A Chemist's View of the Random Phase Approximation

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Acknowledgements

- Organizers: Matthias Scheffler and Claudia Ambrosch-Draxl
- Gustavo E. Scuseria
- Thomas M. Henderson, Joachim Paier
- NSF

Computational Chemistry vs. Physics

- Isolated systems vs. periodic boundary conditions
- Real space vs. Fourier space
- Correlated wavfunction methods vs. GW or RPA

Today's empirical parameters guide tomorrow's work

Outline

- Chemist’s RPA
- Connecting RPA to coupled cluster theory
- Reference states in RPA
- Long-range RPA
- Reference states in RPA (redux)
- Connecting RPA to second-order perturbation theory

Chemist's RPA 1: Derivation

Excitation operator $Q_\nu^\dagger$ for excited states $|\nu\rangle$

$$\begin{aligned} |\nu\rangle &= Q_\nu^\dagger |0\rangle \\ Q_\nu |0\rangle &= 0 \end{aligned}$$

Approximate as one-electron excitations and de-excitations

$$Q_\nu^\dagger = \sum_{ia} X_{ia}^\nu a_a^\dagger a_i + \sum_{ia} Y_{ia}^\nu a_i^\dagger a_a$$

Approximating $|0\rangle$ as $|HF\rangle$ gives equation of motion

$$\begin{aligned} \langle 0| \left[\delta Q, \left[H, Q_\nu^\dagger\right]\right] |0\rangle &= (E_\nu - E_0) \langle 0| \left[\delta Q, Q_\nu^\dagger\right] |0\rangle \\ \langle HF| \left[a_i^\dagger a_a, \left[H, Q_\nu^\dagger\right]\right] |HF\rangle &= (E_\nu - E_0) \langle HF| \left[a_i^\dagger a_a, Q_\nu^\dagger\right] |HF\rangle \\ \langle HF| \left[a_a^\dagger a_i, \left[H, Q_\nu^\dagger\right]\right] |HF\rangle &= (E_\nu - E_0) \langle HF| \left[a_a^\dagger a_i, Q_\nu^\dagger\right] |HF\rangle \end{aligned}$$

Ring & Schuck, *The Nuclear Many-Body Problem*

Chemist's RPA 2: Evaluating $\{X_{ia}^{\nu}, Y_{ia}^{\nu}\}$

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix}$$

$$\begin{aligned} A_{ia,jb} &= (\epsilon_a - \epsilon_i)\,\delta_{ij}\delta_{ab} + \langle ib||aj\rangle \\ B_{ia,jb} &= \langle ij||ab\rangle \end{aligned}$$

$$\begin{aligned} \langle ij||ab\rangle &= \langle ij|ab\rangle - \langle ij|ba\rangle \\ \langle ij|ab\rangle &= \int d^3\mathbf{r} \int d^3\mathbf{r}' \, \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_a^*(\mathbf{r})\phi_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \end{aligned}$$

Ring & Schuck, *The Nuclear Many-Body Problem*

Chemist’s RPA 3: Ground state correlation

Harmonic approach: Difference between correlated and uncorrelated excitation energies gives twice the ground state correlation energy

$$E_c = \frac{1}{2}\left(\sum_{\nu}\omega_{\nu} - \mathrm{Tr}\left[\mathbf{A}\right]\right)$$

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Chemist’s RPA and coupled cluster

Coupled cluster doubles theory invokes an ansatz for the ground-state wavefunction

$$\begin{aligned} |\Psi\rangle &= e^{\hat{T}_2}\,|HF\rangle \\ \hat{T}_2 &= \sum_{ijab} t_{ij}^{ab} a_i a_j a_a^\dagger a_b^\dagger \end{aligned}$$

Scuseria, Henderson, Sorensen: Chemist’s RPA is ”Ring CCD”, a version of CCD containing only particle-hole excitations (ring diagrams)

$$\begin{aligned} E_c &= \frac{1}{4}\mathrm{Tr}\left[\mathbf{BT}\right] \\ 0 &= \mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} \\ \mathbf{T} &= \mathbf{YX}^{-1} \end{aligned}$$

This lets us implement RPA into standard CCSD programs

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

Other ”flavors” of RPA

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix}$$

Scuseria, Henderson, Sorensen approach works on any equation of this form

ACFD RPA

- Adiabatic connection between Kohn-Sham and real systems
- Invokes the fluctuation-dissipation theorem
- Furche, JCP 2008 showed that frequency and adiabatic connection integrals may be done analytically to yield formuals similar to ”chemist’s RPA”

Chemist’s RPA

HF reference

$$\begin{aligned} E_c &= \frac{1}{4}\mathrm{Tr}\left[\mathbf{BT}\right] \\ A_{ia,jb} &= \left(\epsilon_a - \epsilon_i\right)\delta_{ij}\delta_{ab} \\ &- \langle ib||aj\rangle \\ B_{ia,jb} &= \langle ij||ab\rangle \end{aligned}$$

ACFD RPA

KS reference

$$\begin{aligned} E_c &= \frac{1}{2}\mathrm{Tr}\left[\mathbf{BT}\right] \\ A_{ia,jb} &= \left(\epsilon_a - \epsilon_i\right)\delta_{ij}\delta_{ab} \\ &- \langle ib|aj\rangle \\ B_{ia,jb} &= \langle ij|ab\rangle \end{aligned}$$

Comparing chemist's RPA and ACFD

- ACFD RPA has one-electron self-interaction error
  - No exchange integrals (vertex corrections) in $\mathbf{A}$ and $\mathbf{B}$
  - H atom correlation energy $\sim$ 16 mH
- ACFD RPA is stable
  - $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ are positive-definite if orbitals obey the aufbau principle
  - No complex correlation energies!

Implementation Issues

- ACFD RPA is hard to implement into standard CCD codes
  - Diagonal transformed integrals $\langle ii|aa\rangle$ are zero in CCD
  - Corresponding diagonal exciations are zero in CCD
- We evaluate **A** and **B** in the full spin-orbital basis set
  - General for all flavors of RPA
  - Computationally inefficient
  - Probably not something a grad student can do in an afternoon
- Iterative solution of ring CCD equations

$$0 = \mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT}$$

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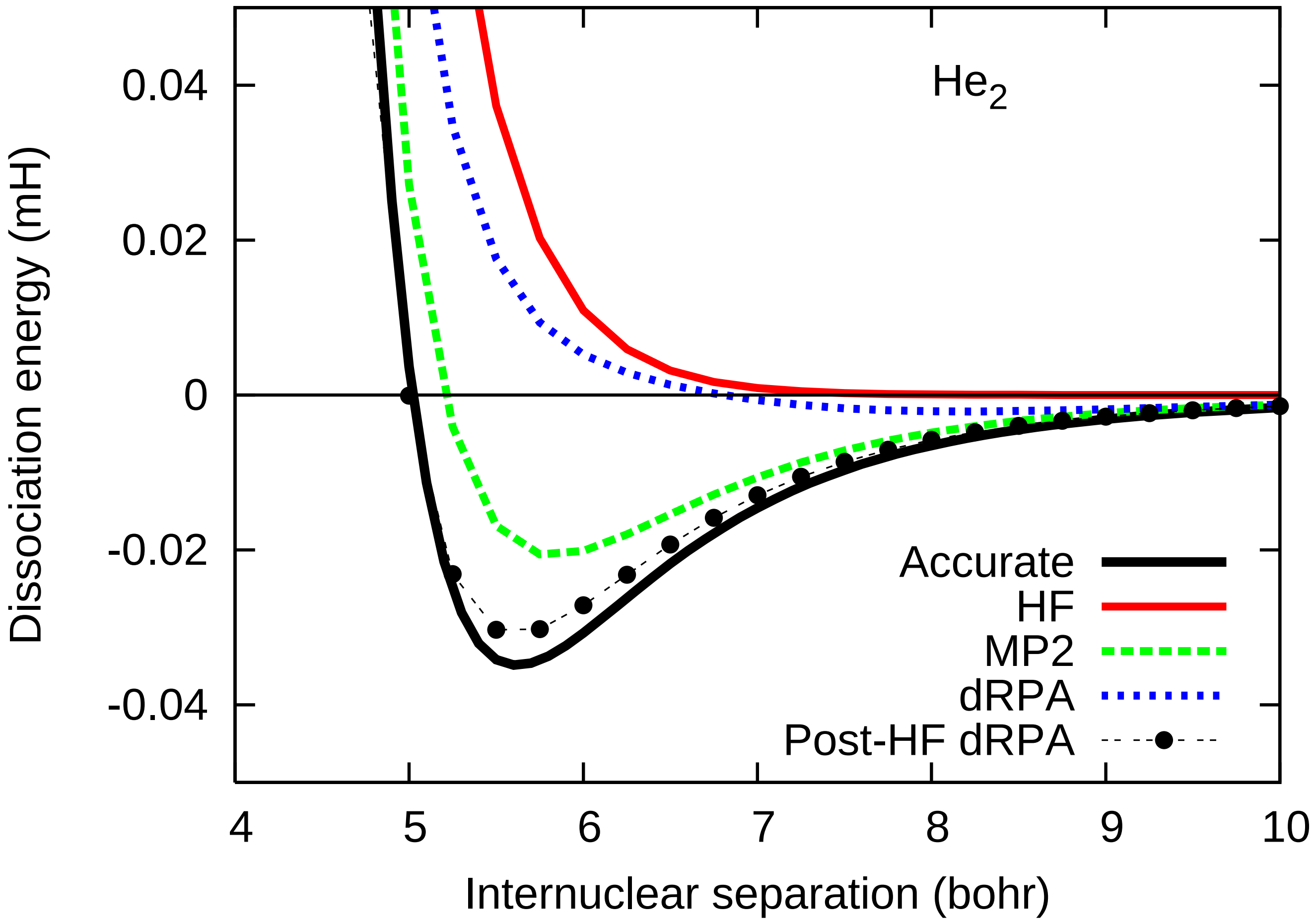
Our initial choice of reference state

