Advanced correlation functionals in density functional theory

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- DFT introduction
- vdW-aware functionals
- ACFDT
- RPA and RPA self consistent potential
- beyond RPA, RPAx and its modifications

Some Remarks on DFT Calculations

- DFT is a formally exact theory for the MB problem

$$E = min_n \left\{ T_s[n] + \int V_{ext}(r) n(r) + \frac{e^2}{2} \int \frac{n(r) n(r')}{|r - r'|} + E_{xc}[n] \right\}$$

- approximations for the exchange-correlation energy are required for practical applications

Local or Semi-Local LDA, GGA functionals

$$E_{xc}^{LDA} = \int d\mathbf{r}\, \varepsilon_{xc}^{LDA}[n(\mathbf{r})]\, n(\mathbf{r})$$

$$E_{xc}^{GGA} = \int d\mathbf{r}\, \varepsilon_{xc}^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})]\, n(\mathbf{r})$$

- LDA, GGAs succesfully predict properties of a wide class of electronic systems

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- LDA, GGAs succesfully predict properties of a wide class of electronic systems but fail qualitatively in a number of situations such as
  weakly vdW bonded compounds,
  strongly correlated materials (ex: H_2),
  molecular dissociation in charged fragments (ex: LiH),
  ...

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- beyond RPA

Truly non local functionals

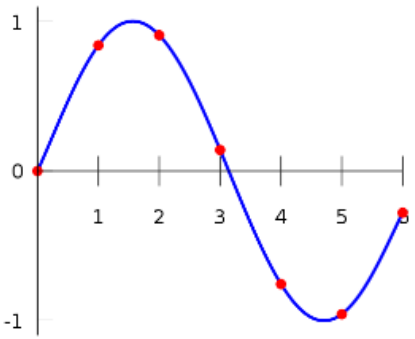
In the last 10 years, starting from the very general Adiabatic Connection Fluctuation-Dissipation Theory formulation of DFT (see later), Langreth and coworkers developped a truly non local functional form aiming at describing vdW interaction.

M.Dion, H.Rydberg, E.Schröder, D.C.Langreth and B.I.Lundqvist, Phys.Rev.Lett. **92**, 246401 (2004).

An efficient integration

Roman-Rerez Soler interpolation scheme
If it's possible to express the complex density dependence on r, r' via a single q(r) (and q(r')) function then ...

$$E_c^{nl} = \frac{1}{2}\int\int n(r)\Phi(q(r), q(r'), |r-r'|)n(r')drdr'$$



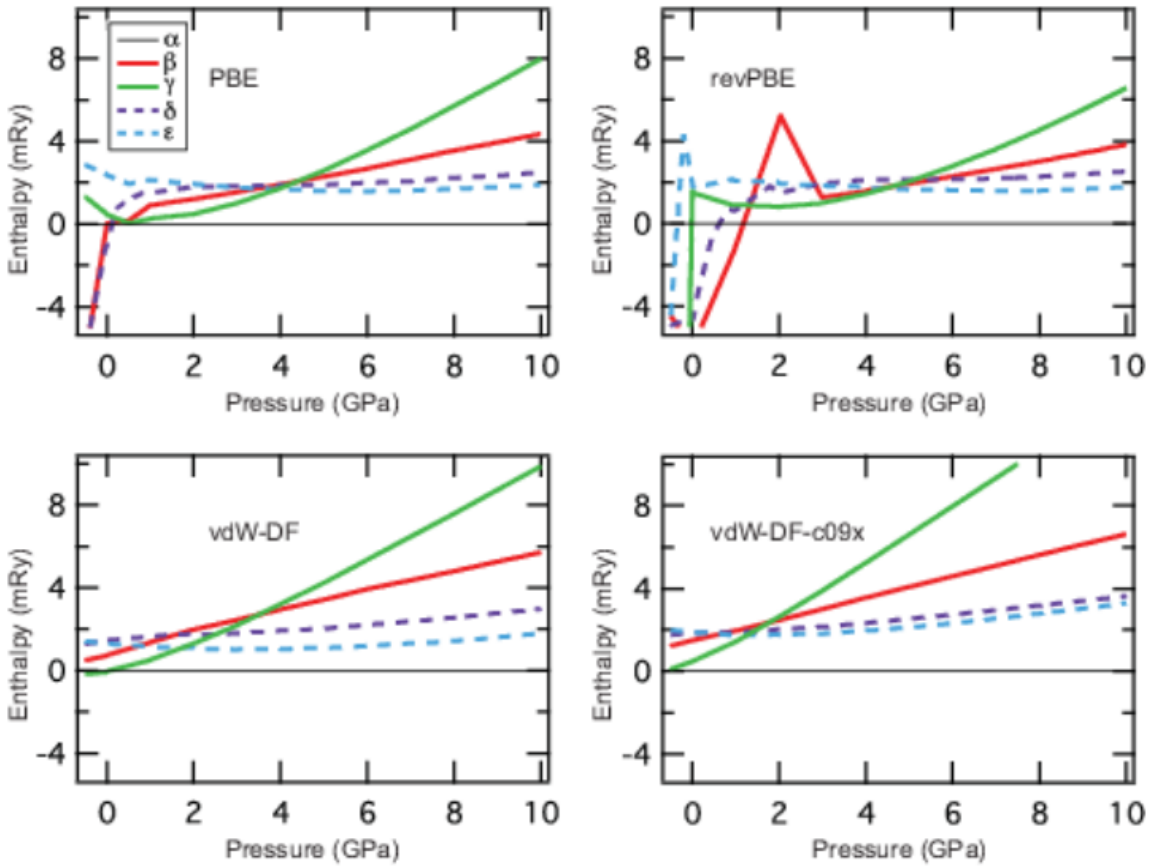
$$\Phi(q_1, q_2, r_{12}) \approx \sum_{\alpha,\beta} \Phi(q_\alpha, q_\beta, r_{12})P_\alpha(q_1)P_\beta(q_2)$$

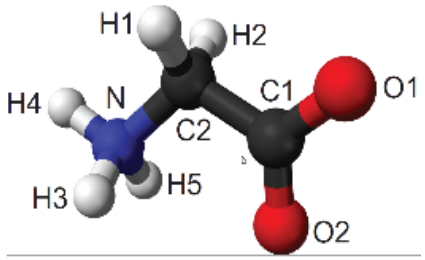
$$E_c^{nl} = \frac{1}{2}\sum_{\alpha,\beta}\int\int \Theta_\alpha(r)\Phi(q_\alpha, q_\beta, |r-r'|)\Theta_\beta(r')\ drdr'$$

$$= \frac{\Omega}{2}\sum_{\alpha,\beta}\sum_{G} \Theta^*_\alpha(G)\Phi(q_\alpha, q_\beta, |G|)\Theta_\beta(G) \qquad \Theta_\alpha(r) = n(r)P_\alpha(q(r))$$

The vdW energy can be expressed as a sum of simple 3d integrals

Glycine polymorphes





$$\gamma < \alpha < \beta < \ldots$$

R.Sabatini, E.Kucukbenli, B.Kolb, T.Thonhauser, and SdG, J. Phys. Cond. Matt. **24**, 424209 (2012).

several Non-local Functionals

	ω_0 in $E_c^{(2)}$		$E_{xc}^{LDA/GGA}$	C_6 error
vdWDF	$\frac{9\hbar}{8\pi m}\left[k_F(1+\mu s^2)\frac{4\pi}{3e^2}\varepsilon_c^{LDA}\right]$	with $\mu = 0.09434$	SLA+PW+RPBE-	18.5%
vdWDF2	$\frac{9\hbar}{8\pi m}\left[k_F(1+\mu s^2)\frac{4\pi}{3e^2}\varepsilon_c^{LDA}\right]$	with $\mu = 0.20963$	SLA+PW+RPW86-	60.9 %
vdWDF-09	$\frac{\hbar}{3m}k_F^2(1+\mu s^2)$	with $\mu = 0.22$	SLA+PW+RPBE-	10.4 %
vv10	$\sqrt{\frac{\omega_p^2}{3}+C\frac{h^2}{m^2}\left\lvert\frac{\nabla n}{n}\right\rvert^4}$	with $C = 0.0089$	SLA+PW+RPW86+PBC	10.7 %

vdWDF – functional can exploit the Roman-Perez Soler interpolation
Vv10 – functional does not fulfill the needed conditions

VV10 functional

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{gg'(g+g')} \qquad k(r) = 3\pi b\left(\frac{n}{9\pi}\right)^{\frac{1}{6}}$$

$$g = \omega_0(r)R^2 + k(r)$$

$$\omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C\left(\frac{\hbar^2}{m^2}\right)\left|\frac{\nabla n}{n}\right|^4, \quad \omega_p^2 = \frac{4\pi n e^2}{m}$$

$$z(r) = \frac{\omega_0(r)}{k(r)}R^2 + 1$$

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{k^{3/2}k'^{3/2}}\frac{1}{zz'\left(\sqrt{\frac{k}{k'}}z + \sqrt{\frac{k'}{k}}z'\right)}$$

VV10 $\longrightarrow$ rVV10 functional

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{gg'(g+g')} \qquad k(r) = 3\pi b\left(\frac{n}{9\pi}\right)^{\frac{1}{6}}$$

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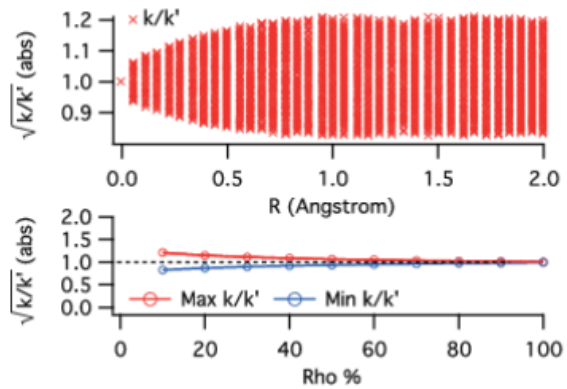

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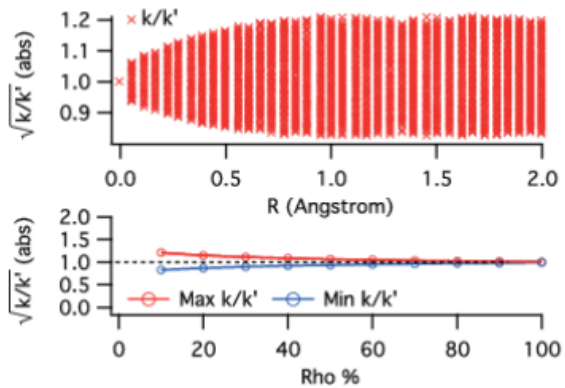
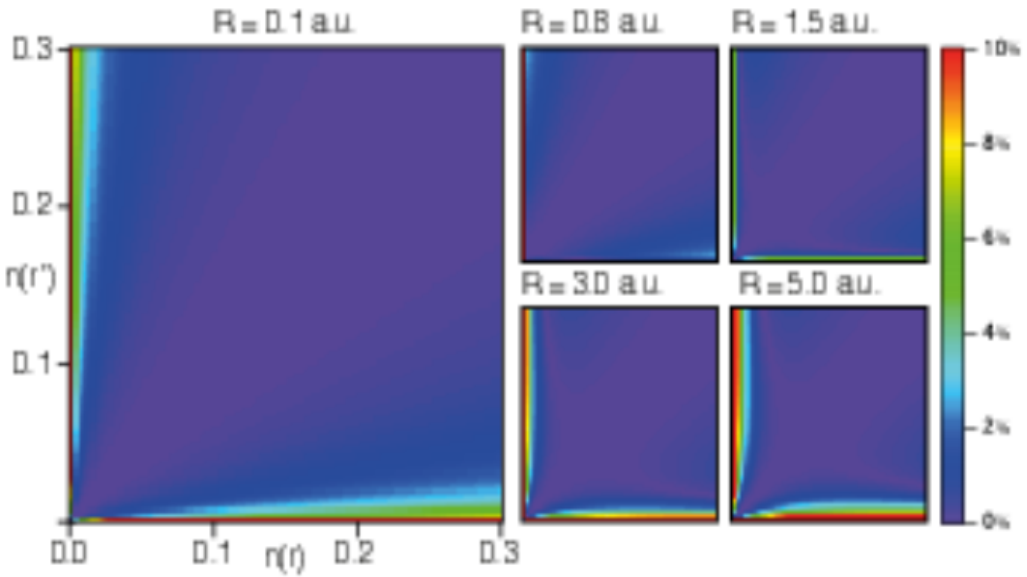
$$q(r) = \omega_0(n(r), \nabla n(r))/k(n(r))$$



$$\Phi^{rVV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{k^{3/2}k'^{3/2}}\frac{1}{(qR^2+1)(q'R^2+1)(qR^2+q'R^2+2)}$$

