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Explicitly Correlated Wave Functions in the Random-Phase Approximation to the Correlation Energy

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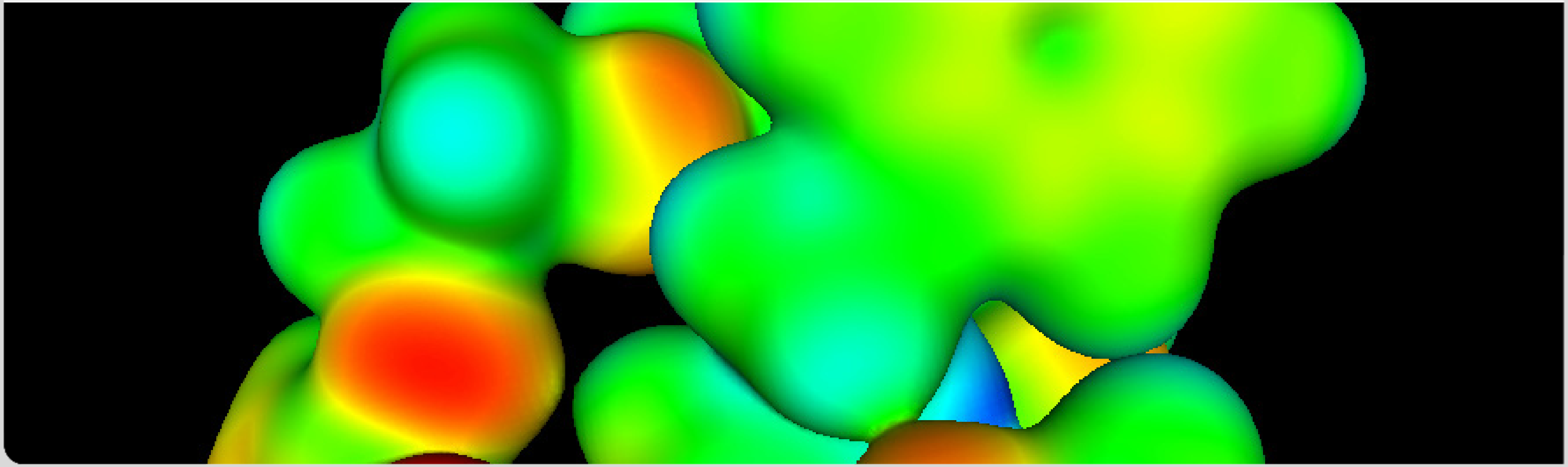

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Adiabatic connection in DFT

$$\hat{H}^{\lambda} = \hat{T} + \hat{V}^{\lambda}[\rho] + \lambda \hat{V}_{\mathrm{ee}}$$

$0 \leq \lambda \leq 1$ (coupling strength)

$$\hat{V}_{\mathrm{ee}} = \sum_{\mu=2}^{n_{\mathrm{e}}} \sum_{\nu=1}^{\mu-1} \frac{1}{r_{\mu\nu}}$$

$$\hat{H}^{\lambda} \left| \Psi_0^{\lambda} \right\rangle = E_0^{\lambda} \left| \Psi_0^{\lambda} \right\rangle; \qquad \forall\ \lambda:\ \left| \Psi_0^{\lambda} \right\rangle \rightarrow \rho$$

$\lambda = 0$ non-interacting particles, $\hat{V}^{\lambda}[\rho]$ is the Kohn−Sham potential

$\lambda = 1$ interacting particles, $\hat{V}^{\lambda}[\rho]$ is the electron−nucleus potential

Adiabatic connection in DFT

If we solve the Schrödinger equations for all values of λ, then we can write the ground-state energy as follows:

$$E_0^1 = \left\langle \Psi_0^0 \middle| \hat{H}^1 \middle| \Psi_0^0 \right\rangle + \int_0^1 W^{\mathrm{C}}(\lambda)\,\mathrm{d}\lambda$$

$$W^{\mathrm{C}}(\lambda) = \left\langle \Psi_0^\lambda \middle| \hat{V}_{\mathrm{ee}} \middle| \Psi_0^\lambda \right\rangle - \left\langle \Psi_0^0 \middle| \hat{V}_{\mathrm{ee}} \middle| \Psi_0^0 \right\rangle$$

Adiabatic connection: Transition densities

The integrand can be written in terms of transition densities:

$$W^{C}(\lambda) = \sum_{n\neq 0}\left\{ J[\rho_{0n}^{\lambda}] - J[\rho_{0n}^{0}] \right\}$$

$$\rho_{0n}^{\lambda}(\mathbf{r}) = \sum_{pq} \varphi_p(\mathbf{r})\ \varphi_q(\mathbf{r})\ \left\langle \Psi_0^{\lambda} \middle| a_p^{+} a_q \middle| \Psi_n^{\lambda} \right\rangle$$

$$J[\rho_{0n}^{\lambda}] = \iint \frac{\rho_{0n}^{\lambda}(\mathbf{r})\rho_{0n}^{\lambda}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$

Direct RPA theory (dRPA)

We now switch to DFT and compute the transition densities using time-dependent density-functional theory (TD-DFT) in the random-phase approximation (RPA):

$$\boxed{\rho_{0n}^{\lambda}(\mathbf{r}) \cong \sum_{ia} \varphi_i(\mathbf{r})\varphi_a(\mathbf{r})\left(X^{\lambda}+Y^{\lambda}\right)_{ia}^{n}}$$

$$\begin{pmatrix} \mathbf{A}^{\lambda} & \mathbf{B}^{\lambda} \\ -\mathbf{B}^{\lambda} & -\mathbf{A}^{\lambda} \end{pmatrix}\begin{pmatrix} \mathbf{X}^{\lambda} & \mathbf{Y}^{\lambda} \\ \mathbf{Y}^{\lambda} & \mathbf{X}^{\lambda} \end{pmatrix} = \begin{pmatrix} \mathbf{X}^{\lambda} & \mathbf{Y}^{\lambda} \\ \mathbf{Y}^{\lambda} & \mathbf{X}^{\lambda} \end{pmatrix}\begin{pmatrix} \mathbf{w}^{\lambda} & \mathbf{0} \\ \mathbf{0} & -\mathbf{w}^{\lambda} \end{pmatrix}$$

$$A_{ia,jb}^{\lambda} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \lambda(ia\,|\,jb); \qquad B_{ia,jb}^{\lambda} = \lambda(ia\,|\,bj)$$

Direct RPA theory (dRPA)

$$
\begin{aligned}
E_0^1 &= \left\langle \Psi_0^0 \middle| \hat{H}^1 \middle| \Psi_0^0 \right\rangle + \int_0^1 W^{\mathrm{C}}(\lambda)\,\mathrm{d}\lambda \\
&= \left\langle \mathrm{KS} \middle| \hat{H} \middle| \mathrm{KS} \right\rangle + E_{\mathrm{dRPA}}^{\mathrm{C}}
\end{aligned}
$$

Expectation value of the
Kohn−Sham determinant
(from DFT)

Correlation energy
(from TD-DFT)

Review: H. Eshuis, J. E. Bates and F. Furche, *Theor. Chem. Acc.* **131**, 1084 (2012).

