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RPA correlation potential in the adiabatic connection fluctuation-dissipation formalism

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RPA Correlation Potential from Adiabatic Connection Fluctuation-Dissipation Theory (ACFDT)

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- ACFDT introduction
- RPA Self-Consistent potential
- going (sistematically) beyond RPA

Some Remarks on DFT Calculations

- DFT is an exact theory BUT approximations for the exchange-correlation energy are required for practical applications
- LDA, GGAs succesfully predict properties of a wide class of electronic systems

Local or Semi-Local nature of LDA, GGAs functionals

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

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

- There are many systems where DFT within LDA and GGAs fails e.g. **strongly correlated materials AND weakly vdW bonded compounds**

ACFDT : an exact definition for the correlation energy

Adiabatic Connection formula for 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

- practical (so to speak) way to calculate xc-energy explicitly
- theoretical framework for **systematic** development of functionals

LIMITATIONS

- computationally very demanding
- affected by a circular argument?

Derivation

Full-Interacting Hamiltonian

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

Non-Interacting (Khon-Sham) Hamiltonian

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

then we introduce fictitious systems with **scaled interaction** λW wich connect the KS ($\lambda = 0$) with the Many-Body system ($\lambda = 1$)

Adiabatic Connection

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

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

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

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

Derivation

According to **Hellmann-Feynman** theorem

$$\frac{dE_\lambda}{d\lambda} = \langle\Psi_\lambda|\frac{dH_\lambda}{d\lambda}|\Psi_\lambda\rangle = \langle\Psi_\lambda|W|\Psi_\lambda\rangle + \langle\Psi_\lambda|\frac{\partial v_{ext}}{\partial\lambda}|\Psi_\lambda\rangle$$

Integrating over λ beetween 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

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

Derivation

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

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

Fluctuation-Dissipation Theorem

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

Exchange-Correlation Energy from ACFDT

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

Derivation

Replacing χ_λ with $\chi_{KS} = \chi_0$

$$E_x = -\frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{|\sum_i^{occ} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

The exchange-correlation energy can thus be separated

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

Adiabatic connection formula for correlation energy

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

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

Random Phase Approximation (RPA)

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

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

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

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

determines the(λ-)interacting response

Implementation

- Define generalized eigenvalue problem

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

- In RPA

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

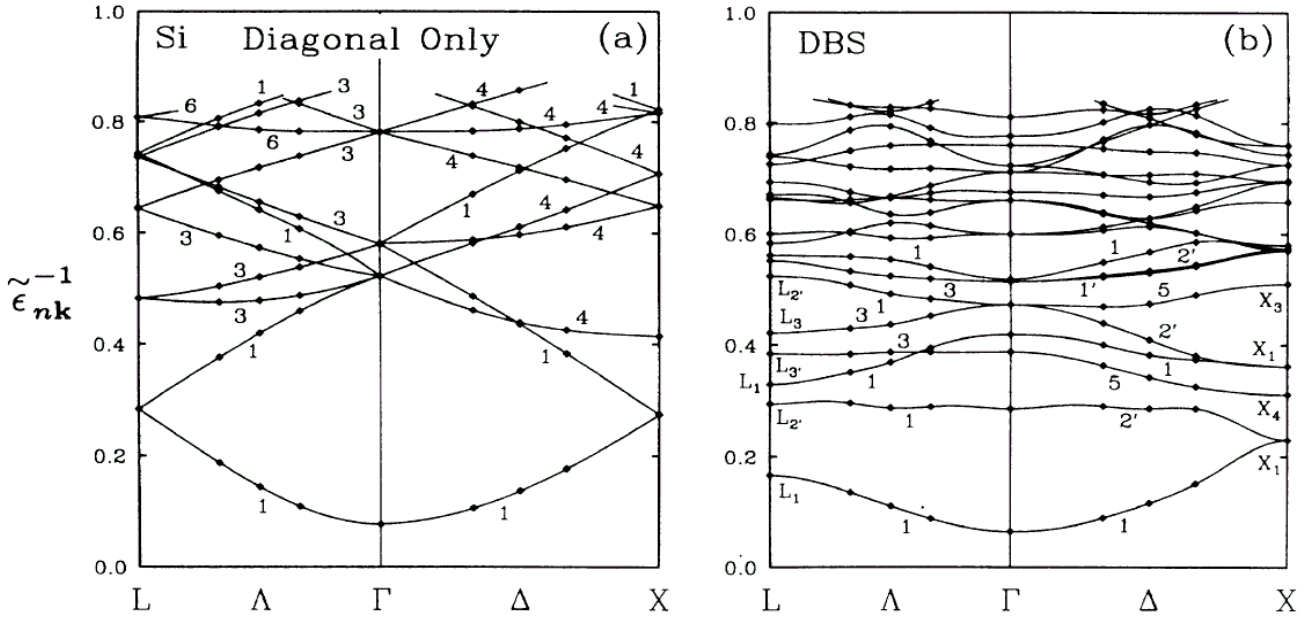
$\Rightarrow$ λ-integration is done analytically

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

dielectric matrix band structure

- Moreover: Most eigenvalues a_α are close to zero

$$\epsilon_{RPA} = 1 - v_c \chi_0$$



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Iterative diagonalizatin of χ_0

- Matrix elements of χ_0 are efficiently computed by Density Functional Perturbation Theory :
  $\Delta n = \chi_0 \Delta V_{SCF} \;\; (= \chi \Delta V_{ext})$
  S.Baroni, A.DalCorso, P.Giannozzi, and SdG, Rev.Mod.Phys. 73, 515 (2001)

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

$$\Delta n(\mathbf{r}) = 2Re\left\{ \sum_{i\in \mathrm{occ.}} \psi_i^* \Delta\psi_i \right\}$$

$$\Delta V_{SCF}(\mathbf{r}) = \cancel{\Delta V_{ext}(\mathbf{r}) + \Delta V_H(\mathbf{r}) + \Delta V_{xc}(\mathbf{r})}$$

