

# Dielectric matrix formulation of correlation energies in the RPA: Inclusion of exchange effects

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# Objective: Developing accurate methods for the electronic correlation within a solid state code based on plane-waves (PWs)

Characteristics of the plane-wave basis set:

- ✓ Large basis set whose convergence can be systematically improved by increasing a single parameter, the kinetic energy cut-off: In principle no need for complete basis set extrapolation.
- ✓ No basis set superposition error.
- ✓ Straightforward treatment of molecules and solids within the same framework.
- x Because of the large size of this basis set the applicability of “quantum chemical” methods is numerically challenging.
- x The information contained in the PW basis set is redundant (especially for molecules or low dimensional systems).
- x Explicit inclusion of core electrons is problematic and pseudopotentials or PAW are routinely used.

# Outline

- ❑ Introduction
- ❑ Improving the efficiency of (direct) RPA calculations within a PW basis set implementation
- ❑ Applications to molecules and solids
- ❑ Improving the accuracy of RPA including exchange effects: The AC-SOSEX and eh-TDHF methods
- ❑ Applications to reaction energies and weakly bound dimers
- ❑ Extension of the methodology to MP2
- ❑ Conclusions

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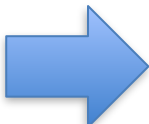
## ❑ Introduction

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# Correlation energy within the adiabatic connection fluctuation and dissipation theorem (ACFDT)

$$E_c^{\text{ACFDT}} = -\frac{1}{2\pi} \int_0^1 d\lambda \int_0^\infty du \text{Tr} \{ \chi_\lambda(iu) V - \chi_0(iu) V \}$$

$\chi_0$   Independent-electron polarizability

$\chi_\lambda$   Polarizability of a fictitious system whose electrons interact with a scaled Coulomb potential  $\lambda v_c$

# (direct) Random-phase approximation (RPA)

TDDFT or Bethe-Salpeter Equation

$$\chi_\lambda(iu) = (I - \lambda \chi_0(iu) \Xi)^{-1} \chi_0(iu)$$

with a kernel that contains the Hartree contribution only

$$\Xi = V = \begin{pmatrix} V & V \\ V & V \end{pmatrix}$$

$$V_{vc,v'c'} = 2 \langle \phi_v \phi_c | v_c | \phi_{v'} \phi_{c'} \rangle$$



After analytical integration over  $\lambda$  the correlation energy becomes

$$E_c^{\text{RPA}} = \frac{1}{2\pi} \int_0^\infty du \text{Tr} \{ \ln(I - \chi_0(iu)V) + \chi_0(iu)V \}$$

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# Challenges in the numerical calculation of RPA correlation energies

$$E_c^{\text{RPA}} = \frac{1}{2\pi} \int_0^\infty du \text{Tr} \{ \ln(I - \chi_0(iu)V) + \chi_0(iu)V \}$$

$$\chi_0(\mathbf{r}, \mathbf{r}', iu) = 4\text{Re} \sum_{cv} \frac{\phi_v(\mathbf{r})\phi_c(\mathbf{r})\phi_c(\mathbf{r}')\phi_v(\mathbf{r}')}{iu + \epsilon_v - \epsilon_c}$$

**v valence states**  
**c conduction states**

- ❑ To evaluate  $\chi_0$  it is necessary to compute several conduction states  $\phi_c$ . Convergence is slow with respect to this parameter.
- ❑ It is necessary to compute an integral between 0 and  $+\infty$ .
- ❑ It is necessary to store in memory and compute the logarithm of the large matrix  $\chi_0$ .



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**RESUMMATION AND  
ELIMINATION OF THE EMPTY  
STATES (STERNHEIMER-DFPT)**

❑ It is necessary to compute an integral between 0 and  $+\infty$ . →

**LANCZOS ALGORITHM**

❑ It is necessary to store in memory and compute the logarithm of the large matrix  $\chi_0$ . →

**OPTIMAL AUXILIARY  
BASIS SET**

# Construction of the optimal basis set: A few observations

Let us consider the static response function ( $i\omega=0$ )

$$\begin{aligned}\chi_{ij} &= \int U_i(\mathbf{r})\chi_0(\mathbf{r}, \mathbf{r}')U_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \\ &= 4\text{Re} \sum_{cv} \frac{\langle \phi_v | U_i | \phi_c \rangle \langle \phi_c | U_j | \phi_v \rangle}{\epsilon_v - \epsilon_c}\end{aligned}$$