- For convenience, we tried evaluating ACFD RPA from a HF reference state
  - Formally derived from a Kohn-Sham state with a local exchange-correlation potential
- We had to rescale the ACFD RPA correlation energy

$$\begin{aligned} E_{XC} &= E_X^{HF} + c_{RPA} E_C^{dRPA} \\ c_{RPA} &= \frac{3}{2} \end{aligned}$$

Janesko, Henderson, Scuseria, JCP 130, 081105 (2009)

vdW dimers with ACFD RPA



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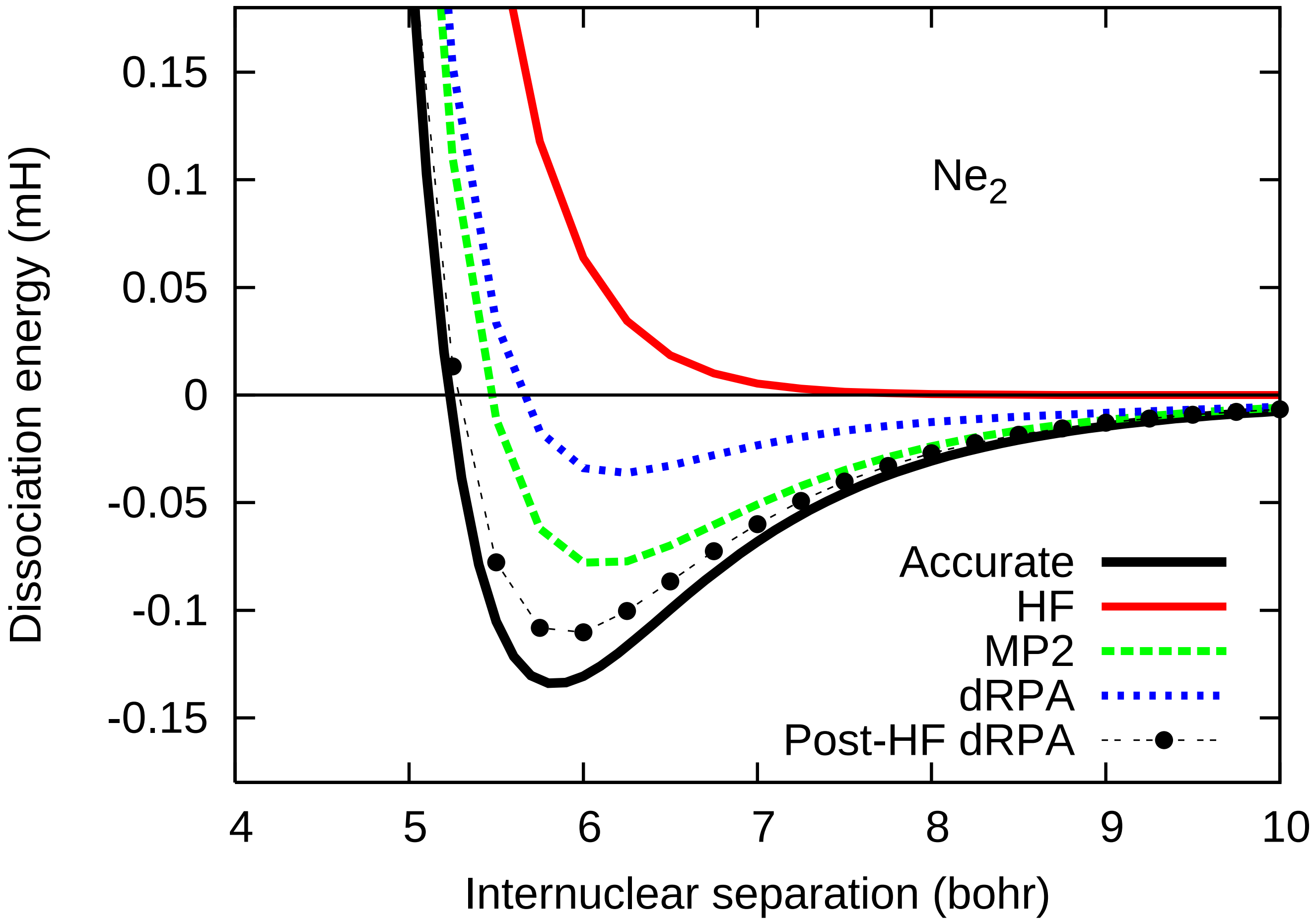

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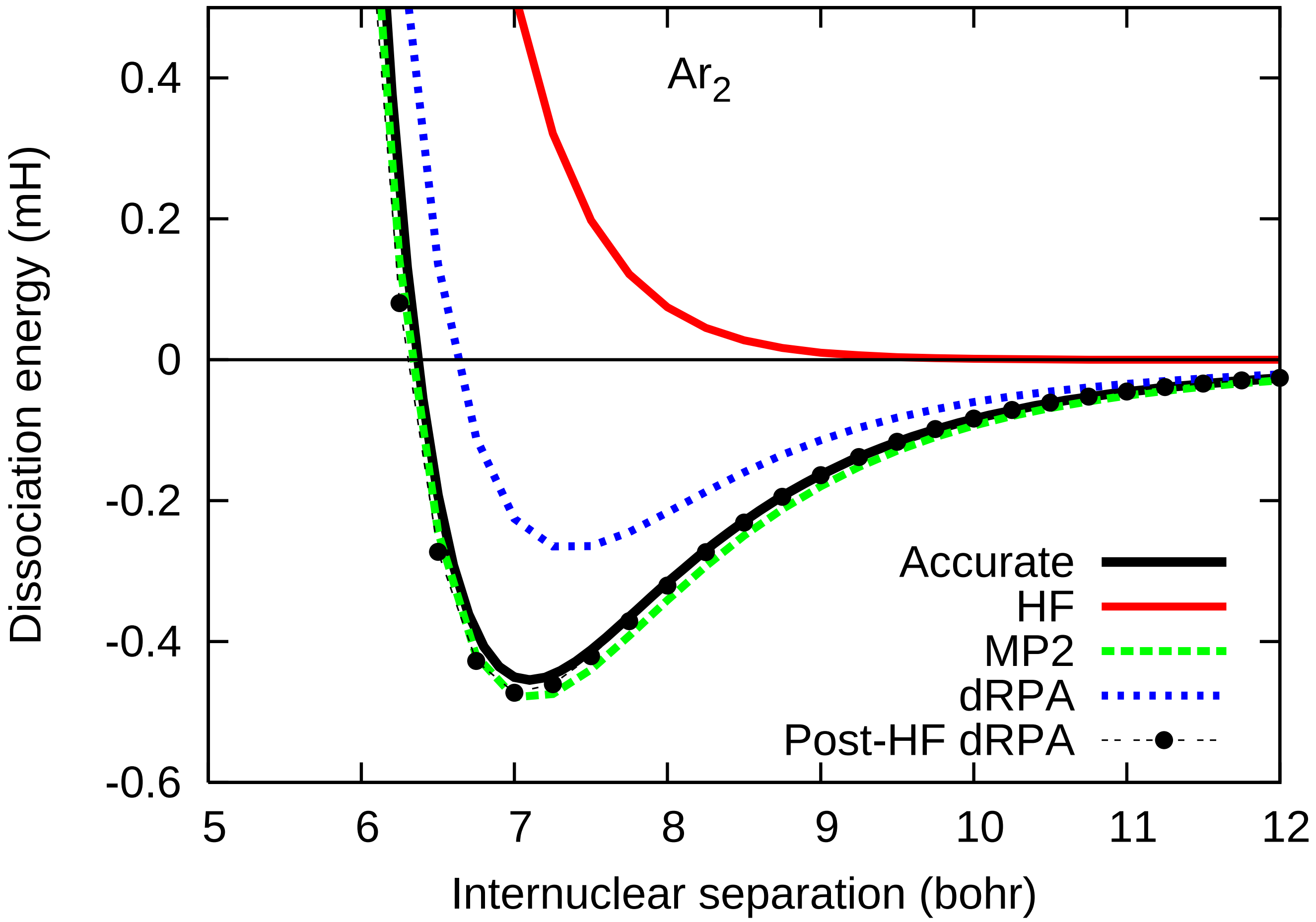

Janesko, Henderson, Scuseria, JCP 130, 081105 (2009)

What just happened here?

- MP2 underbinds light atoms, overbinds heavy ones
- ACFD RPA from a PBE reference underbinds light atoms, overbinds heavy ones
- Rescaled post-HF RPA is accurate for all atoms

Operationally, the reference state makes a big difference to ACFD RPA!

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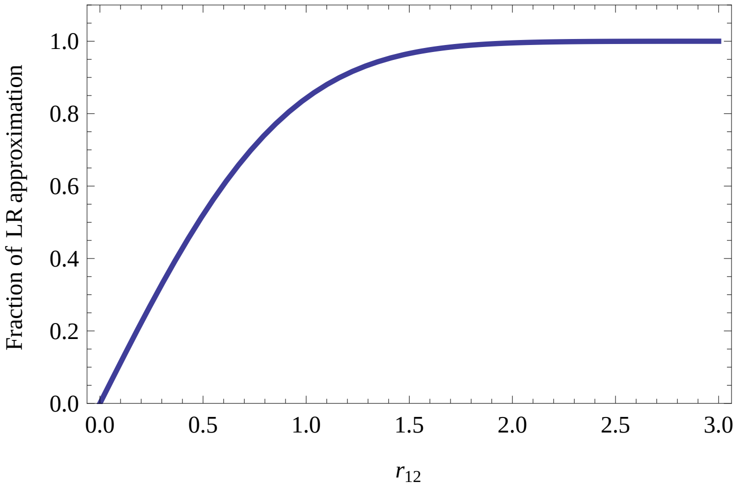
Invoking range separation



$$\frac{1}{r_{12}} = \frac{\mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}$$

- Separate Coulomb interaction into SR and LR parts
- SR semilocal DFT, LR multideterminant Ψ
- Savin, Stoll, Ángyán, and others
- ω selected empirically