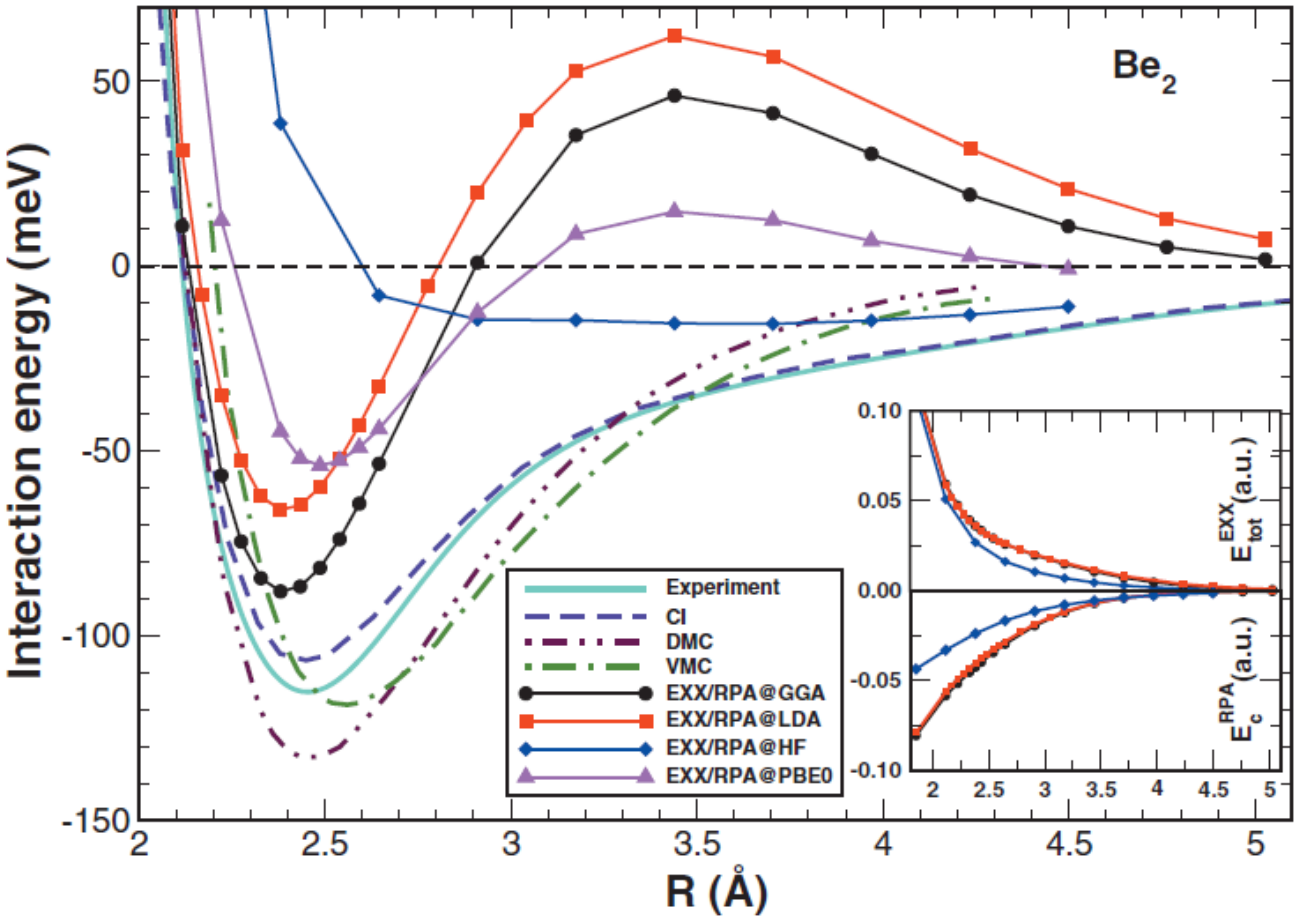
A number of applications have been made ...

- Molecular Crystals (Benzene and Methane)
- Self assembled Monolayers on Au
- Water
- vdW-dimers

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

Importance of a self-consistent potential

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



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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

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

where

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

- The first line can trivially be calculated for any perturbing potential δV_{KS}, hence $\longrightarrow \frac{\delta a_\alpha}{\delta V_{KS}}$
- The second line is more complicated but can also be re-expressed in a way that it can be calculated easily for any perturbing potential δV_{KS}.

For $iu = 0$

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

where

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

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

solution of the OEP problem

$v_c(\mathbf{r}) = \frac{\delta E_c}{\delta n(\mathbf{r})}$ can be obtained by

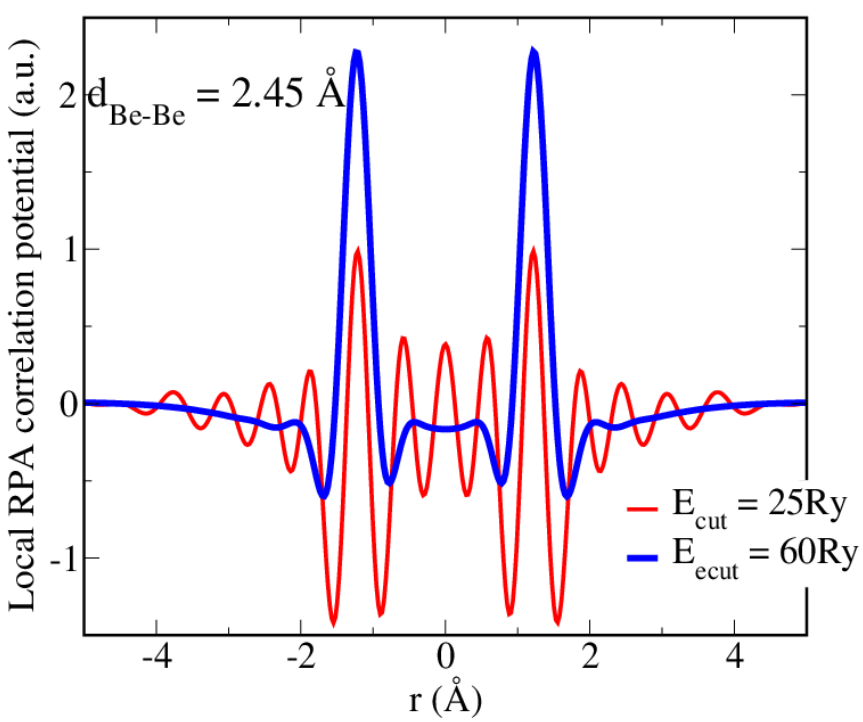
$$\boxed{v_c(\mathbf{r}) = \int \chi_0^{-1}(\mathbf{r},\mathbf{r}') \frac{\delta E_c}{\delta V_{KS}(\mathbf{r}')} d\mathbf{r}'}$$