The basis set elements needs to accurately represent the products

$$\phi_v(\mathbf{r})\phi_c(\mathbf{r})$$

The products of valence (v) and conduction (c) states have a strong linear dependence

keeping into account the weight

$$\frac{1}{\epsilon_v - \epsilon_c}$$

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Important Contribution!!!

$$\phi_{HOMO}(\mathbf{r})\phi_{LUMO}(\mathbf{r})$$

$$\frac{1}{\epsilon_{HOMO} - \epsilon_{LUMO}}$$

Small contribution (because of the weight)

$$\phi_{HOMO}(\mathbf{r})\phi_{LUMO+50000}(\mathbf{r})$$

Just an example

$$\frac{1}{\epsilon_{HOMO} - \epsilon_{LUMO+50000}} \approx 0$$

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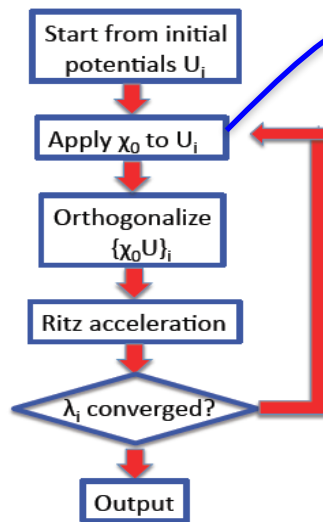
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Just an example

$$\frac{1}{\epsilon_{HOMO} - \epsilon_{LUMO+50000}} \approx 0$$

kinetic energy only

# Construction of the optimal basis set by iterative diagonalization of a $\chi_0$ containing **only the kinetic energy term**



$$\begin{aligned}
 \chi_0 \cdot U_j &= \int \chi_0(\mathbf{r}, \mathbf{r}', iu) U_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\
 &= 4Re \sum_{cv} \frac{\phi_v(\mathbf{r}) \phi_c(\mathbf{r}) \langle \phi_c | U_j | \phi_v \rangle}{\epsilon_v - \epsilon_c} \\
 &= 4Re \sum_v \phi_v(\mathbf{r}) \hat{Q}(\mathbf{r}) (\epsilon_v - \hat{H})^{-1} \hat{Q}(\mathbf{r}) | U_j \phi_v \rangle \\
 &\approx 4Re \sum_v \phi_v(\mathbf{r}) \hat{Q}(\mathbf{r}) (\epsilon_v + \boxed{\nabla^2/2})^{-1} \hat{Q}(\mathbf{r}) | U_j \phi_v \rangle
 \end{aligned}$$

**KINETIC ENERGY ONLY**

- ❑ This procedure takes advantage of the **low-rank** of  $\chi_0$ . This is a consequence of the linear dependence of valence-conduction state products and of the presence of the energy weight at the denominator.
- ❑ The kinetic energy is **diagonal** in reciprocal space (proportional to  $G^2$ ) and the inverse is easily computed.
- ❑ The kinetic energy approximation is used only to compute the optimal basis set, which is then used to compute the matrix elements of the “exact”  $\chi_0$  through the Lanczos algorithm.
- ❑ This auxiliary basis set allows for a **fast convergence of the eigenvalues** of the “exact”  $\chi_0$
- ❑ This approach is a numerically efficient approximation of the **projective dielectric eigenpotential** method (Wilson, Gygi, and Galli, PRB 2008; Lu, Li, Rocca, and Galli, PRL 2009).