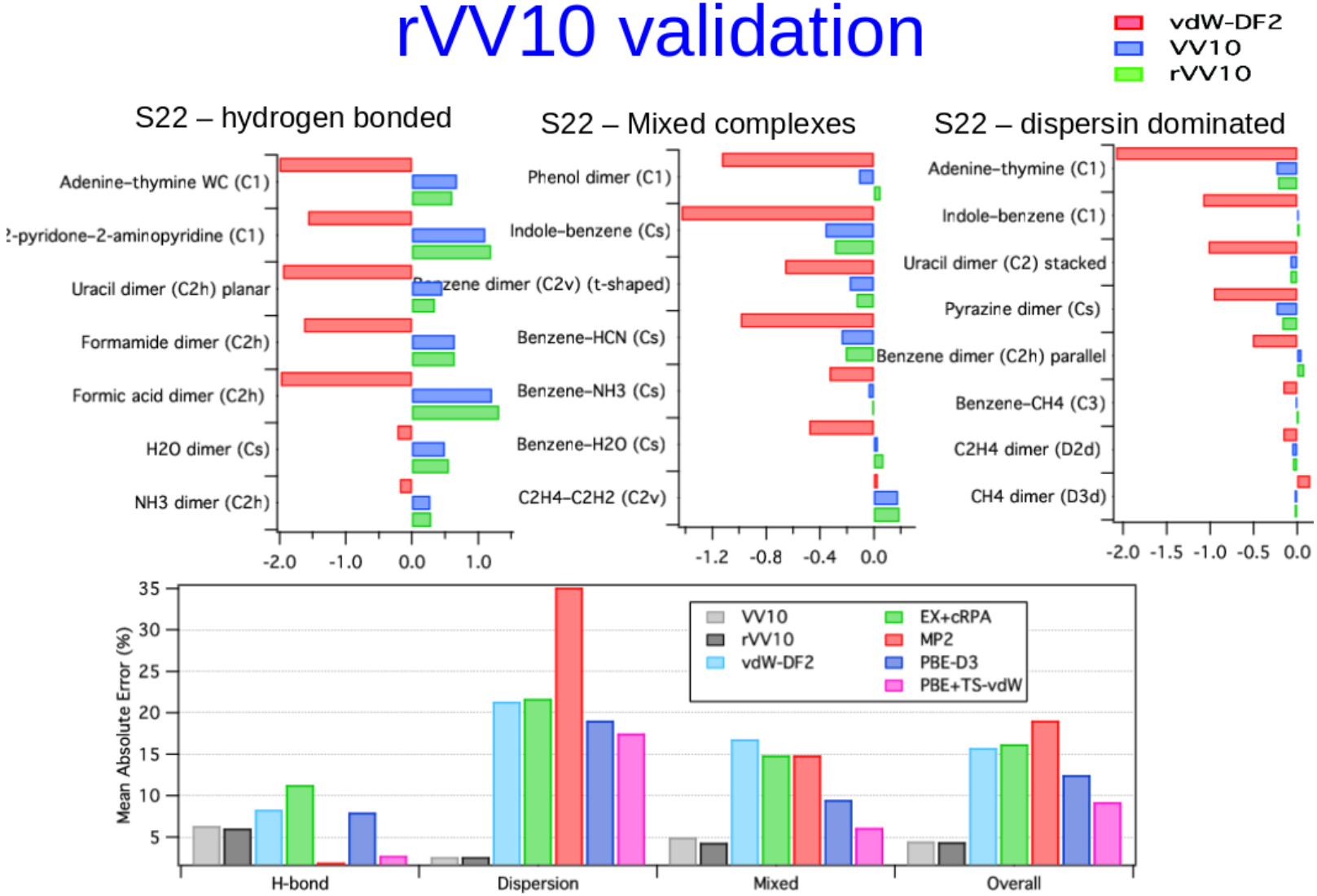
VV10 vs rVV10

$$\Delta\Phi^{VV10} = \Phi^{VV10}(r, r') - \Phi^{rVV10}(r, r')$$



The error in the kernel is small except when the density itself is very small !

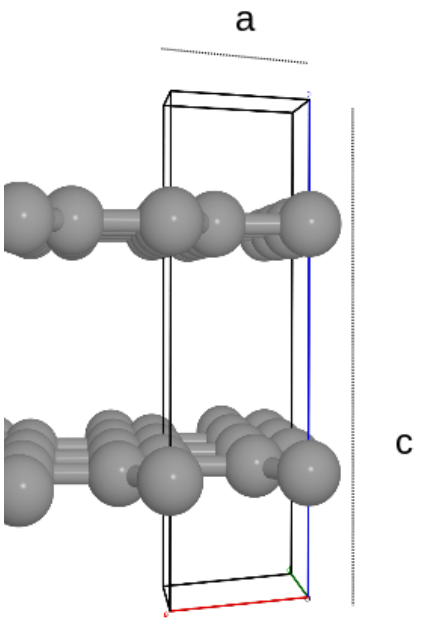
rVV10 validation

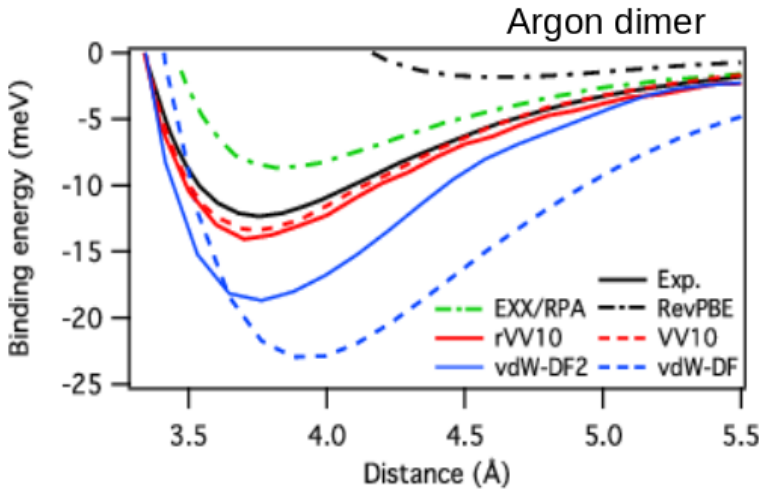


R.Sabatini, T.Gorni, SdG, Phys. Rev. B **87**, 041108 (2013).

rVV10 applications

Noble gas dimer are classical examples of dispersion dominated systems where the quality of different functionals can be explored.



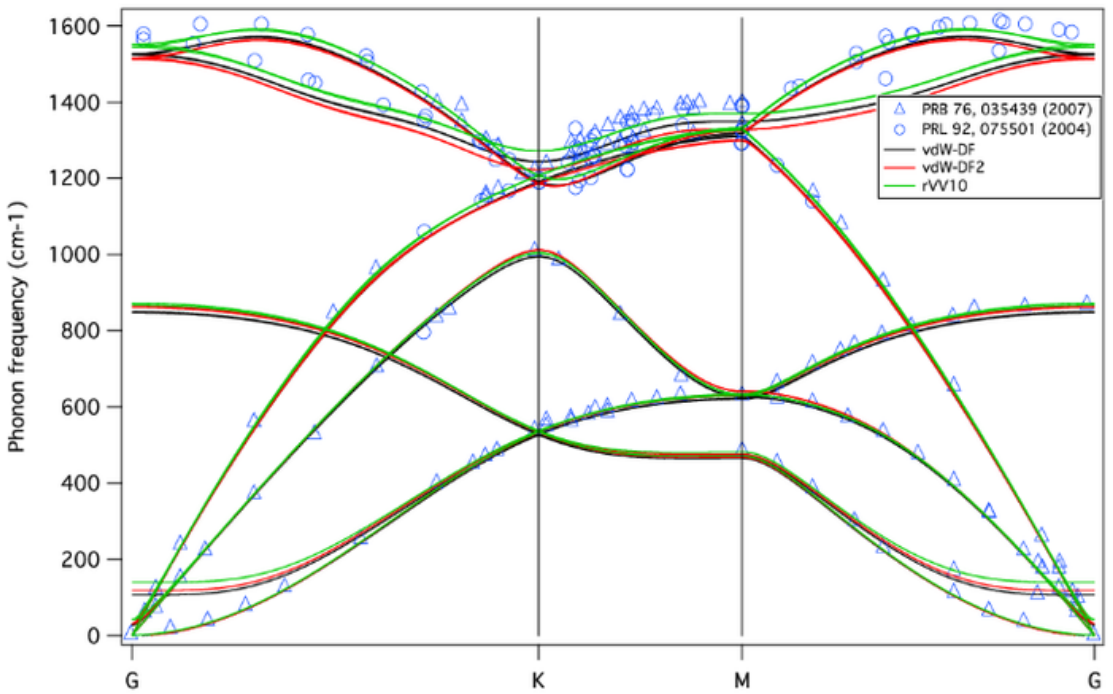


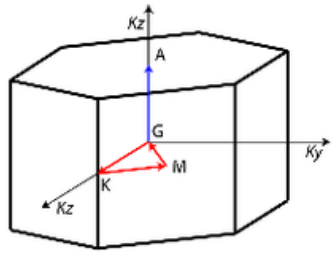
Graphite cel parameters (A)

	a	c
vdW-DF	2.48	7.19
vdW-DF2	2.47	7.06
rVV10	2.46	6.72
exp	2.46	6.71

R.Sabatini, T.Gorni, SdG, Phys. Rev. B **87**, 041108 (2013).

Phonons in Graphite





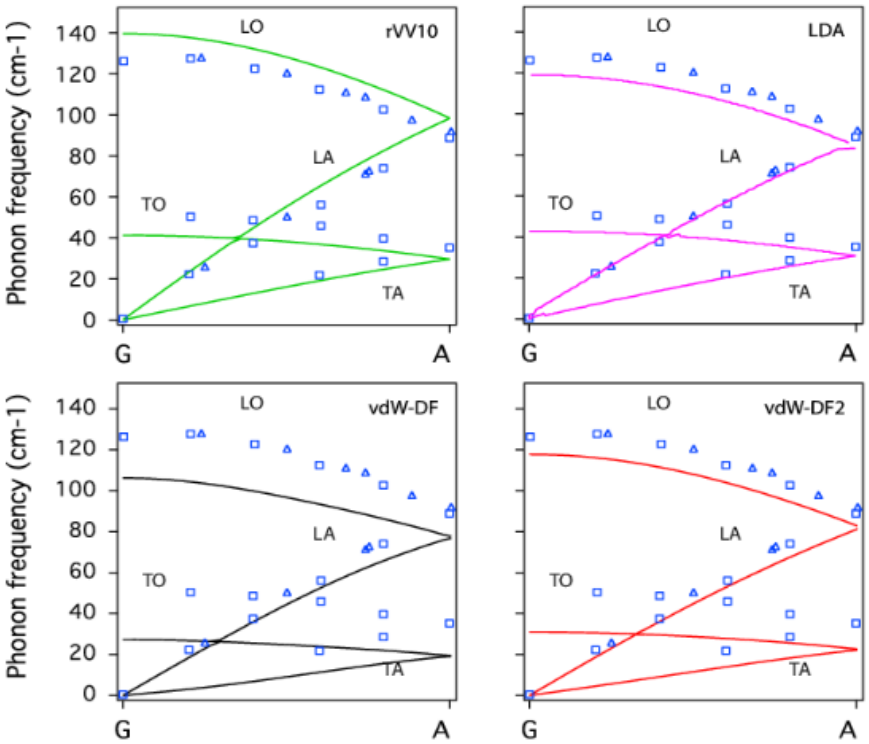
Stiff intralayer modes

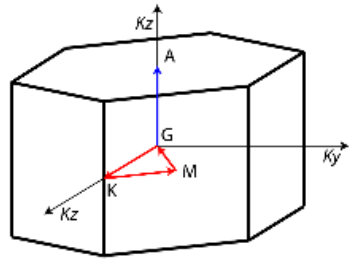
	LDA	vdW-DF	vdW-DF2	rVV10
MAE (cm-1)	39.86	24.57	28.29	18.29
MARE (%)	3.21	1.85	2.04	1.36

Comparison of DFPT results at high symmetry points

R.Sabatini, E. Kucukbenli, C.H. Pham, SdG, Phys. Rev. B **93**, 235120 (2016).

Phonons in Graphite





Soft interlayer modes

	LDA	vdW-DF	vdW-DF2	rVV10
MAE (cm-1)	5.50	13.50	10.00	7.50
MARE (%)	10.51	28.17	22.50	13.63

R.Sabatini, E. Kucukbenli, C.H. Pham, SdG, Phys. Rev. B **93**, 235120 (2016).

vdWDF functionals

- Calculations with vdW-aware functionals are now possible and efficient.
- Implemented in the Quantum ESPRESSO suite of codes
- including forces, stress, phonons etc.

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ACFDT Derivation

Full-Interacting Hamiltonian

$$H = T + W + v_{ext} \quad \Rightarrow \quad |\Psi^{GS}\rangle,\ n(\mathbf{r})$$

Non-Interacting (Kohn-Sham) Hamiltonian

$$H_{KS} = T_s + v_{KS} \quad \Rightarrow \quad |\Phi^{GS}_{KS}\rangle,\ n(\mathbf{r})$$

One can introduce fictitious systems with **scaled interaction** λW which connect the KS ($\lambda = 0$) with the fully interacting system ($\lambda = 1$)

Adiabatic Connection

$$H_\lambda = T + \lambda W + v^\lambda_{ext}$$

$$v^{\lambda=0}_{ext} = v_{KS}$$

$$v^{\lambda=1}_{ext} = v_{ext}$$

$$n_\lambda(\mathbf{r}) = \langle \Psi^{GS}_\lambda | \hat{n}(\mathbf{r}) | \Psi^{GS}_\lambda \rangle = n(\mathbf{r})$$

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ACFDT Derivation

According to **Hellmann-Feynman** theorem

$$\frac{dE_\lambda}{d\lambda} = \langle \Psi_\lambda | \frac{dH_\lambda}{d\lambda} | \Psi_\lambda \rangle = \langle \Psi_\lambda | W | \Psi_\lambda \rangle + \int d\mathbf{r}\; n(\mathbf{r}) \frac{\partial v_{ext}^\lambda}{\partial \lambda}$$

Integrating over λ between 0 and 1

$$E_{\lambda=1} = E_{\lambda=0} + \int_0^1 d\lambda\, \langle \Psi_\lambda | W | \Psi_\lambda \rangle + \int d\mathbf{r}\; n(\mathbf{r})[v_{ext}(\mathbf{r}) - v_{KS}(\mathbf{r})]$$

With the usual decomposition of energy functional

$$E_{\lambda=1} = T_s + E_H + E_{xc} + \int d\mathbf{r}\; n(\mathbf{r}) v_{ext}(\mathbf{r})$$

$$E_{\lambda=0} = T_s + \int d\mathbf{r}\; n(\mathbf{r}) v_{KS}(\mathbf{r})$$

we end up with

$$\boxed{E_H + E_{xc} = \int_0^1 d\lambda\, \langle \Psi_\lambda | W | \Psi_\lambda \rangle}$$

ACFDT Derivation

$$\langle \Psi_\lambda | W | \Psi_\lambda \rangle = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}')$$

$$n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle_\lambda + n(\mathbf{r}) n(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') n(\mathbf{r})$$

using the **Fluctuation-Dissipation Theorem**
Density Fluctuations $\Rightarrow$ Energy Dissipation i.e. $Im[\chi]$

$$n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}') = -\int_0^\infty \frac{du}{\pi} \chi_\lambda(\mathbf{r}, \mathbf{r}'; iu) + n(\mathbf{r}) n(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') n(\mathbf{r})$$

Exchange-Correlation Energy from ACFDT

$$E_{xc} = -\frac{1}{2\pi} \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left\{ \int_0^\infty du \chi_\lambda(\mathbf{r}, \mathbf{r}'; iu) + \pi\delta(\mathbf{r} - \mathbf{r}') n(\mathbf{r}) \right\}$$

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Replacing χ_λ with χ_0 the exchange energy is recovered.