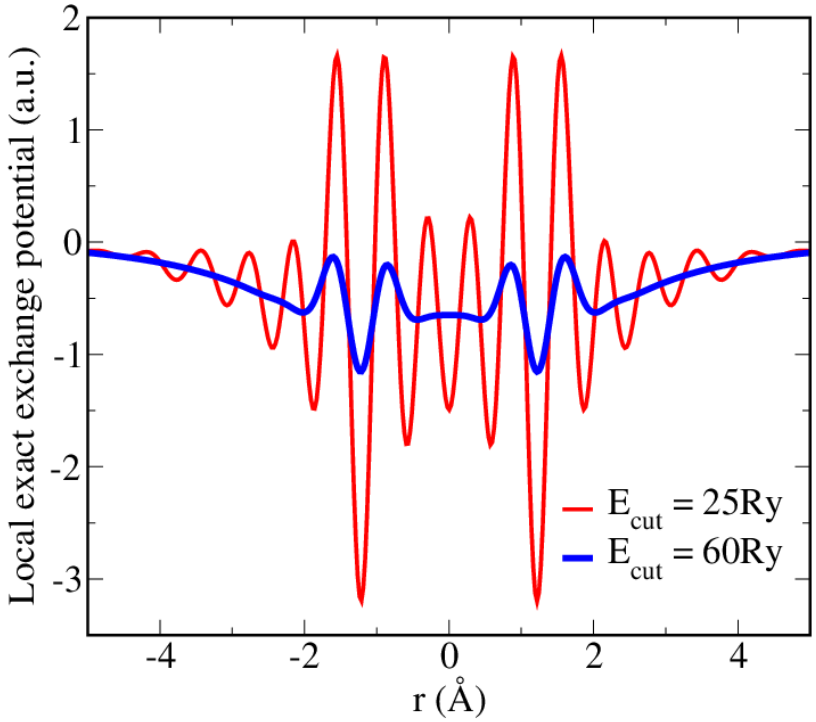
exploiting the eigenvalue decomposition of $\chi_0^{-1}(\mathbf{r},\mathbf{r}')$.

$$\boxed{v_c(\mathbf{r}) = \sum_\alpha \omega_\alpha(\mathbf{r}) \frac{1}{a_\alpha} \langle \omega_\alpha | \frac{\delta E_c}{\delta V_{KS}} \rangle}$$

OEP solution requires many χ_0 eigenpotentials.

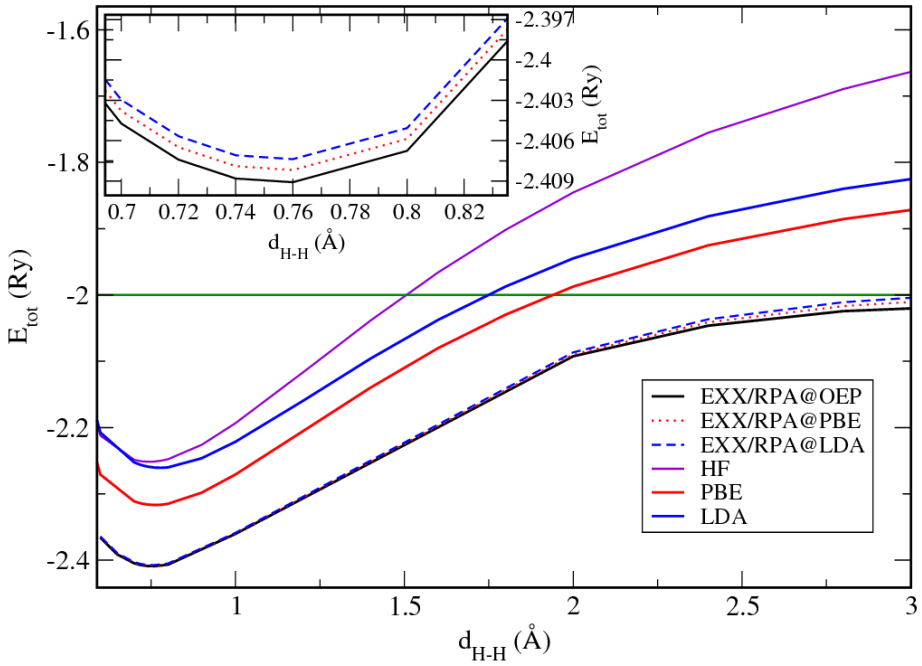
Self-consistent potential





Numerical stability is somewhat a problem but can be kept under control.

