Review of several formulations and variants of the random-phase approximation

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The random-phase approximation (RPA)

- RPA is a method for calculating **excitation energies** and the **ground-state correlation energy** in quantum many-body systems.
- RPA is used in **condensed-matter physics**, **quantum chemistry**, and **nuclear physics**.
- RPA is an old method started in the 1950s. In condensed-matter physics and quantum chemistry, there is a **revived interest in RPA since the 2000s** in the context of ground-state DFT: RPA is seen as the simplest many-body method beyond second-order perturbation theory which can improve over usual density-functional approximations.
- There are **several formulations of RPA** for calculating the ground-state correlation energy:
  - **Adiabatic-connection formulation**
  - **Plasmon-formula formulation**
  - **Ring coupled-cluster doubles formulation**
  - **Dielectric-matrix formulation**
- Within each formulation, one can define **several variants of RPA**, differing in the way **exchange terms** are included:
  - There is one unique variant without exchange: **direct RPA (dRPA)**
  - There are many non-equivalent variants of **RPA with exchange (RPAx)**
- dRPA suffers from **self-interaction errors** and many RPAx variants suffer from **static-correlation errors** $\Longrightarrow$ Which RPA variant should we use?

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The quantum many-body electronic-structure problem

- ***N*-electron Hamiltonian** in the Born-Oppenheimer and non-relativistic approximations:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Stationary states are determined by the **time-independent Schrödinger equation**:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is an **antisymmetric wave function** written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i = \uparrow$ or $\downarrow$), and E is the associated energy.

- Introducing an **orthonormal basis of spin orbitals** $\psi_p(\mathbf{x}) = \phi_p(\mathbf{r})\chi_{\sigma_p}(\sigma)$ which are products of spatial orbitals $\phi_p(\mathbf{r})$ (assumed to be real valued) with a spin function $\chi_{\sigma_p}(\sigma) = \delta_{\sigma_p,\sigma}$, the Schrödinger equation can be rewritten using second quantization:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad \text{with} \quad \hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}$$

with

$$\hat{T} = \sum_{pq} T_{p,q}\ \hat{a}_p^\dagger \hat{a}_q, \quad \hat{V}_{\text{ne}} = \sum_{pq} (V_{\text{ne}})_{p,q}\ \hat{a}_p^\dagger \hat{a}_q, \quad \hat{W} = \frac{1}{2}\sum_{pqrs} W_{rs,pq}\ \hat{a}_p^\dagger \hat{a}_s^\dagger \hat{a}_r \hat{a}_q$$

where $T_{p,q}$ and $(V_{\text{ne}})_{p,q}$ are the one-electron integrals and $W_{rs,pq} = \langle rq|sp\rangle$ are the two-electron integrals.

The Hartree-Fock (HF) starting point

- Even though DFT is nowadays mostly used as reference for RPA, we will use here HF.
- In HF, we approximate the wave function by a **single Slater determinant**:

$$|\Psi\rangle \approx |\Phi\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger ... \hat{a}_N^\dagger |\text{vac}\rangle$$

- The spin orbitals are determined by **minimizing the HF energy** $E_{\text{HF}} = \langle \Phi | \hat{H} | \Phi \rangle$ (with orthonormalization constraints) leading to the self-consistent **HF equations**:

$$\hat{H}_0 |\psi_p\rangle = \varepsilon_p |\psi_p\rangle$$

with the **non-interacting HF Hamiltonian**:

$$\hat{H}_0 = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{Hx}}$$

involving the HF Hartree-exchange potential $\hat{V}_{\text{Hx}} = \sum_{pq} (V_{\text{Hx}})_{p,q} \, \hat{a}_p^\dagger \hat{a}_q$ with matrix elements $(V_{\text{Hx}})_{p,q} = \sum_{i=1}^{N} \overline{W}_{ii,pq}$, where $\overline{W}_{rs,pq} = W_{rs,pq} - W_{rp,sq}$ are the antisymmetrized two-electron integrals.

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Adiabatic-connection formula

- **Adiabatic connection** from the non-interacting HF Hamiltonian ($\boldsymbol{\lambda} = 0$) to the interacting Hamiltonian ($\boldsymbol{\lambda} = 1$) by linearly switching on the perturbation $\hat{\mathcal{W}} = \hat{W} - \hat{V}_{\text{Hx}}$:

$$\left(\hat{H}_0 + \boldsymbol{\lambda}\hat{\mathcal{W}}\right)|\Psi^{\boldsymbol{\lambda}}\rangle = E^{\boldsymbol{\lambda}}|\Psi^{\boldsymbol{\lambda}}\rangle$$

  Note: Contrary to the usual DFT adiabatic connection, here the ground-state density is not kept constant.

