

Application of RPA and Beyond-RPA methods to the A24 and S22 Test Sets

Julien Claudot, Anant Dixit, Sébastien Lebègue, and Dario Rocca
 Université de Lorraine and CNRS, CRM² Laboratory, Vandoeuvre-lès-Nancy, France



The adiabatic connection fluctuation dissipation theorem (ACFDT) is a powerful theoretical framework to determine the Exchange-Correlation (xc) energy functional of DFT. Within the context of the ACFDT, it was shown that the dielectric matrix formulation, which is usually applied to calculate the random phase approximation (RPA) correlation energy, can be used for alternative RPA expressions including exchange effects. By using an approximate electron-hole exchange kernel two approximations were derived: An adiabatic connection analog of the second order screened exchange (AC-SOSEX) and the electron-hole time-dependent Hartree-Fock (eh-TDHF)[1]. It has been shown that this formalism is suitable for an efficient implementation within the plane-wave basis set[2].

This work introduces a new version of the code that optimizes the number of basis vectors involved in the response functions calculations. This is achieved by Gram-Schmidt orthogonalization and elimination of the linearly dependent vectors. The A24 test set, composed mostly of small dimers, is used to test the numerical accuracy of this procedure against the original implementation. This new efficient approach with Gram-Schmidt orthogonalization will then be used to compute the binding energies in the S22 test set, which involves weakly bound dimers with up to about 100 valence electrons.

Correlation Energies within ACFDT[2]

Within the adiabatic connection fluctuation dissipation theorem,

$$E_c^{ACFDT} = -\frac{1}{2} \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr} [\tilde{\Pi}^\lambda(i\omega) \tilde{K} - \tilde{\Pi}^0(i\omega) \tilde{K}]$$

$$\tilde{\Pi}_{\text{RPA}}^\lambda(i\omega) = (\tilde{I} - \lambda \tilde{\Pi}^0(i\omega) \tilde{K})^{-1} \tilde{\Pi}^0(i\omega),$$

Approximations for $\tilde{\Pi}_{\text{RPA}}^\lambda$:

- Random Phase Approximation (RPA) is the most used

$$\mathbb{F} = \mathbb{G} = \mathbb{V} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}, \quad K_{v_c, v'_c} = 2 \langle \phi_v \phi_c | V | \phi_{v'} \phi_{c'} \rangle$$

$$E_c^{\text{RPA}} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \{ \log(\mathbf{I} - \Pi_0(i\omega) \mathbf{K}) + \Pi_0 \mathbf{K} \}$$

Approximations beyond the RPA can be obtained by introducing an approximation in the exchange kernel [1, 2]:

$$\tilde{\mathbb{E}} = \tilde{\mathbb{B}} + (\tilde{\mathbb{E}} - \tilde{\mathbb{B}}) = \begin{pmatrix} \mathbf{B} & \mathbf{B} \\ \mathbf{B} & \mathbf{B} \end{pmatrix} + \begin{pmatrix} \mathbf{A} - \mathbf{B} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} - \mathbf{B} \end{pmatrix} \approx \begin{pmatrix} \mathbf{B} & \mathbf{B} \\ \mathbf{B} & \mathbf{B} \end{pmatrix}$$

$$A_{v_c, v'_c} = 2 \langle \phi_v \phi_c | V | \phi_{v'} \phi_{c'} \rangle - \langle \phi_v \phi_{v'} | V | \phi_c \phi_{c'} \rangle$$

$$B_{v_c, v'_c} = 2 \langle \phi_v \phi_c | V | \phi_{v'} \phi_{c'} \rangle - \langle \phi_v \phi_{c'} | V | \phi_{v'} \phi_c \rangle.$$

- Adiabatic Connection Second Order Screened Exchange (AC-SOSEX)

$$\mathbb{F} = \mathbb{V} \text{ and } \mathbb{G} = \mathbb{W} \quad \Rightarrow \quad E_c^{\text{AC-SOSEX}} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \{ \log(\mathbf{I} - \Pi_0(i\omega) \mathbf{K}) \mathbf{K}^{-1} \mathbf{B} + \Pi_0 \mathbf{B} \}$$

- Electron-Hole Time-Dependent Hartree-Fock (eh-TDHF)

$$\mathbb{F} = \mathbb{W} \text{ and } \mathbb{G} = \mathbb{V} \quad \Rightarrow \quad E_c^{\text{eh-TDHF}} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \{ \log(\mathbf{I} - \Pi_0(i\omega) \mathbf{B}) \mathbf{B}^{-1} \mathbf{K} + \Pi_0 \mathbf{K} \}$$