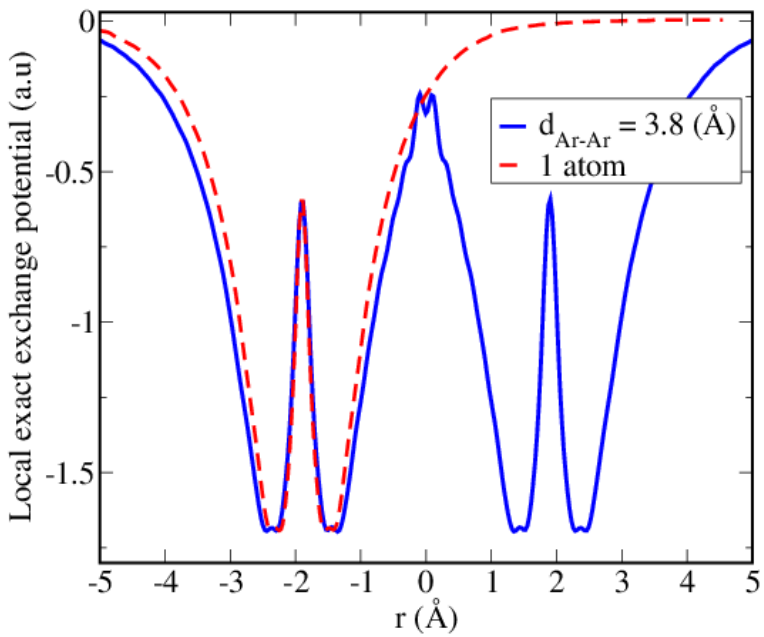
Hydrogen dimer dissociation

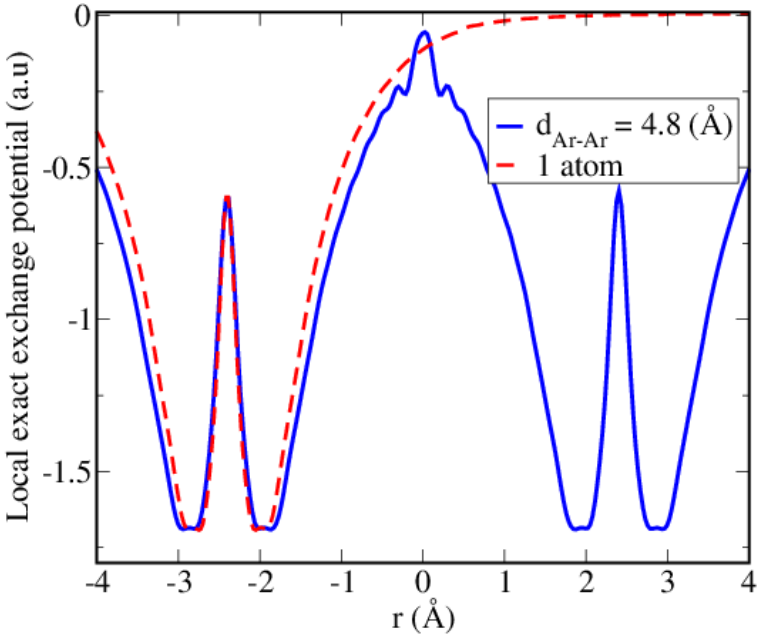


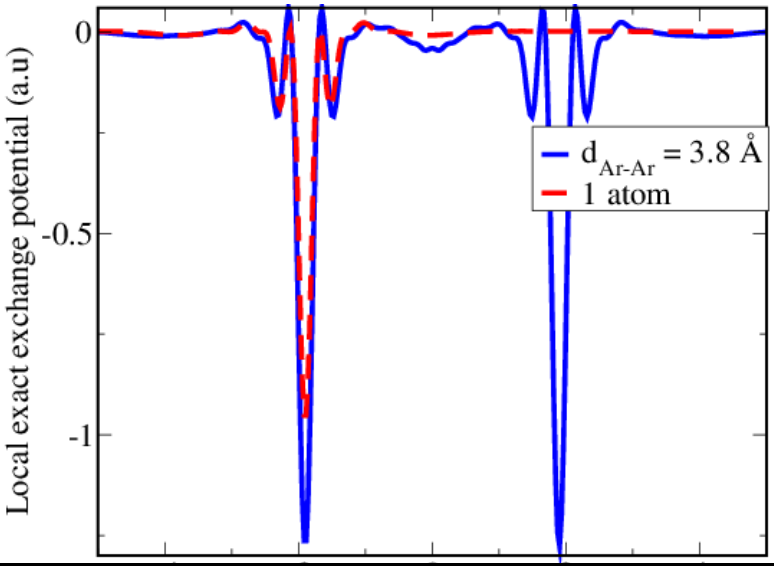
dissociation behaviour correctly described

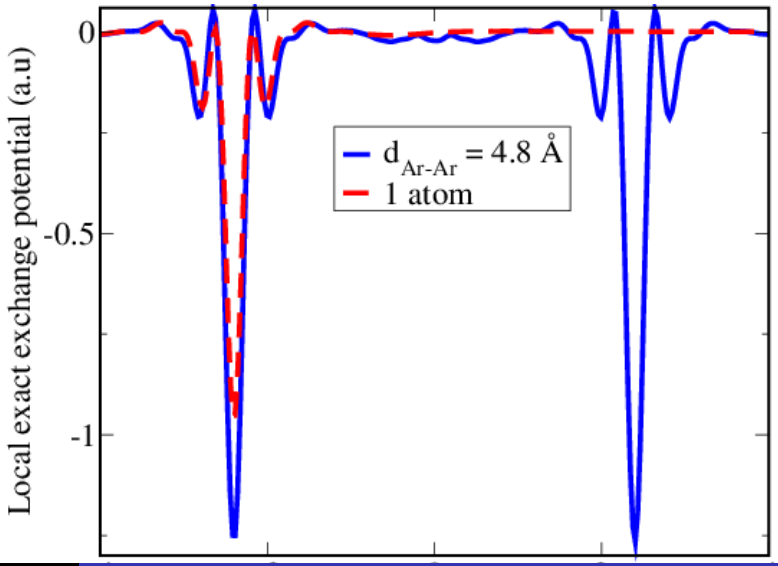
self-consistent potential is not very important