- The ground-state energy E of the interacting Hamiltonian can be expressed as

$$E = E^{\boldsymbol{\lambda}=1} = E^{\boldsymbol{\lambda}=0} + \int_0^1 \mathrm{d}\boldsymbol{\lambda} \frac{\mathrm{d}E^{\boldsymbol{\lambda}}}{\mathrm{d}\boldsymbol{\lambda}} = E^{\boldsymbol{\lambda}=0} + \int_0^1 \mathrm{d}\boldsymbol{\lambda} \langle\Psi^{\boldsymbol{\lambda}}|\hat{\mathcal{W}}|\Psi^{\boldsymbol{\lambda}}\rangle$$

  where the Hellmann-Feynman theorem was used.

- Noting that the HF energy is $E_{\text{HF}} = E^{\boldsymbol{\lambda}=0} + \langle\Psi^{\boldsymbol{\lambda}=0}|\hat{\mathcal{W}}|\Psi^{\boldsymbol{\lambda}=0}\rangle$ where $\Psi^{\boldsymbol{\lambda}=0} = \Phi$ is the HF wave function, we arrive at the following expression for the **correlation energy**:

$$E_{\text{c}} = E^{\boldsymbol{\lambda}=1} - E_{\text{HF}} = \int_0^1 \mathrm{d}\boldsymbol{\lambda}\, \langle\Psi^{\boldsymbol{\lambda}}|\hat{\mathcal{W}}|\Psi^{\boldsymbol{\lambda}}\rangle - \langle\Psi^{\boldsymbol{\lambda}=0}|\hat{\mathcal{W}}|\Psi^{\boldsymbol{\lambda}=0}\rangle$$

Adiabatic-connection formula in a spin-orbital basis

- In the HF real-valued spin-orbital basis, the perturbation operator is expressed as

$$\hat{\mathcal{W}} = \frac{1}{2} \sum_{pqrs} W_{rs,pq} \; \hat{a}_p^\dagger \hat{a}_s^\dagger \hat{a}_r \hat{a}_q - \sum_{pq} (V_{\text{Hx}})_{q,p} \; \hat{a}_p^\dagger \hat{a}_q$$

- Let us introduce the correlation part of the two-body density matrix

$$(P_{\text{c}}^{\boldsymbol{\lambda}})_{pq,rs} = \langle \Psi^{\boldsymbol{\lambda}} | \hat{a}_p^\dagger \hat{a}_s^\dagger \hat{a}_r \hat{a}_q | \Psi^{\boldsymbol{\lambda}} \rangle - \langle \Psi^{\boldsymbol{\lambda}=0} | \hat{a}_p^\dagger \hat{a}_s^\dagger \hat{a}_r \hat{a}_q | \Psi^{\boldsymbol{\lambda}=0} \rangle$$

  and the correlation part of the one-body density matrix

$$(\gamma_{\text{c}}^{\boldsymbol{\lambda}})_{p,q} = \langle \Psi^{\boldsymbol{\lambda}} | \hat{a}_p^\dagger \hat{a}_q | \Psi^{\boldsymbol{\lambda}} \rangle - \langle \Psi^{\boldsymbol{\lambda}=0} | \hat{a}_p^\dagger \hat{a}_q | \Psi^{\boldsymbol{\lambda}=0} \rangle$$

- The correlation energy can be written as

$$E_{\text{c}} = \frac{1}{2} \int_0^1 \text{d}\boldsymbol{\lambda} \sum_{pqrs} W_{rs,pq} (P_{\text{c}}^{\boldsymbol{\lambda}})_{pq,rs} - \int_0^1 \text{d}\boldsymbol{\lambda} \sum_{p,q} (V_{\text{Hx}})_{q,p} (\gamma_{\text{c}}^{\boldsymbol{\lambda}})_{p,q}$$

  or, using matrix notations,

$$E_{\text{c}} = \frac{1}{2} \int_0^1 \text{d}\boldsymbol{\lambda} \, \text{tr}[\mathbf{W} \, \mathbf{P}_{\text{c}}^{\boldsymbol{\lambda}}] - \int_0^1 \text{d}\boldsymbol{\lambda} \, \text{tr}[\mathbf{V}_{\text{Hx}} \, \boldsymbol{\gamma}_{\text{c}}^{\boldsymbol{\lambda}}]$$