# Implementation

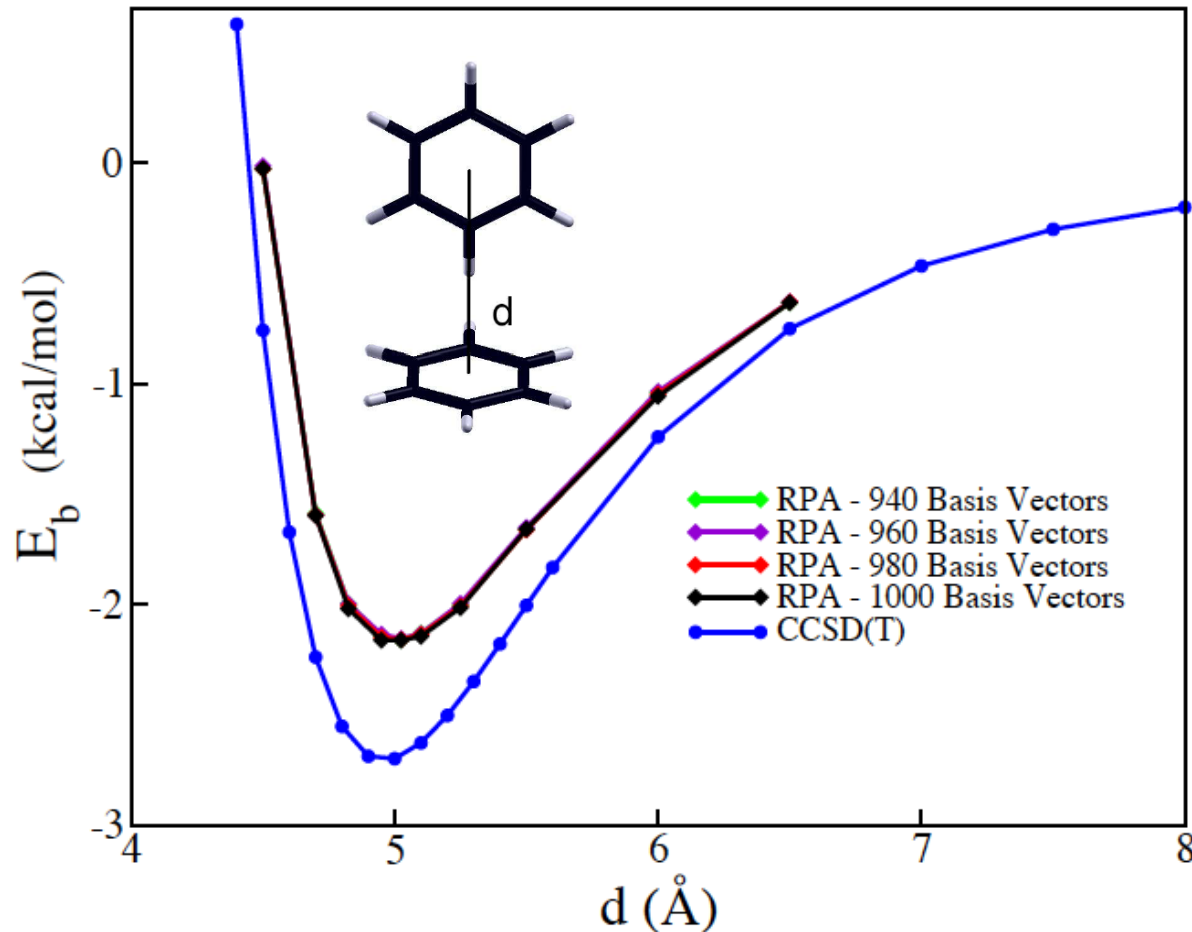
- ❑ The following numerical applications use dielectric matrix-based methods implemented within the QUANTUM ESPRESSO package, that uses plane-waves and pseudopotentials
- ❑ Density functional theory orbitals and energies are used to build dielectric matrices (LDA or GGA approximation)



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# Application of the RPA to the weakly bound benzene dimer



- ❑ 60 Ry cut-off
- ❑ 165000 plane-waves for the wavefunctions
- ❑ 1.3 millions of PWs for the charge/potential
- ❑ Curves are shown for different sizes of the optimal basis set: Only 1000 basis vectors are sufficient to converge
- ❑ RPA gives the correct equilibrium distance and 80% of the coupled cluster binding energy