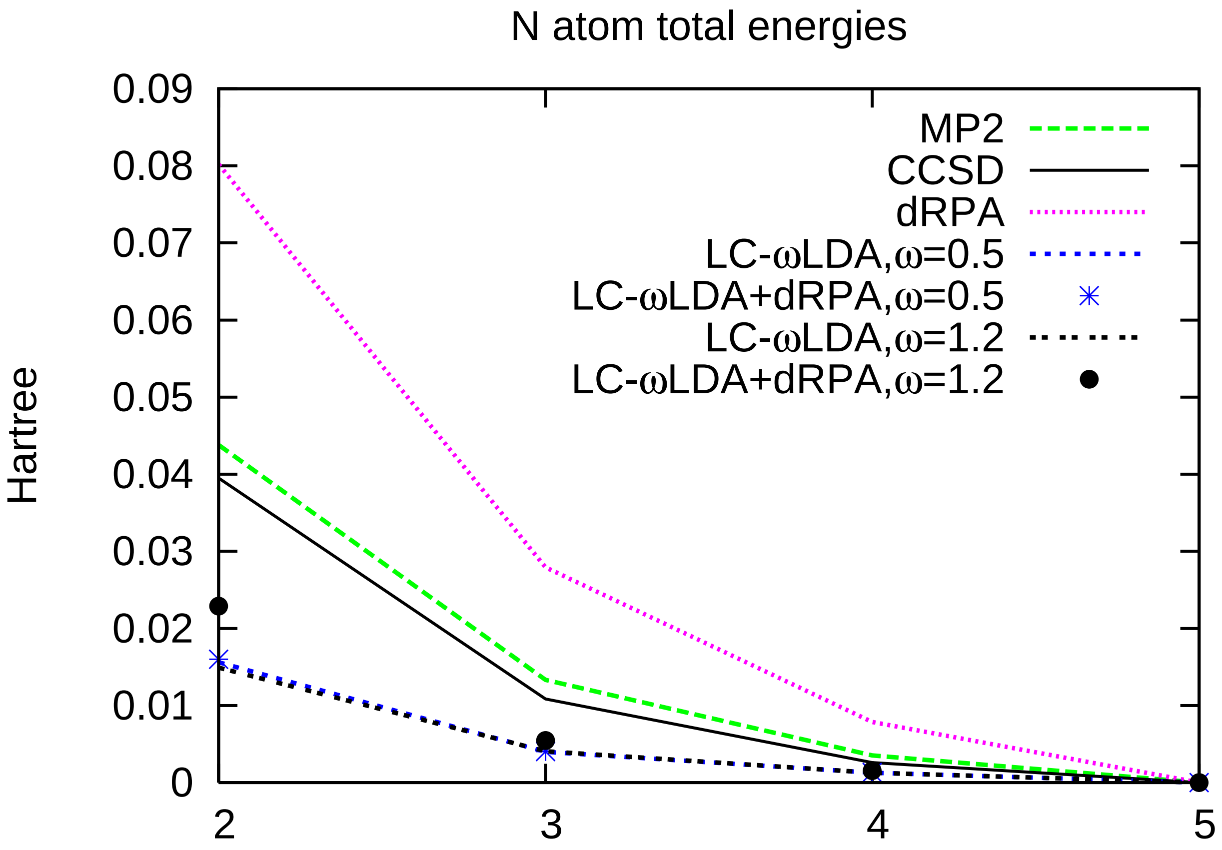
Range-separated RPA

LC-ωLDA+dRPA

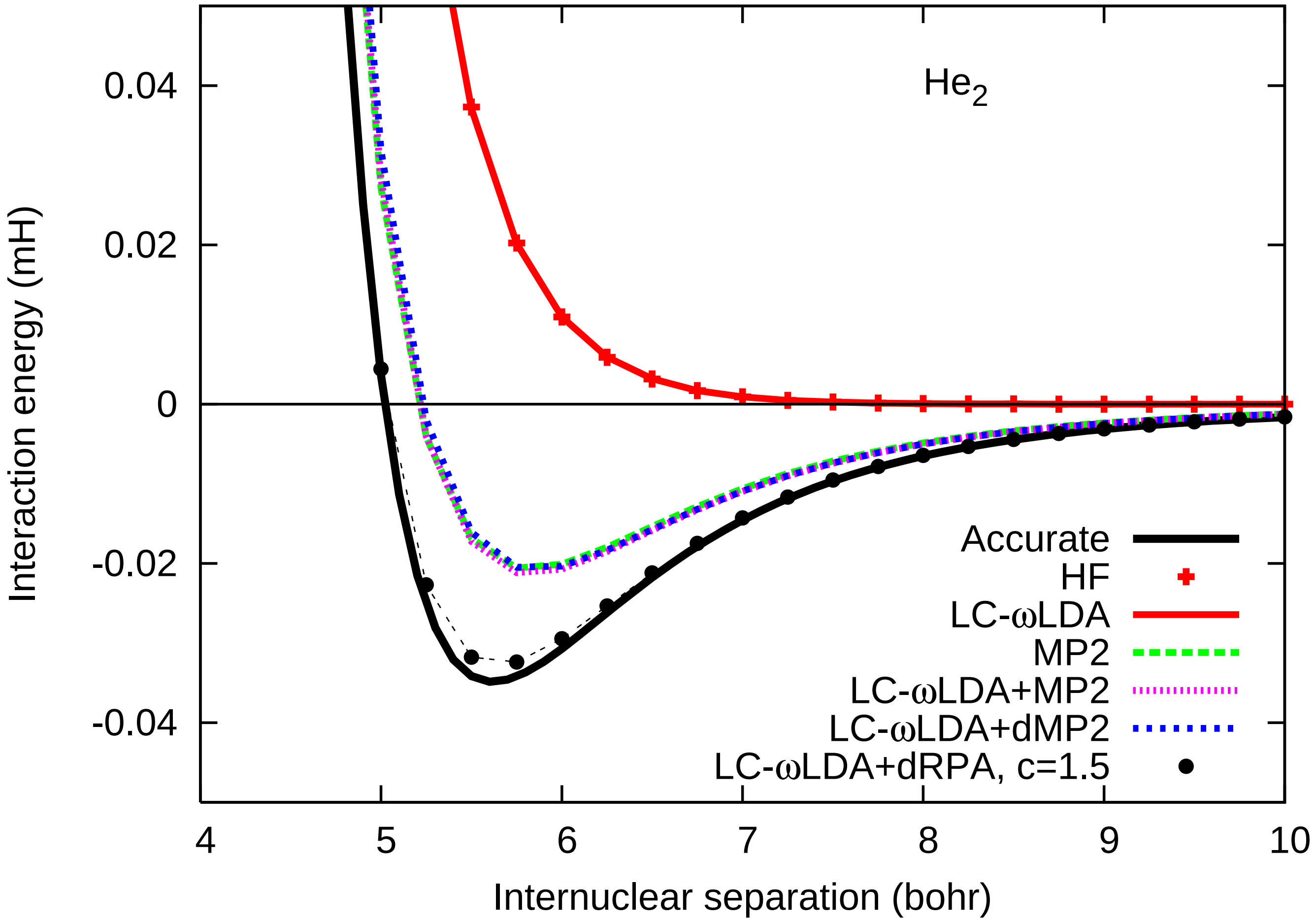
- Short range: LSDA exchange-correlation
- Long range: HF exchange, RPA correlation
- Range separation $\omega = 1.2\,\mathrm{bohr}^{-1}$
- Evaluate RPA correlation from short-range LSDA, long-range HF orbitals and orbital energies
- Rescale RPA correlation by $\frac{3}{2}$

Janesko, Henderson, Scuseria, JCP 130, 081105 (2009)

Basis set convergence of long-range RPA



vdW dimers with LC-ωLDA+dRPA



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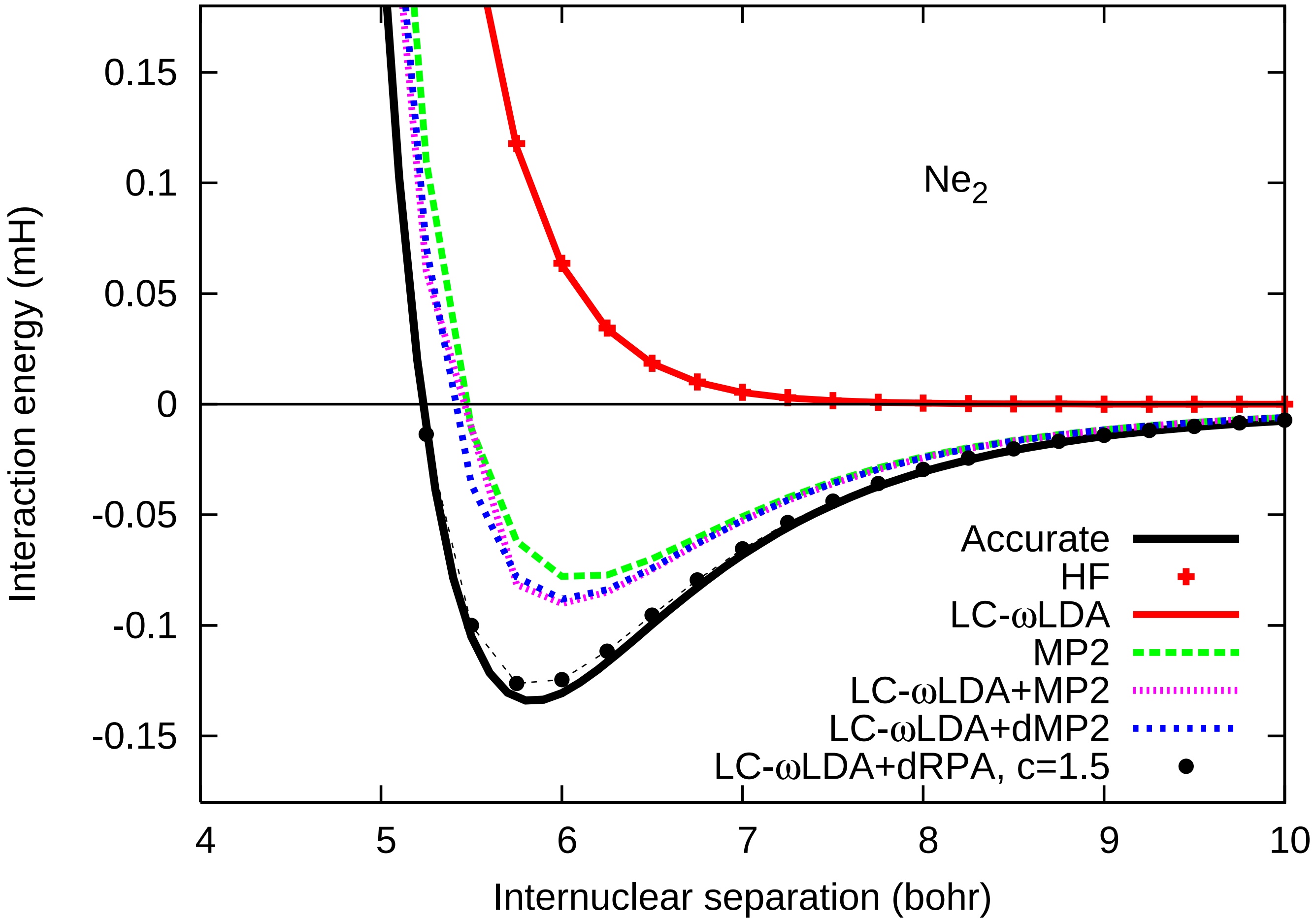