Fluctuation-dissipation theorem

- $\mathbf{P}_c^{\boldsymbol{\lambda}}$ can be obtained from the **fluctuation-dissipation theorem**:

$$(P_c^{\boldsymbol{\lambda}})_{pq,rs} = -\int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{-i\omega 0^+} \left(\chi^{\boldsymbol{\lambda}}_{pq,rs}(\omega) - \chi^{\boldsymbol{\lambda}=0}_{pq,rs}(\omega)\right) + \Delta^{\boldsymbol{\lambda}}_{pq,rs}$$

where $\chi^{\boldsymbol{\lambda}}_{pq,rs}(\omega)$ is the polarization propagator (or linear-response function):

$$\chi^{\boldsymbol{\lambda}}_{pq,rs}(\omega) = \sum_{n\neq \text{g.s.}} \frac{\langle \Psi^{\boldsymbol{\lambda}}|\hat{a}_p^\dagger \hat{a}_q|\Psi^{\boldsymbol{\lambda}}_n\rangle\langle\Psi^{\boldsymbol{\lambda}}_n|\hat{a}_s^\dagger \hat{a}_r|\Psi^{\boldsymbol{\lambda}}\rangle}{\omega - \omega_n^{\boldsymbol{\lambda}} + i0^+} - \frac{\langle \Psi^{\boldsymbol{\lambda}}|\hat{a}_s^\dagger \hat{a}_r|\Psi^{\boldsymbol{\lambda}}_n\rangle\langle\Psi^{\boldsymbol{\lambda}}_n|\hat{a}_p^\dagger \hat{a}_q|\Psi^{\boldsymbol{\lambda}}\rangle}{\omega + \omega_n^{\boldsymbol{\lambda}} - i0^+}$$

where $\omega_n^{\boldsymbol{\lambda}} = E_n^{\boldsymbol{\lambda}} - E^{\boldsymbol{\lambda}}$ are the excitation energies and $\Delta^{\boldsymbol{\lambda}}_{pq,rs}$ is a term coming from the variation of the one-body density matrix with $\boldsymbol{\lambda}$:

$$\Delta^{\boldsymbol{\lambda}}_{pq,rs} = \left(\gamma^{\boldsymbol{\lambda}}_{pq}\gamma^{\boldsymbol{\lambda}}_{sr} - \delta_{qs}\gamma^{\boldsymbol{\lambda}}_{pr}\right) - \left(\gamma^{\boldsymbol{\lambda}=0}_{pq}\gamma^{\boldsymbol{\lambda}=0}_{sr} - \delta_{qs}\gamma^{\boldsymbol{\lambda}=0}_{pr}\right)$$

Note: The theorem is easily proved by contour integrating over the lower-half complex ω-plane and using the residue theorem.

- Similarly, $\gamma_c^{\boldsymbol{\lambda}}$ can be obtained from the one-body Green function:

$$(\gamma_c^{\boldsymbol{\lambda}})_{p,q} = \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{-i\omega 0^+} \left(G^{\boldsymbol{\lambda}}_{p,q}(\omega) - G^{\boldsymbol{\lambda}=0}_{p,q}(\omega)\right)$$

- $\mathbf{G}^{\boldsymbol{\lambda}}(\omega)$ and $\boldsymbol{\chi}^{\boldsymbol{\lambda}}(\omega)$ can be directly calculated from the **Dyson equation** and the **Bethe-Salpeter equation**, respectively.

RPA approximations

- In **direct RPA (dRPA)**, we take $\mathbf{G}^{\lambda}_{\mathrm{dRPA}}(\omega) = \mathbf{G}^{\lambda=0}(\omega)$ (implying $\gamma^{\lambda}_{\mathrm{c,dRPA}} = 0$) and $\chi^{\lambda}_{\mathrm{dRPA}}(\omega)$ from time-dependent Hartree (TDH):

$$\chi^{\lambda}_{\mathrm{dRPA}}(\omega)^{-1} = \chi^{\lambda=0}(\omega)^{-1} - \lambda \mathbf{W}$$

leading to the **dRPA correlation energy**:

$$E_{\mathrm{c,dRPA}} = -\frac{1}{2}\int_0^1 \mathrm{d}\lambda \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{-i\omega 0^+} \mathrm{tr}\left[\mathbf{W}\left(\chi^{\lambda}_{\mathrm{dRPA}}(\omega) - \chi^{\lambda=0}(\omega)\right)\right]$$