D. Rocca, J. Chem. Phys. (2014), special issue Advances in DFT Methodology



# Applications to solids: Lattice parameters and bulk moduli (in parenthesis)

	<b>Covalent bonds</b>			<b>vdW interactions</b>		
<i>Method</i>	Si	C	SiC	Ar	Kr	Ne
LDA	10.20 (92.10)	6.67 (449.7)	8.21 (216.1)	9.32 (6.71)	10.09 (6.15)	7.27 (8.25)
<b>RPA@LDA</b>	<b>10.11 (102.1)</b>	<b>6.68 (441.1)</b>	<b>8.17 (222.4)</b>	<b>10.23 (1.58)</b>	<b>10.83 (2.24)</b>	<b>8.97 (0.26)</b>
GGA	10.33 (85.70)	6.73 (416.2)	8.26 (204.4)	11.22 (0.70)	12.12 (0.61)	8.69 (1.17)
<b>RPA@GGA</b>	<b>10.21 (97.30)</b>	<b>6.73 (417.0)</b>	<b>8.21 (215.0)</b>	<b>10.00 (2.79)</b>	<b>10.72 (2.98)</b>	<b>8.18 (1.47)</b>
Experiment	10.26 (99.00)	6.74 (443.0)	8.24 (225.0)	10.04 (2.66)	10.60 (3.34)	8.22 (0.99)

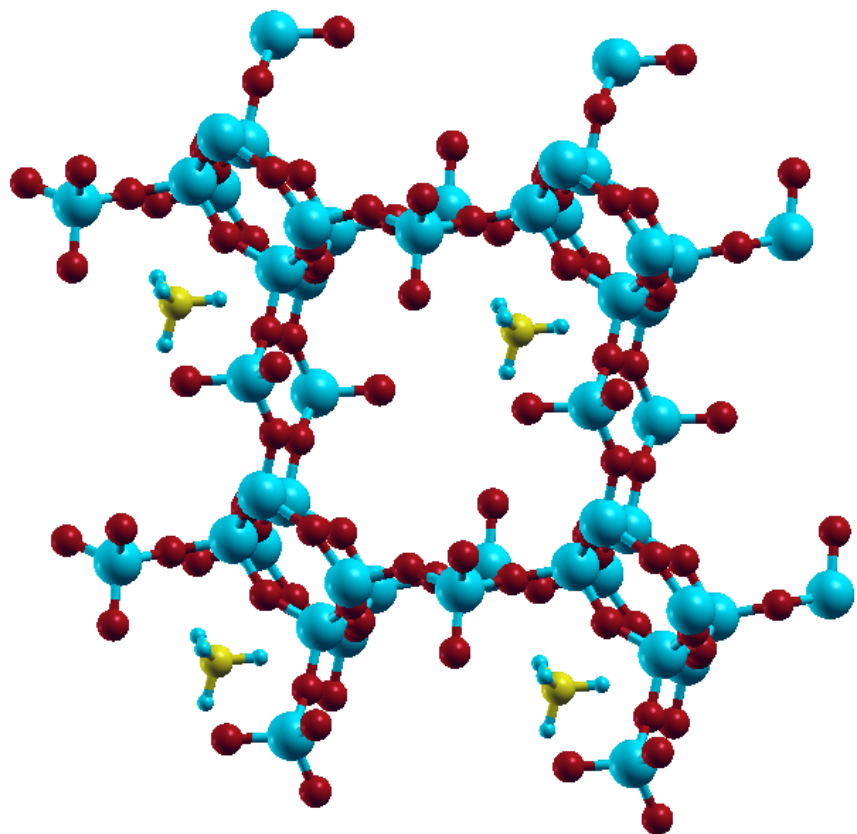
**The RPA preserves the accuracy of traditional DFT methods for covalent solids while is significantly more reliable for weakly interacting solids**

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**The RPA based on GGA gives very accurate results for all the solids considered**

# Application of the RPA to compute molecular adsorption energies in zeolites (work in progress)



- ❑ Adsorption of  $\text{CH}_4$  and  $\text{CO}_2$  on chabazite
- ❑ Periodic model with 200 electrons per unit cell
- ❑ Preliminary results at 0K (see table)
- ❑ In order to introduce temperature effects we are performing single-shot RPA calculations on different configurations generated by molecular dynamics

Molecule adsorbed	PBE	RPA	Exp. (300K)
Methane	+1.60 kJ/mol	-10.99 kJ/mol	n.a.
Carbon dioxide	-1.36 kJ/mol	-18.17 kJ/mol	-22.5 kJ/mol

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# Improving over the RPA: Time-dependent Hartree Fock (TDHF)