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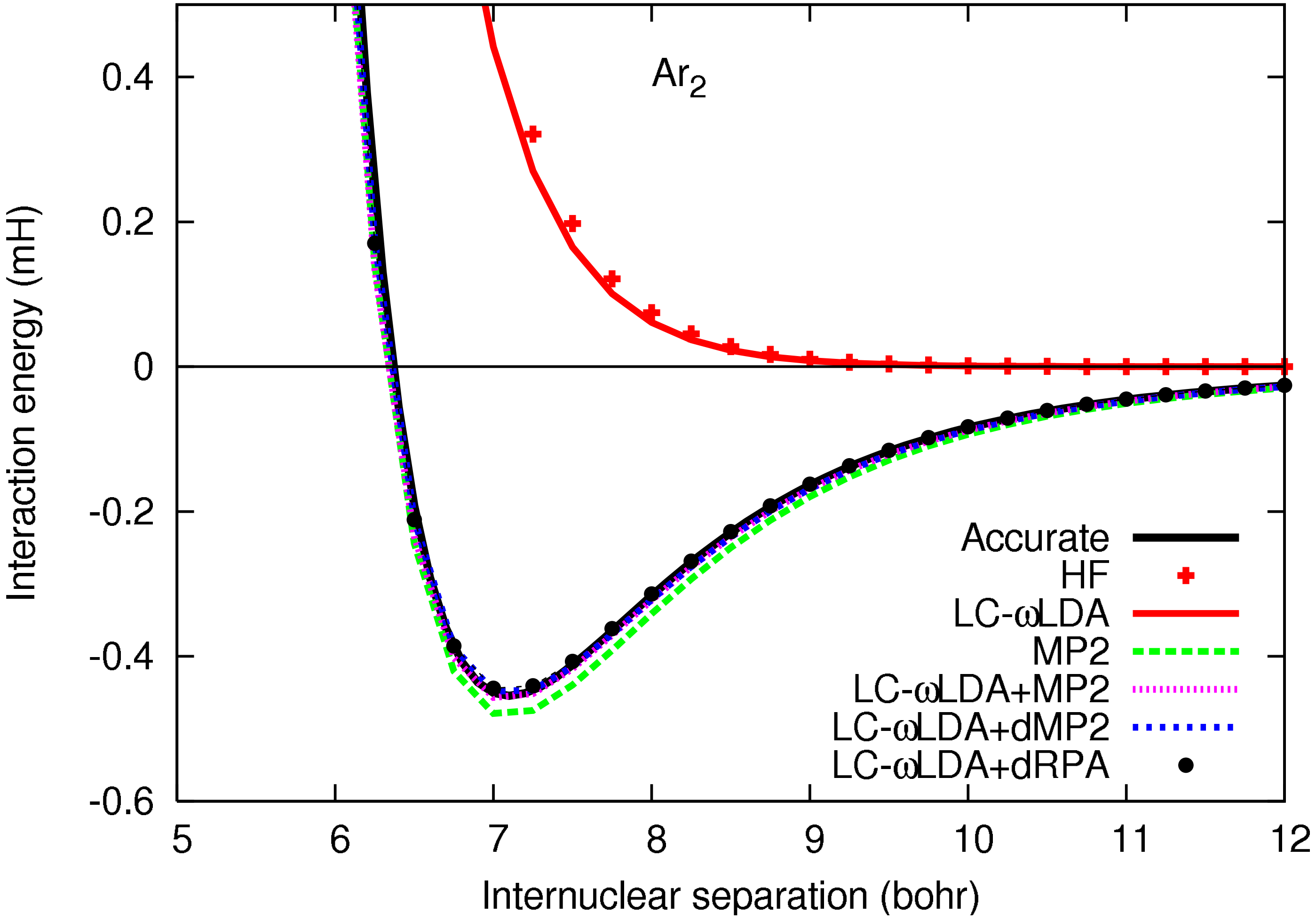

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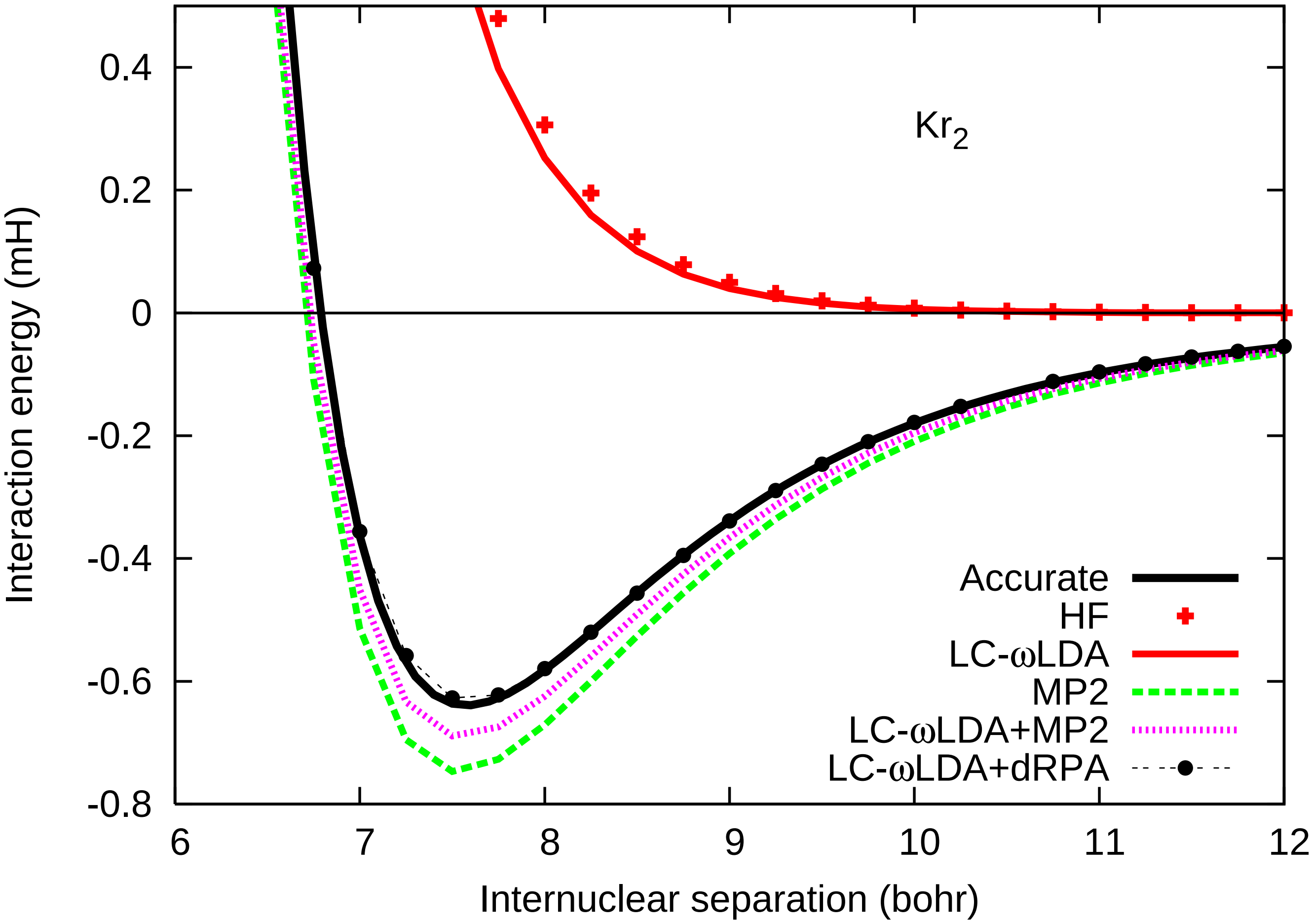
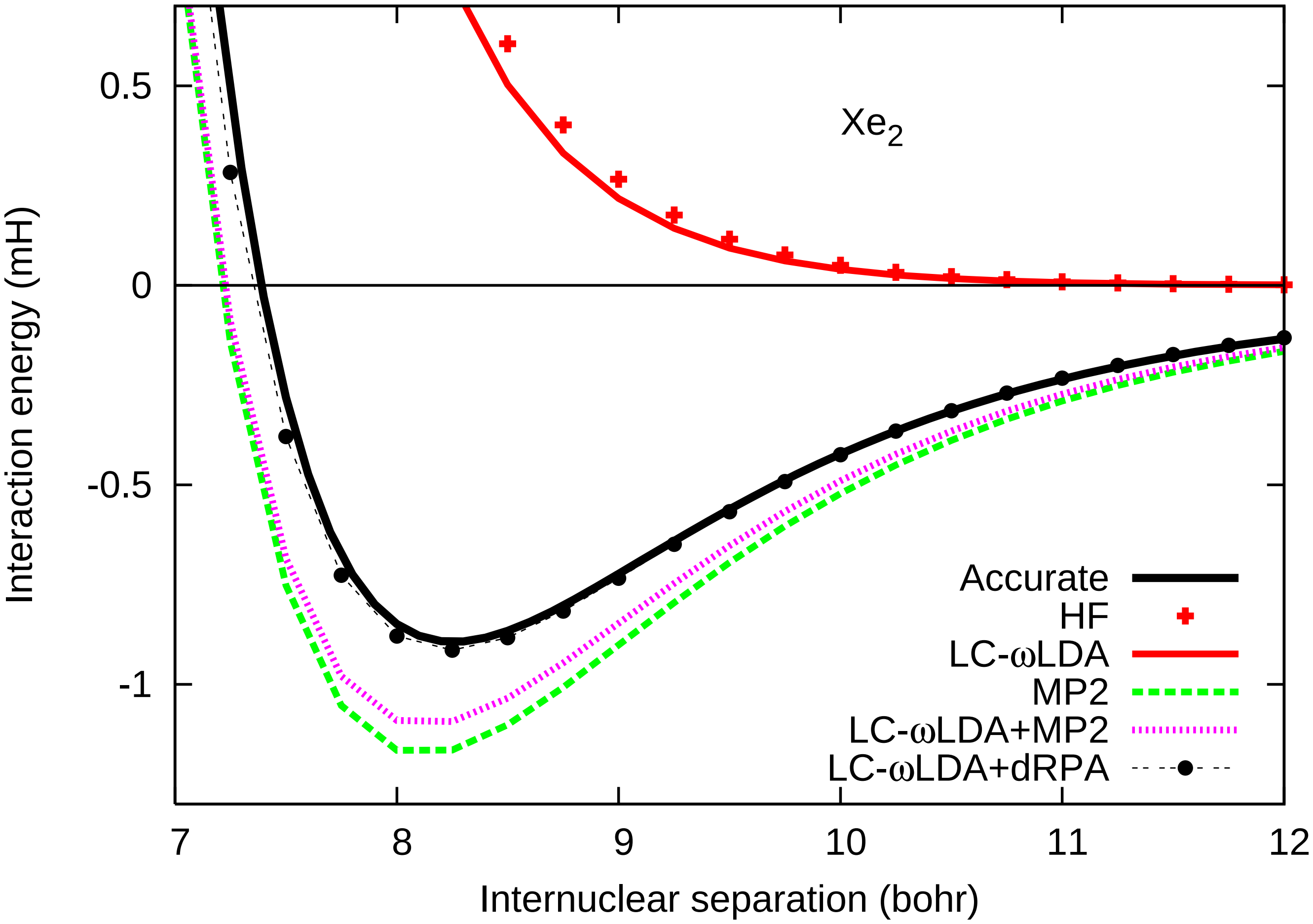