Implementation Details

Using an auxiliary basis set $\Phi_Q(\mathbf{r})$ to more compactly represent the dielectric matrix, the RPA correlation energy requires evaluation of matrix elements of the type:

$$C_{QR}(i\omega) = 4 \sum_v \langle U_Q^v | \mathcal{R}(i\omega + \epsilon_v - \hat{H})^{-1} | U_R^v \rangle$$

$$\text{with } |U_G^v\rangle = \hat{P} V^{\frac{1}{2}} \Phi_G | \phi_v \rangle$$

Beyond-RPA methods require additional terms such as,

$$J_{QG}^{vv'}(i\omega) = 2 \langle U_Q^v | \mathcal{R}(i\omega + \epsilon_v - \hat{H})^{-1} | U_G^{v'} \rangle$$

Inclusion of different occupied states v and v' are the reason for the higher numerical complexity of Beyond-RPA methods.

To overcome this difficulties

- Reduce the large number of right and left vectors by applying a Gram-Schmidt orthogonalization procedure

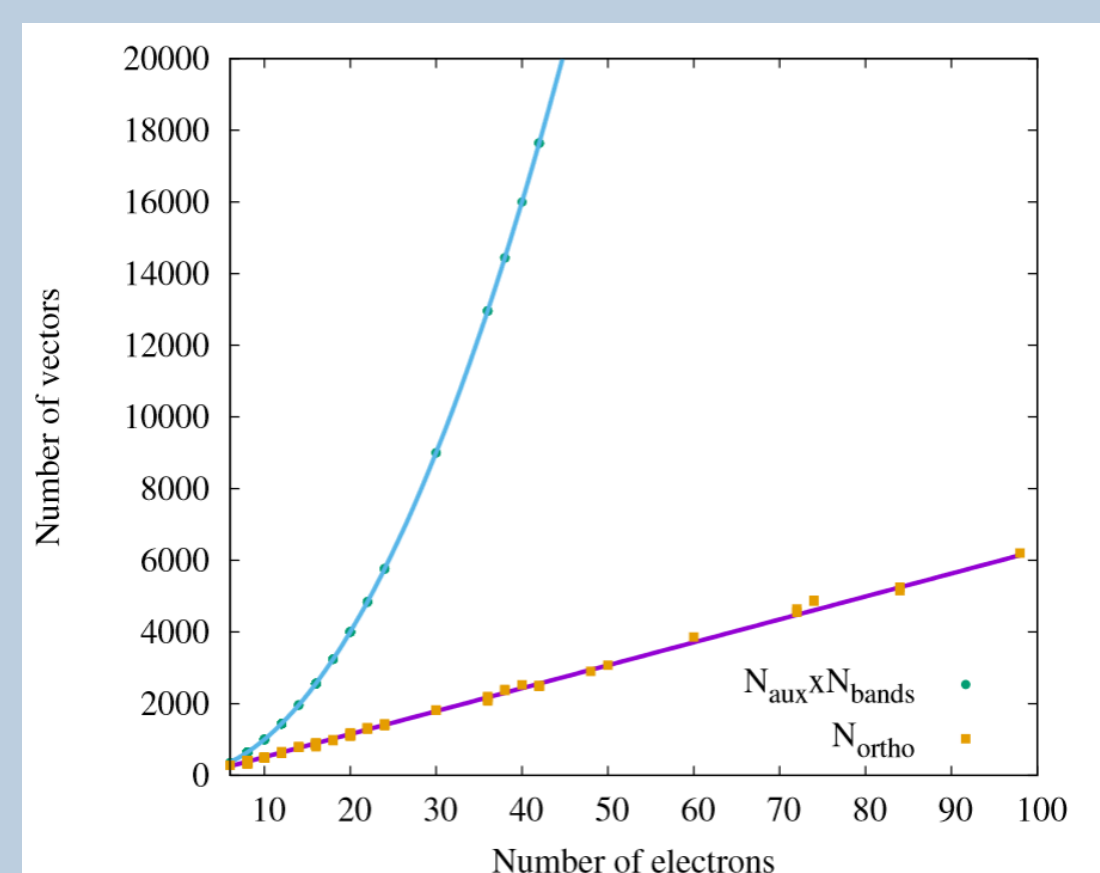
$$|O_1\rangle = |U_1^1\rangle / N_1$$

$$|O_2\rangle = [|U_1^2\rangle - \langle U_1^2 | O_1 \rangle |O_1\rangle] / N_2$$