## Bethe-Salpeter Equation

$$\chi_\lambda(iu) = (I - \lambda \chi_0(iu) \Xi)^{-1} \chi_0(iu)$$

with a kernel that contains the Hartree and exchange contributions

$$\Xi = \begin{pmatrix} A & B \\ B & A \end{pmatrix}$$

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

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



- ❑ Expression of the correlation energy hard to simplify
- ❑ It is not possible to take advantage of techniques to eliminate conduction states and to compactly represent response functions

# A practical approximation: The electron-hole (eh) exchange kernel

The exchange kernel can be split in two parts

$$\mathbf{E} = \begin{pmatrix} A & B \\ B & A \end{pmatrix} = \begin{pmatrix} B & B \\ B & B \end{pmatrix} + \begin{pmatrix} A - B & 0 \\ 0 & A - B \end{pmatrix}$$

# A practical approximation: The electron-hole (eh) exchange kernel

The exchange kernel can be split in two parts

$$\mathbf{E} = \begin{pmatrix} A & B \\ B & A \end{pmatrix} = \begin{pmatrix} B & B \\ B & B \end{pmatrix} + \begin{pmatrix} A & \text{X} \\ \text{X} & A \end{pmatrix}$$

**Electron-hole approximation**

- ❑ The approximate kernel contains **valence-conduction state products only** and the equations for the correlation energy can be significantly simplified.
- ❑ This approximation leads to expressions for the correlation energy that correctly **reduce to MP2 to the second order**.
- ❑ The **f-sum rule is satisfied** even when using DFT states as starting point.
- ❑ Within the optimized effective potential framework this approximation is **exact for a system with two electrons** (Hesselman and Gorling PRL 2011).
- ❑ In numerical applications **this kernel significantly improves over RPA results**.

# Equations for the correlation energy obtained from the electron-hole exchange kernel

## Random Phase Approximation (RPA)

$$E_c^{\text{RPA}} = \frac{1}{2\pi} \int_0^\infty du \operatorname{Tr} \{ \ln(I - \chi_0(iu)V) + \chi_0(iu)V \}$$

## Adiabatic connection second order screened exchange (AC-SOSEX)

$$E_c^{\text{AC-SOSEX}} = \frac{1}{2\pi} \int_0^\infty du \operatorname{Tr} \{ \ln(I - \chi_0(iu)V) V^{-1}B + \chi_0(iu)B \}$$

## Electron-hole TDHF (eh-TDHF)

$$E_c^{\text{eh-TDHF}} = \frac{1}{2\pi} \int_0^\infty du \operatorname{Tr} \{ \ln(I - \chi_0(iu)B) B^{-1}V + \chi_0(iu)V \}$$

Logarithmic equations similar to RPA

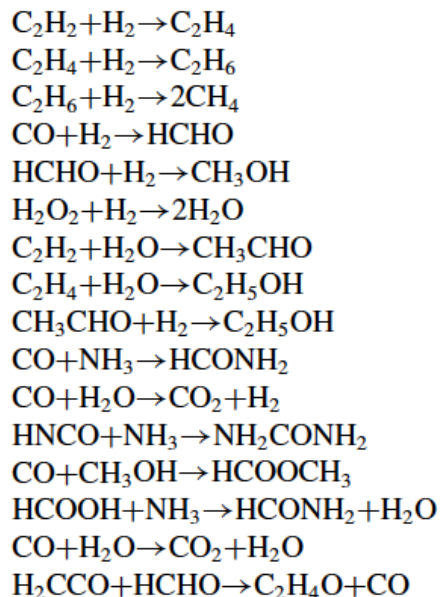
These expressions allow for the elimination of the empty states and are suitable for an optimal basis set representation