Self-consistent potential for Ar_2

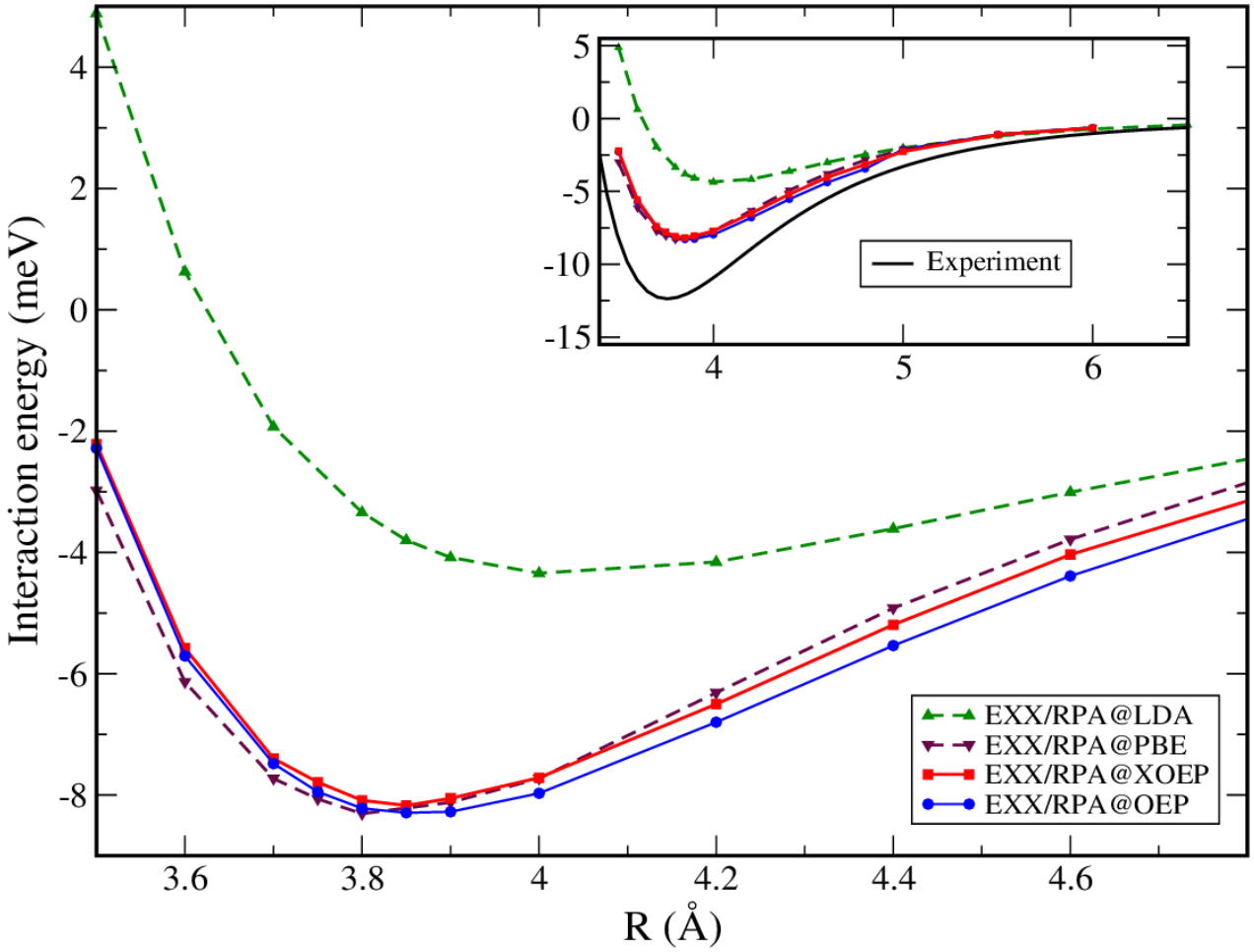






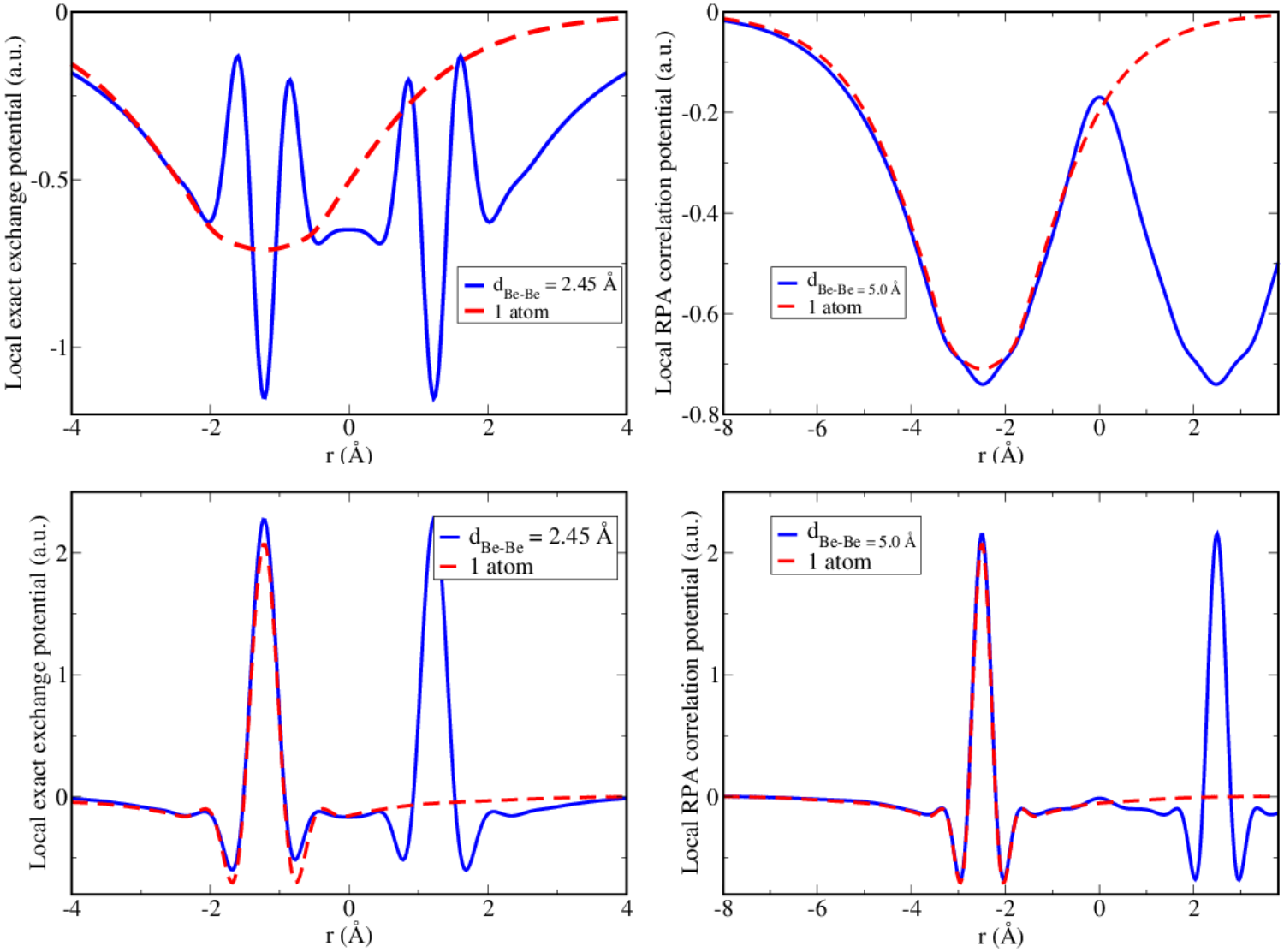


Ar_2 binding energy



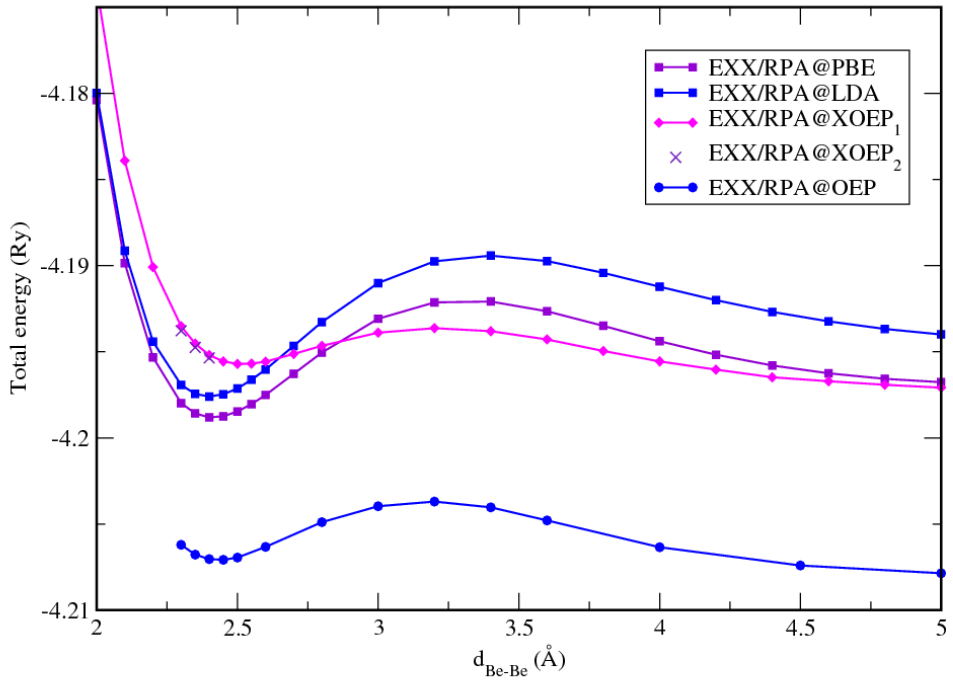
dissociation behaviour correctly described
binding underestimated
self-consistent potential is not very important