- In **RPA with exchange (RPAx)**, we take $\mathbf{G}^{\lambda}_{\mathrm{RPAx}}(\omega) = \mathbf{G}^{\lambda=0}(\omega)$ (implying $\gamma^{\lambda}_{\mathrm{c,RPAx}} = 0$) and $\chi^{\lambda}_{\mathrm{RPAx}}(\omega)$ from time-dependent Hartree-Fock (TDHF):

$$\chi^{\lambda}_{\mathrm{RPAx}}(\omega)^{-1} = \chi^{\lambda=0}(\omega)^{-1} - \lambda \overline{\mathbf{W}}$$

leading to the **RPAx-I correlation energy**:

$$E_{\mathrm{c,RPAx\text{-}I}} = -\frac{1}{2}\int_0^1 \mathrm{d}\lambda \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{-i\omega 0^+} \mathrm{tr}\left[\mathbf{W}\left(\chi^{\lambda}_{\mathrm{RPAx}}(\omega) - \chi^{\lambda=0}(\omega)\right)\right]$$

Inverse HF and RPA polarization propagators

- $\chi^{\lambda=0}(\omega)$ has non-zero matrix elements only on the occ/vir and vir/occ subspaces, and since it is diagonal it can easily be inverted:

$$\chi^{\lambda=0}(\omega)^{-1} = -\left[\begin{pmatrix} \Delta\varepsilon & 0 \\ 0 & \Delta\varepsilon \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right]$$

where $\Delta\varepsilon_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$.

- We thus find the inverse of $\chi^{\lambda}_{\text{dRPA}}(\omega)$:

$$\chi^{\lambda}_{\text{dRPA}}(\omega)^{-1} = -\left[\begin{pmatrix} \mathbf{A}^{\lambda} & \mathbf{B}^{\lambda} \\ \mathbf{B}^{\lambda} & \mathbf{A}^{\lambda} \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right]$$

where $A^{\lambda}_{ia,jb} = \Delta\varepsilon_{ia,jb} + \lambda W_{ia,jb}$ and $B^{\lambda}_{ia,jb} = \lambda W_{ia,bj}$.

- Similarly, the inverse of $\chi^{\lambda}_{\text{RPAx}}(\omega)$ is

$$\chi^{\lambda}_{\text{RPAx}}(\omega)^{-1} = -\left[\begin{pmatrix} \overline{\mathbf{A}}^{\lambda} & \overline{\mathbf{B}}^{\lambda} \\ \overline{\mathbf{B}}^{\lambda} & \overline{\mathbf{A}}^{\lambda} \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right]$$

where $\overline{A}^{\lambda}_{ia,jb} = \Delta\varepsilon_{ia,jb} + \lambda \overline{W}_{ia,jb}$ and $\overline{B}^{\lambda}_{ia,jb} = \lambda \overline{W}_{ia,bj}$.

Spectral representation of the RPA polarization propagator

- We consider the **dRPA or RPAx pseudo-Hermitian generalized eigenvalue equation**:

$$\begin{pmatrix} \mathbf{A}^{\lambda} & \mathbf{B}^{\lambda} \\ \mathbf{B}^{\lambda} & \mathbf{A}^{\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n^{\lambda} \\ \mathbf{Y}_n^{\lambda} \end{pmatrix} = \omega_n^{\lambda} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X}_n^{\lambda} \\ \mathbf{Y}_n^{\lambda} \end{pmatrix}$$

or, more compactly,

$$\mathbf{\Lambda}^{\lambda}\, \mathbf{C}_n^{\lambda} = \omega_n^{\lambda}\, \mathbf{\Delta}\, \mathbf{C}_n^{\lambda}$$