Direct RPA theory (dRPA)

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dRPA correlation energy (in E_h) of the He-atom ground state

aug-cc-pVXZ basis sets

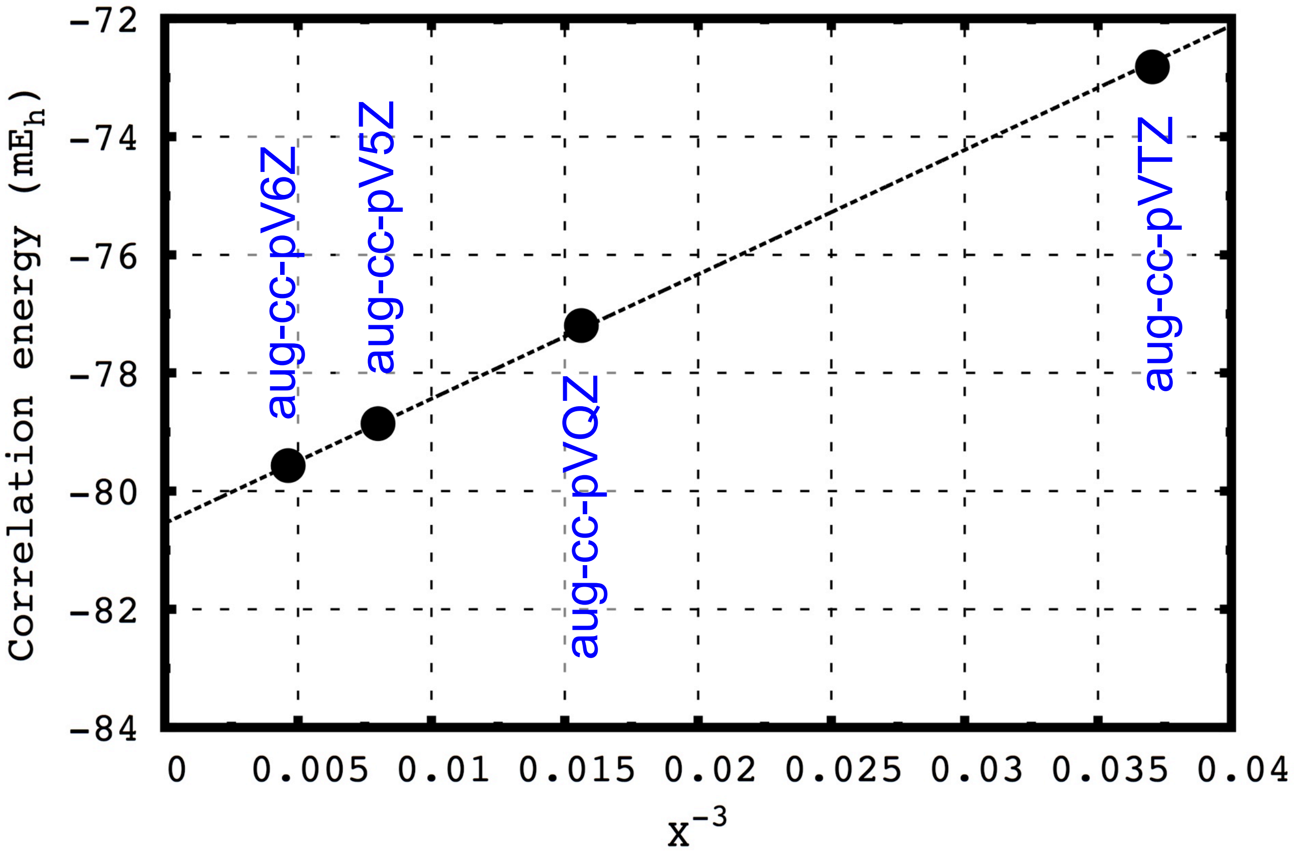
TPSSh Kohn−Sham orbitals

X	$\langle KS\|\hat{H}\|KS\rangle$	E^{c}_{dRPA}
2	−2.8554	−0.0589
3	−2.8609	−0.0728
4	−2.8612	−0.0772
5	−2.8613	−0.0789
6	−2.8613	−0.0796
:	:	:
∞	**−2.8613**	**−0.0805**

Direct RPA theory (dRPA)

dRPA correlation energy (in mE_h) of the He-atom ground state

aug-cc-pVXZ basis sets TPSSh Kohn−Sham orbitals



Direct RPA theory (dRPA)

- Basis-set convergence of the dRPA method is X^{-3}.
- This is the same slow basis-set convergence as in wave-function-based electron-correlation methods.

- This can be understood by noting that the dRPA correlation energy can be obtained by solving the **direct ring-coupled-cluster-doubles** (drCCD) equation:

$$E^{\mathrm{C}}_{\mathrm{dRPA}} = \frac{1}{2}\operatorname{tr}\left(\mathbf{BT}\right), \quad \text{with} \quad \mathbf{B} \equiv \mathbf{B}^{1} \quad \text{and} \quad \mathbf{A} \equiv \mathbf{A}^{1}$$

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

(Riccati equation)

The dRPA(F12) method

- The CCSD(F12) method uses two-electron functions $f(r_{12})$ that explicitly depend on the interelectronic distance r_{12}.

- The dRPA(F12) method can very easily be implemented when a program code for the CCSD(F12) approach is already available.