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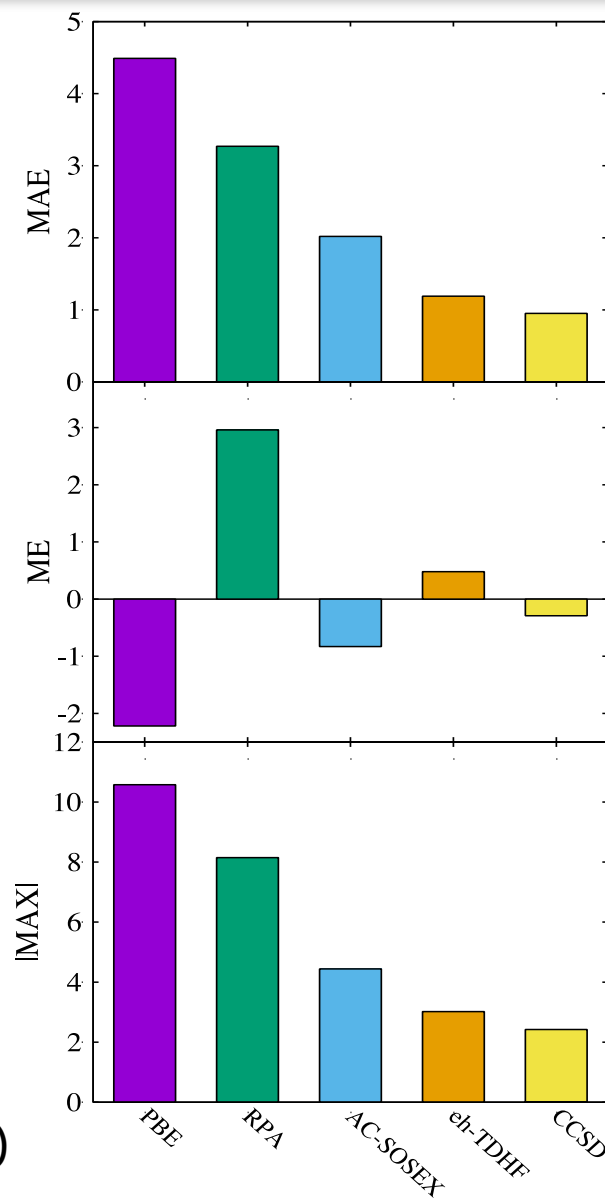
# RPA, AC-SOSEX, and eh-TDHF applied to a reaction energy test set



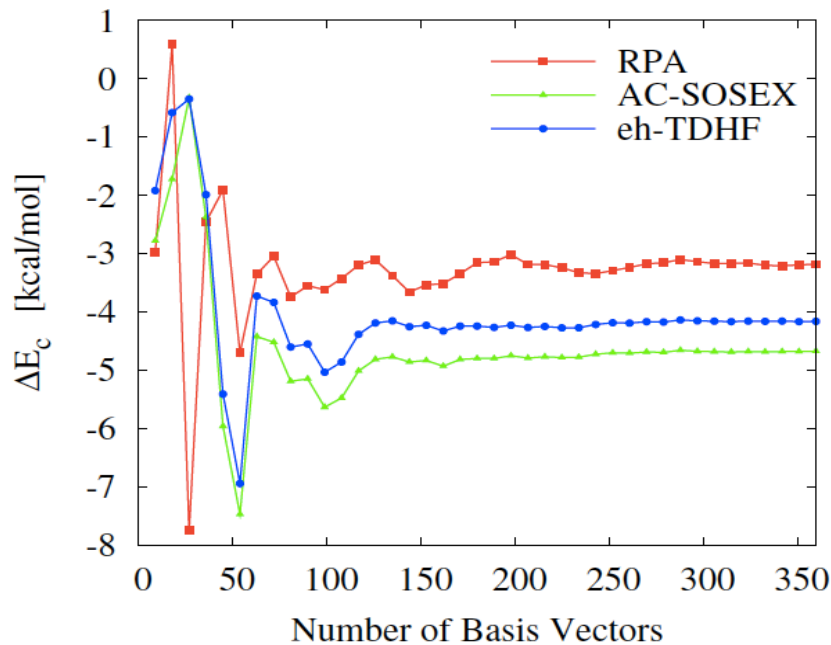
☐ Test set of reaction energies from A. Hesselmann  
PRA 85, 012517 (2012)

☐ Mean absolute error (MAE), mean error (ME), and  
maximum absolute deviation ( $|\text{MAX}|$ ) in kcal/mol  
computed with respect to CCSD(T)