- For **dRPA**, $\mathbf{\Lambda}^{\lambda}$ is always positive definite which implies that the dRPA problem is diagonalizable and all eigenvalues ω_n^{λ} are non-zero real numbers.
  For **RPAx**, $\mathbf{\Lambda}^{\lambda}$ may not be positive definite, the RPAx problem may not be diagonalizable and some eigenvalues ω_n^{λ} may be zero or complex $\Longrightarrow$ "instability problems".
- **The solutions come in pairs**: If ω_n^{λ} is an eigenvalue with eigenvector $\mathbf{C}_n^{\lambda} = \begin{pmatrix} \mathbf{X}_n^{\lambda} \\ \mathbf{Y}_n^{\lambda} \end{pmatrix}$, then -$\omega_n^{\lambda}$ is an eigenvalue with eigenvector $\mathbf{C}_{-n}^{\lambda} = \begin{pmatrix} \mathbf{Y}_n^{\lambda} \\ \mathbf{X}_n^{\lambda} \end{pmatrix}$.
- The **spectral representation** of the RPA polarization propagator is:

$$\chi_{\mathrm{RPA}}^{\lambda}(\omega) = \sum_{n>0} \frac{\mathbf{C}_n^{\lambda}(\mathbf{C}_n^{\lambda})^{\mathsf{T}}}{\omega - \omega_n^{\lambda} + i0^{+}} - \frac{\mathbf{C}_{-n}^{\lambda}(\mathbf{C}_{-n}^{\lambda})^{\mathsf{T}}}{\omega + \omega_n^{\lambda} - i0^{+}}$$

using the normalization $(\mathbf{C}_n^{\lambda})^{\mathsf{T}}\mathbf{\Delta}\mathbf{C}_n^{\lambda} = 1$ and $(\mathbf{C}_{-n}^{\lambda})^{\mathsf{T}}\mathbf{\Delta}\mathbf{C}_{-n}^{\lambda} = -1$.

RPA variants in the adiabatic-connection formulation

- Using the spectral representation of $\chi^{\lambda}_{\text{dRPA}}(\omega)$, we find $\mathbf{P}^{\lambda}_{\text{c,dRPA}}$

$$\mathbf{P}^{\lambda}_{\text{c,dRPA}} = -\int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{-i\omega 0^+} [\chi^{\lambda}_{\text{dRPA}}(\omega) - \chi^{\lambda=0}(\omega)] = \sum_{n>0} \mathbf{C}^{\lambda}_n (\mathbf{C}^{\lambda}_n)^{\mathsf{T}} - \mathbf{C}^{\lambda=0}_n (\mathbf{C}^{\lambda=0}_n)^{\mathsf{T}}$$

leading to the **dRPA correlation energy**:

$$E_{\text{c,dRPA}} = \frac{1}{2} \int_0^1 \mathrm{d}\lambda \sum_{n>0} \mathrm{tr}[\mathbf{W}\, \mathbf{C}^{\lambda}_n (\mathbf{C}^{\lambda}_n)^{\mathsf{T}} - \mathbf{W}\, \mathbf{C}^{\lambda=0}_n (\mathbf{C}^{\lambda=0}_n)^{\mathsf{T}}]$$

(Furche *et al.* PRB 2001)

- Similarly, the **RPAx-I correlation energy** is expressed with the RPAx eigenvectors:

$$E_{\text{c,RPAx-I}} = \frac{1}{2} \int_0^1 \mathrm{d}\lambda \sum_{n>0} \mathrm{tr}[\mathbf{W}\, \overline{\mathbf{C}}^{\lambda}_n (\overline{\mathbf{C}}^{\lambda}_n)^{\mathsf{T}} - \mathbf{W}\, \overline{\mathbf{C}}^{\lambda=0}_n (\overline{\mathbf{C}}^{\lambda=0}_n)^{\mathsf{T}}]$$

(Toulouse *et al.* PRL 2009)

- We can also define other variants:

$$E_{\text{c,RPAx-II}} = \frac{1}{4} \int_0^1 \mathrm{d}\lambda \sum_{n>0} \mathrm{tr}[\overline{\mathbf{W}}\, \overline{\mathbf{C}}^{\lambda}_n (\overline{\mathbf{C}}^{\lambda}_n)^{\mathsf{T}} - \overline{\mathbf{W}}\, \overline{\mathbf{C}}^{\lambda=0}_n (\overline{\mathbf{C}}^{\lambda=0}_n)^{\mathsf{T}}]$$

(McLachlan & Ball RMP 1964)

$$E_{\text{c,dRPA-II}} = \frac{1}{2} \int_0^1 \mathrm{d}\lambda \sum_{n>0} \mathrm{tr}[\overline{\mathbf{W}}\, \mathbf{C}^{\lambda}_n (\mathbf{C}^{\lambda}_n)^{\mathsf{T}} - \overline{\mathbf{W}}\, \mathbf{C}^{\lambda=0}_n (\mathbf{C}^{\lambda=0}_n)^{\mathsf{T}}]$$