CCSD(F12)

↓ No single excitations

CCD(F12)

↓ Ring diagrams only

rCCD(F12)

↓ No exchange terms

drCCD(F12) ≅ dRPA(F12)

The F12 double excitations

$$\hat{T}_{2'} = \sum_{i<j}\sum_{\alpha<\beta}\sum_{x<y} c^{ij}_{xy}\, w^{xy}_{\alpha\beta}\, a^{+}_{\alpha} a_i a^{+}_{\beta} a_j$$

(Kutzelnigg, TCA, 1985;
Klopper, CPL, 1991)

$$w^{xy}_{\alpha\beta} = \langle \alpha\beta |\, \hat{Q}_{12} \left(\tfrac{3}{8} + \tfrac{1}{8}\hat{S}_{xy} \right) f(r_{12})\, | xy \rangle$$

(Ten-no, JCP, 2004)

$$f(r_{12}) = \gamma^{-1}(1 - e^{-\gamma\, r_{12}})$$

(Ten-no, CPL, 2004)

$$\hat{Q}_{12} = (1-\hat{O}_1)(1-\hat{O}_2) - \hat{V}_1\hat{V}_2 \longleftarrow$$

Removes conventional doubles

(Valeev, CPL, 2004)

$$\hat{S}_{xy} \longleftarrow$$

Permutes the spatial components of spin orbitals x and y in the determinant $| xy >$

CCSD(F12) approximation

(Fliegl *et al*., JCP, 2005)

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}$$

$$\hat{\tilde{H}} = \exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1)$$

Simplifications in the doubles equations

$$E_{\mathrm{CCSD(F12)}} = \langle \mathrm{HF}|\, \hat{\tilde{H}} + \left[\hat{H},\, \hat{T}_2 + \hat{T}_{2'}\right] |\mathrm{HF}\rangle$$

$$0 = \Omega_a^i = \left\langle {}^{i}_{a} \right|\, \hat{\tilde{H}} + \left[\hat{\tilde{H}},\, \hat{T}_2 + \hat{T}_{2'}\right] |\mathrm{HF}\rangle$$

$$0 = \Omega_{ab}^{ij} = \left\langle {}^{ij}_{ab} \right|\, \hat{\tilde{H}} + \left[\hat{\tilde{H}},\, \hat{T}_2 + \hat{T}_{2'}\right] + \tfrac{1}{2}\left[\left[\hat{H},\, \hat{T}_2 + 2\hat{T}_{2'}\right],\, \hat{T}_2\right] |\mathrm{HF}\rangle$$

$$0 = \Omega_{xy}^{ij} = \left\langle {}^{ij}_{xy} \right|\, \hat{\tilde{H}} + \left[\hat{F}_D,\, \hat{T}_{2'}\right] + \left[\hat{\tilde{H}},\, \hat{T}_2\right] |\mathrm{HF}\rangle$$

Explicit correlation: dRPA(F12)

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dRPA(F12) correlation energy (in E_h) of the He-atom ground state

aug-cc-pVXZ basis sets TPSSh Kohn−Sham orbitals

X	$\langle KS\|\hat{H}\|KS\rangle$	$E^{c}_{\mathrm{dRPA(F12)}}$
2	−2.8554	−0.0827
3	−2.8609	−0.0805
4	−2.8612	−0.0803
5	−2.8613	−0.0805
6	−2.8613	−0.0805
:	:	:
∞	**−2.8613**	**−0.0805**

Direct RPA theory (dRPA)

- The drCCD equation can be written as follows:
(using Einstein summation convention)

$$\underset{\mathbf{B}}{g_{ij}^{ab}} + \underbrace{\left(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j\right) t_{ij}^{ab}}_{\mathbf{A}^{(0)}\mathbf{T}+\mathbf{T}\mathbf{A}^{(0)}} + \underbrace{g_{ic}^{ak} t_{kj}^{cb} + t_{ik}^{ac} g_{cj}^{kb}}_{\mathbf{A}^{(1)}\mathbf{T}+\mathbf{T}\mathbf{A}^{(1)}} + \underset{\mathbf{TBT}}{t_{il}^{ad} g_{dc}^{lk} t_{kj}^{cb}} = 0$$

The dRPA(F12) method

- The equation for the **conventional doubles amplitudes** becomes:

$$g_{ij}^{ab}+\left(\varepsilon_a+\varepsilon_b-\varepsilon_i-\varepsilon_j\right)t_{ij}^{ab}+g_{ic}^{ak}t_{kj}^{cb}+t_{ik}^{ac}g_{cj}^{kb}+t_{il}^{ad}g_{dc}^{lk}t_{kj}^{cb}+$$

$$\boxed{C_{op}^{ab}c_{ij}^{op}}+\boxed{g_{ic'}^{ak}f_{op}^{c'b}c_{kj}^{op}+c_{ik}^{op}f_{op}^{ac'}g_{c'j}^{kb}}+\boxed{t_{il}^{ad}g_{dc'}^{lk}f_{op}^{c'b}c_{kj}^{op}+c_{il}^{op}f_{op}^{ad'}g_{d'c}^{lk}t_{kj}^{cb}}=0$$

- The equation for the **F12 amplitudes** is:

$$\boxed{V_{ij}^{mn}+B_{op}^{mn}(ij)c_{ij}^{op}+C_{ab}^{mn}t_{ij}^{ab}}+\boxed{f_{a'b}^{mn}g_{ic}^{a'k}t_{kj}^{cb}+t_{ik}^{ac}g_{cj}^{kb'}f_{ab'}^{mn}}=0$$