The correlation energy can thus be separated

Adiabatic connection formula for correlation energy

$$E_c = -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^\infty du \mathrm{Tr}\left\{v_c\left[\chi_\lambda(iu) - \chi_0(iu)\right]\right\}$$

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_\lambda(iu)[\lambda v_c + f_{xc}^\lambda(iu)]\chi_0(iu)$$

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$$\chi_\lambda(iu) = \chi_0(iu) + \chi_\lambda(iu)[\lambda v_c + f_{xc}^\lambda(iu)]\chi_0(iu)$$

Adiabatic Connection Fluctuation-Dissipation Theory

An exact definition for the correlation energy :

$$E_c = -\frac{1}{2\pi}\int_0^1 d\lambda \int d\mathbf{r}d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\{\int_0^\infty du\,[\chi_\lambda(iu)-\chi_{KS}(iu)]\right\}$$

where $\chi_\lambda(iu)$ is given by

$$\chi_\lambda(iu) = \chi_{KS}(iu) + \chi_\lambda(iu)\left[\lambda v_c + f_{xc}{}^\lambda(iu)\right]\chi_{KS}(iu)$$

ADVANTAGES

- a practical way to calculate xc-energy (almost) exactly
- theoretical framework for a **systematic** development of functionals

LIMITATIONS

- computationally very demanding
- f_{xc} **needed**

Adiabatic Connection Fluctuation-Dissipation Theory

An exact definition for the correlation energy :

$$E_c = -\frac{1}{2\pi}\int_0^1 d\lambda \int d\mathbf{r}d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\{\int_0^\infty du\,[\chi_\lambda(iu)-\chi_{KS}(iu)]\right\}$$

where $\chi_\lambda(iu)$ is given by

$$\chi_\lambda(iu) = \chi_{KS}(iu) + \chi_\lambda(iu)\left[\lambda v_c + f_{xc}{}^\lambda(iu)\right]\chi_{KS}(iu)$$

ADVANTAGES

- a practical way to calculate xc-energy (almost) exactly
- theoretical framework for a **systematic** development of functionals

LIMITATIONS

- computationally very demanding
- f_{xc} **needed**

- DFT introduction
- vdW-aware functionals
- ACFDT
- RPA and RPA self consistent potential
- beyond RPA

Random Phase Approximation (RPA)

Random Phase Approximation: $f_{xc}^{\lambda} = 0$

$$\chi_{\lambda}^{RPA} = \chi_0 + \chi_0[\lambda v_c]\chi_{\lambda}^{RPA}$$

- We can define a generalized eigenvalue problem

$$\chi_0(iu)\,|\omega_\alpha(iu)\rangle = a_\alpha(iu) v_c^{-1}\,|\omega_\alpha(iu)\rangle$$

$$\chi_{\lambda}^{RPA} = \chi_0 + \lambda\chi_0 v_c \chi_{\lambda}^{RPA} \Rightarrow \quad \chi_{\lambda}^{RPA}|\omega_\alpha\rangle = \frac{a_\alpha}{1-\lambda a_\alpha} v_c^{-1}|\omega_\alpha\rangle$$

$\Rightarrow$ λ-integration is done analytically

$$E_c = \frac{1}{2\pi}\int_0^\infty du \sum_\alpha \{a_\alpha(iu) + \ln(1 - a_\alpha(iu))\}$$

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$\Rightarrow$ λ-integration is done analytically

$$E_c = \frac{1}{2\pi}\int_0^{\infty} du \sum_{\alpha}\{a_\alpha(iu) + \ln(1-a_\alpha(iu))\}$$

Iterative diagonalization of χ_0

- The Kohn-Sham (non-interacting) response function

$$\chi_0(\mathbf{r},\mathbf{r}';iu) = \sum_{i,j}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j + iu}$$

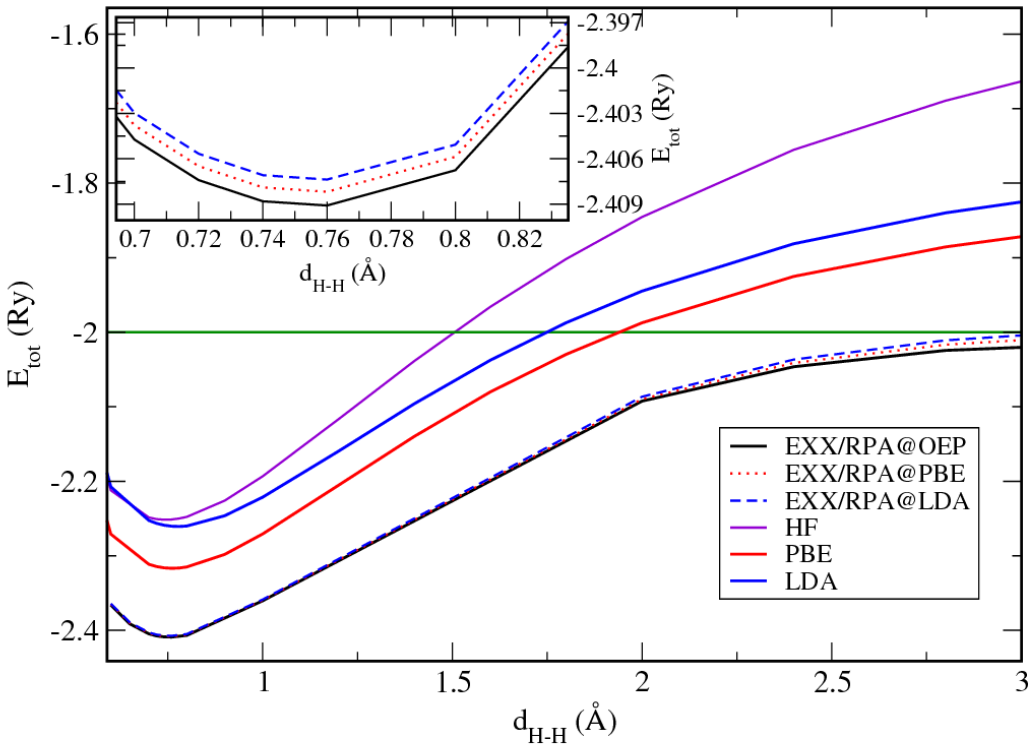
- Matrix elements of χ_0 are efficiently computed by Density Functional Perturbation Theory :

  S.Baroni, A.DalCorso, P.Giannozzi, and SdG, Rev.Mod.Phys. 73, 515 (2001)

$$\Delta n(\mathbf{r}) = \int \chi_0(\mathbf{r},\mathbf{r}')\Delta V_{SCF}(\mathbf{r})d\mathbf{r} \quad = \quad 2Re\left\{\sum_{i\in \mathrm{occ.}} \psi_i^*\Delta\psi_i\right\}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i - iu\right]\Delta\psi_i(\mathbf{r}) \quad = \quad -\Delta V_{SCF}(\mathbf{r})\psi_i(\mathbf{r})$$

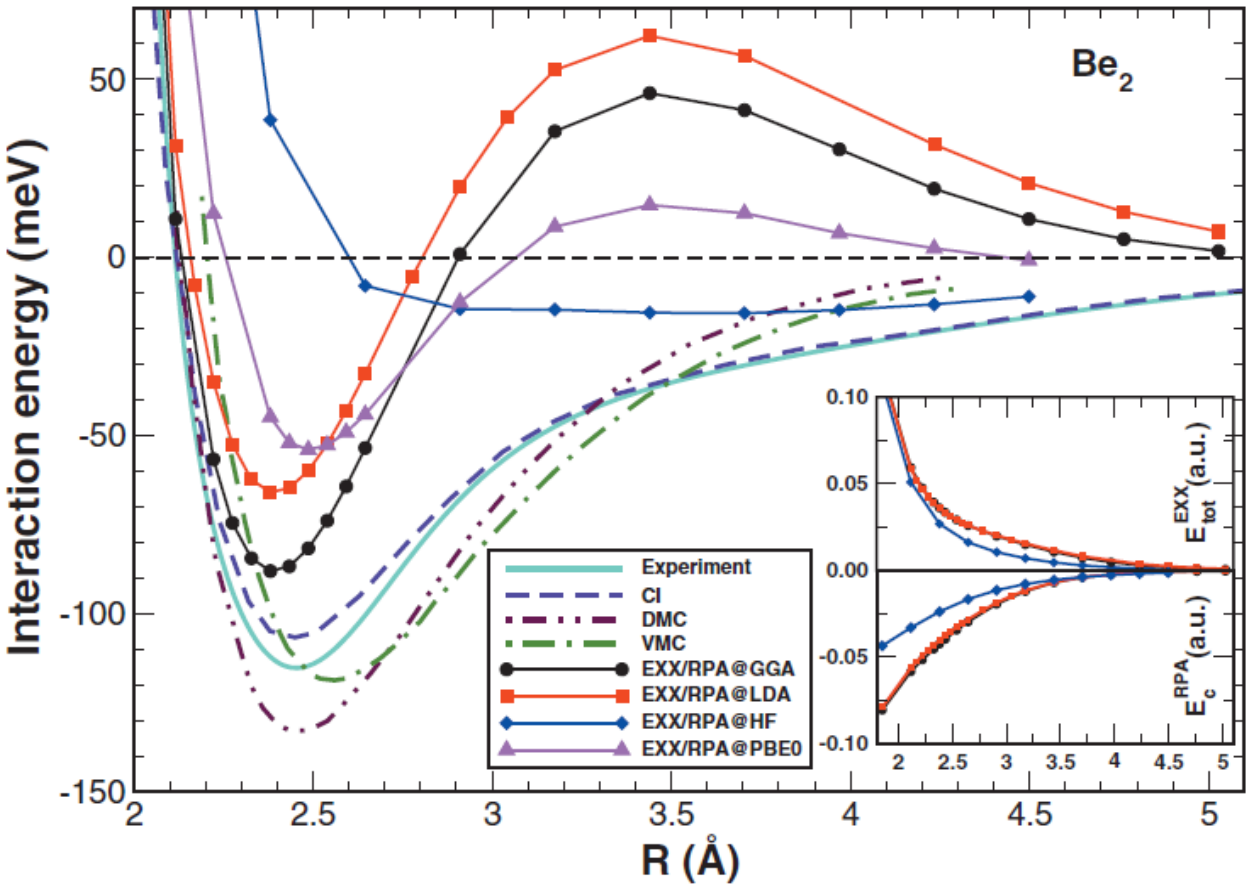
Hydrogen dimer dissociation



Dissociation behaviour correctly described

Importance of a self-consistent potential

E_c^{RPA} has been computed so far as a post-scf correction...



H.V. Nguyen, and G. Galli, J.Chem. Phys.**132**, 044109 (2010)

RPA correlation potential

$v_c(\mathbf{r}) = \frac{\delta E_c}{\delta n(\mathbf{r})}$ can be calculated via an OEP costruction

$$v_c(\mathbf{r}) = \int \frac{\delta E_c}{\delta V_{KS}(\mathbf{r}')} \times \frac{\delta V_{KS}(\mathbf{r}')}{\delta n(\mathbf{r})} d\mathbf{r}' = \int \chi_0^{-1}(\mathbf{r}, \mathbf{r}') \frac{\delta E_c}{\delta V_{KS}(\mathbf{r}')} d\mathbf{r}'$$

requires the knowledge of

$$\frac{\delta a_\alpha(iu)}{\delta V_{KS}(\mathbf{r})}$$

where a_α is an eigenvalue of the generalized eigenvalue problem and is a second order derivative of the KS energy w.r.t. the eigenpotential ω_α

$$a_\alpha(iu) = \langle \omega_\alpha(iu) | \chi_0(iu) | \omega_\alpha(iu) \rangle = 2Re \left\{ \sum_{i \in \text{occ.}} \langle \psi_i | \omega_\alpha | \Delta\psi_i^\alpha \rangle \right\}$$

The derivative of the energy w.r.t the effective potential

Applying the 2N+1 theorem, after some manipulations ($iu = 0$)

$$\begin{aligned}\delta a_\alpha &= \sum_{i\in\text{occ.}} \langle \Delta\psi_i^\alpha | \delta V_{KS} | \Delta\psi_i^\alpha \rangle - \langle \Delta\psi_i^\alpha | \Delta\psi_i^\alpha \rangle \langle \psi_i | \delta V_{KS} | \psi_i \rangle \\ &+ \sum_{i\in\text{occ.}} \langle \psi_i | \delta V_{KS} | \Delta^{(2)}\psi_i^\alpha \rangle + c.c.\end{aligned}$$

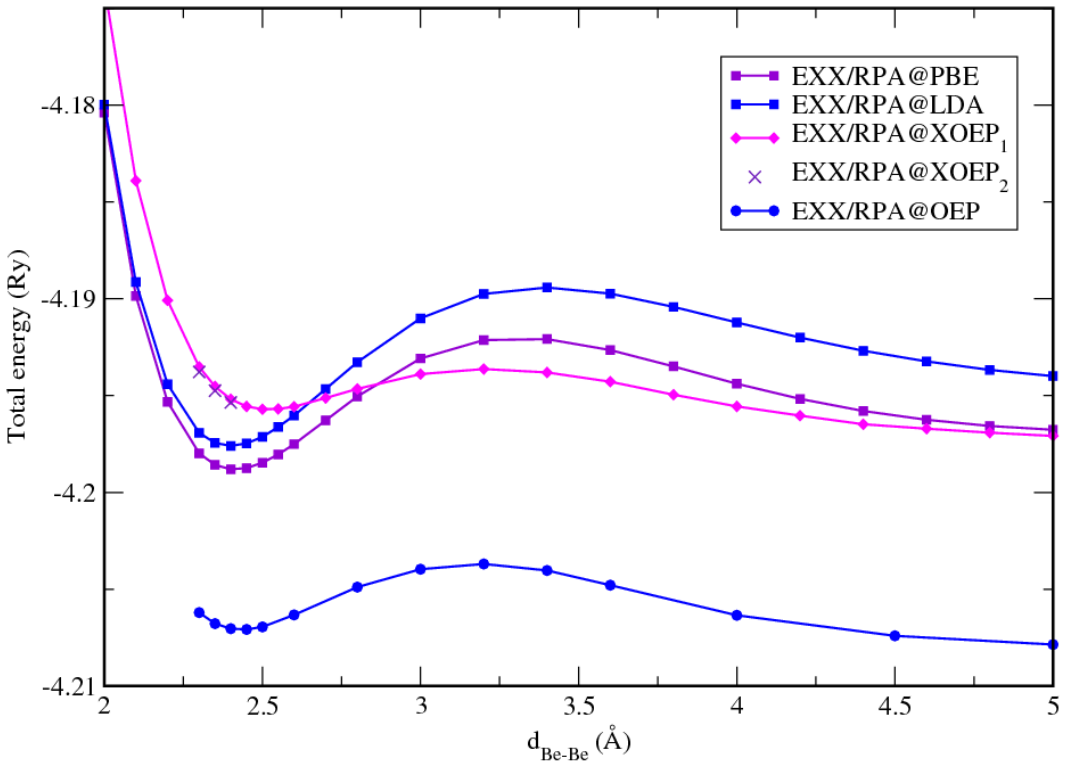
where

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i \right] \Delta\psi_i(\mathbf{r}) = -\omega_\alpha(\mathbf{r})\psi_i(\mathbf{r})$$

$$\begin{aligned}\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i \right] \Delta^{(2)}\psi_i(\mathbf{r}) &= -\omega_\alpha(\mathbf{r})\Delta\psi_i^\alpha(\mathbf{r}) \\ &+\Delta\psi_i^\alpha(\mathbf{r})\langle\psi_i|\omega_\alpha|\psi_i\rangle\end{aligned}$$

- The cost is affordable: Obtaning $\frac{\delta E_c}{\delta V_{KS}(\mathbf{r})}$ costs only twice E_c

Beryllium dimer dissociation



The effect of the self-consistent potential is very important
In scf RPA Beryllium dimer is only metastable...

