{\text{as}} = \langle ij||ab\rangle \end{aligned}$$

Exchange term corrects for all self-interaction terms $\langle ii|aa\rangle$, i.e. $i = j$ and $a = b$.





Last few bullets on RPA

- **Long-range HF + dRPA** looks very promising combined with **short-range semilocal xc DFT**
- **Molecules:** **RPA** is better than **MP2** but not as accurate as **CCSD(T)**
- **Solids:** neither **MP2** nor **(T)** are useful for small band gap systems
- Cost of **dRPA** correlation with **ring-CCD** is between **$O(N^5) \rightarrow O(N^3)$** and asymptotically **$O(N)$**
- **Better (self-consistent) orbitals** are crucial for ground-state **RPA** correlation

**One important additional
ingredient**

Strong/static correlation

Static/Strong Correlation

New Method Desideratum:

1. Should preserve **space** and **spin** symmetries (avoid spatial symmetry breaking and spin contamination)
2. Should have low-computational cost (**mean-field** instead of **CASSCF** exponential blowup)
3. Should cleanly separate **static** & **dynamic** correlation

How do we accomplish this?

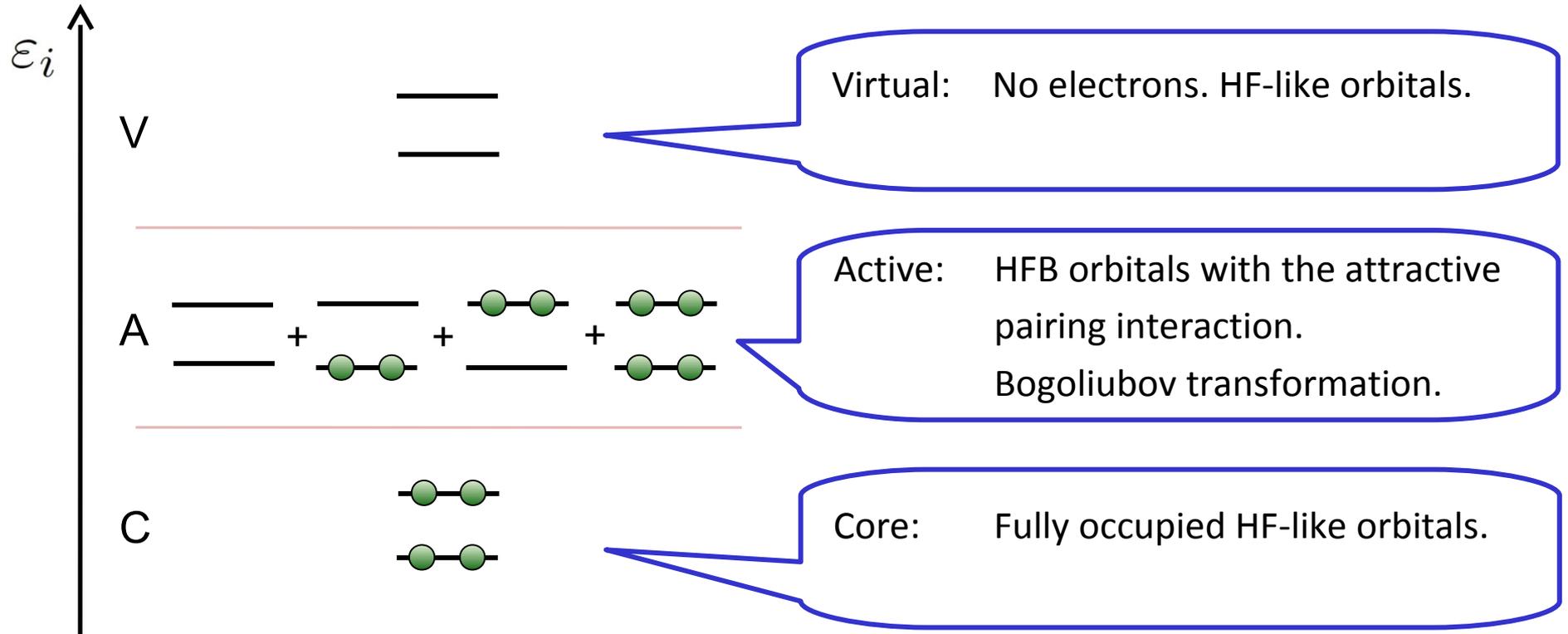
- **Break** a different (new!) symmetry in mean-field:
electron number conservation
- Introduce electron number fluctuations
- The theory that accomplishes this is **BCS (HFB)** but for Coulombic Fermionic systems, **HFB** always reduces to **HF** (Lieb 1994)
- We introduce an attractive pairing interaction ($-1/r_{12}$) in a "hybrid" **HFB** scheme with **HF** ($2/r_{12}$)
- Is mean-field (roughly same computational cost as **KS** or **HF**)
- Is "exact" at dissociation (Σ **ROHF** atomic energies)