...

$$|O_{N_{aux} \times N_v}\rangle = \left[|U_{N_{aux}}^{N_v}\rangle - \sum_{i=1}^{N_{aux} \times N_v} \langle U_{N_{aux}}^{N_v} | O_i \rangle |O_i\rangle \right] / N_{N_{aux} \times N_v},$$

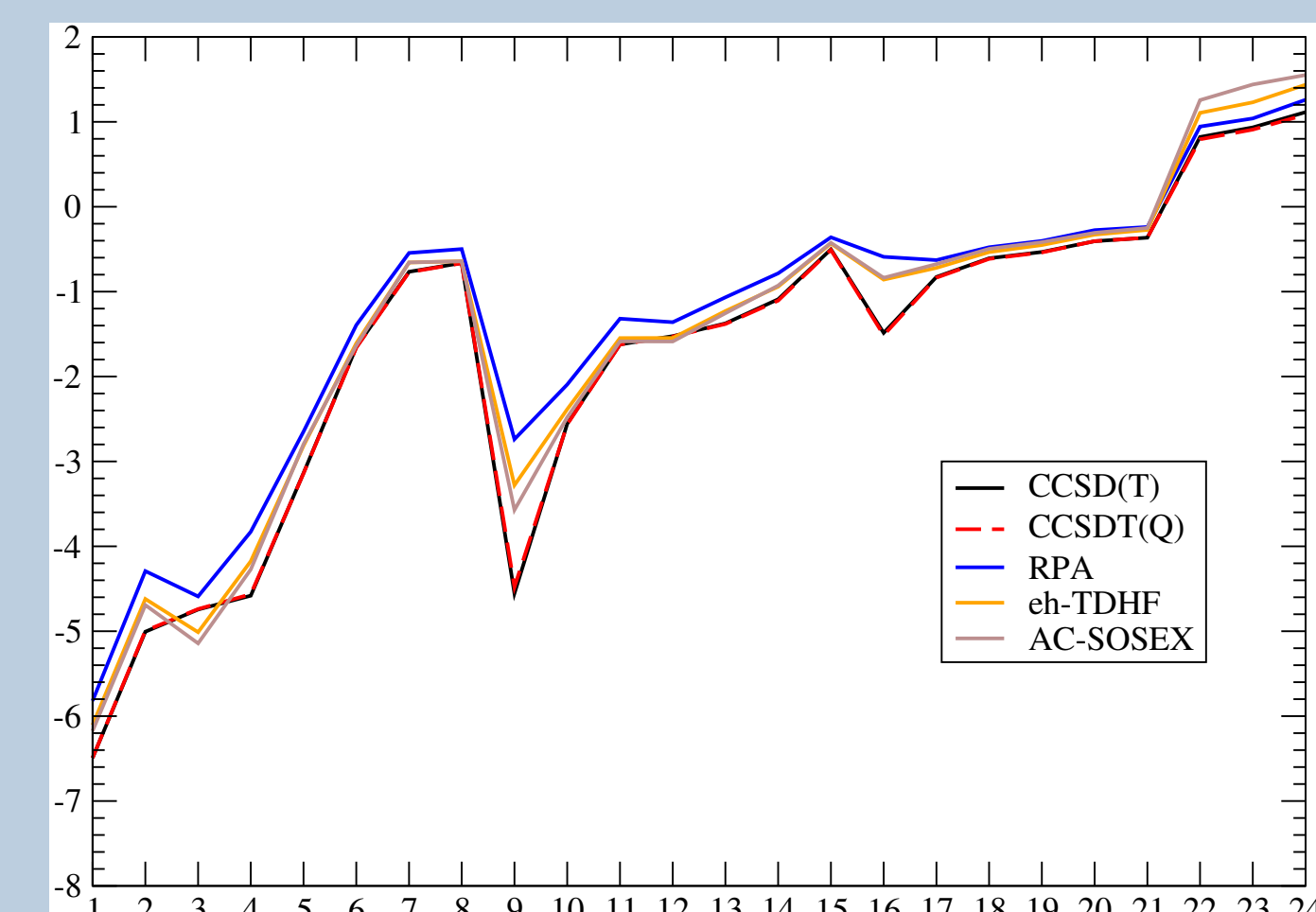