Janesko, Henderson, Scuseria JCP 131, 034110 (2009)

vdW dimers with LC-ωLDA+dRPA



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Noncovalent interactions with LC-ωLDA+dRPA

Method	H-bond	D-D	CT	Weak	Average
PBE	3	80	10	56	37
M06-2X	3	9	8	71	23
B2PLYP-D	3	17	3	18	10
LC-ωLDA+dRPA	5	11	2	14	8

aug-cc-pVTZ basis, MA%E vs. CCSD(T)/CBS extrapolations

Janesko, Henderson, Scuseria JCP 131, 034110 (2009)

Chemistry with LC-ωLDA+dRPA

Method	ω	ΔH_f^o	HT	NHT
LC-ωPBE	0.4	4.2	1.3	2.0
LC-ωLDA	0.5	7.0	3.0	4.4
LC-ωLDA+dRPA	1.2	4.4	1.6	3.5

6-311+G(2d,2p) basis, MAE (kcal/mol) in G2-97 thermochemistry, HTBH38/04 & NHTBH38/04 reaction barrier heights

Janesko, Henderson, Scuseria, JCP 130, 081105 (2009)

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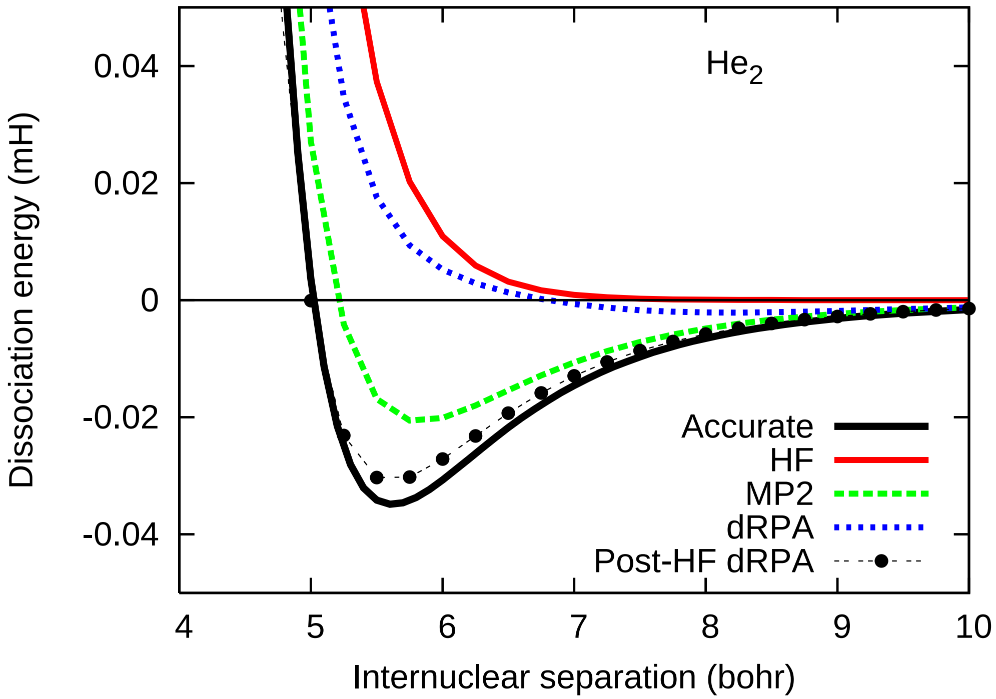
Role of the reference state



Differences between RPA calculations: rescaling c_{RPA}, orbitals and orbital energies used to build **A** and **B**

Janesko, Henderson, Scuseria, JCP 130, 081105 (2009)

Role of the reference state

- Most RPA calculations use Kohn-Sham DFT with semilocal XC functionals
- Furche and van Voorhis 2005 showed global hybrid reference states were useful for beyond-RPA
- HF reference states (nonlocal XC potential) with empirical rescaling are accurate for many properties
- Motivates a systematic study of the reference state in LC-ωLDA+dRPA

RPA rescaling vs. band gap

	Average Gap (eV)	c_{RPA}
LR-HF	0.48	1.11
LR-Slater	0.23	0.93
PBE	0.21	0.85

HOMO-LUMO gap for the 21 molecules in the AE6 and BH6 test sets.

Janesko and Scuseria, JCP 131, 154106 (2009)

Performance for Chemistry

Reference	Optimial rescaling	Atomization energies	Barrier heights
LC-ωLDA	1.50	4.6	0.9
LR-Slater	1.22	5.2	3.5
PBE	1.00	4.3	1.9

LC-ωLDA+dRPA, $\omega = 1.2$ bohr^{-1}, MAE (kcal/mol) in AE6 atomization energies, BH6 hydrogen-transfer barrier heights, evaluated from different reference states. Optimal rescaling fit to AE6 MAE.

Janesko and Scuseria, JCP 131, 154106 (2009)

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Re-examining the connection to coupled cluster

$$\begin{aligned} E_c &= \frac{1}{2}\mathrm{Tr}\left[\mathbf{BT}\right] \\ 0 &= \mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} \end{aligned}$$

- We solve the ring CCD equations iteratively as

$$\begin{aligned} t_{ij}^{ab} &= -D_{ij}^{ab}\Big(\langle ij|ab\rangle + \sum_{kc} t_{ik}^{ac}\,\langle kb|cj\rangle \\ &+ \sum_{kc}\langle ic|ak\rangle\, t_{kj}^{cb} + \sum_{klcd} t_{ik}^{ac}\,\langle kl|cd\rangle\, t_{lj}^{db}\Big), \\ D_{ij}^{ab} &= \left(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j\right)^{-1} \end{aligned}$$

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

Re-examining the connection to coupled cluster

- With $\mathbf{T}_0 = 0$, iteration 1 of regular CCD gives second order MBPT correlation

$$E_C^{MP2} = -\frac{1}{4}\sum_{ijab}\frac{|\langle ij||ab\rangle|^2}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j}$$

- Iteration 1 of ACFD ring CCD gives a ″Coulomb-only″ version of second-order perturbative correlation

$$E_c^{JMP2} = -\frac{1}{2}\sum_{ijab}\frac{|\langle ij|ab\rangle|^2}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j}$$

- Chemists call this second-order Møller-Plesset (MP2) correlation

Janesko and Scuseria, PCCP 11, 9677 (2009)

Coulomb-only MP2

$$E_c^{JMP2} = -\frac{1}{2}\sum_{ijab}\frac{|\langle ij|ab\rangle|^2}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j}$$

- Perturbative variant of ACFD RPA
- No exchange integrals
- One-electron self-interaction error
- Related to new developments in MP2

Janesko and Scuseria, PCCP 11, 9677 (2009)

Spin-scaled MP2

- MP2 is the least expensive ”conventional” correlated method
- Improve MP2 with semiempirical parameters
- HF exchange correlates like-spin electrons, doesn’t affect opposite-spin electrons
- Rescale MP2 correlation between opposite-spin electrons
- Grimme 2003: Rescale $\uparrow\uparrow$, $\downarrow\downarrow$ by 0.33, $\uparrow\downarrow$ by 1.2
- Head-Gordon 2004: Keep **only** $\uparrow\downarrow$ correlation, rescale by 1.3
  - Contains no exchange intgrals
  - **Exchange integrals are expensive!** $\mathcal{O}(N^5)$ vs. $\mathcal{O}(N^4)$