Our CPMFT model

- Yields a "**definition**" for static correlation from the **2pdm** ansatz
- Reduces to **HF** in the **absence** of strong correlation
- Yields correct symmetry-adapted orbitals
- **BCS**-type (**HFB**) wavefunction w/ determinants of different N_e
- Has correct number of electrons on average $\langle N \rangle = N_e$
- Has correct number of **correlated electron pairs**
- Recent papers:
 - I. *J. Chem. Phys.* **131**, 121102 (2009)
 - II *J. Chem. Phys.* **131**, 164119 (2009)
 - III. *J. Chem. Phys.* **132**, 024111(2010)

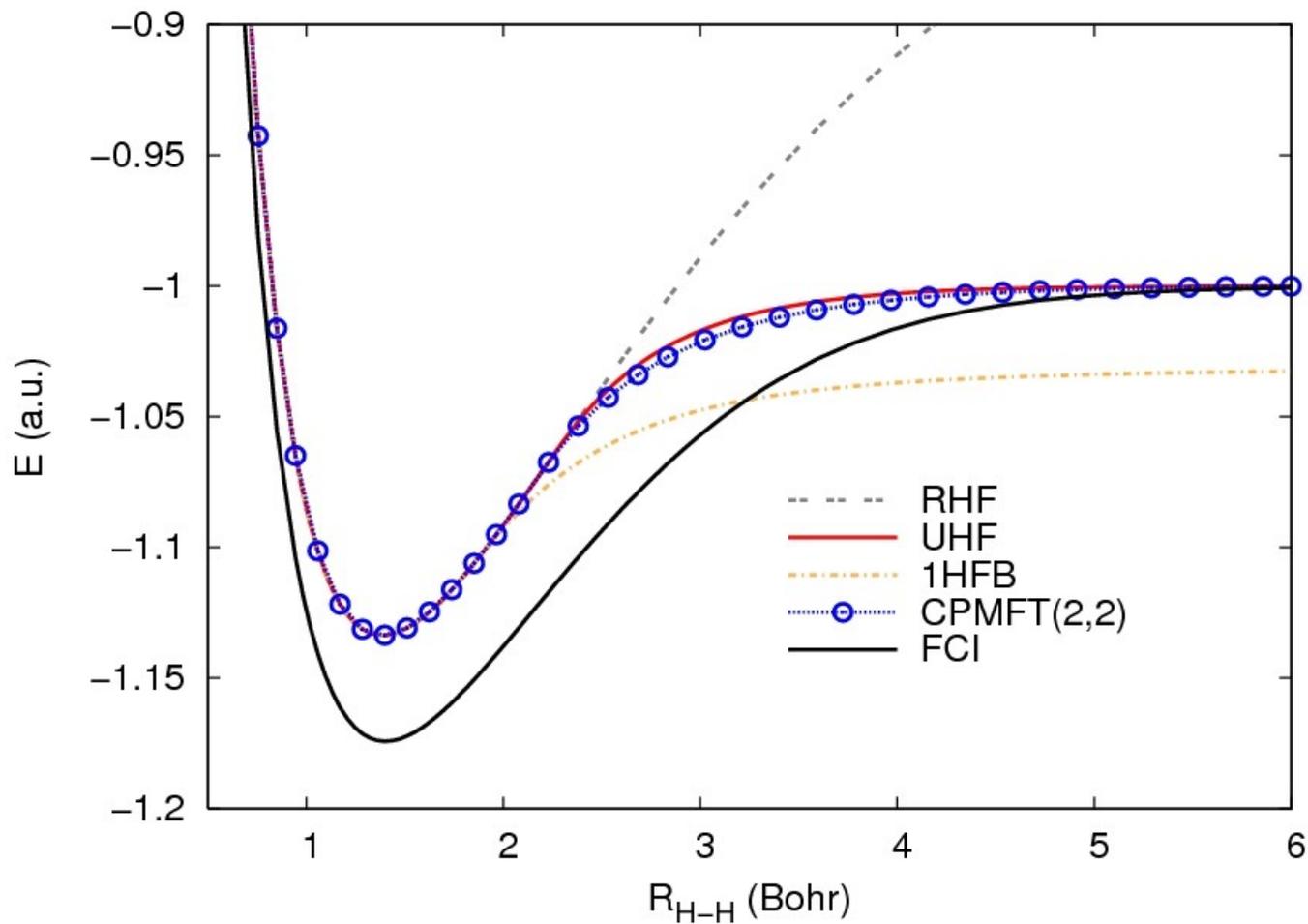
Constrained-Pairing Mean-Field Theory

We **constrain** pairings to the entangled region of the orbital space:

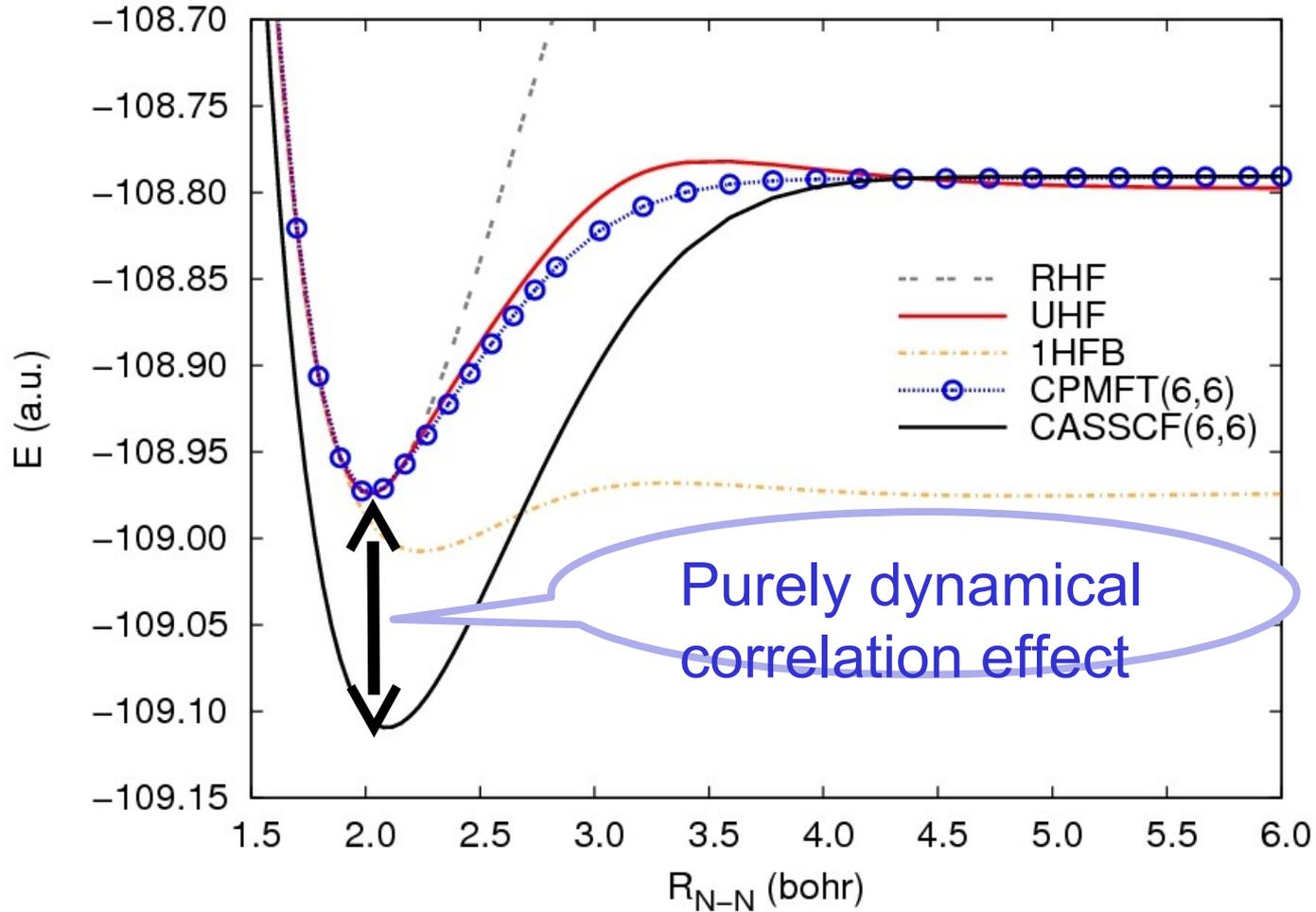


$$|\Psi_{\text{CPMFT}}\rangle = \prod_c^{\text{core}} a_{c\alpha}^\dagger a_{c\beta}^\dagger \prod_i^{\text{active}} \left(x_i + y_i a_{i\alpha}^\dagger a_{i\beta}^\dagger \right) |-\rangle$$

H₂ cc-pV5Z



N_2 6-311++G**



Dynamical Correlation

- **CPMFT** orbitals and density are symmetry-adapted
- How do we add **dynamical correlation** only?
- Answer: use "alternative" densities derived from the **CPMFT 2pdm** ansatz
- Use total and on-top densities as fundamental variables
- Feed **alternative** densities into regular DFT correlation subroutines

Alternative Densities

We define **alternative** densities (χ) from **total** (ρ) and **on-top** (Γ) densities:

$$\chi_{\alpha}(\mathbf{r}) = \frac{1}{2} \left(\rho(\mathbf{r}) + \sqrt{\rho^2(\mathbf{r}) - 2\Gamma(\mathbf{r})} \right)$$

$$\chi_{\beta}(\mathbf{r}) = \frac{1}{2} \left(\rho(\mathbf{r}) - \sqrt{\rho^2(\mathbf{r}) - 2\Gamma(\mathbf{r})} \right)$$

where $\chi_{\alpha}(\mathbf{r}) + \chi_{\beta}(\mathbf{r}) = \rho(\mathbf{r})$ and $\Gamma(\mathbf{r}) = 2\rho_{\alpha}(\mathbf{r})\rho_{\beta}(\mathbf{r}) - (\kappa_{\alpha\beta}^2(\mathbf{r}) + \kappa_{\beta\alpha}^2(\mathbf{r}))$