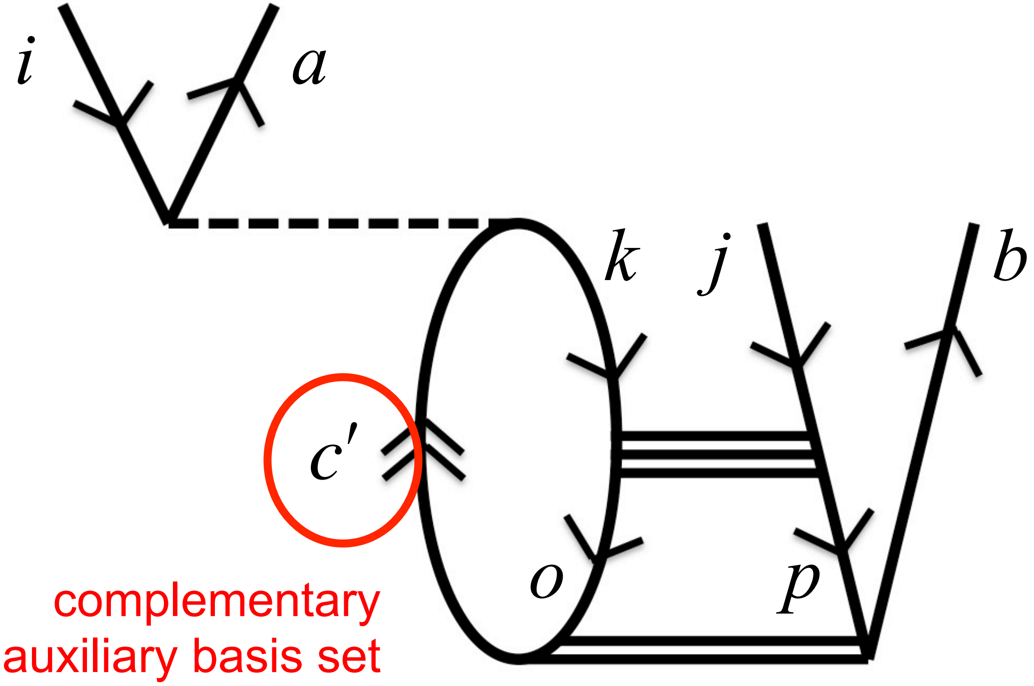
dMP2-F12

$$g_{pq}^{rs}=\left\langle rs\middle|r_{12}^{-1}\middle|pq\right\rangle;\quad f_{pq}^{rs}=\left\langle rs\middle|f(r_{12})\middle|pq\right\rangle$$

Diagrammatic dRPA(F12) theory

- 1st F12 diagram added to the **conventional doubles amplitudes**:

$$g_{ic'}^{ak} f_{op}^{c'b} c_{kj}^{op}$$

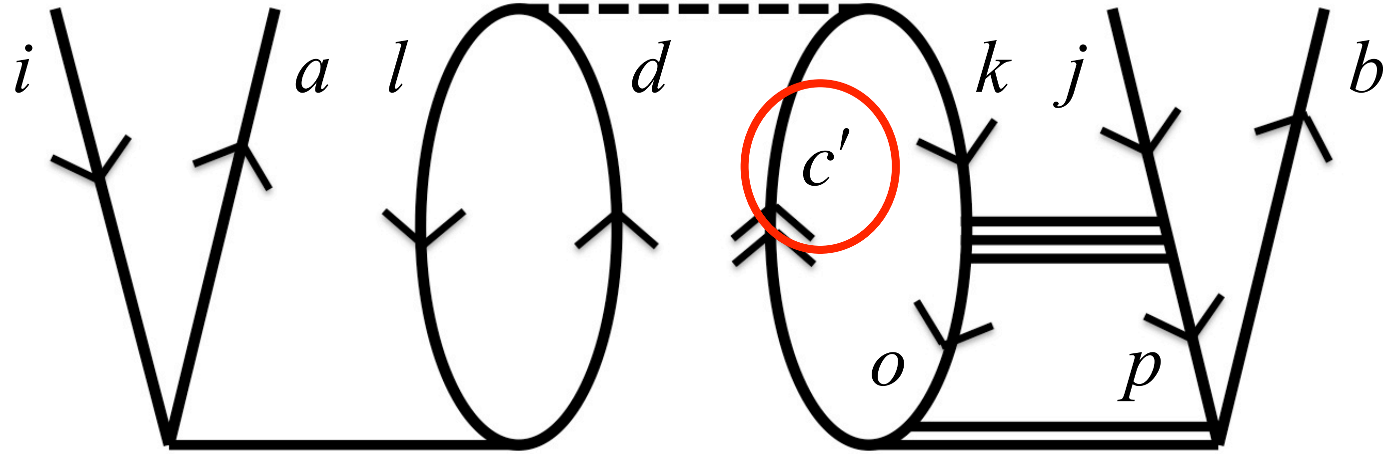


complementary auxiliary basis set

(diagram d4.8 in J. Noga and W. Kutzelnigg, *J. Chem. Phys*. **1994**, *101*, 7738)

Diagrammatic dRPA(F12) theory

- 2nd F12 diagram added to the **conventional doubles amplitudes**:

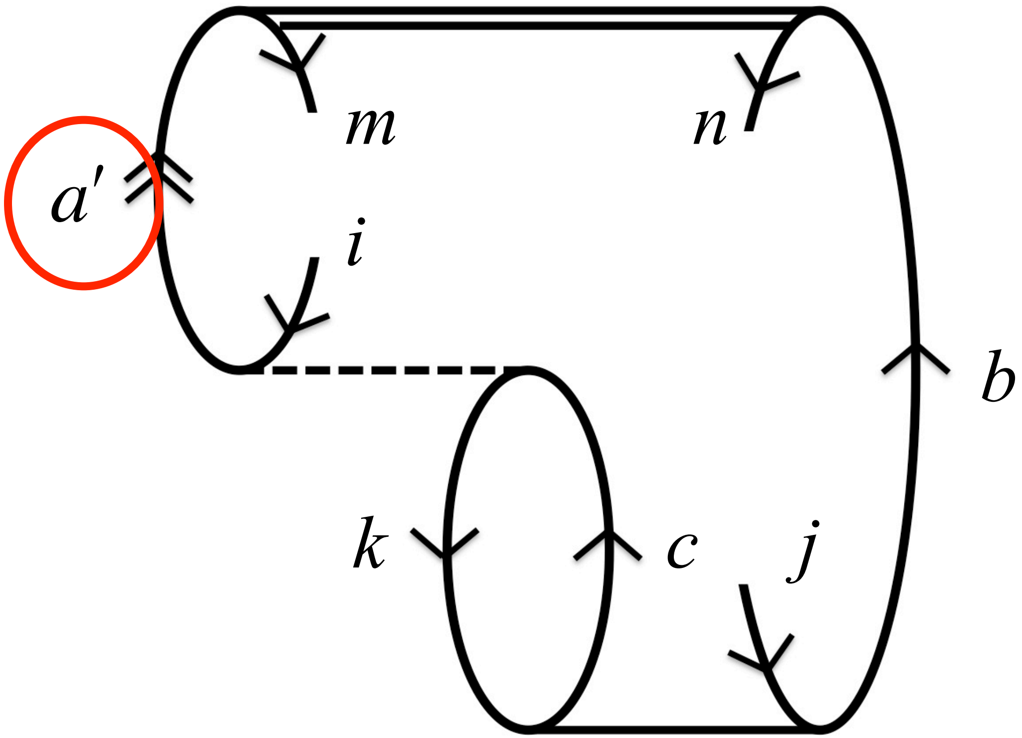


$$t_{il}^{ad}\, g_{dc'}^{lk}\, f_{op}^{c'b}\, c_{kj}^{op}$$

(diagram d4.12 in J. Noga and W. Kutzelnigg, *J. Chem. Phys*. **1994**, *101*, 7738)