Self-consistent potential for Be_2



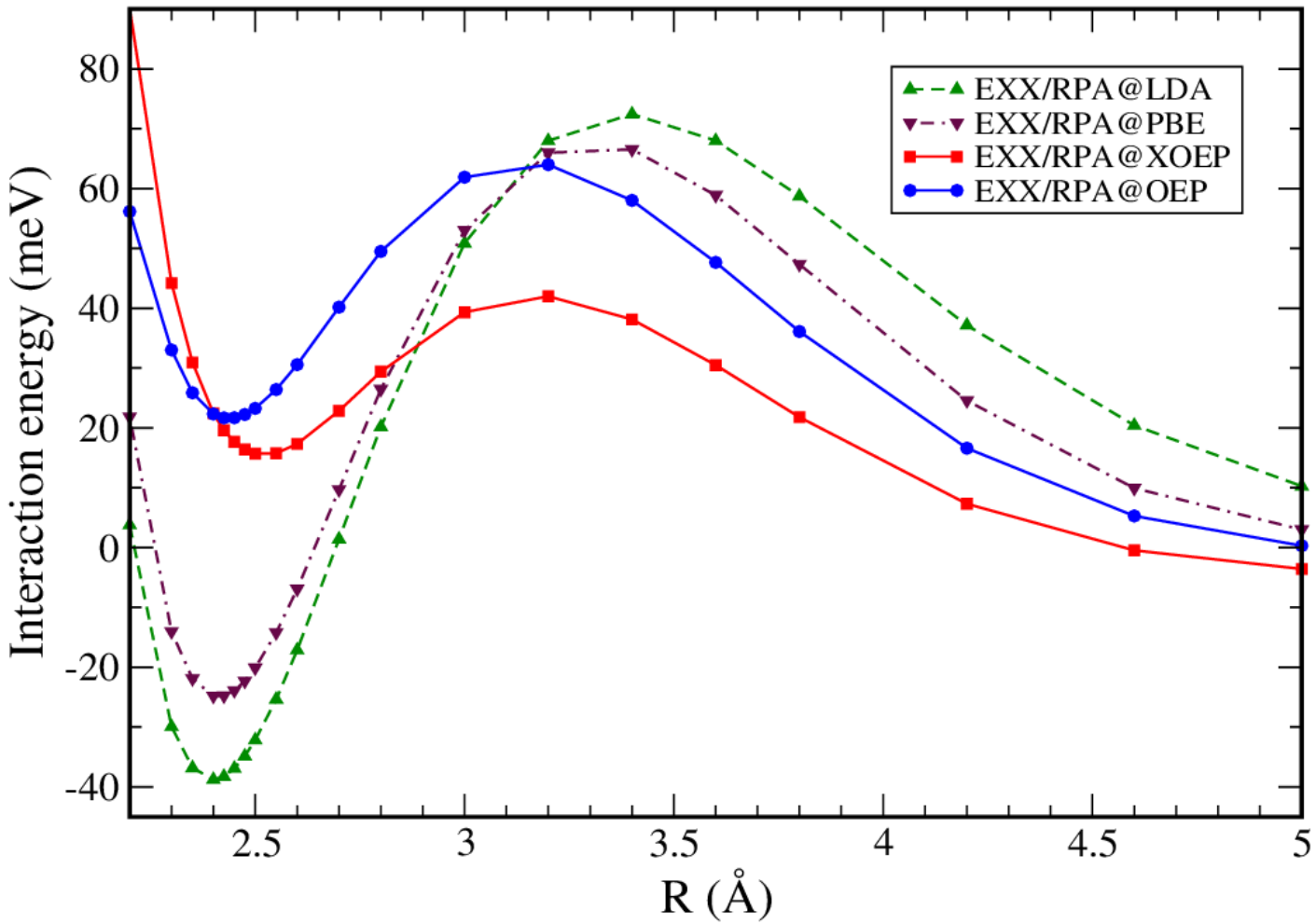
Beryllium dimer dissociation

Self-consistent potential makes a significant difference in this case

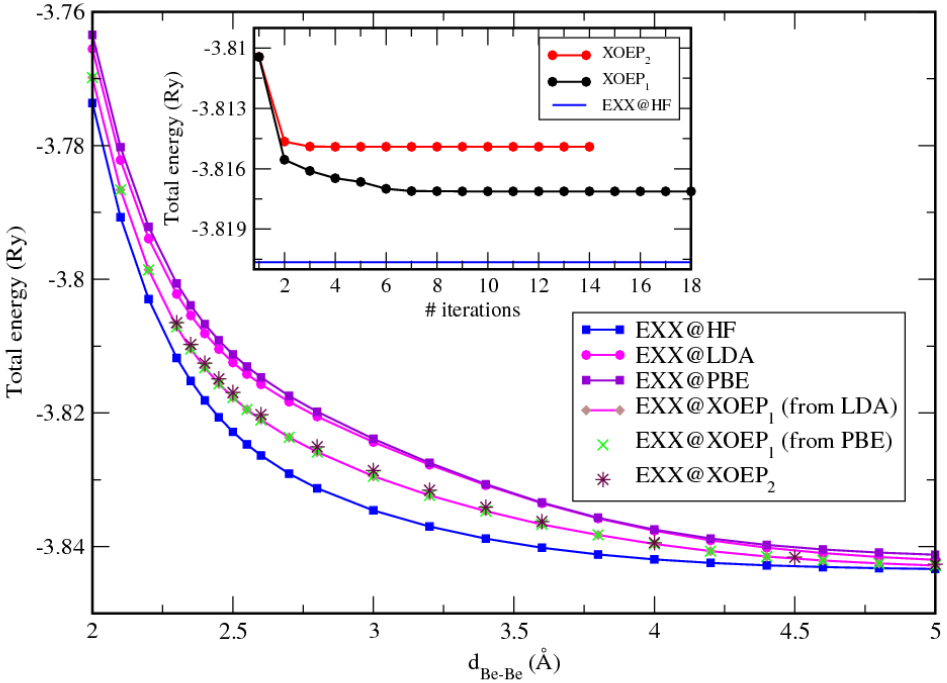


Beryllium dimer is unstable...

Beryllium dimer dissociation



Beryllium dimer dissociation



XOEP potential gives "significantly" higher energies w.r.t. HF

- should we use HF exchange instead ?
- is it a problem of the 2-el pseudopotential we're using ?
- is it a real feature of RPA ?

Beyond Random Phase Approximation (RPA)

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

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

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

$$\Downarrow$$

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

Beyond RPA: including exchange kernel

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

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

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

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

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

$\chi_{\lambda}^{(1)}$ Kernel $\propto \lambda \quad \Longrightarrow \quad E_{c,\lambda}^{(2)} \sim \mathrm{o}(\lambda^2)$

Furthermore one can show that

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

χ_{λ} Kernel $\sim \mathrm{o}(\lambda^2) \quad \Longrightarrow \quad \Delta^{(2)} E_{c,\lambda} \sim \mathrm{o}(\lambda^3)$

A systematic improvement for E_{xc}

Next step: $\frac{\delta^2 E_{c,\lambda}^{(2)}}{\delta n \delta n} \rightarrow \lambda^2 f_c^{(2)} \rightarrow \chi_\lambda^{(2)} = \chi_\lambda^{(1)} + \chi_\lambda^{(1)}[\lambda^2 f_c^{(2)}]\chi_\lambda^{(2)}$

$$E_{xc}^\lambda = \lambda E_x - \frac{1}{2\pi}\int_0^\lambda d\mu \int_0^\infty du \mathrm{Tr}\left\{v_c\left[\chi_\mu^{(1)}(iu) - \chi_0(iu)\right]\right\} +$$
$$- \frac{1}{2\pi}\int_0^\lambda d\mu \int_0^\infty du \mathrm{Tr}\left\{v_c\left[\chi_\mu^{(2)}(iu) - \chi_\mu^{(1)}(iu)\right]\right\} +$$
$$- \frac{1}{2\pi}\int_0^\lambda d\mu \int_0^\infty du \mathrm{Tr}\left\{v_c\left[\chi_\mu(iu) - \chi_\mu^{(2)}(iu)\right]\right\} =$$
$$= \lambda E_x + E_{c,\lambda}^{(2)} + E_{c,\lambda}^{(3)} + \Delta^{(3)} E_{c,\lambda}$$

$\chi_\lambda^{(2)}$ Kernel $\propto \lambda^2 \quad \Longrightarrow \quad E_{c,\lambda}^{(3)} \sim o(\lambda^3),\ \Delta E_{c,\lambda}^{(3)} \sim o(\lambda^4)$