SOS-MP2 & JMP2: Closed shells

- For closed shells, JMP2 is SOS-MP2 with rescaling factor 2

$$E_c(OS-MP2) \;=\; -\sum_{I\bar{J}A\bar{B}} D_{I\bar{J}}^{A\bar{B}} \left|\langle I\bar{J}|A\bar{B}\rangle\right|^2$$

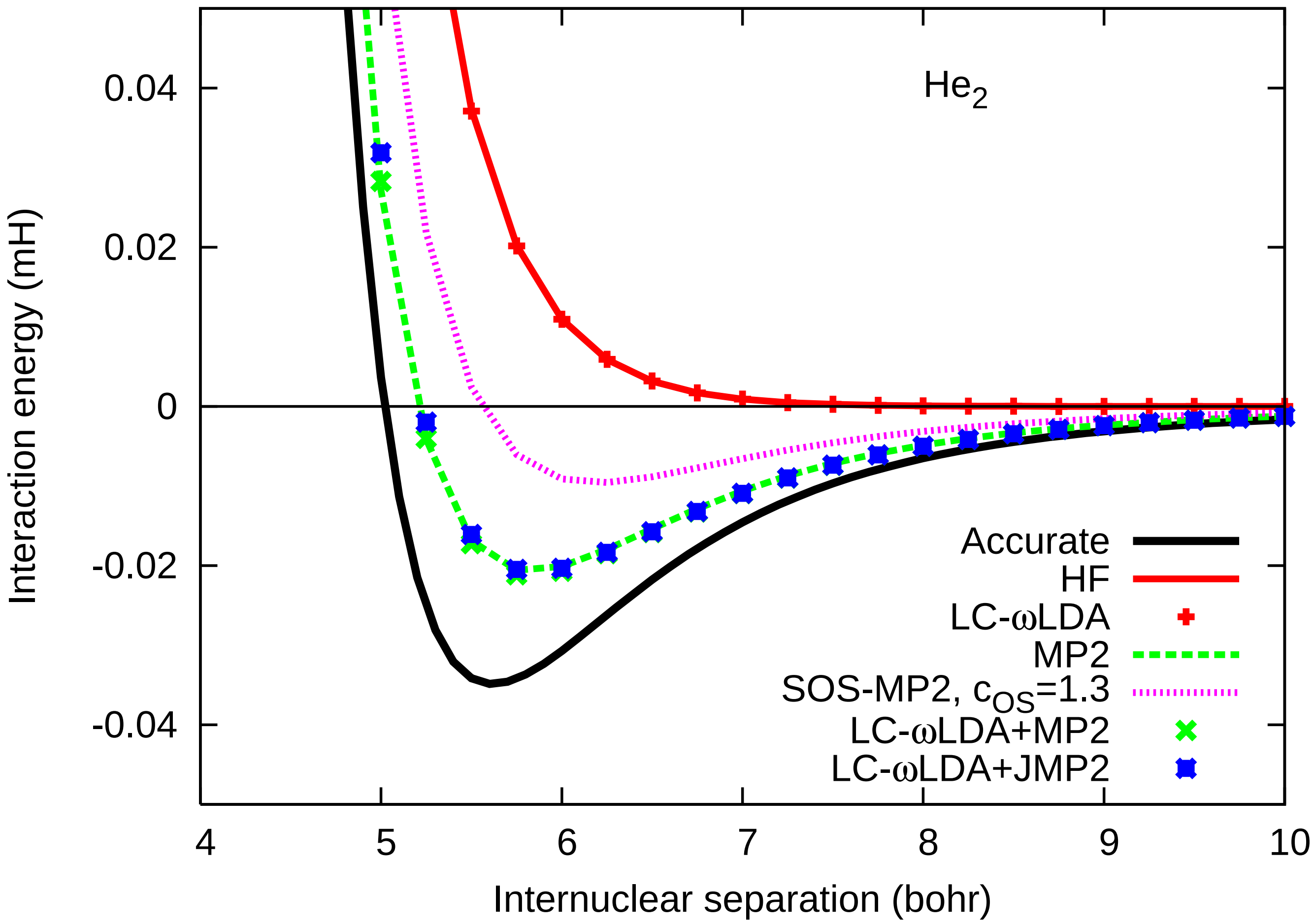
$$\begin{aligned} E_c(JMP2) \;&=\; -\sum_{I\bar{J}A\bar{B}} D_{I\bar{J}}^{A\bar{B}} \left|\langle I\bar{J}|A\bar{B}\rangle\right|^2 \\ &\quad - \frac{1}{2}\Big(\sum_{IJAB} D_{IJ}^{AB} \left|\langle IJ|AB\rangle\right|^2 + \sum_{\bar{I}\bar{J}\bar{A}\bar{B}} D_{\bar{I}\bar{J}}^{\bar{A}\bar{B}} \left|\langle \bar{I}\bar{J}|\bar{A}\bar{B}\rangle\right|^2 \Big) \end{aligned}$$

$$D_{ij}^{ab} \;=\; \left(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j\right)^{-1}$$

Long-range SOS-MP2 and JMP2

- SOS-MP2 with rescaling=2 reproduces MP2 interaction of distant closed-shell fragments
- Exchange integrals decay faster than Coulomb, and are generally less important at long range
- Long-range RPA works well

Closed-shell vdW dimers with SOS-MP2/JMP2



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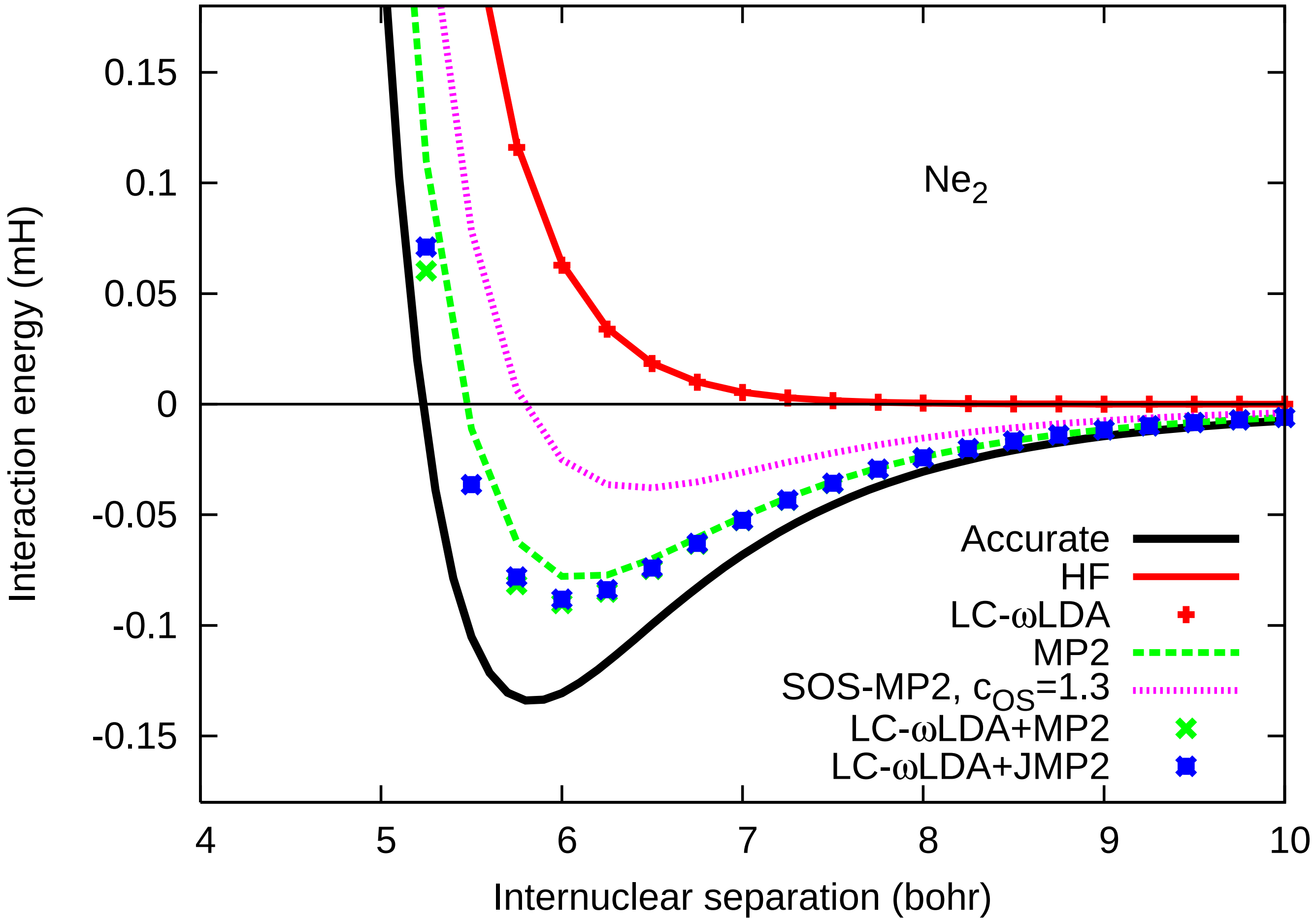