- DFT introduction
- vdW-aware functionals
- ACFDT
- RPA and RPA self consistent potential
- beyond RPA, RPAx and its modifications

Beyond Random Phase Approximation

Random Phase Approximation: $f_{xc}^{\lambda} = 0$

$$\chi_{\lambda}^{RPA} = \chi_0 + \chi_0[\lambda v_c]\chi_{\lambda}^{RPA}$$

λv_c is not the only term in the kernel linear in λ

$$E_{xc}^{\lambda} = \lambda E_x - \frac{1}{2\pi}\int_0^{\lambda} d\mu \int_0^{\infty} du \mathrm{Tr}\left\{v_c\left[\chi_{\mu}(iu) - \chi_0(iu)\right]\right\} =$$

$$= \lambda E_x + o(\lambda^2)$$

$$\Downarrow$$

$$f_{xc}^{\lambda} = \frac{\delta^2 E_{xc}^{\lambda}}{\delta n \delta n} = \lambda f_x + o(\lambda^2)$$

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$$f_{xc}^{\lambda} = \frac{\delta^2 E_{xc}^{\lambda}}{\delta n \delta n} = \lambda f_x + o(\lambda^2)$$

Beyond RPA: including exchange kernel

From **Exact Exchange** : $f_{xc}^{\lambda} = \lambda f_x$

$$\chi_{\lambda}^{(1)} = \chi_0 + \chi_0[\lambda v_c + \lambda f_x]\chi_{\lambda}^{(1)}$$

$$E_{xc}^{\lambda} = \lambda E_x - \frac{1}{2\pi}\int_0^{\lambda} d\mu \int_0^{\infty} du \mathrm{Tr}\left\{v_c\left[\chi_{\mu}^{(1)}(iu) - \chi_0(iu)\right]\right\} +$$

$$- \frac{1}{2\pi}\int_0^{\lambda} d\mu \int_0^{\infty} du \mathrm{Tr}\left\{v_c\left[\chi_{\mu}(iu) - \chi_{\mu}^{(1)}(iu)\right]\right\} =$$

$$= \lambda E_x + E_{c,\lambda}^{(2)} + \Delta^{(2)} E_{c,\lambda}$$

$$E_{c,\lambda}^{(2)} \sim o(\lambda^2) \qquad \Delta^{(2)} E_{c,\lambda} \sim o(\lambda^3)$$

all other terms in the xc-kernel are higher order.

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Calculating the Trace

$$E_c^{(2)} = -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^\infty du \mathrm{Tr}\left\{v_c\left[\chi_\lambda^{(1)}(iu) - \chi_0(iu)\right]\right\}$$

$$\chi_\lambda^{(1)} = \chi_0 + \chi_\lambda^{(1)}[\lambda v_c + \lambda f_x]\chi_0$$

consider the generalized eigenvalue problem

$$\chi_0[v_c + f_x]\chi_0|\omega_\alpha\rangle = -a_\alpha[-\chi_0]|\omega_\alpha\rangle \qquad \langle\omega_\alpha|[-\chi_0]|\omega_\beta\rangle = \delta_{\alpha\beta}$$

$$\chi_\lambda^{(1)}|\omega_\alpha\rangle = \frac{1}{1-\lambda a_\alpha}\chi_0|\omega_\alpha\rangle$$

$$\mathrm{Tr}[v_c(\chi_\lambda^{(1)} - \chi_0)] = \sum_\alpha \left(1 - \frac{1}{1-\lambda a_\alpha}\right)\langle\omega_\alpha|\chi_0 v_c \chi_0|\omega_\alpha\rangle$$

Performing integration over λ

$$E_c^{(2)} = -\frac{1}{2\pi}\int_0^\infty du \sum_\alpha \frac{\langle\omega_\alpha|\chi_0 v_c \chi_0|\omega_\alpha\rangle}{a_\alpha(iu)}\left\{\mathrm{Log}[1 - a_\alpha(iu)] + a_\alpha(iu)\right\}$$

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Perturbation Theory (PT) along the adiabatic path

Only $\chi_0(v_c + f_x)\chi_0$ is needed (and not f_x) in the diagonalization

$$\chi_\lambda^{(1)} = \chi_0 + \lambda\{\chi_0[v_c + f_x]\chi_0\} + o(\lambda^2)$$

$$\chi_0[v_c + f_x]\chi_0 = \left[\frac{d\chi_\lambda^{(1)}}{d\lambda}\right]_{\lambda=0}$$

$$H_\lambda = T + \lambda W + v_{ext}^\lambda = H_0 + \lambda(W - v_H - v_x) + o(\lambda^2)$$

with

$$H_0 = T_s + v_{KS}(\mathbf{r}, t) = T_s + v_{KS}(\mathbf{r}) + v_p(\mathbf{r}, t)$$

Perturbation Theory (PT) along the adiabatic path

$$H^{\lambda=0} = H_{KS} + v_p(\mathbf{r}, t) \quad \text{with} \quad v_p(\mathbf{r}, t) = \Delta V(\mathbf{r}) e^{ut}$$

From standard time dependent PT

$$\Delta n(\mathbf{r}; iu) = \langle \Phi_0 | \hat{n}(\mathbf{r}) | \Delta\Phi_0^{(+)} + \Delta\Phi_0^{(-)} \rangle$$

$$\left[H_{KS} - (E_0 \pm iu) \right] | \Delta\Phi_0^{(\pm)} \rangle + \Delta V | \Phi_0 \rangle = 0$$

The generic response function matrix element is

$$\chi^{\beta\alpha} = \langle \Delta^\beta V | \chi | \Delta^\alpha V \rangle = \int d\mathbf{r} d\mathbf{r}' \, \Delta^\beta V(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}'; iu) \Delta^\alpha V(\mathbf{r}')$$

$$= \int d\mathbf{r} \, \Delta^\beta V(\mathbf{r}) \Delta^\alpha n(\mathbf{r}; iu) = \langle \Phi_0 | \Delta^\beta V | \Delta^\alpha \Phi_0^{(+)} + \Delta^\alpha \Phi_0^{(-)} \rangle$$

Perturbation Theory (PT) along the adiabatic path

Switching on the AC perturbation: $\delta V = W - v_H - v_x$

$$\delta\chi^{\beta\alpha} = \langle \delta\Phi_0 | \Delta^\beta V | \Delta^\alpha \Phi_0^{(+)} + \Delta^\alpha \Phi_0^{(-)} \rangle + \langle \Phi_0 | \Delta^\beta V | \delta\Delta\Phi_0^{(+)} + \delta\Delta^\alpha \Phi_0^{(-)} \rangle$$

$$[H_{KS} - E_0)] \, |\delta\Phi_0\rangle + [\delta V - \delta E_0] \, |\Phi_0\rangle = 0$$

$$[H_{KS} - (E_0 \pm iu)] \, |\delta\Delta^\alpha \Phi_0^{(\pm)}\rangle + [\delta V - \delta E_0] \, |\Delta^\alpha \Phi_0^{(\pm)}\rangle + \Delta^\alpha V |\delta\Phi_0\rangle = 0$$

$\delta\chi$ is the third derivative of the energy $\Rightarrow$ must depend only on first order correction of the wf (**"2n+1" Theorem**)

$$\begin{aligned}\delta\chi^{\beta\alpha} = {} & \langle \Delta^\beta \Phi_0^{(+)} | \delta V | \Delta^\alpha \Phi_0^{(-)} \rangle + \langle \Delta^\beta \Phi_0^{(-)} | \delta V | \Delta^\alpha \Phi_0^{(+)} \rangle + \\ & - \left[\langle \Delta^\beta \Phi_0^{(+)} | \Delta^\alpha \Phi_0^{(-)} \rangle + \langle \Delta^\beta \Phi_0^{(-)} | \Delta^\alpha \Phi_0^{(+)} \rangle \right] \langle \Phi_0 | \delta V | \Phi_0 \rangle + \\ & + \langle \Delta^\beta \Phi_0^{(+)} + \Delta^\beta \Phi_0^{(-)} | \Delta^\alpha V | \delta\Phi_0 \rangle + \langle \delta\Phi_0 | \Delta^\beta V | \Delta^\alpha \Phi_0^{(+)} + \Delta^\alpha \Phi_0^{(-)} \rangle\end{aligned}$$

Matrix element of $\chi_0 f_x \chi_0$

$$
\begin{aligned}
\delta\chi^{\alpha\beta} \quad = \quad & + \sum_{ab} \langle \phi_b \Delta^\beta \phi_a^{(-)} | W | \phi_a \Delta^\alpha \phi_b^{(+)} \rangle + \langle \phi_b \Delta^\beta \phi_a^{(+)} | W | \phi_a \Delta^\alpha \phi_b^{(-)} \rangle \\
& + \sum_{ab} \langle \phi_b \Delta^\beta \phi_a^{(+)} | W | \phi_a \Delta^\alpha \phi_b^{(+)} \rangle + \langle \phi_b \Delta^\beta \phi_a^{(-)} | W | \phi_a \Delta^\alpha \phi_b^{(-)} \rangle \\
& - \sum_{ab} \langle \phi_b \Delta^\beta \phi_a^{(-)} | W | \Delta^\alpha \phi_b^{(+)} \phi_a \rangle + \langle \Delta^\beta \phi_b^{(+)} \phi_a | W | \phi_b \Delta^\alpha \phi_a^{(-)} \rangle \\
& - \sum_{ab} \langle \phi_b \phi_a | W | \Delta^\beta \phi_b^{(+)} \Delta^\alpha \phi_a^{(-)} \rangle + \langle \Delta^\beta \phi_b^{(+)} \Delta^\alpha \phi_a^{(-)} | W | \phi_b \phi_a \rangle \\
& + \sum_{a} \langle \Delta^\beta \phi_a^{(-)} | V_x - v_x | \Delta^\alpha \phi_a^{(+)} \rangle - \sum_{ab} \langle \Delta^\beta \phi_a^{(-)} | \Delta^\alpha \phi_b^{(+)} \rangle \langle \phi_b | V_x - v_x | \phi_a \rangle \\
& + \sum_{a} \langle \Delta^\beta \phi_a^{(+)} | V_x - v_x | \Delta^\alpha \phi_a^{(-)} \rangle - \sum_{ab} \langle \Delta^\beta \phi_a^{(+)} | \Delta^\alpha \phi_b^{(-)} \rangle \langle \phi_b | V_x - v_x | \phi_a \rangle \\
& + \sum_{a} \langle \delta\phi_a | \Delta^\beta V | \Delta^\alpha \phi_a^{(+)} \rangle + \sum_{a} \langle \delta\phi_a | \Delta^\beta V | \Delta^\alpha \phi_a^{(-)} \rangle \\
& - \sum_{ab} \langle \delta\phi_a | \Delta^\beta \phi_b^{(+)} \rangle \langle \phi_b | \Delta^\alpha V | \phi_a \rangle - \sum_{ab} \langle \delta\phi_a | \Delta^\beta \phi_b^{(-)} \rangle \langle \phi_b | \Delta^\alpha V | \phi_a \rangle \\
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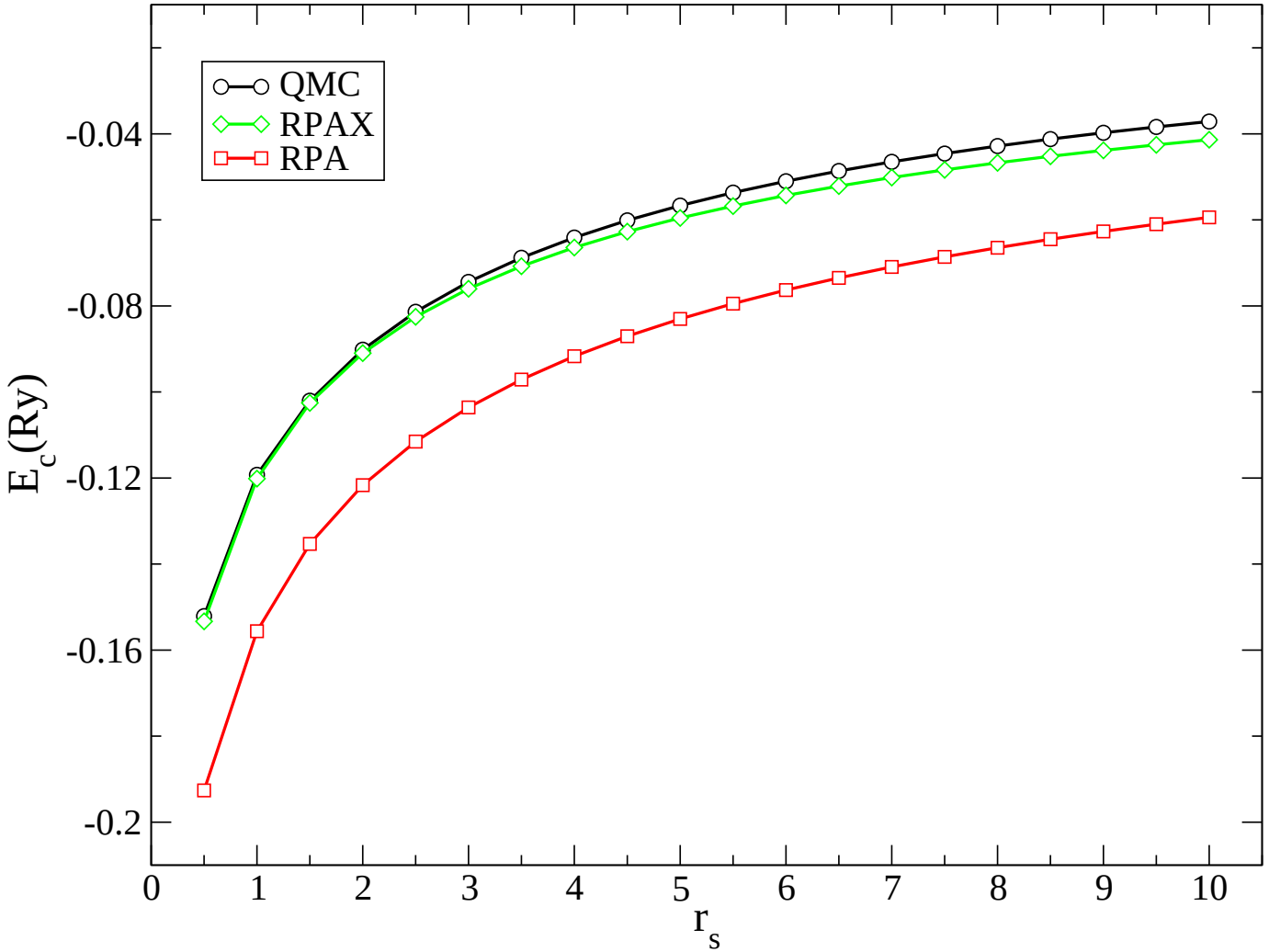
& - \sum_{ab} \langle \Delta^\beta \phi_b^{(+)} | \delta\phi_a \rangle \langle \phi_a | \Delta^\alpha V | \phi_b \rangle - \sum_{ab} \langle \Delta^\beta \phi_b^{(-)} | \delta\phi_a \rangle \langle \phi_a | \Delta^\alpha V | \phi_b \rangle
\end{aligned}
$$