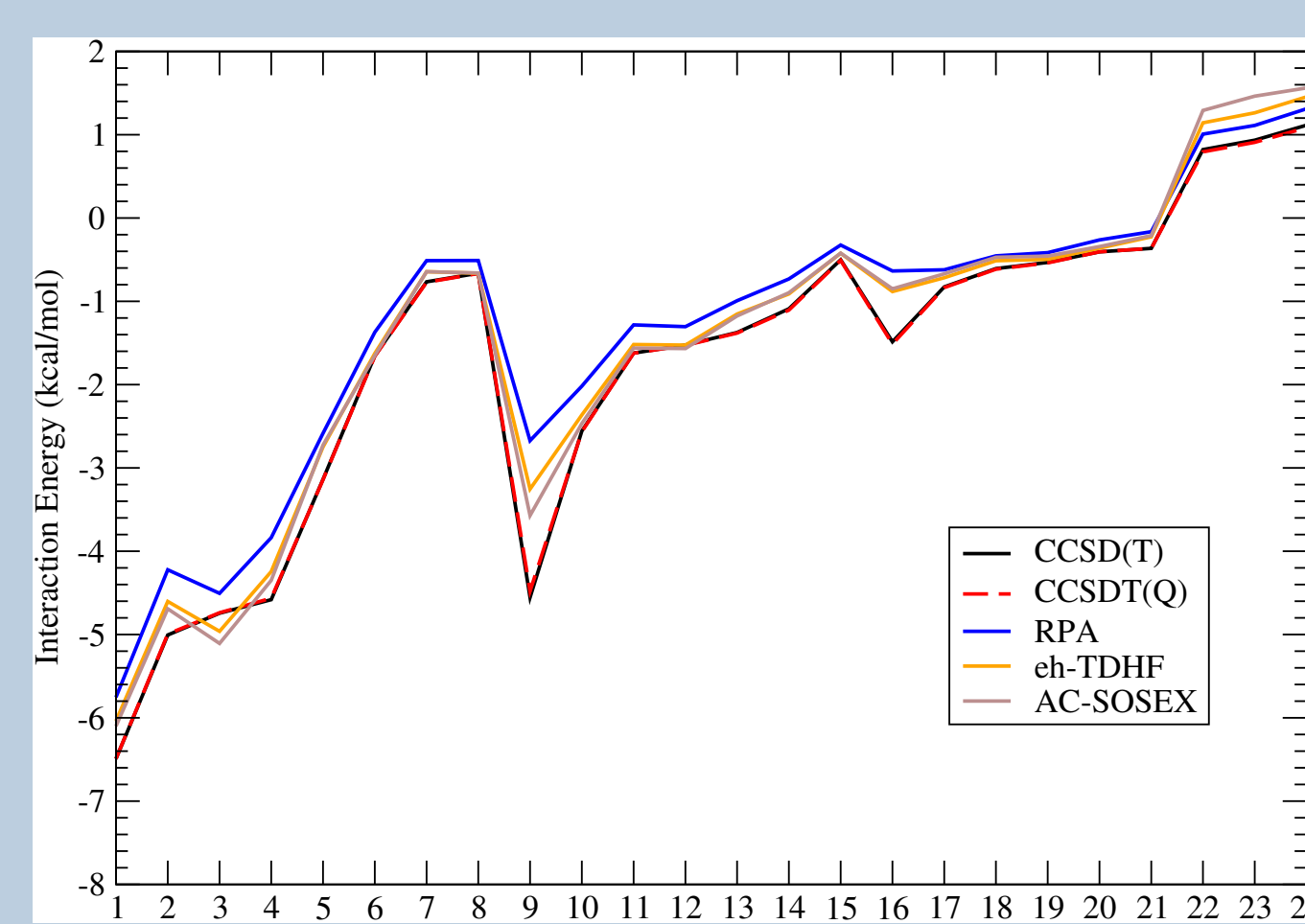
- If a certain $|O_n\rangle$ is linearly dependent to all previous ones ($|O_1\rangle, \dots, |O_{n-1}\rangle$) then it does not need to be included in the orthonormalized basis set.