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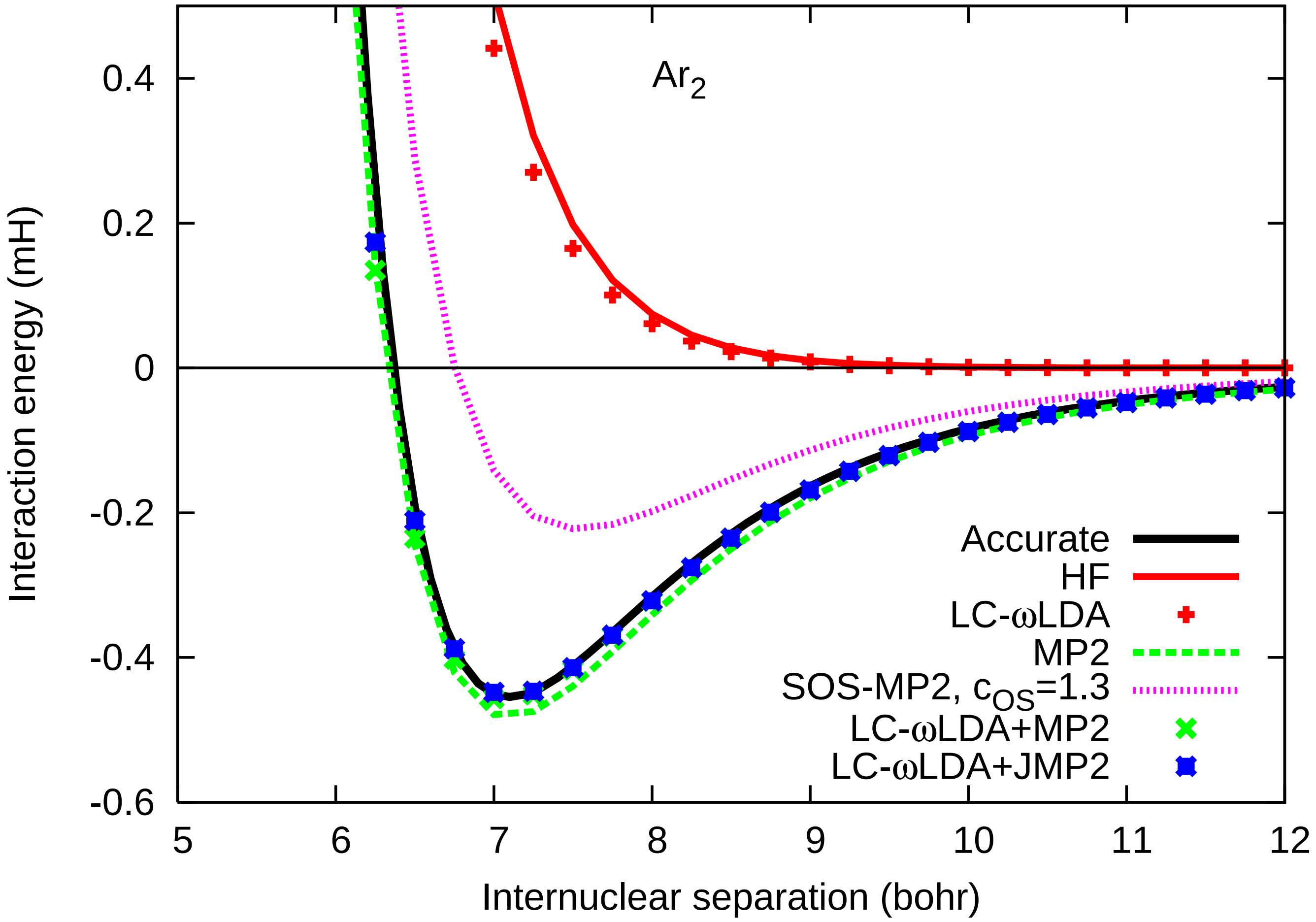
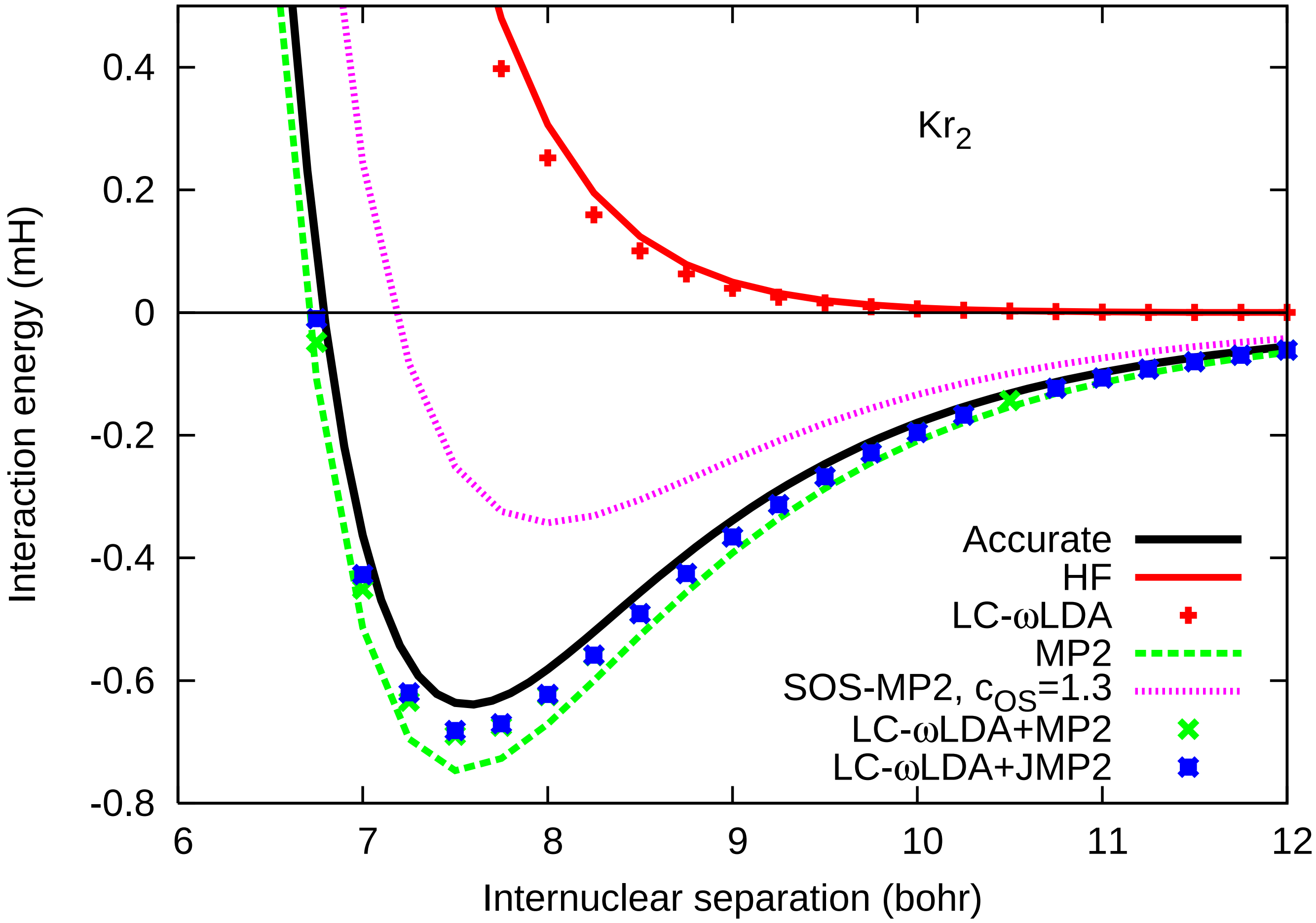


Closed-shell vdW dimers with SOS-MP2/JMP2



Noncovalent interactions with SOS-MP2/JMP2

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B2PLYP-D	3	17	3	18	10
LC-ωLDA+dRPA	5	11	2	14	8
LC-ωLDA+JMP2	1	6	2	29	10

aug-cc-pVTZ basis, compare to CCSD(T)/CBS extrapolations

SOS-MP2 & JMP2: Open shells

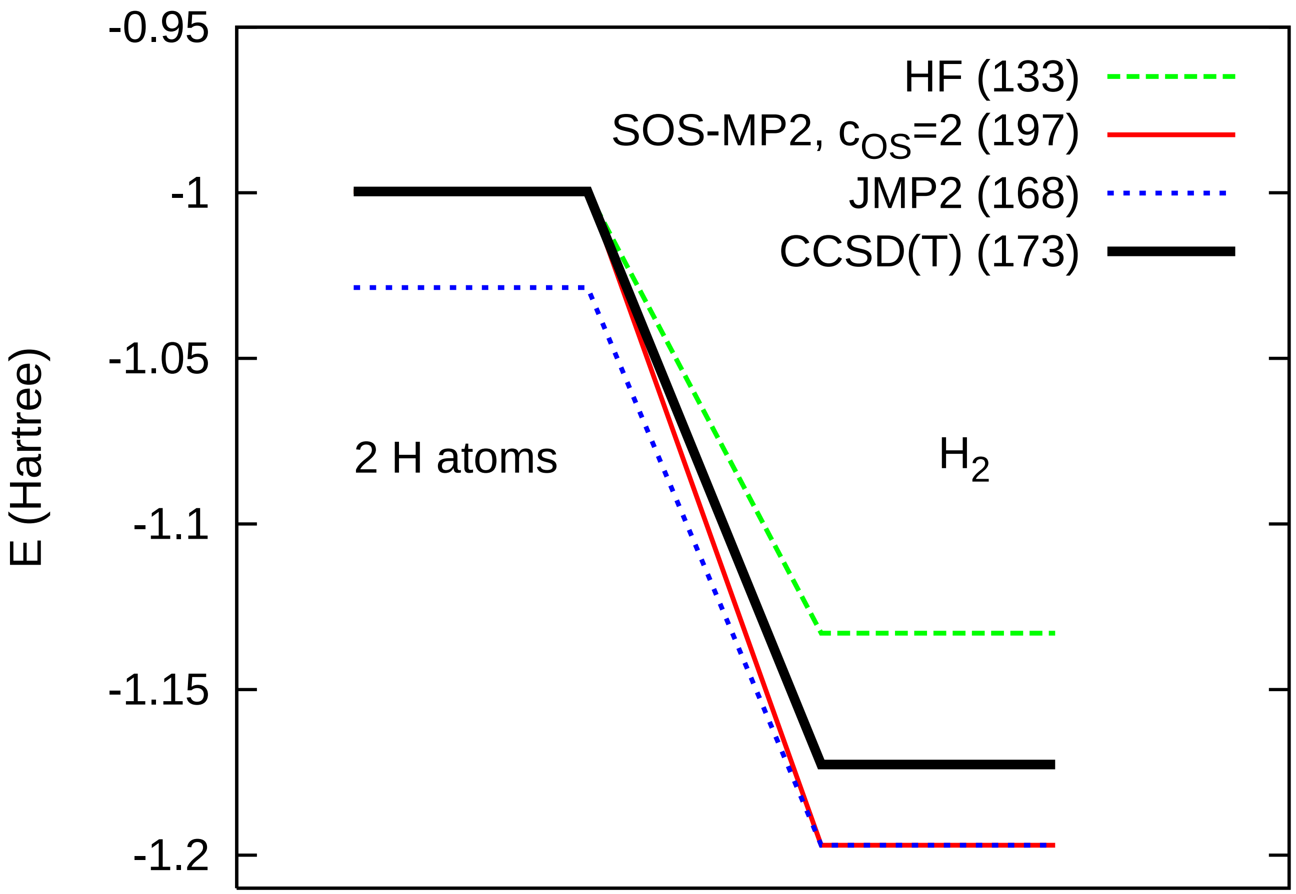
- For open shells, JMP2 and SOS-MP2 are different
- JMP2 has **approximate** like-spin correlation
- This is a problem for one-electron systems!
  - Probably also a problem for Rydberg states, charge-transfer excitations
- Is it a problem everywhere?