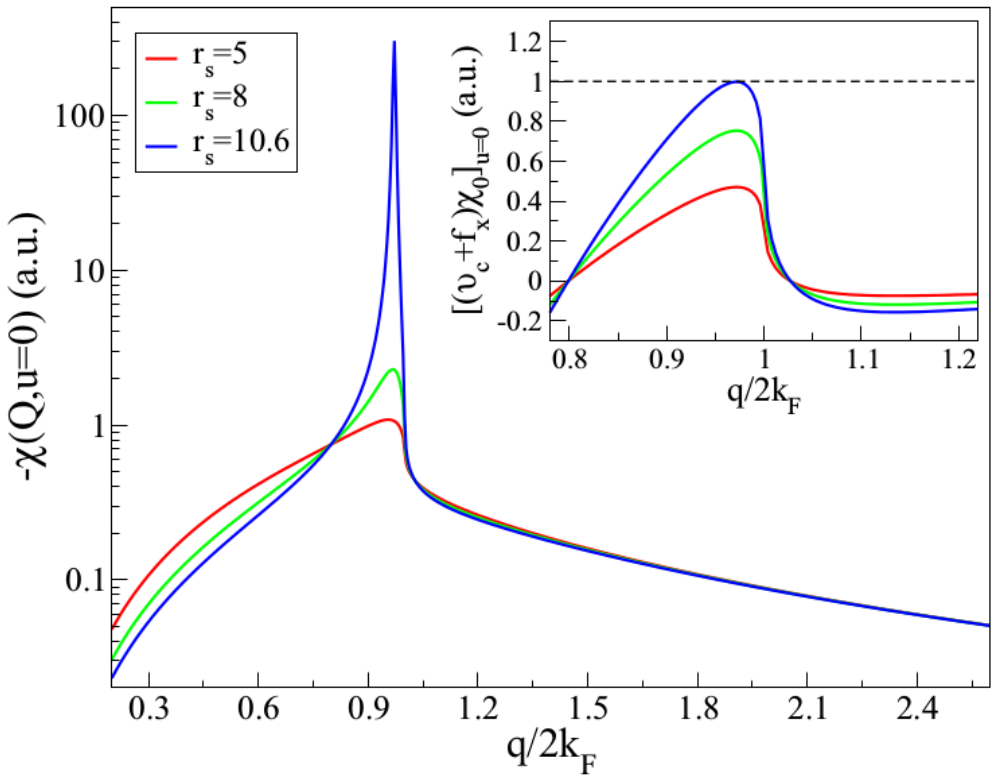
Testing on the Homogeneous Electron Gas (HEG)



- RPA not very good, RPAx much better.

Testing on the Homogeneous Electron Gas (HEG)

- RPAx breakes down at low densities (beyond $r_s \approx 10$)



modified exchange-correlation kernels

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_\lambda(iu)[\lambda v_c + f_{xc}^\lambda(iu)]\chi_0(iu)$$

Original kernel

$$f_{xc}^\lambda(iu) = \lambda f_x(iu)$$

Approximate kernel 1 (inspired by work by Engel & Vosko)

$$f_{xc}^\lambda(iu) = \lambda f_x(iu)[1 + \chi_0(iu)\lambda f_x(iu)]^{-1}$$

Approximate kernel 2 (inspired by work by Furche)

$$f_{xc}^\lambda(iu) = \lambda f_x(iu)[1 + \chi_{RPA,\lambda}(iu)\lambda f_x(iu)]^{-1}$$

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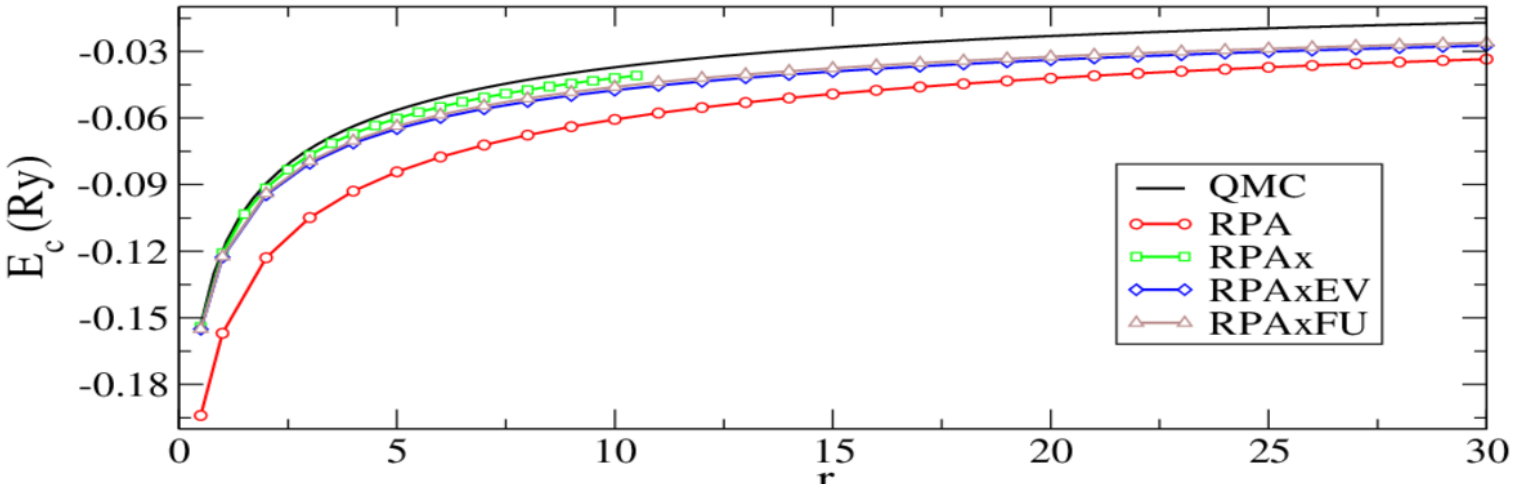
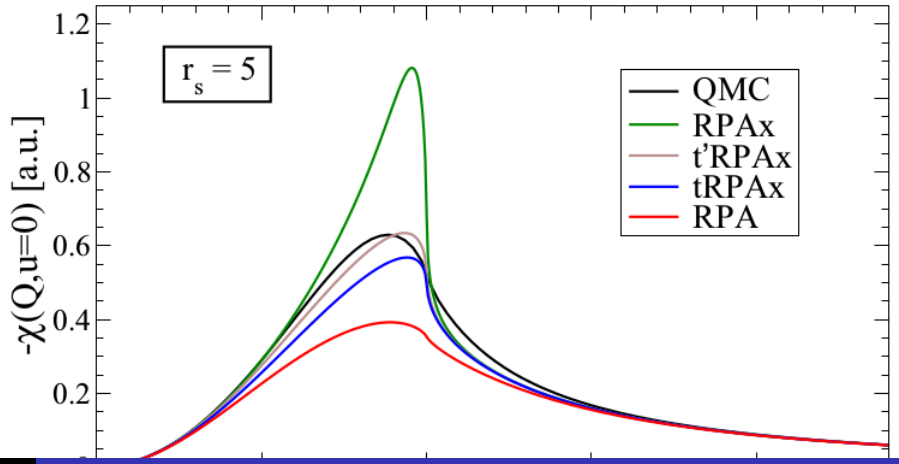
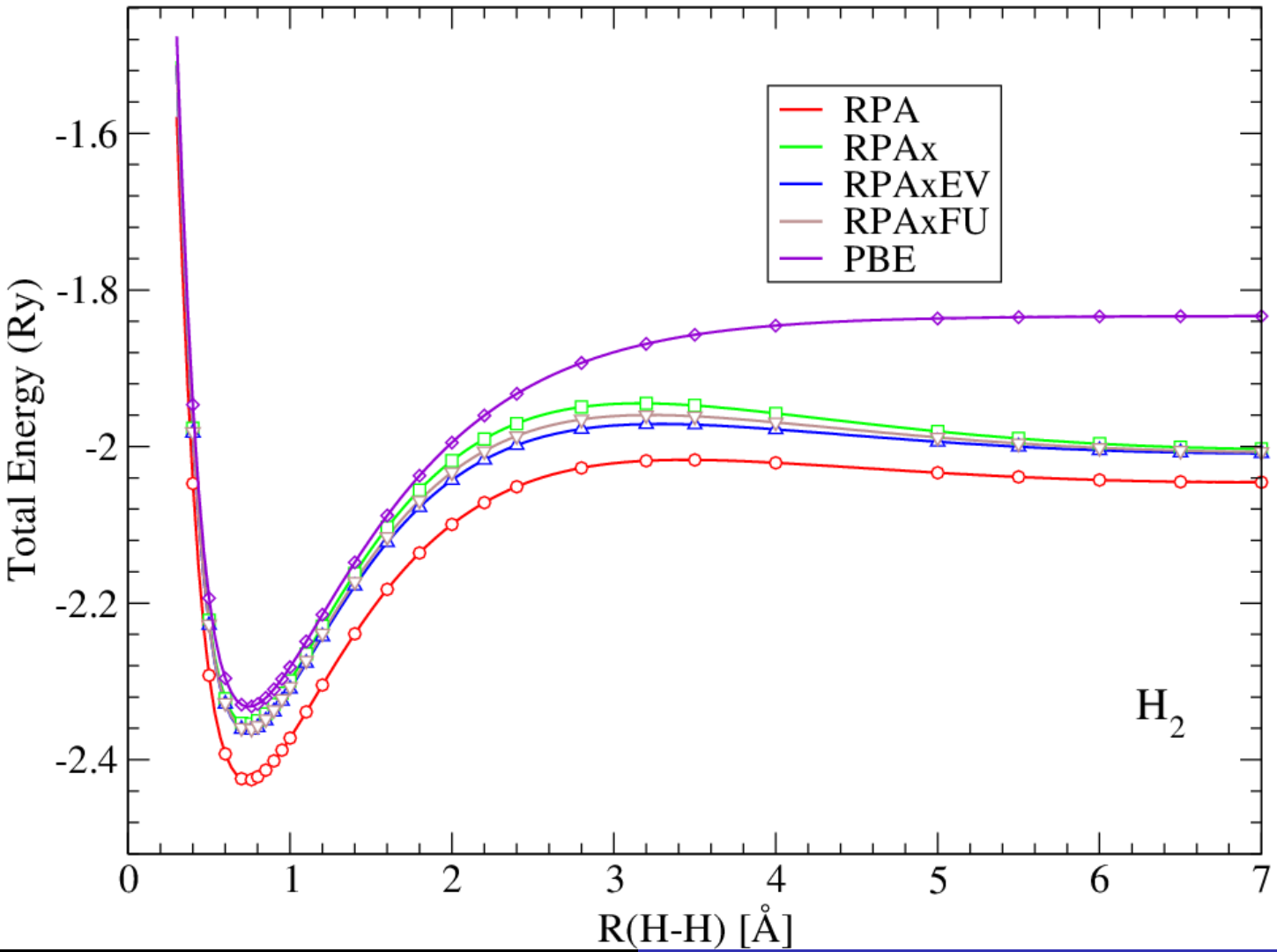
Testing on the Homogeneous Electron Gas (HEG)

- modified fx kernels can be found that are well-behaved without loosing much accuracy.