Route for a **systematic improvement** of E_{xc}

$$E_{xc,\lambda}^{(1)}(=\lambda E_x) \longrightarrow f_{xc}^{(1)}(=f_x) \longrightarrow E_{c,\lambda}^{(2)} \longrightarrow f_c^{(2)} \longrightarrow E_{c,\lambda}^{(3)} \longrightarrow f_c^{(3)} \ldots$$

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

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

Perturbation Theory (PT) along the adiabatic path

Only $h_{vx} = \chi_0(v_c + f_x)\chi_0$ is needed (and not f_x)

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

$$h_{vx} = \left[\frac{d\chi_\lambda^{(1)}}{d\lambda}\right]_{\lambda=0}$$

$$H_\lambda = T + \lambda W + v_{ext}^\lambda = H_0 + \lambda\left(W + \left[\frac{dv_{ext}^\lambda}{d\lambda}\right]_{\lambda=0}\right) + o(\lambda^2)$$

with

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

$$\left[\frac{dv_{ext}^\lambda}{d\lambda}\right]_{\lambda=0} = -v_H - v_x$$

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 on the MB system

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

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

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

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

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

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

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

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

Matrix element of $h_{\upsilon x}$

$$
\begin{aligned}
h^{\alpha\beta}_{\upsilon x} \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 - \upsilon_x | \Delta^\alpha \phi_a^{(+)} \rangle - \sum_{ab} \langle \Delta^\beta \phi_a^{(-)} | \Delta^\alpha \phi_b^{(+)} \rangle \langle \phi_b | V_x - \upsilon_x | \phi_a \rangle \\
& + \sum_{a} \langle \Delta^\beta \phi_a^{(+)} | V_x - \upsilon_x | \Delta^\alpha \phi_a^{(-)} \rangle - \sum_{ab} \langle \Delta^\beta \phi_a^{(+)} | \Delta^\alpha \phi_b^{(-)} \rangle \langle \phi_b | V_x - \upsilon_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 \\
& + \sum_{a} \langle \Delta^\beta \phi_a^{(+)} | \Delta^\alpha V | \delta\phi_a \rangle + \sum_{a} \langle \Delta^\beta \phi_a^{(-)} | \Delta^\alpha V | \delta\phi_a \rangle \\
& - \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}
$$