SOS-MP2 & JMP2: Thermochemistry & barriers

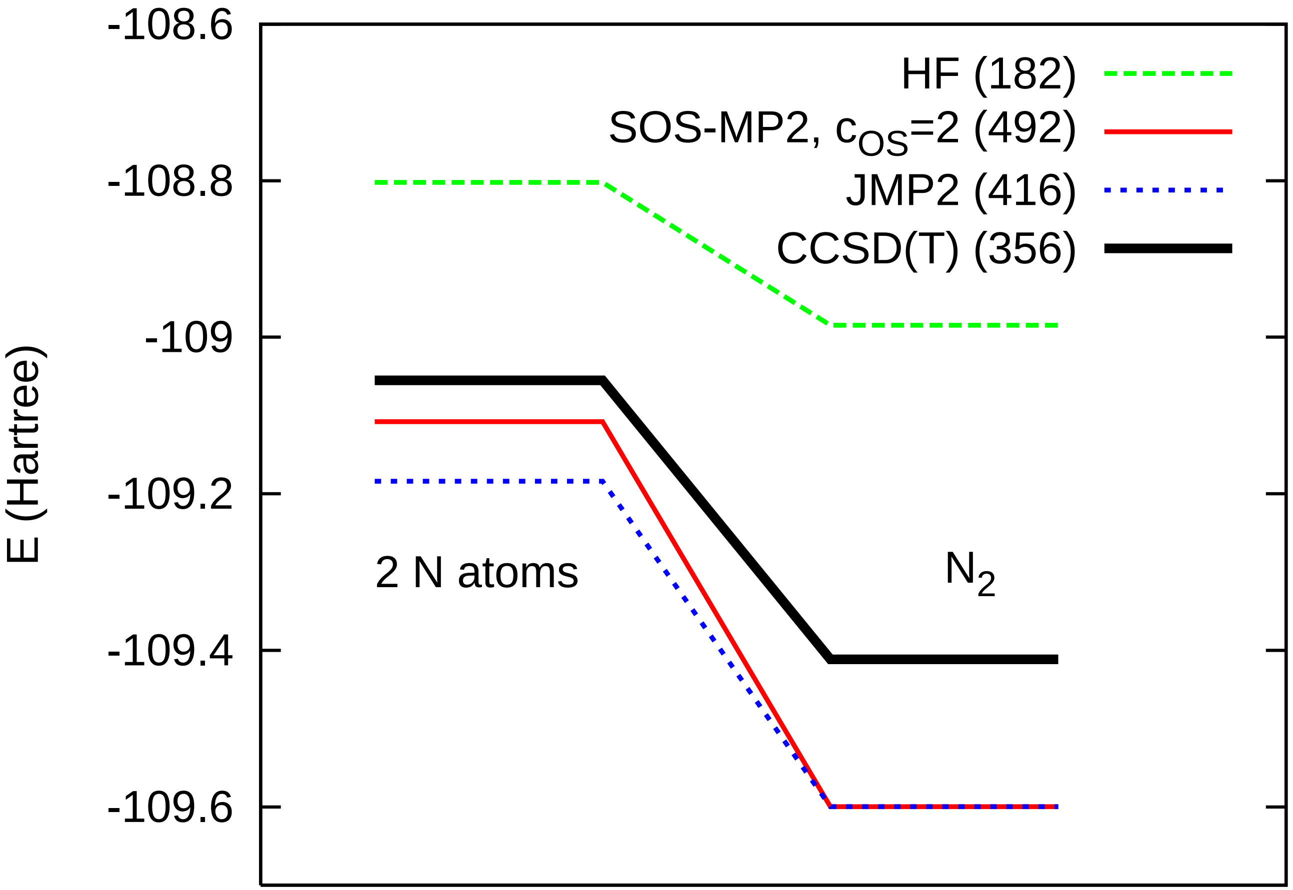
Method	Thermochemistry	Barriers
MP2	9.8	3.3
LC-ωLDA+MP2	9.9	2.9
LC-ωLDA+SOS-MP2	24.2	1.5
LC-ωLDA+JMP2	5.4	1.5

Complete basis set aug-cc-pV(D,T)Z extrapolations, G2-97 ΔH_f^o and HTBH38/04 reaction barrier MAE (kcal/mol)

What happened to the thermochemistry?



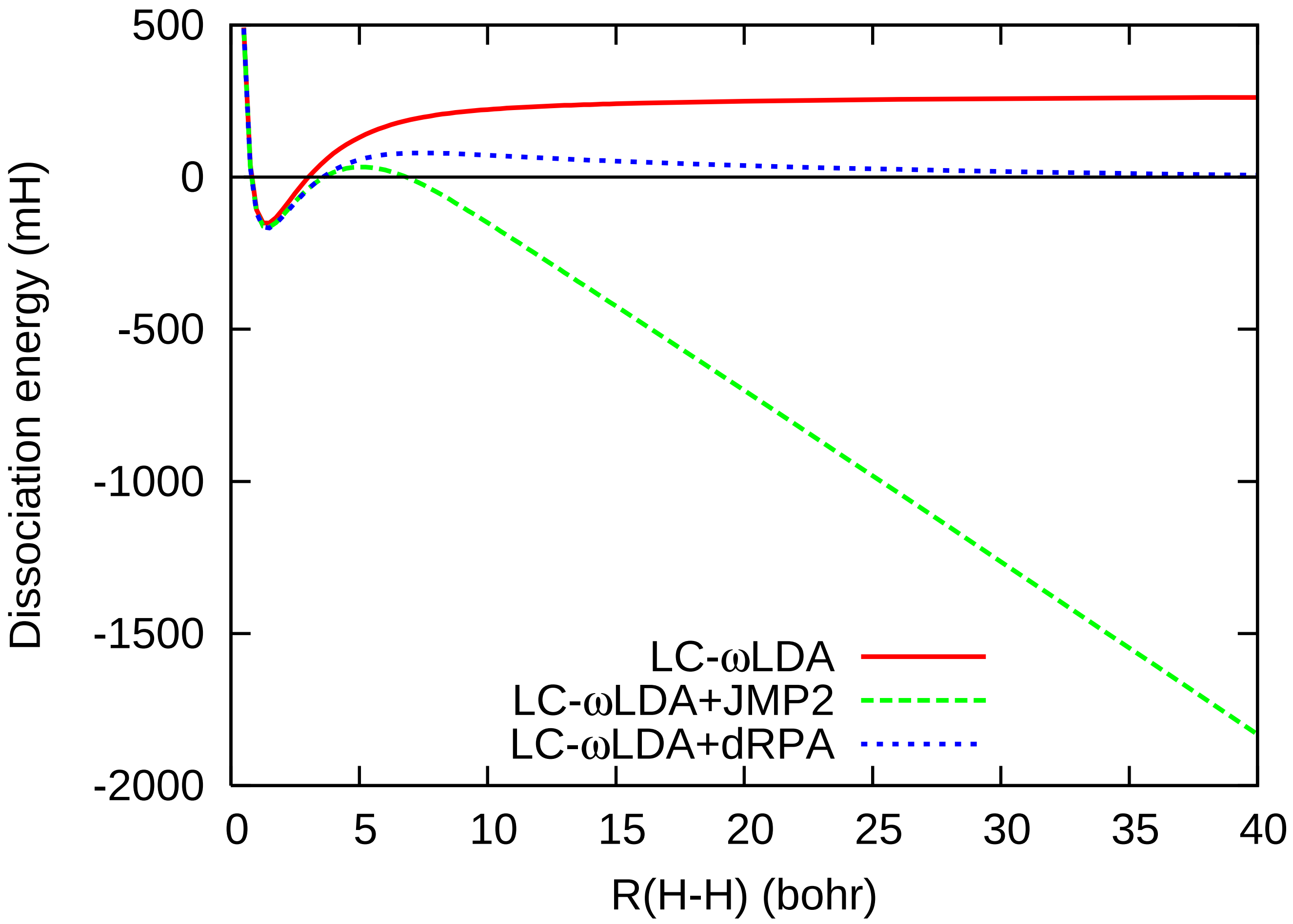
What happened to the thermochemistry?



Take-home messages

- Scuseria, Henderson, Sorensen approach is a simple way to evaluate RPA
- The reference state is important in RPA
- Direct RPA from a nonlocal HF potential seems to work well
  - ”Hybrid” of physicist’s and chemist’s RPA
  - Rederive RPA from a generalized Kohn-Sham reference with a nolocal $v_{XC}(\mathbf{r}, \mathbf{r}')$
  - Explore other Kohn-Sham reference states for RPA
- Long-range exact exchange + RPA, short-range semilocal functionals seem to work well
  - Promising alternative to RPA+

Degenerate orbitals with LC-ωLDA+dRPA



RPA is nonperturbative