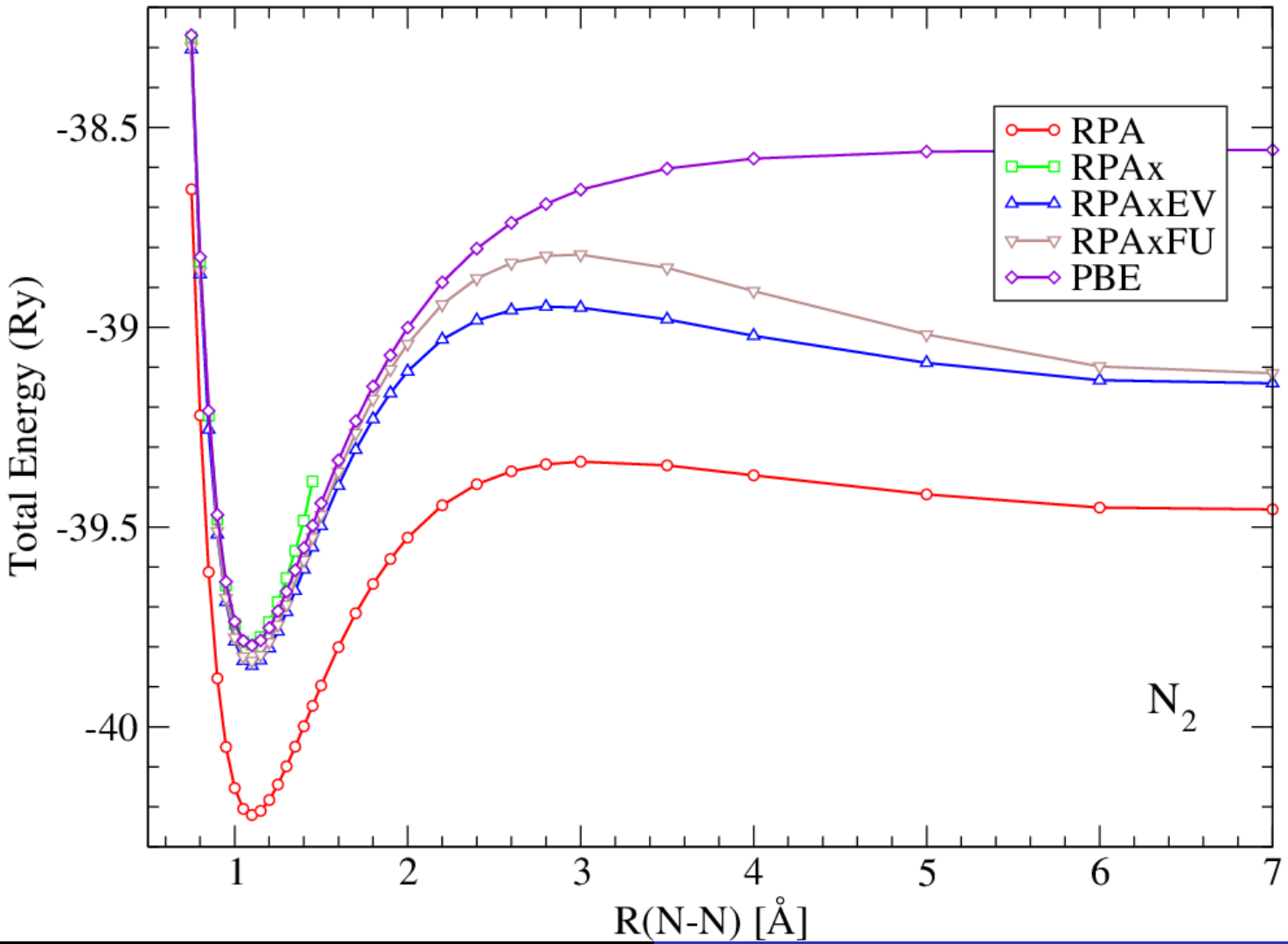




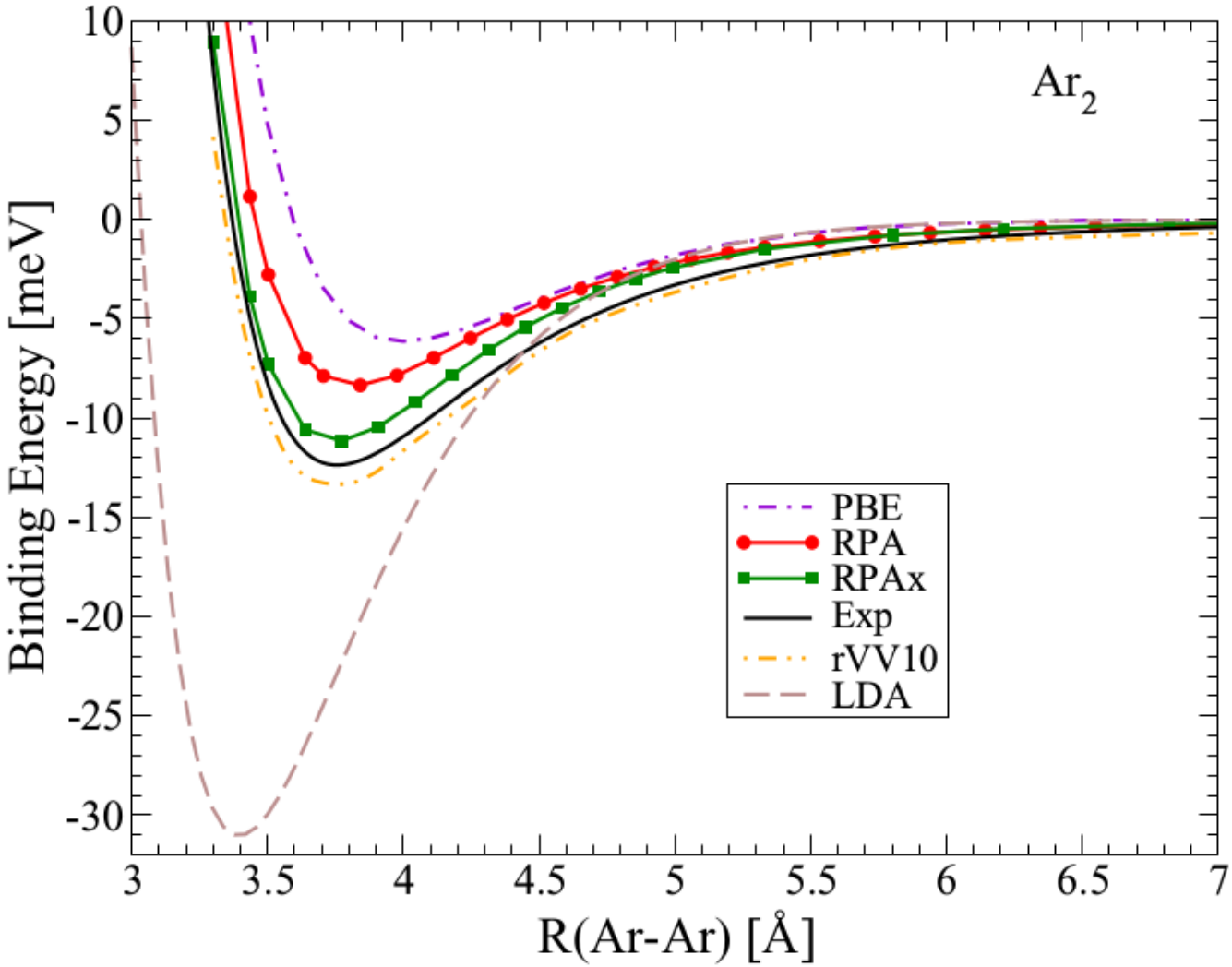
Testing on small molecules



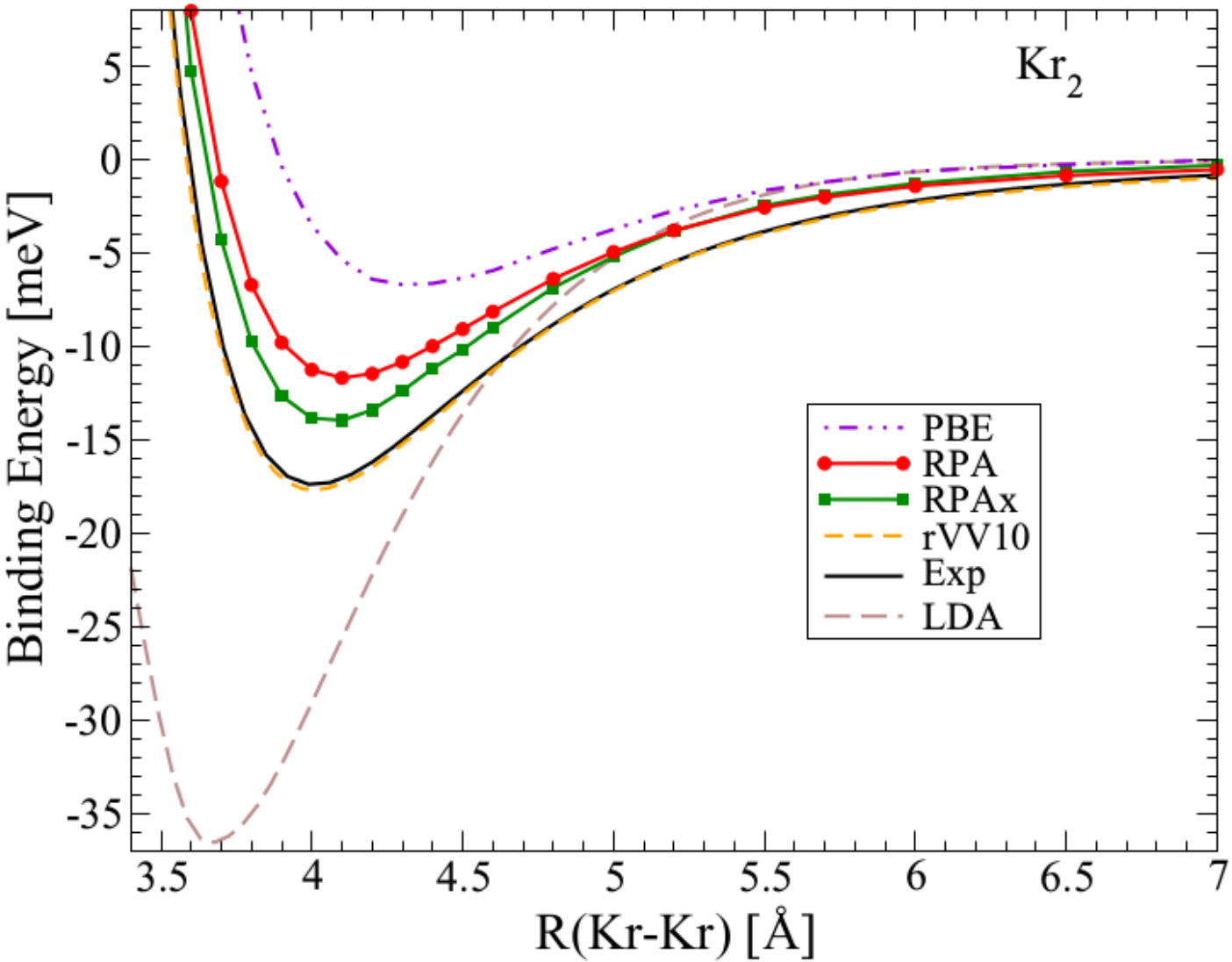
Testing on small molecules



Testing on small molecules: vdW-dimers



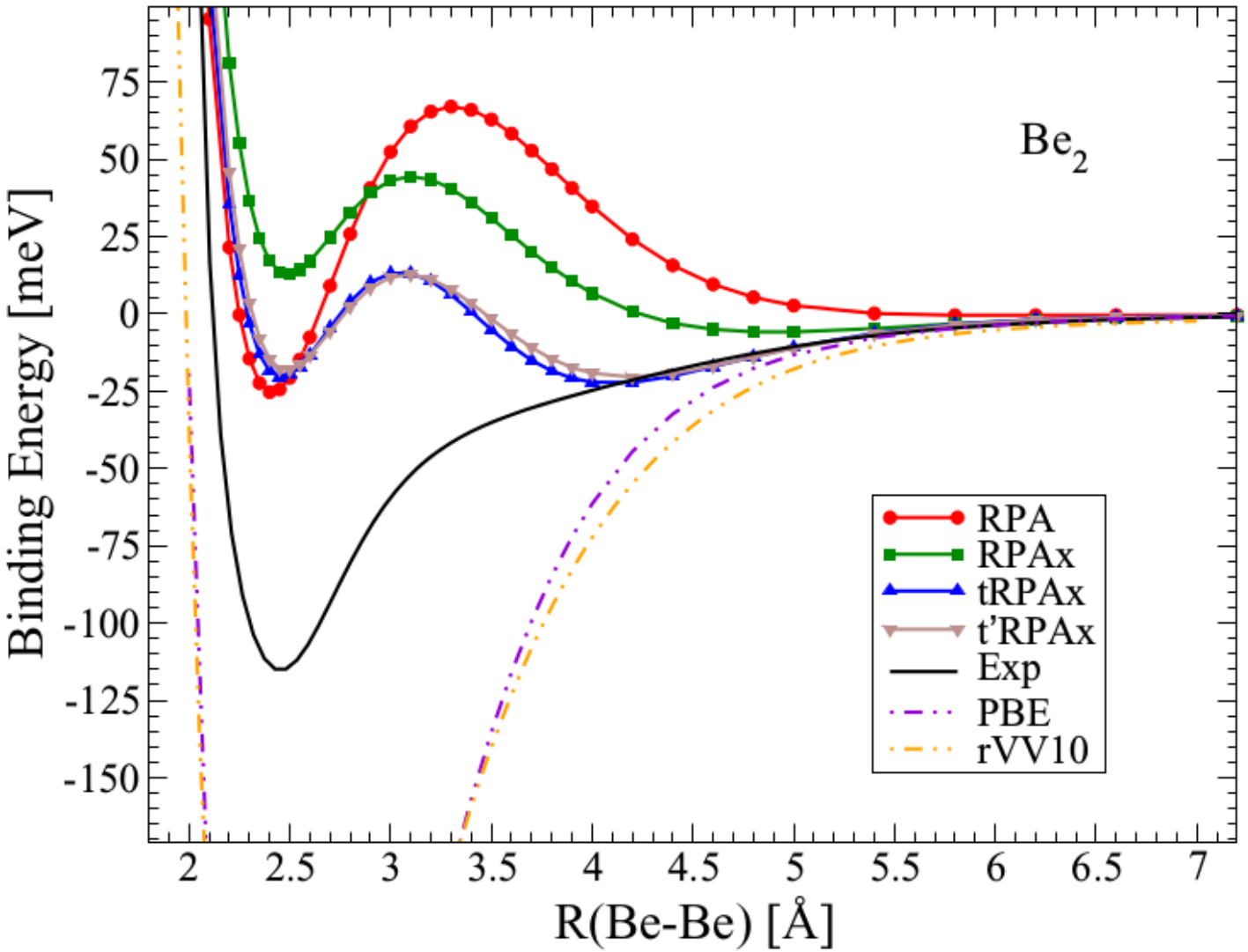
Testing on small molecules: vdW-dimers



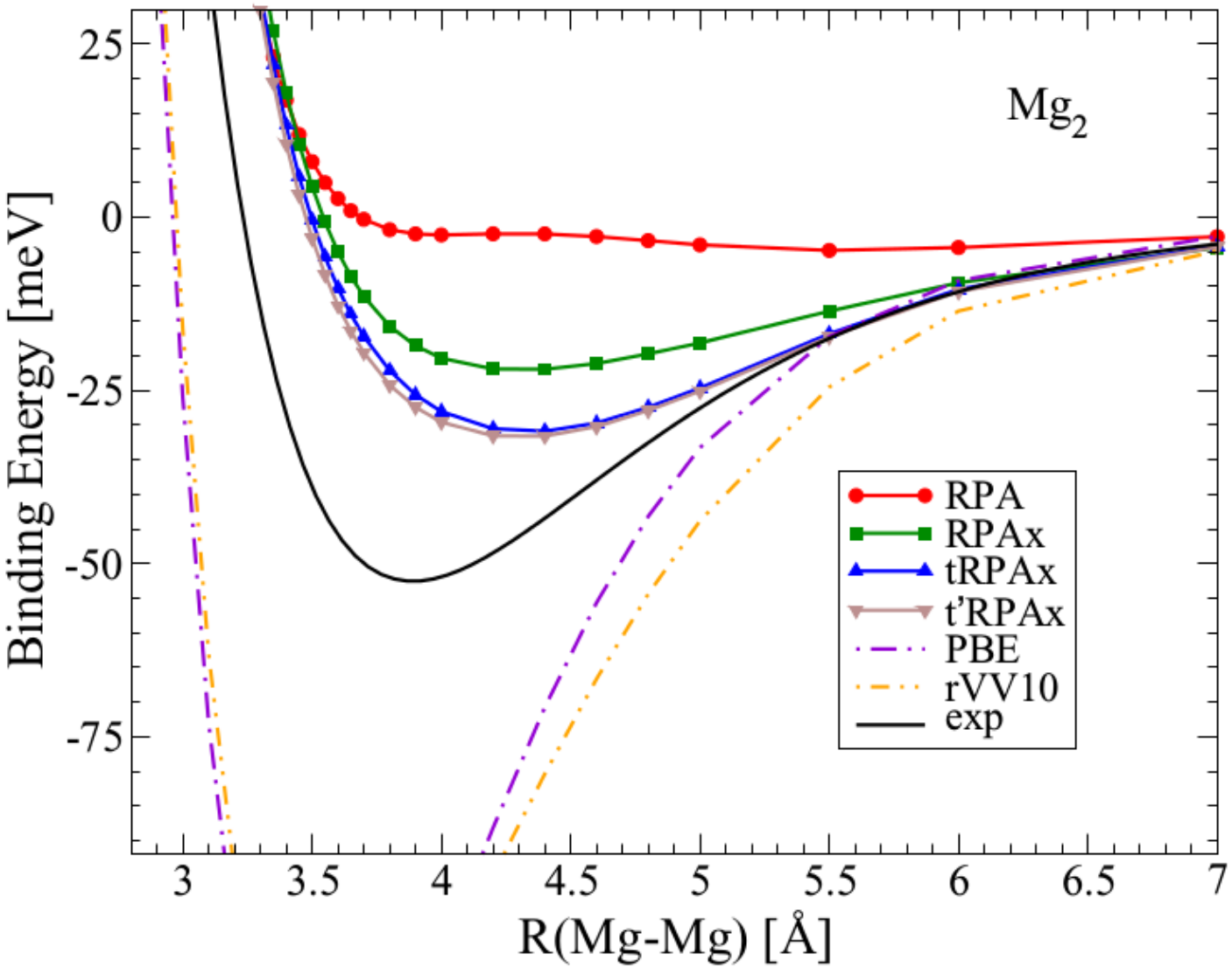
Testing on small molecules: vdW-dimers

	LDA	PBE	RPA	RPAx	rVV10	Expt.
Ar_2						
R_0(Å)	3.39	3.99	3.84	3.75	3.75	3.76
E_b(meV)	31.0	6.1	8.3	11.1	13.4	12.4
$\omega_0(\mathrm{cm}^{-1})$	58.3	23.4	26.8	30.8	32.3	31.2
Kr_2						
R_0(Å)	3.67	4.33	4.11	4.06	4.01	4.01