A24 Test Set[3]

Version with Re-orthogonalization

Original Version



1. Water... Ammonia
2. Water... Water
3. HCN... HCN
4. HF... HF
5. Ammonia... Ammonia
6. Methane... HF
7. Ammonia... Methane
8. Methane... Water

9. Formaldehyde... Formaldehyde
10. Ethene... Water
11. Ethene... Formaldehyde
12. Ethyne... Ethyne (C2v)
13. Ethene... Ammonia
14. Ethene... Ethene (C2v)
15. Methane... Ethene
16. Borane... Methane

17. Methane... Ethane
18. Methane... Ethane
19. Methane... Methane
20. Methane... Ar
21. Ethene... Ar
22. Ethene... Ethyne
23. Ethene... Ethene (D2h)
24. Ethyne... Ethyne (D2h)

	CCSD(T)	RPA	Original-version eh-TDHF	AC-SOSEX	Orthogonalized-version RPA	eh-TDHF	AC-SOSEX
MAE	0.013	0.375	0.246	0.252	0.415	0.256	0.260
ME	-0.004	-0.375	-0.221	-0.213	-0.415	-0.237	-0.226
[MAX]	0.075	1.740	1.199	0.908	1.805	1.224	0.907

→ Good agreement with CCSD(T) for both versions
 → MAE (kcal/mol) between two versions: 0.047 (RPA), 0.033 (eh-TDHF), 0.029 (AC-SOSEX)

S22 Test Set[4]

System	CCSD(T)	RPA	eh-TDHF	AC-SOSEX
Hydrogen-bonded systems				
1 ammonia dimer	-3.17	-2.54	-2.72	-2.71
2 water dimer	-5.02	-4.20	-4.58	-4.65
3 formic acid dimer	-18.80	-17.05	-18.24	-18.60
4 formamide dimer	-16.12	-14.75	-15.57	-15.71
5 uracil dimer (c2h)	-20.69	-18.78	-20.32	-21.02
6 2-pyridoxine... 2-aminopyridine	-17.00	-15.78	-16.46	-16.61
7 adenine... thymine (WC)	-16.74	<i>in progress</i>	<i>in progress</i>	<i>in progress</i>
Mixed-type systems				
8 methane dimer	-0.53	-0.47	-0.52	-0.48
9 ethene dimer	-1.50	-1.15	-1.33	-1.31
10 benzene... methane	-1.45	<i>in progress</i>	<i>in progress</i>	<i>in progress</i>
11 benzene dimer	-2.62	<i>in progress</i>	<i>in progress</i>	<i>in progress</i>
12 pyrazine dimer	-4.20	-3.40	-3.39	-3.24
13 uracil dimer	-9.74	-8.61	-9.11	-9.26
14 indole... benzene (stack)	-4.59	-3.41	-3.35	-3.19
15 adenine... thymine (stack)	-11.66	-10.36	-10.59	-10.62
Dispersion-dominated systems				
16 ethene... ethene	-1.51	-1.29	-1.50	-1.57
17 benzene... water	-3.29	-2.89	-3.10	-3.10
18 benzene... ammonia	-2.32	-1.91	-2.07	-2.06
19 benzene... hydrogen cyanide	-4.55	-4.03	-4.49	-4.61
20 benzene dimer	-2.71	-2.31	-2.45	-2.42
21 indole... benzene (T-shape)	-5.62	<i>in progress</i>	<i>in progress</i>	<i>in progress</i>
22 phenol dimer	-7.09	-6.31	-6.76	-6.79
MAE		0.847	0.441	0.437
ME		-0.06	-0.01	-0.05
[MAX]		1.91	1.24	1.4

Good agreement of Beyond-RPA methods with CCSD(T) methods.

Further Reading

- [1] B. Mussard, D. Rocca, G. Jansen, and J. Ángyán. *JCTC*, 12:2191, 2016.
- [2] A. Dixit, J. Ángyán, and D. Rocca. *JCP*, 145:104105, 2016.
- [3] J. Řezáč and P. Hobza. *J. Chem. Theory Comput.*, 9:2151, 2013.
- [4] P. Jurečka, J. Šponer, J. Černý, and P. Hobza. *Phys. Chem. Chem. Phys.*, 8:1985, 2006.

Funding

Work supported by Agence Nationale de la Recherche under grant number ANR-15-CE29-0003-01.

Computation resources using GENCI-CCRT/CINES under grant x2017-085106 and the DECI resource ARCHER (United Kingdom) with support from the PRACE aisbl.