☐ The eh-TDHF method presents an accuracy  
similar to CCSD



# Auxiliary basis set convergence: The $C_2H_2+H_2O \rightarrow CH_3CHO$ reaction

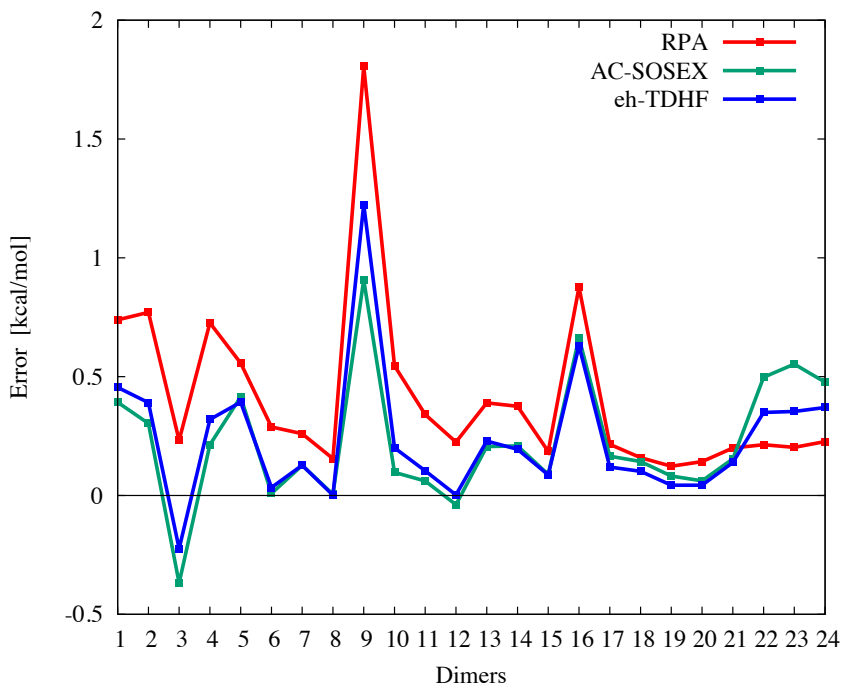


$\square \Delta E_c = E_c(CH_3CHO) - E_c(C_2H_2) - E_c(H_2O)$

$\square$  By increasing the basis set from 270 to 360 the values of  $\Delta E_c$  are all within a 0.04 kcal/mol interval for AC-SOSEX and eh-TDHF and within a 0.1 kcal/mol interval for RPA.

$\square$  In general convergence rates of the eh-TDHF and AC-SOSEX approximations are similar or sometimes better than RPA

# Application to weakly bound molecular dimers: A24 test set



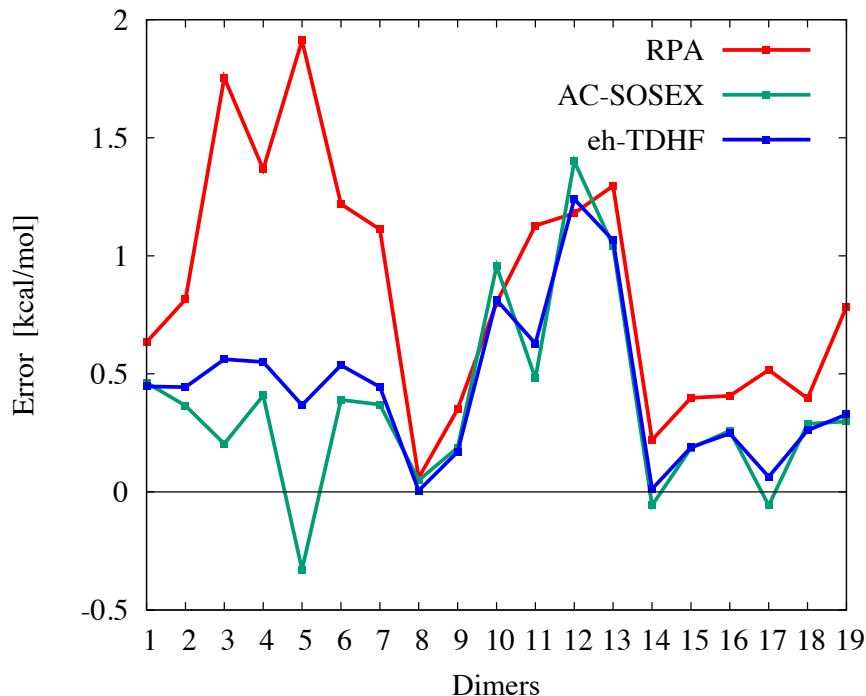
	RPA	AC-SOSEX	eh-TDHF
MAE	0.42	0.26	0.26
ME	-0.42	-0.24	-0.23
MAX	1.81	1.22	0.90