E_b(meV)	36.6	6.7	11.7	14.0	17.7	17.4
$\omega_0(\mathrm{cm}^{-1})$	39.8	15.4	20.1	22.8	23.8	23.6

A very difficult case: Beryllium dimer



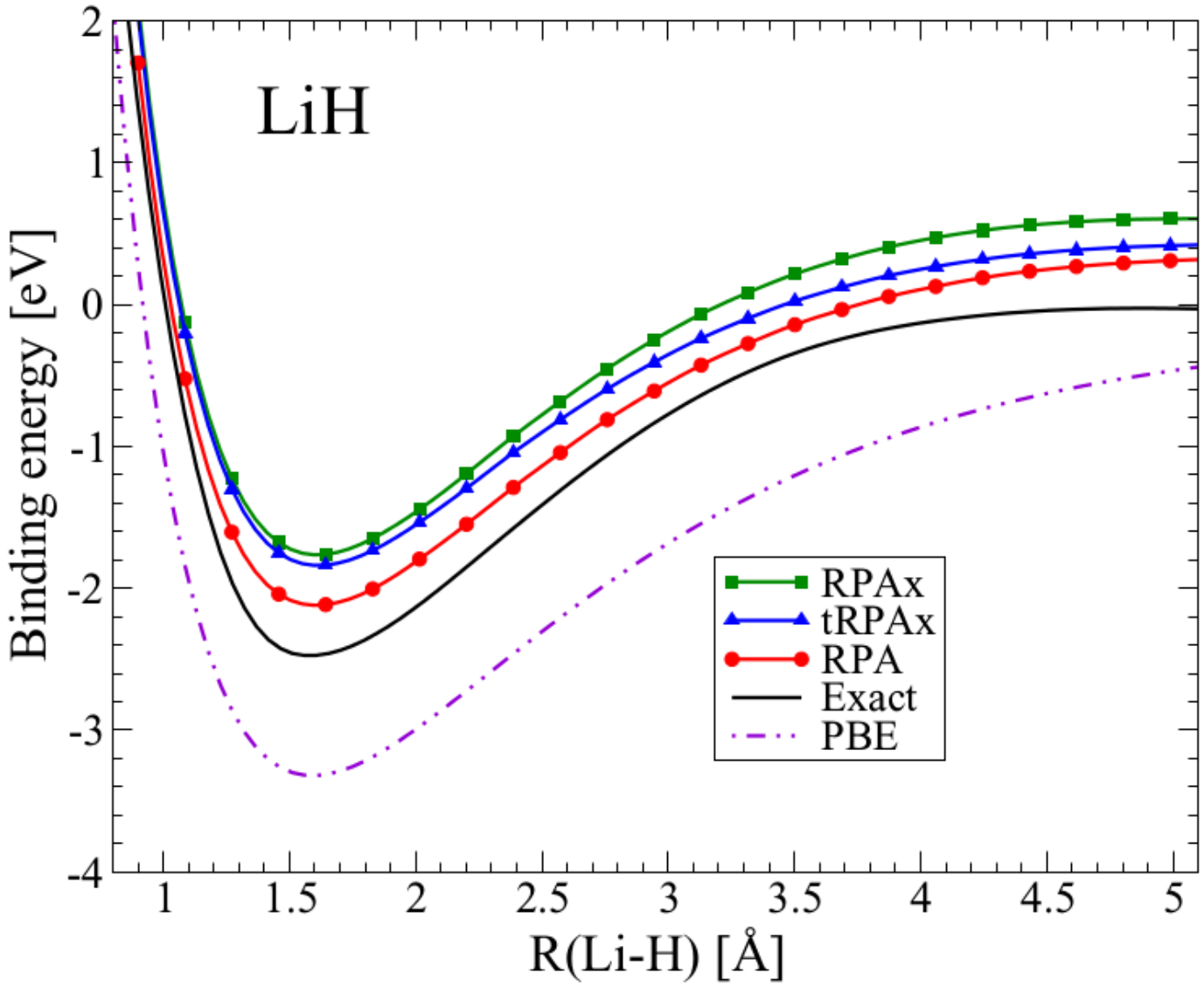
A less difficult case: Magnesium dimer



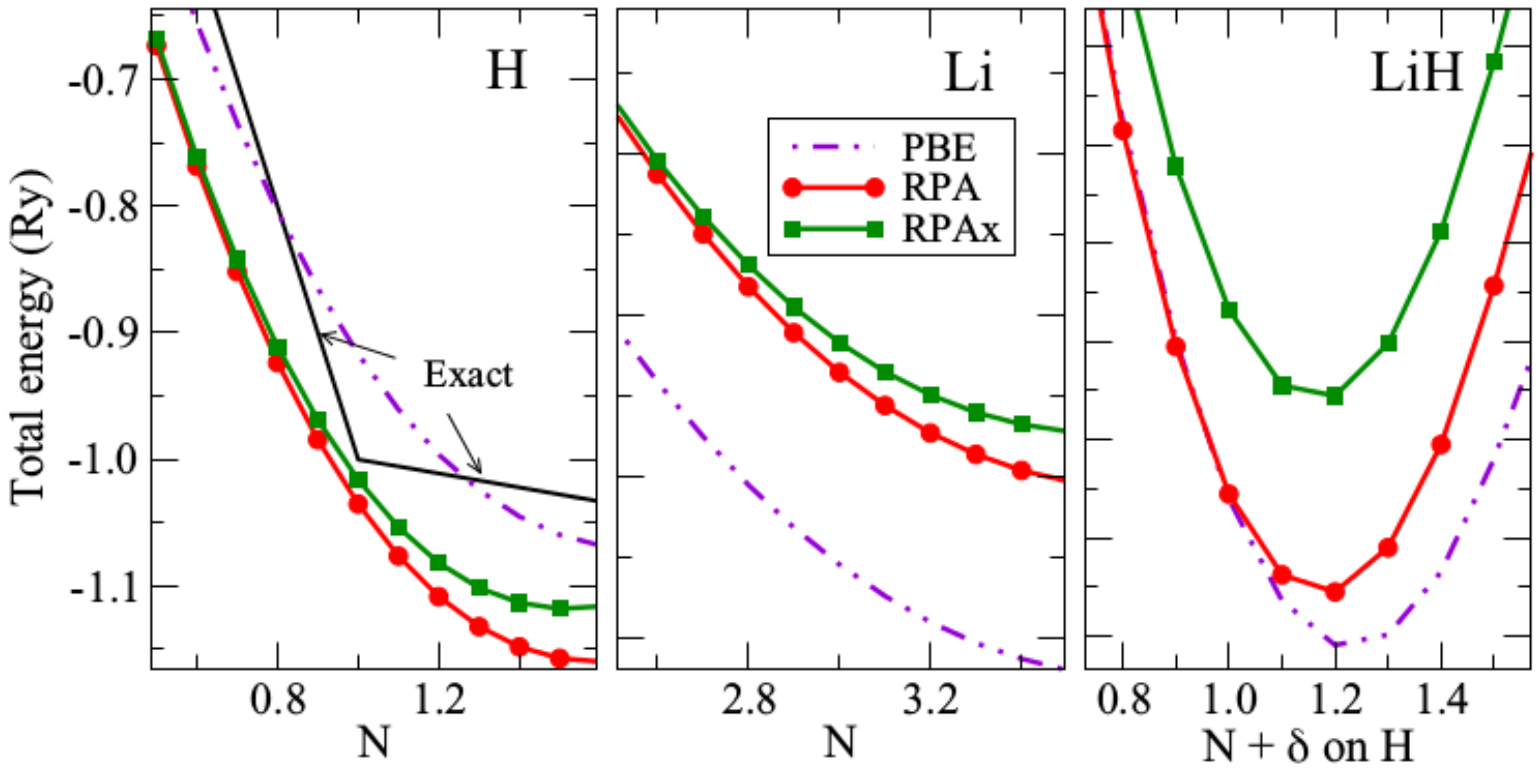
Difficult cases: Be and Mg dimers

	PBE	RPA	RPAx	tRPAx	rVV10	Expt.
Be_2						
R_0(Å)	2.46	2.40	2.49	2.46	2.44	2.45
E_b(meV)	399.4	25.1	–13.1	20.0	387.7	115.3
$\omega_0(cm^{-1})$	336	293	221	231	326	276
Mg_2						
R_0(Å)	3.51		4.31	4.30	3.56	3.89
E_b(meV)	137.1		22.3	30.9	131.1	52.57
$\omega_0(cm^{-1})$	101.5		27.0	31.2	90.2	51.1