Example: H₂ molecule

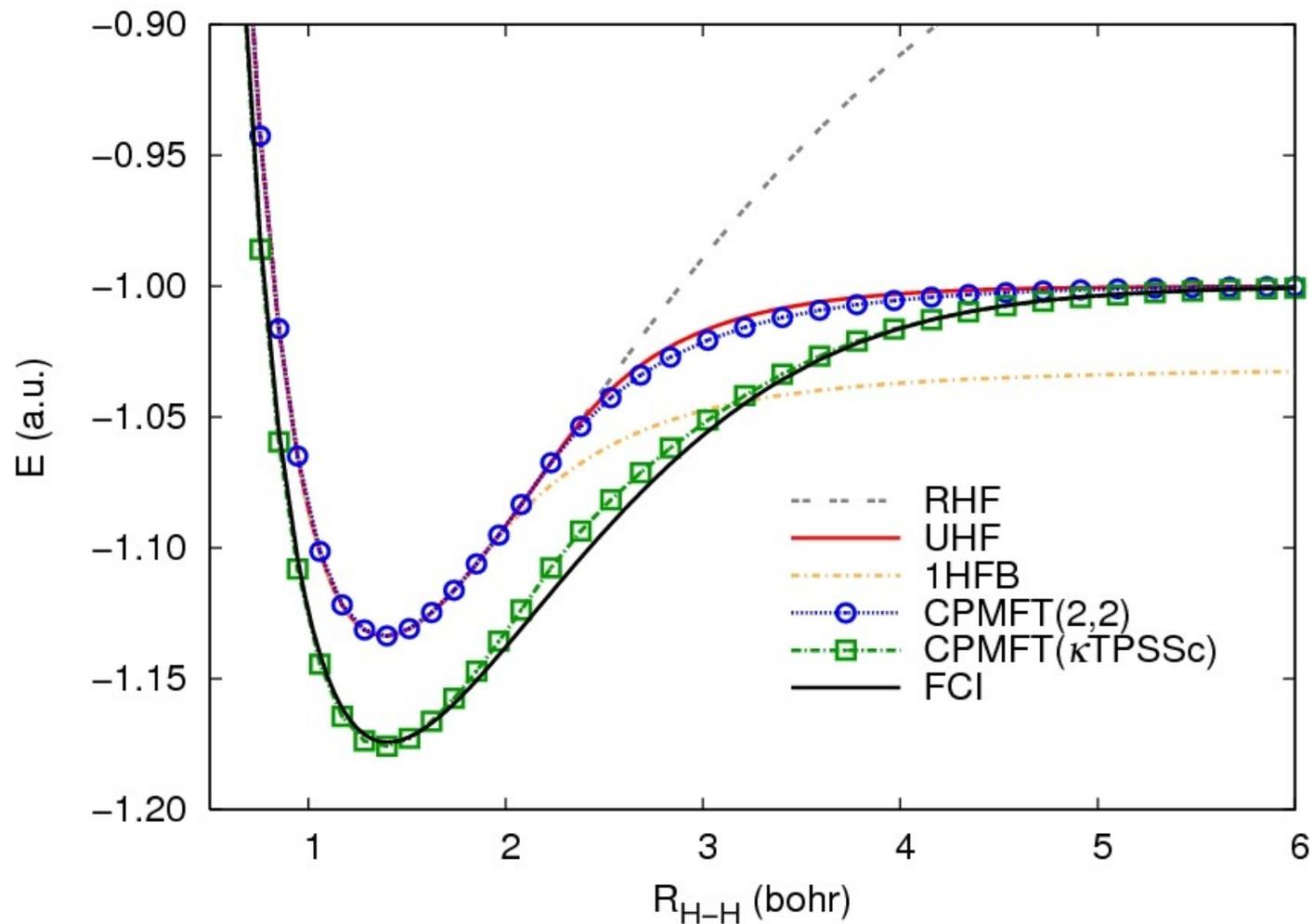
(1) **At R_e,** $\chi_{\alpha}(\mathbf{r}) = \chi_{\beta}(\mathbf{r}) = \rho_{\alpha}(\mathbf{r}) = \rho_{\beta}(\mathbf{r})$ (**RKS density**)

(2) **At dissociation,** $\chi_{\alpha}(\mathbf{r}) = \rho(\mathbf{r})$ and $\chi_{\beta}(\mathbf{r}) = 0$ (**UKS-like density**)

We change variables of E_{xc} :

$$E_{XC}[\rho_{\alpha}, \rho_{\beta}, \dots] \rightarrow E_{XC}[\chi_{\alpha}, \chi_{\beta}, \dots]$$

H₂ cc-pV5Z



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