Diagrammatic dRPA(F12) theory

- Diagram added to the **F12 amplitudes**:



$$f_{a'b}^{mn}\, g_{ic}^{a'k}\, t_{kj}^{cb}$$

(diagram d6.23 in J. Noga and W. Kutzelnigg, *J. Chem. Phys*. **1994**, *101*, 7738)

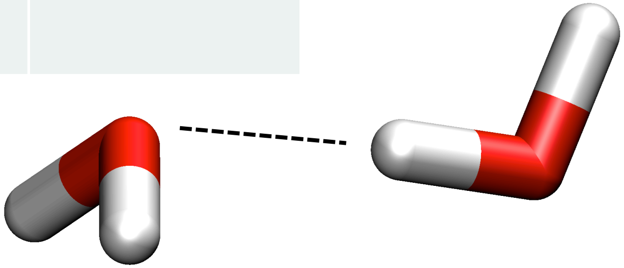
dRPA(F12) theory: The water dimer

Counterpoise (CP) corrected dRPA and **dRPA(F12)** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)

X	$\langle KS\|\hat{H}\|KS\rangle$	E^{C}_{dRPA}	$E^{C}_{\mathrm{dRPA(F12)}}$
2	−2.59	−0.77	**−1.58**
3	−2.60	−1.25	**−1.62**
4	−2.63	−1.46	**−1.63**
5	−2.63	−1.54	**−1.64**
6	−2.64	−1.58	
⋮	⋮	⋮	
∞	**−2.64**	**−1.64**	

aug-cc-pVXZ basis

PBE Kohn−Sham orbitals



CABS singles correction

- We have a complementary auxiliary basis set (CABS).
- How can single excitations into this CABS be included into the computation of the ground-state energy?

CABS singles correction in CCSD(F12) theory

- Singles amplitudes equation when an auxiliary basis is present:

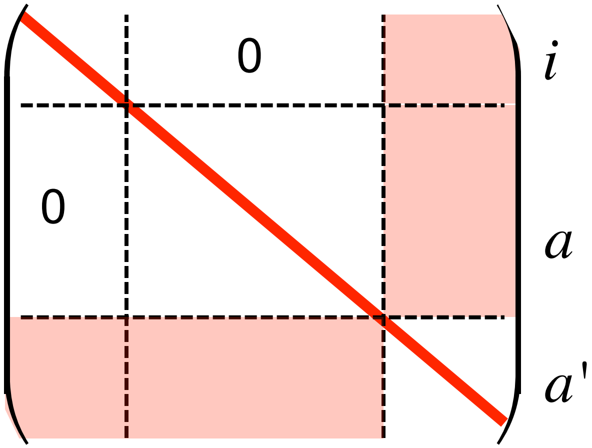
$$f_a^i + f_a^{b'} t_{b'}^i + \left(\varepsilon_a - \varepsilon_i\right) t_a^i = 0 \qquad \{a''\} = \{a\} \cup \{a'\}$$

$$f_{a'}^i + f_{a'}^{b'} t_{b'}^i + \left(\varepsilon_{a'} - \varepsilon_i\right) t_{a'}^i = 0$$

- The CABS singles correction is obtained from:

$$E_{\mathrm{CABS}} = f_i^a t_a^i + f_i^{a'} t_{a'}^i$$

Hartree−Fock matrix



CABS singles correction in dRPA(F12) theory

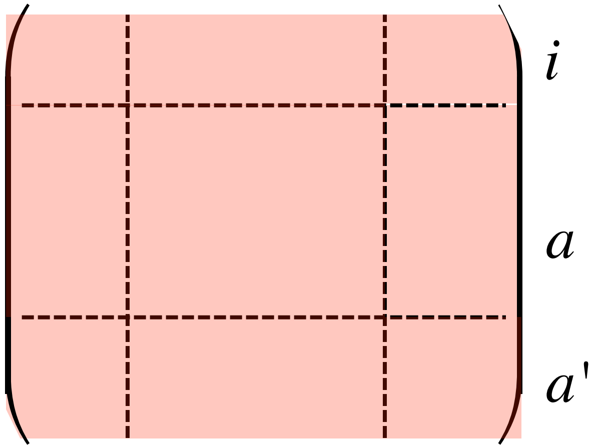
- Singles amplitudes equation when an auxiliary basis is present:

$$f_a^i + f_a^{b'} t_{b'}^i + \left(\varepsilon_a - \varepsilon_i\right) t_a^i = 0 \qquad \{a''\} = \{a\} \cup \{a'\}$$

$$f_{a'}^i + f_{a'}^{b'} t_{b'}^i + \left(\varepsilon_{a'} - \varepsilon_i\right) t_{a'}^i = 0$$

Kohn−Sham matrix

Hartree−Fock matrix



- The CABS singles correction is obtained from:

$$E_{\text{CABS}} = f_i^a t_a^i + f_i^{a'} t_{a'}^i$$

dRPA(F12) theory: The water dimer

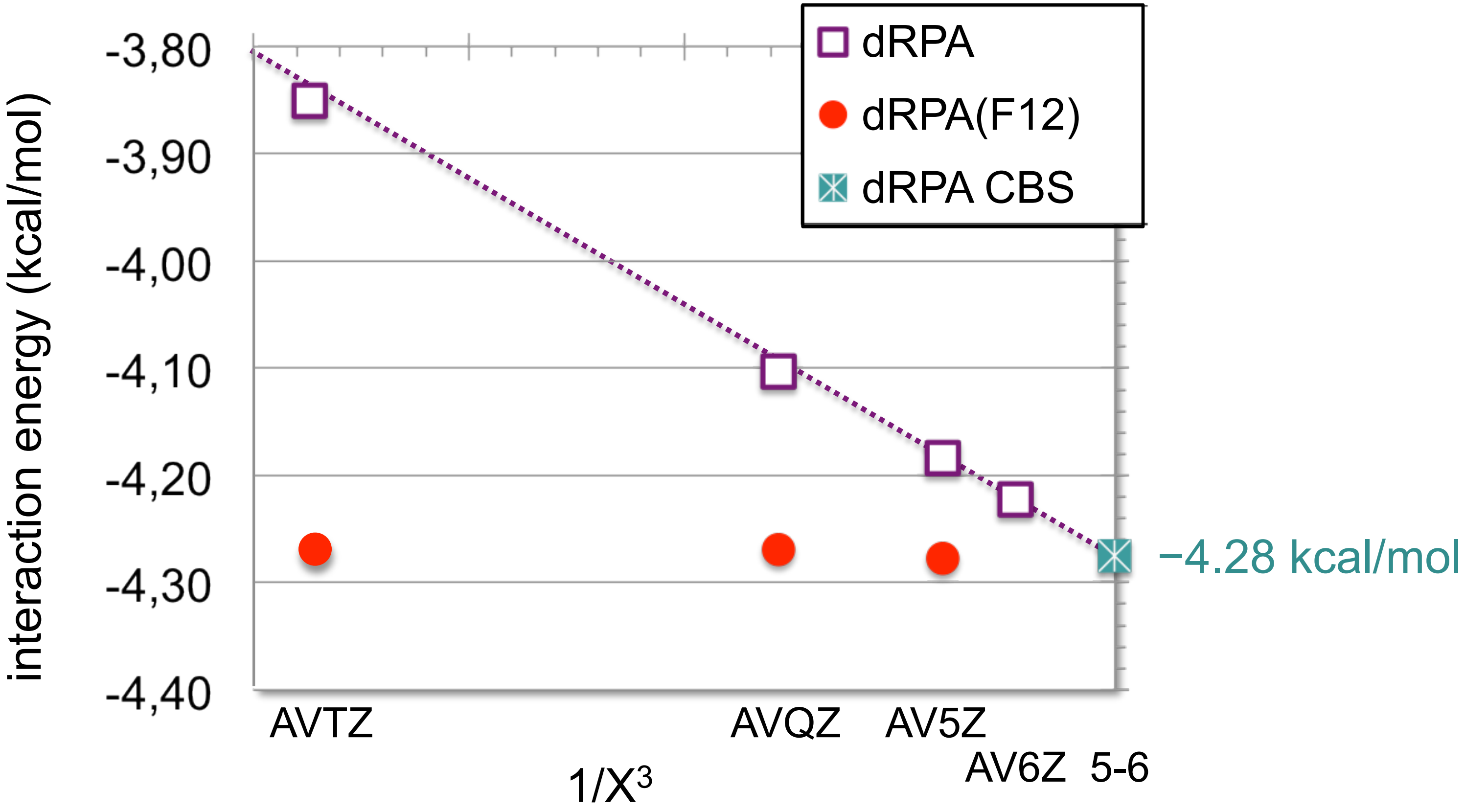
Counterpoise (CP) corrected dRPA and **dRPA(F12)** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)

Including a CABS singles correction to the expectation value

X	$\langle KS\vert\hat{H}\vert KS\rangle$ + CABS	E^{C}_{dRPA}	$E^{C}_{\text{dRPA(F12)}}$
2	−2.60	−0.77	**−1.58**
3	−2.63	−1.25	**−1.62**
4	−2.64	−1.46	**−1.63**
5	−2.64	−1.54	**−1.64**
6	−2.64	−1.58	
⋮	⋮	⋮	
∞	**−2.64**	**−1.64**	

dRPA(F12) theory: The water dimer

Counterpoise (CP) corrected dRPA and **dRPA(F12)** interaction energies (kcal/mol) for the water dimer (fixed geometry from the S22 test set)



Including exchange: The RPA(F12) method

- Why don’t we stop at the rCCD(F12) level?
- **Spin-flipped excitations must be accounted for.**
- **Hard to converge.**
- **Suffers from triplet instabilities.**

CCSD(F12)

↓ No single excitations

CCD(F12)

↓ Ring diagrams only

rCCD(F12) ≅ RPA(F12)

SO1 and SO2 approaches for closed shells

- In the 1970s, Szabo and Ostlund (SO) proposed to solve **singlet (*s*=1) and triplet (*s*=3) equations** (for closed-shell systems):

$$ {}^{s}\mathbf{B} + {}^{s}\mathbf{A}\,{}^{s}\mathbf{T} + {}^{s}\mathbf{T}\,{}^{s}\mathbf{A} + {}^{s}\mathbf{T}\,{}^{s}\mathbf{B}\,{}^{s}\mathbf{T} = \mathbf{0} $$

$$ {}^{1}A_{IJ}^{AB} = 2(AI\,|\,JB) - (AB\,|\,JI) $$

$$ {}^{1}B_{IJ}^{AB} = 2(AI\,|\,BJ) - (AJ\,|\,BI) $$

$$ {}^{3}A_{IJ}^{AB} = -(AB\,|\,JI) $$

$$ {}^{3}B_{IJ}^{AB} = -(AJ\,|\,BI) $$

A. Szabo and N. S. Ostlund, *J. Chem. Phys*. **67,** 4351 (1977).
A. Szabo and N. S. Ostlund, *Int. J. Quantum Chem*. **S11**, 389 (1977).

See also: B. Mussard, P. Reinhardt J. G. Ángyán, and J. Toulouse, *J. Chem. Phys*. **142**, 154123 (2015).