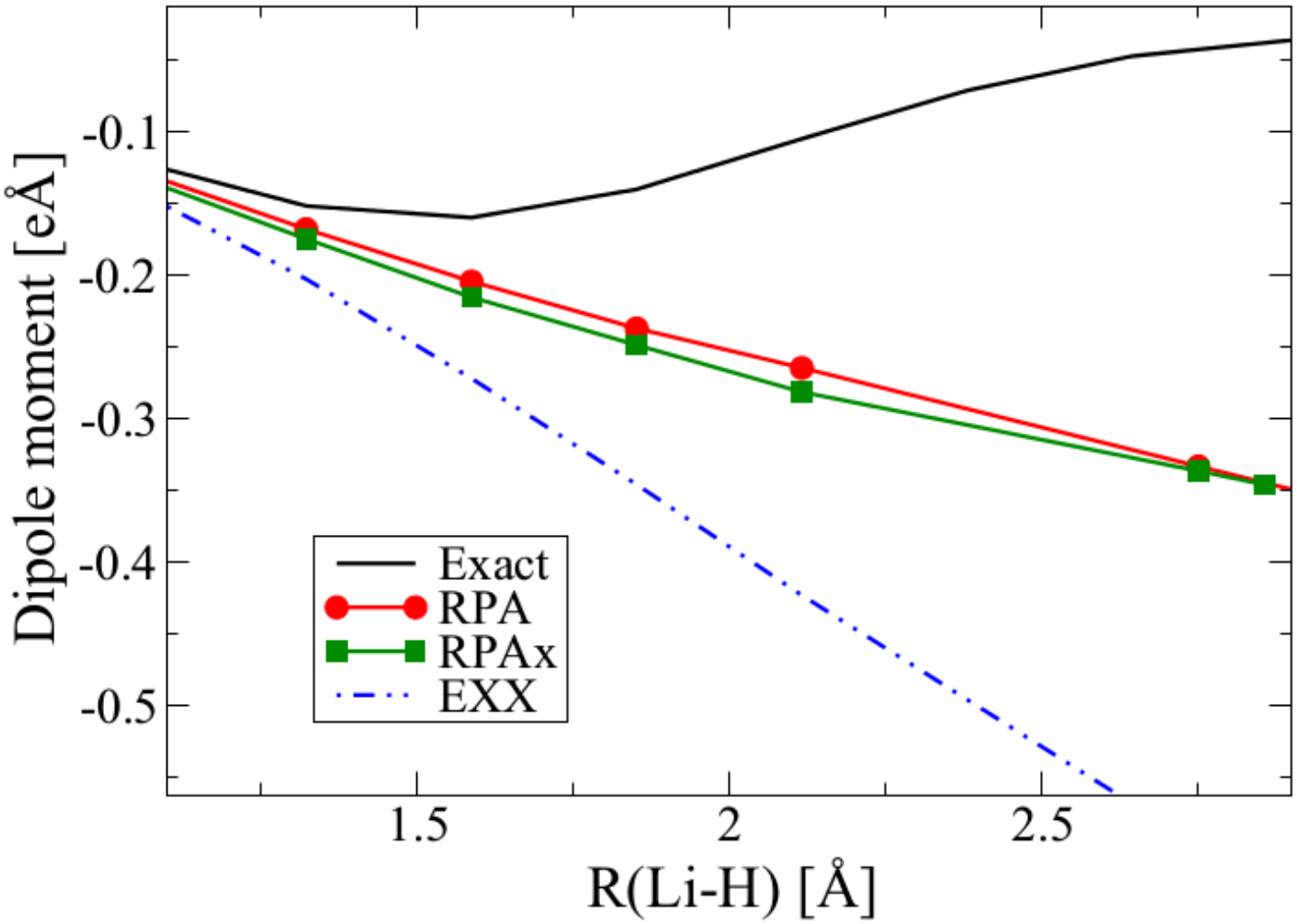
Heteropolar dissociation: LiH



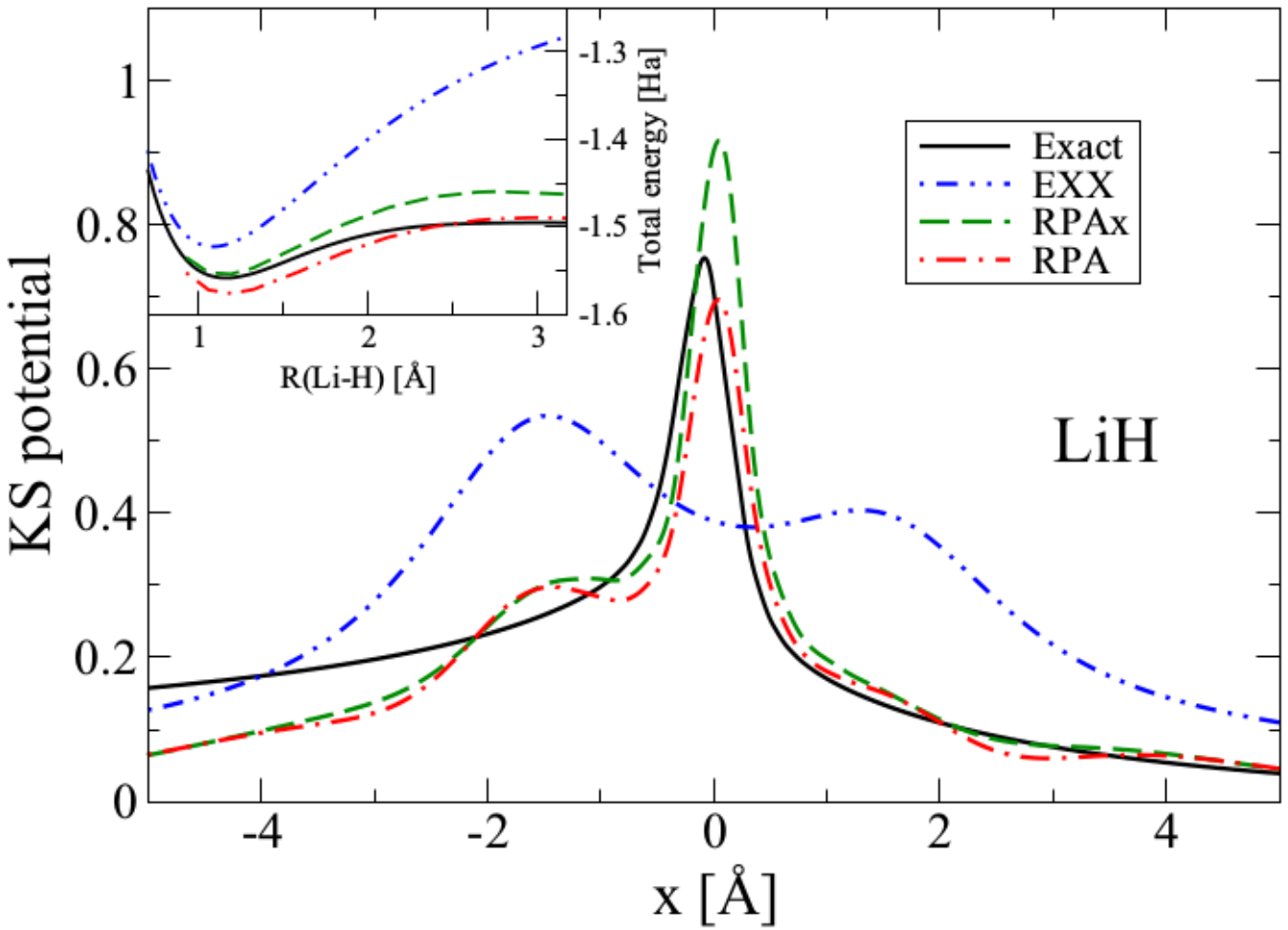
Heteropolar dissociation: LiH



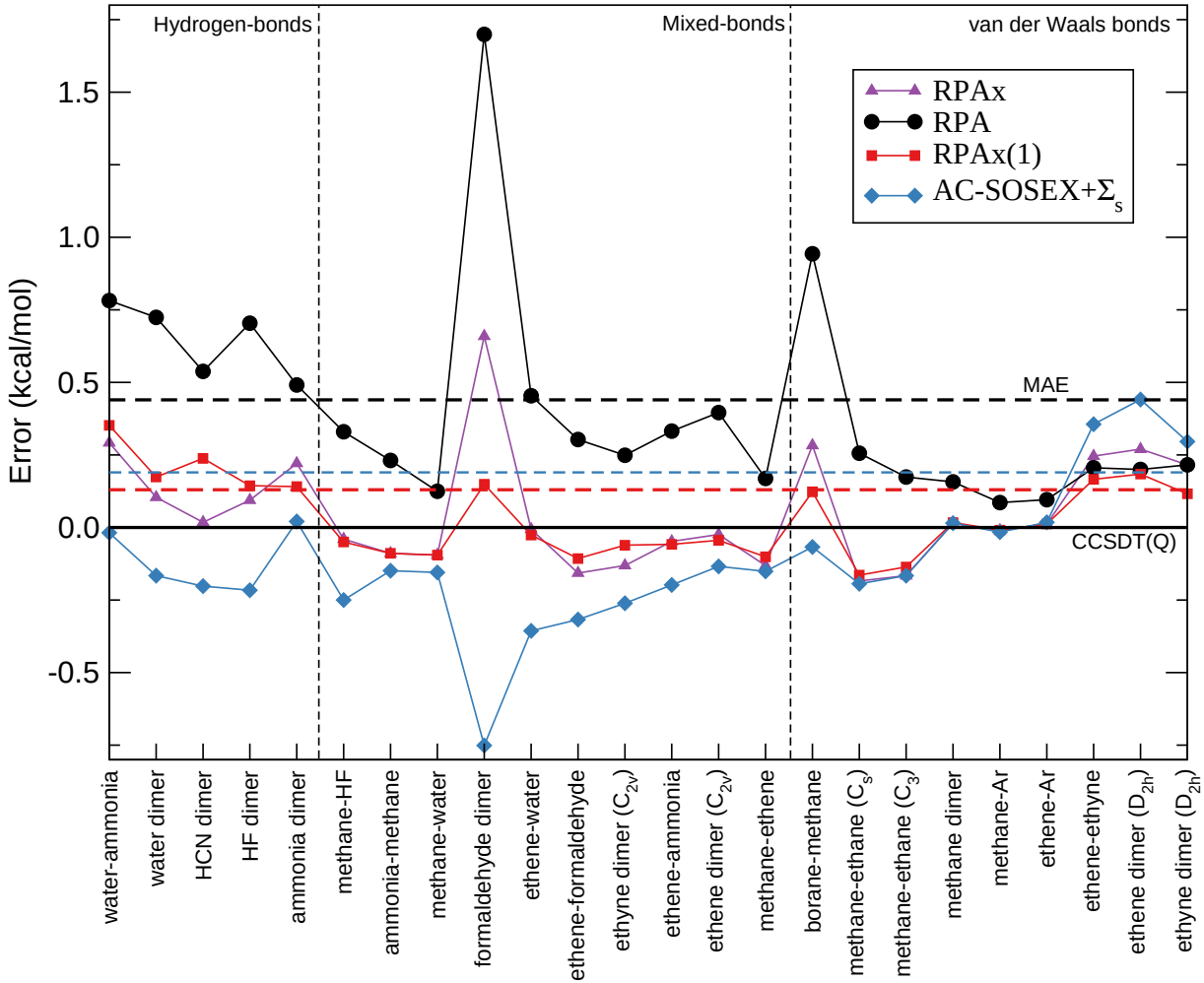
Heteropolar dissociation: LiH



Heteropolar dissociation: LiH



Comparison with the A24 test set



Conclusions

- ACFDT is a promising framework for a systematic generation of improved functionals in terms of coupling constant strength.
- RPA is the simplest approximation, not pathological but not very accurate (in the HEG for instance)
- RPAx includes all linear coupling terms but becomes pathological at low densities. There are well behaved and accurate modified kernels.

- vdW interaction correctly accounted for.
- Dissociation limit is well described for homopolar dimers
- Weak vdW-covalent bonds in Beryllium dimer is problematic
- Heteropolar dissociation still not satisfatory

THANK YOU

A systematic improvement for E_{xc}

Root for a **systematic improvement** of E_{xc};

$$E^{(1)}_{xc,\lambda}(=\lambda E_x) \longrightarrow f^{(1)}_{xc}(=f_x) \longrightarrow E^{(2)}_{c,\lambda} \longrightarrow f^{(2)}_{c} \longrightarrow E^{(3)}_{c,\lambda} \longrightarrow f^{(3)}_{c} \dots$$

Hierarchy for E_{xc}

$$E^{\lambda}_{xc} = \lambda E_x + \sum_{m=1}^{\infty} E^{(m+1)}_{c,\lambda}$$

$$E^{(m+1)}_{c,\lambda} = -\frac{1}{2\pi}\int_0^{\lambda} d\mu \int_0^{\infty} du \mathrm{Tr}\left\{ v_c \left[\chi^{(m)}_{\mu}(iu) - \chi^{(m-1)}_{\mu}(iu) \right] \right\}$$

$$\chi^{(m)}_{\lambda} - \chi^{(m-1)}_{\lambda} = \chi^{(m)}_{\lambda}[\lambda^m f^{(m)}_c]\chi^{(m-1)}_{\lambda}$$

$$f^{(m)}_c = \frac{1}{m!}\frac{d^m}{d\lambda^m}\left[\frac{\delta^2 E^{\lambda}_{xc}}{\delta n \delta n}\right]_{\lambda=0} \equiv \frac{1}{m!}\frac{d^m}{d\lambda^m}\left[\sum_{l\leq m}\frac{\delta^2 E^{(l)}_{c,\lambda}}{\delta n \delta n}\right]_{\lambda=0}$$

Calculating the Trace

Consider the generalized eigenvalue problem

$$\chi_0[v_c + f_x]\chi_0|\omega_\alpha\rangle = -a_\alpha[-\chi_0]|\omega_\alpha\rangle \qquad \langle\omega_\alpha|[-\chi_0]|\omega_\beta\rangle = \delta_{\alpha\beta}$$

Multipling on the left by $\lambda\chi_\lambda^{(1)}\chi_0^{-1}$

$$\lambda\chi_\lambda^{(1)}[v_c + f_x]\chi_0|\omega_\alpha\rangle = \lambda a_\alpha\chi_\lambda^{(1)}|\omega_\alpha\rangle$$

$$(\chi_\lambda^{(1)} - \chi_0)|\omega_\alpha\rangle = \lambda a_\alpha\chi_\lambda^{(1)}|\omega_\alpha\rangle \quad \Rightarrow \quad \chi_\lambda^{(1)}|\omega_\alpha\rangle = \frac{1}{1-\lambda a_\alpha}\chi_0|\omega_\alpha\rangle$$

$$\mathrm{Tr}[v_c(\chi_\lambda^{(1)} - \chi_0)] = \sum_\alpha \left(1 - \frac{1}{1-\lambda a_\alpha}\right)\langle\omega_\alpha|\chi_0 v_c\chi_0|\omega_\alpha\rangle$$

Performing integration over λ

$$E_c^{EXX} = -\frac{1}{2\pi}\int_0^\infty du \sum_\alpha \frac{\langle\omega_\alpha|\chi_0 v_c\chi_0|\omega_\alpha\rangle}{a_\alpha(iu)}\{\mathrm{Log}[1 - a_\alpha(iu)] + a_\alpha(iu)\}$$

Perturbation Theory along Adiabatic Path

$$\left(\frac{dE_\lambda}{d\lambda}\right)_{\lambda=0} = \frac{d}{d\lambda}\langle\Psi_\lambda|T+\lambda W+V_\lambda|\Psi_\lambda\rangle_{\lambda=0} = \langle\Psi_0|W+\left(\frac{dV_\lambda}{d\lambda}\right)_{\lambda=0}|\Psi_0\rangle =$$

$$= \langle\Psi_0|W|\Psi_0\rangle + \int n\left(\frac{dV_\lambda}{d\lambda}\right)_{\lambda=0} == E_H + E_x + \int n\left(\frac{dV_\lambda}{d\lambda}\right)_{\lambda=0}$$

On the other hand

$$\left(\frac{dE_\lambda}{d\lambda}\right)_{\lambda=0} = \left(\frac{dF_\lambda}{d\lambda}\right)_{\lambda=0} + \int n\left(\frac{dV_\lambda}{d\lambda}\right)_{\lambda=0}$$

Hence

$$\left(\frac{dF_\lambda}{d\lambda}\right)_{\lambda=0} = E_H + E_x$$

Becouse of the stationarity of the functional E_λ

$$\frac{\delta F_\lambda}{\delta n} + V_\lambda = 0 \Rightarrow \qquad \frac{\delta}{\delta n}\left[\frac{dF_\lambda}{d\lambda}\right]_{\lambda=0} + \left[\frac{dV_\lambda}{d\lambda}\right]_{\lambda=0} = 0 \Rightarrow$$

$$\Rightarrow \frac{\delta}{\delta n}[E_H+E_x] + \left[\frac{dV_\lambda}{d\lambda}\right]_{\lambda=0} = 0 \Rightarrow \left[\frac{dV_\lambda}{d\lambda}\right]_{\lambda=0} = -\upsilon_H - \upsilon_x$$