Errors in kcal/mol with respect to CCSDT(Q)

- ❑ The exchange contribution significantly decrease the MAE of RPA
- ❑ For three systems far from the equilibrium position beyond-RPA methods perform slightly worst

A. Dixit, J. Claudot, S. Lebègue, and D. Rocca, in preparation

# Application to weakly bound molecular dimers: S22 test set



	RPA	AC-SOSEX	eh-TDHF
MAE	0.86	0.41	0.44
ME	-0.86	-0.36	-0.44
MAX	1.91	1.40	1.24

Errors in kcal/mol with respect to CCSD(T)

- ❑ This test set includes systems with up to **98 valence electrons** and requiring **390k PWs** (adenine-thymine dimer).
- ❑ The exchange contribution significantly decrease the MAE of RPA.
- ❑ Work is still in progress for three dimers.

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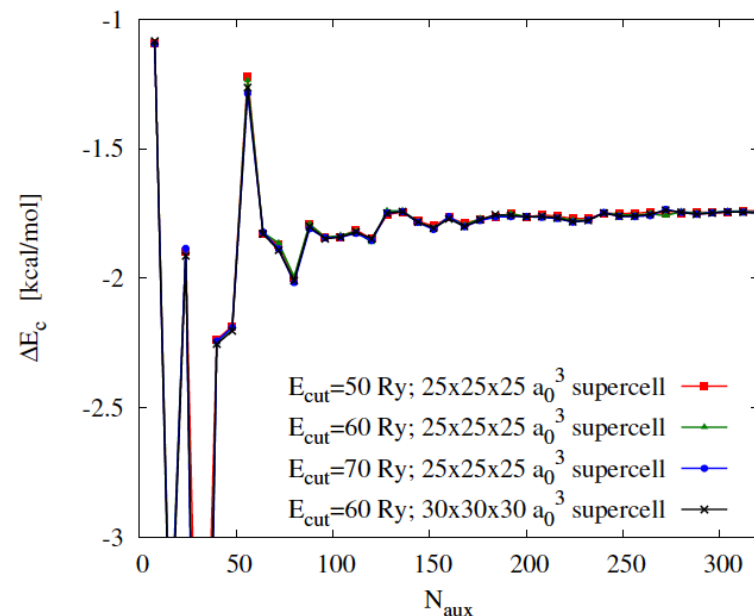
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# MP2 correlation energies in a response function framework

$$E_c^{\text{MP2}} = -\frac{1}{4} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr} \{ \chi^0(i\omega) B \chi^0(i\omega) K \}$$

$$= -\frac{1}{2} \sum_{vc,v'c'} \frac{K_{vc,v'c'} B_{v'c',vc}}{\epsilon_c + \epsilon_{c'} - \epsilon_v - \epsilon_{v'}}.$$

□ Approach analogous to the ACFDT methods but a scf HF reference state is used



System	This work	CBS (Ref. 43)	CBS (Ref. 44)	CBS (Ref. 44) with CP corrections
	Plane-waves	GTO	GTO	GTO
NH <sub>3</sub> dimer	-3.20	-3.20	-3.19	-3.15
C <sub>2</sub> H <sub>4</sub> dimer	-1.64	-1.62	-1.60	-1.58
C <sub>2</sub> H <sub>4</sub> -C <sub>2</sub> H <sub>2</sub> dimer	-1.72	-1.69	-1.68	-1.66

Ref. 43: P. Jurecka et al.  
Phys. Chem. Chem. Phys.  
(2006)

Ref. 44: T. Takatani et al.  
J. Chem. Phys. (2010)

# Conclusions

- ❑ New promising approximations to introduce exchange effects within the ACFDT have been discussed that allow for an efficient implementation within a plane-wave basis set code.
- ❑ Work is in progress to extend these methodologies to solids.



# Acknowledgements

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- Tomas Bucko
- Bastien Mussard
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- Sébastien Lebègue
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