SO1 and SO2 approaches for closed shells

- In the 1970s, Szabo and Ostlund (SO) proposed to solve **singlet (*s*=1) and triplet (*s*=3) equations** (for closed-shell systems):

$$E_{\mathrm{rCCD}} = \frac{1}{4}\mathrm{tr}\left({}^{1}\mathbf{B}\,{}^{1}\mathbf{T} + 3\,{}^{3}\mathbf{B}\,{}^{3}\mathbf{T}\right)$$

$$E_{\mathrm{rCCD\text{-}SO1}} = \frac{1}{2}\mathrm{tr}\left({}^{1}\mathbf{B}({}^{1}\mathbf{T} - {}^{3}\mathbf{T})\right)$$

$$E_{\mathrm{rCCD\text{-}SO2}} = \frac{1}{2}\mathrm{tr}\left({}^{1}\mathbf{K}\,{}^{1}\mathbf{T}\right) \qquad \text{with} \quad {}^{1}K_{IJ}^{AB} = 2(AI\,|\,BJ)$$

SO1 and SO2 approaches for closed shells

- For the respective (F12) variants (using *fixed amplitudes*), we obtain:

$$E_{\text{rCCD(F12)-SO1}} = \frac{1}{2}\,\text{tr}\left({}^{1}\mathbf{B}({}^{1}\mathbf{T} - {}^{3}\mathbf{T})\right) + E_{\text{F12}}^{(2)} + \text{tr}\left({}^{1}\mathbf{L}\,{}^{1}\mathbf{T}\right)$$

$$E_{\text{rCCD(F12)-SO2}} = \frac{1}{2}\,\text{tr}\left({}^{1}\mathbf{K}\,{}^{1}\mathbf{T}\right) + E_{\text{F12}}^{(2)} + \text{tr}\left({}^{1}\mathbf{M}\,{}^{1}\mathbf{T}\right)$$

$${}^{1}L_{IJ}^{AB} = \sum_{KD'} {}^{1}A_{IK}^{AD'}\left({}^{1}F_{KJ}^{D'B} - {}^{3}F_{KJ}^{D'B}\right)$$

$${}^{1}M_{IJ}^{AB} = \sum_{KD'} \left({}^{1}A_{IK}^{AD'} - {}^{3}A_{IK}^{AD'}\right){}^{1}F_{KJ}^{D'B}$$

SO1 and SO2 approaches for closed shells

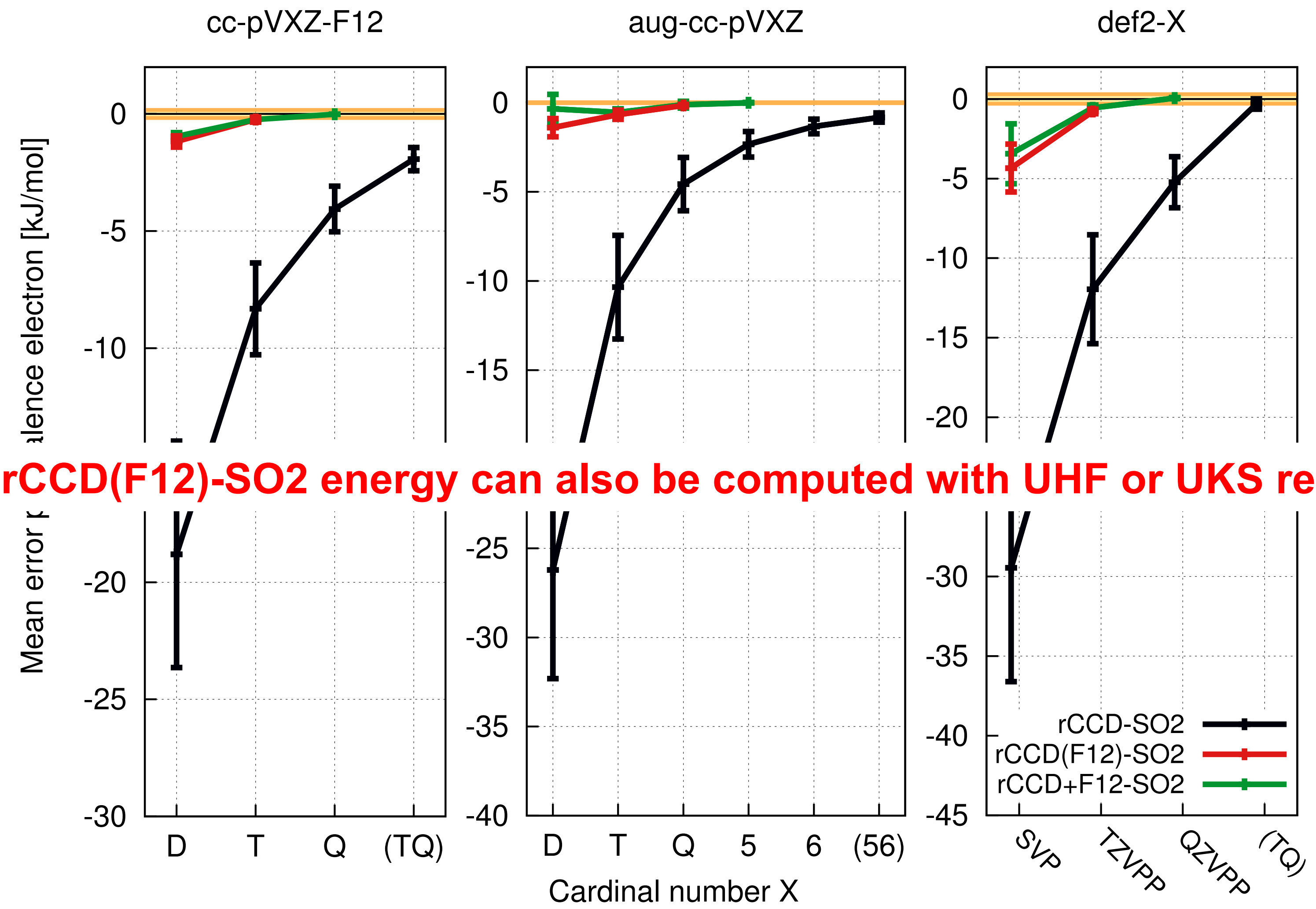
- The (F12) terms in the amplitudes equation (using *fixed F12 amplitudes* and *neglecting coupling terms*), are:

$$\mathbf{0} = {}^{s}\boldsymbol{\Omega}_{IJ}^{AB}(\text{conventional}) + {}^{s}\mathbf{Z} + {}^{s}\mathbf{T}\,{}^{s}\mathbf{Y} + \left({}^{s}\mathbf{Z} + {}^{s}\mathbf{T}\,{}^{s}\mathbf{Y}\right)^{\mathrm{T}}$$

$${}^{s}Y_{IJ}^{AB} = \sum_{KD'} {}^{s}B_{IK}^{AD'}\,{}^{s}F_{KJ}^{D'B}$$

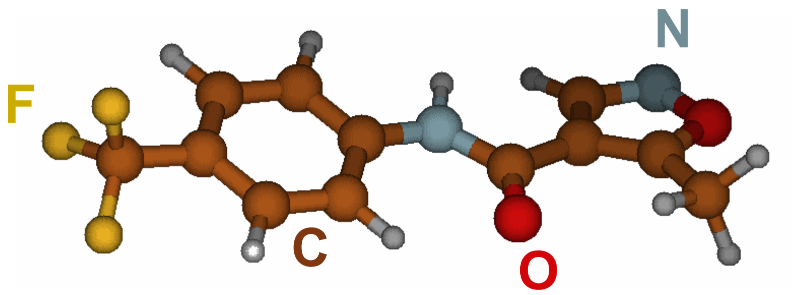
$${}^{s}Z_{IJ}^{AB} = \sum_{KD'} {}^{s}A_{IK}^{AD'}\,{}^{s}F_{KJ}^{D'B}$$