Consistent with Goerling (*Int. J. Quan. Chem.* 68, 265)

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

$$h_{vx}|\Delta^\alpha V\rangle = -a_\alpha[-\chi_0]|\Delta^\alpha V\rangle \qquad \langle \Delta^\alpha V|[-\chi_0]|\Delta^\beta V\rangle = \delta_{\alpha\beta}$$

$$\begin{array}{cc} \langle \delta\phi_a|\Delta^\beta V|\Delta^\alpha \phi_a^{(+)}\rangle & \textbf{OK} \\ \langle \Delta^\beta \phi_a^{(-)}|V_x - v_x|\Delta^\alpha \phi_a^{(+)}\rangle & \textbf{NO} \end{array}$$

BUT $\langle \Delta^\beta \phi_a^{(-)}|$ is such that

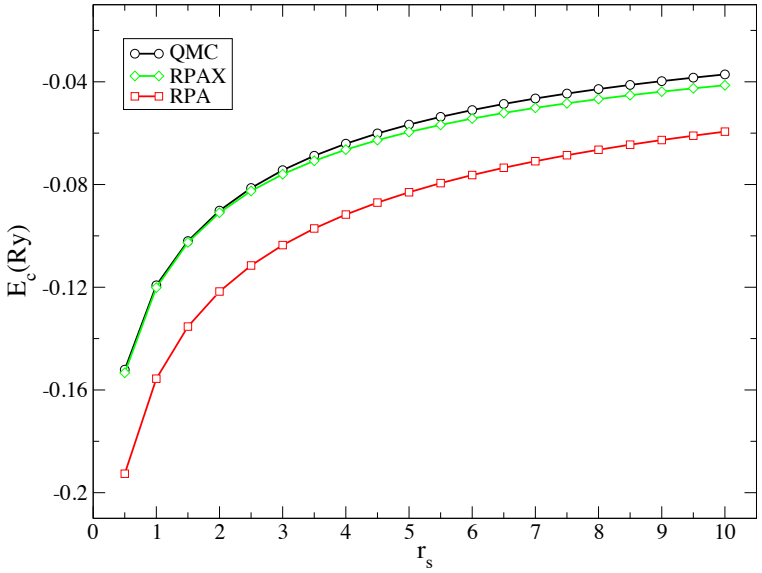
$$\begin{array}{c} \langle \Delta^\beta \phi_a^{(-)}|\,[H_0 - (\varepsilon_a + iu)] = -\langle \phi_a|\Delta^\beta V \Rightarrow \\ \Rightarrow \qquad \langle \Delta^\beta \phi_a^{(-)}| = \langle \phi_a|\Delta^\beta V\, G(\varepsilon_a + iu) \end{array}$$

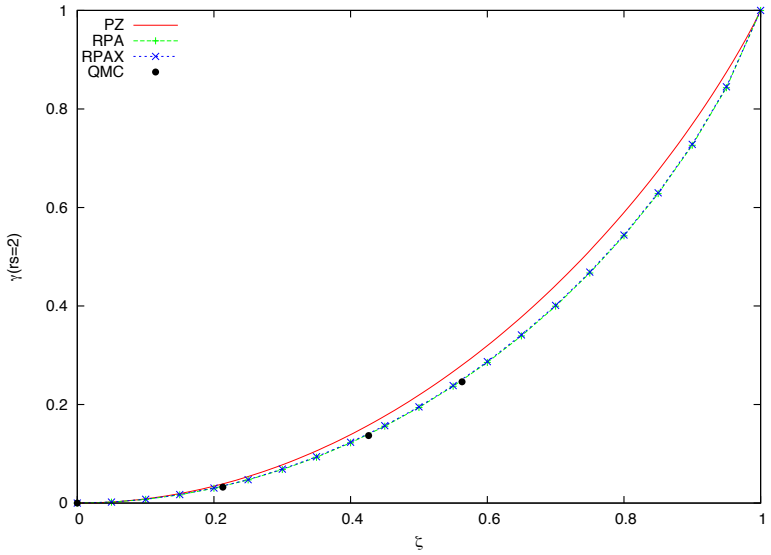
$$\begin{array}{cc} \langle \delta\phi_a|\Delta^\beta V|\Delta^\alpha \phi_a^{(+)}\rangle & \textbf{OK} \\ \langle \phi_a|\Delta^\beta V|\, G(\varepsilon_a + iu)[V_x - v_x]\Delta^\alpha \phi_a^{(+)}\rangle & \textbf{OK} \end{array}$$

Computational cost $\sim \chi_0|\Delta^\beta V\rangle$

Testing on Homogeneous Electron Gas (HEG)

- Local Density like Approximation for $\Delta^{(2)} E_c$ in the RPA+ spirit..





- RPA not very good, RPA+fx much better, however RPA+fx becomes pathological beyond $r_s \approx 10$ ...
- RPA, RPA+fx magnetic polarization dependence in very good agreement with QMC data [Ortiz & Ballone, PRB 50, 1391 (1994)]

Conclusions

- ACFDT is a framework for a systematic generation of improved functionals in terms of coupling constant strenght.
- RPA is the simplest approximation, not pathological but not very accurate (in the HEG for instance)
- RPA+fx includes all linear coupling terms but becomes pathological at low densities
- self-consistent potential for RPA is possible (hence forces, relaxation, Molecular Dynamics... (in due time)) but does not bind Be_2 ...
- scf potential for RPA+fx or going beyond RPA+fx in the correlation energy expansion appears quite involved...