Atomization energies



The rCCD(F12)-SO2 energy can also be computed with UHF or UKS reference!

dRPA+F12 theory: Correlation energy (in E_h) of leflunomide

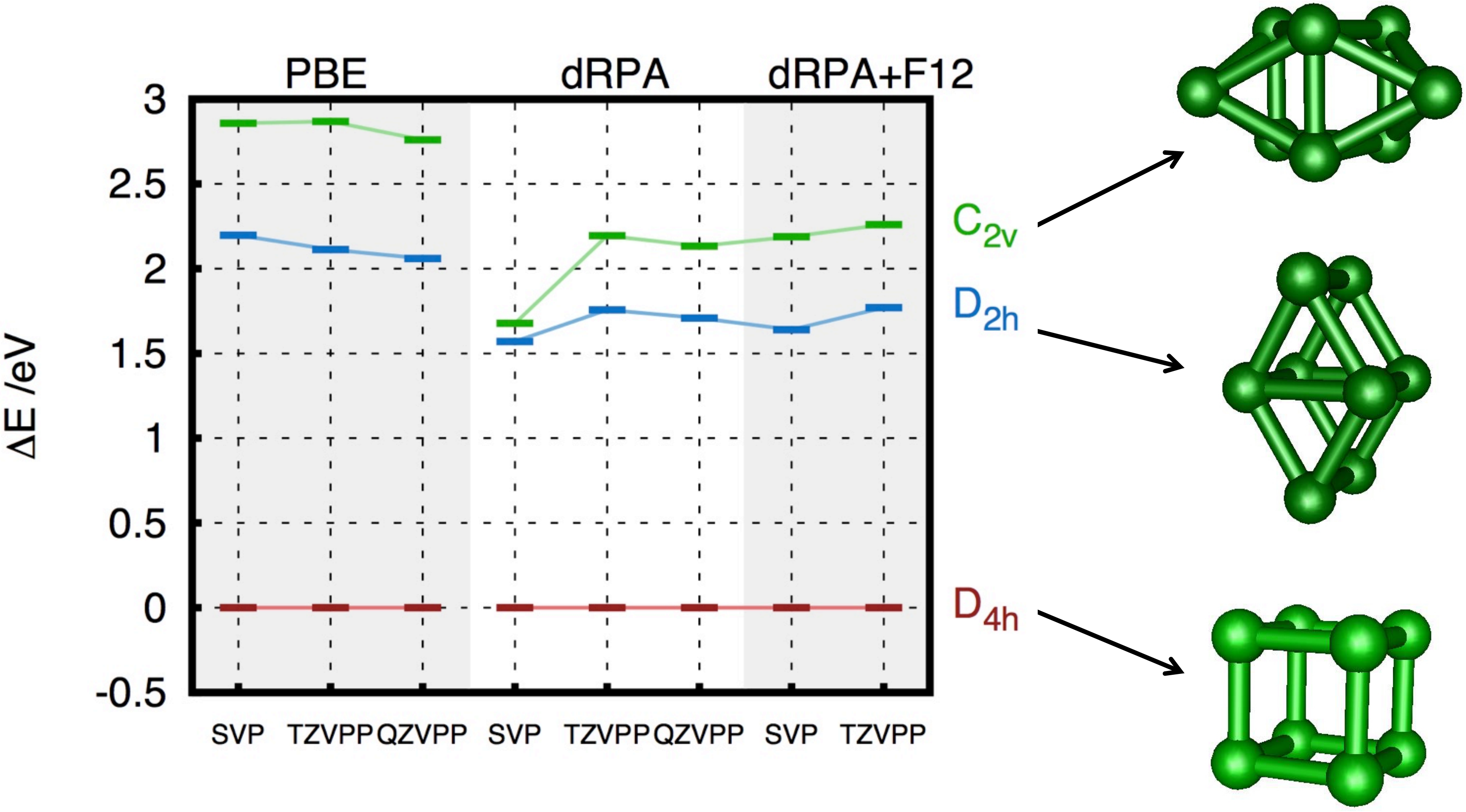


MP2/aug-cc-pVTZ
optimized equilibrium
geometry

Limit: −6.21(1) E_h

Basis	**Size**	$E^\mathrm{C}_\mathrm{dRPA}$	**%**	$E^\mathrm{C}_\mathrm{dRPA+F12}$	**%**
aug-cc-pVDZ	518	−4.426	71.3	−6.228	100.3
aug-cc-pVTZ	1081	−5.466	88.0	−6.186	99.6
aug-cc-pVQZ	1934	−5.858	94.3	−6.197	99.8
aug-cc-pV5Z	3133	−6.020	96.9	−6.202	99.9

dRPA+F12 theory:
Relative energies of Ru_8^- isomers



Conclusions

- The basis-set convergence of methods that compute the correlation energy in the random-phase approximation (RPA) can be accelerated using Slater-type geminals.
- This is not unexpected in view of the close relation to ring-coupled-cluster-doubles (rCCD) theory.
- It is not straightforward to account for exchange, however.
- In this respect, the rCCD(F12)-SO2 variant looks very promising.
- We plan to use the method for computations of interaction energies between ground-state systems.

Acknowledgments

David P.
Tew

Anna-Sophia
Hehn

Christof
Holzer

- *Chem. Phys. Lett.* **2011**, *510*, 147
- *J. Chem. Phys.* **2013**, *138*, 181104
- *J. Chem. Phys.* **2015**, *142*, 194106
- *Chem. Phys.* **2016**, *479*, 160

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