(Ángyán *et al.* JCTC 2011)

Outline

Analytical integration over λ for dRPA

- Using the cyclic invariance of the trace

$$\begin{aligned} E_{\text{c,dRPA}} &= \frac{1}{2}\int_0^1 \mathrm{d}\boldsymbol{\lambda} \sum_{n>0} \mathrm{tr}[\mathbf{W}\,\mathbf{C}_n^{\boldsymbol{\lambda}}(\mathbf{C}_n^{\boldsymbol{\lambda}})^{\mathsf{T}} - \mathbf{W}\,\mathbf{C}_n^{\boldsymbol{\lambda}=0}(\mathbf{C}_n^{\boldsymbol{\lambda}=0})^{\mathsf{T}}] \\ &= \frac{1}{2}\int_0^1 \mathrm{d}\boldsymbol{\lambda} \sum_{n>0} \left[(\mathbf{C}_n^{\boldsymbol{\lambda}})^{\mathsf{T}}\,\mathbf{W}\,\mathbf{C}_n^{\boldsymbol{\lambda}} - (\mathbf{C}_n^{\boldsymbol{\lambda}=0})^{\mathsf{T}}\mathbf{W}\,\mathbf{C}_n^{\boldsymbol{\lambda}=0}\right] \end{aligned}$$

- Since the eigenvalues $\omega_{n,\text{dRPA}}^{\boldsymbol{\lambda}}$ are stationary with respect to the eigenvector $\mathbf{C}_n^{\boldsymbol{\lambda}}$, we have a Hellmann-Feynman theorem giving

$$\omega_{n,\text{dRPA}}^{\boldsymbol{\lambda}} = (\mathbf{C}_n^{\boldsymbol{\lambda}})^{\mathsf{T}}\,\mathbf{\Lambda}^{\boldsymbol{\lambda}}\,\mathbf{C}_n^{\boldsymbol{\lambda}} \quad\Longrightarrow\quad \frac{\mathrm{d}\omega_{n,\text{dRPA}}^{\boldsymbol{\lambda}}}{\mathrm{d}\boldsymbol{\lambda}} = (\mathbf{C}_n^{\boldsymbol{\lambda}})^{\mathsf{T}}\,\frac{\mathrm{d}\mathbf{\Lambda}^{\boldsymbol{\lambda}}}{\mathrm{d}\boldsymbol{\lambda}}\,\mathbf{C}_n^{\boldsymbol{\lambda}} = (\mathbf{C}_n^{\boldsymbol{\lambda}})^{\mathsf{T}}\,\mathbf{W}\,\mathbf{C}_n^{\boldsymbol{\lambda}}$$

- **Integration over $\boldsymbol{\lambda}$ can be done analytically for the dRPA correlation energy:**

$$\begin{aligned} E_{\text{c,dRPA}} &= \frac{1}{2}\int_0^1 \mathrm{d}\boldsymbol{\lambda} \sum_{n>0} \left[\frac{\mathrm{d}\omega_{n,\text{dRPA}}^{\boldsymbol{\lambda}}}{\mathrm{d}\boldsymbol{\lambda}} - (\mathbf{C}_n^{\boldsymbol{\lambda}=0})^{\mathsf{T}}\mathbf{W}\,\mathbf{C}_n^{\boldsymbol{\lambda}=0}\right] \\ &= \frac{1}{2}\sum_{n>0} \left[\omega_{n,\text{dRPA}}^{\boldsymbol{\lambda}=1} - \omega_{n,\text{dRPA}}^{\boldsymbol{\lambda}=0} - (\mathbf{C}_n^{\boldsymbol{\lambda}=0})^{\mathsf{T}}\mathbf{W}\,\mathbf{C}_n^{\boldsymbol{\lambda}=0}\right] \\ &= \frac{1}{2}\sum_{n>0} \left[\omega_{n,\text{dRPA}}^{\boldsymbol{\lambda}=1} - (\mathbf{C}_n^{\boldsymbol{\lambda}=0})^{\mathsf{T}}\mathbf{\Lambda}^{\boldsymbol{\lambda}=1}\,\mathbf{C}_n^{\boldsymbol{\lambda}=0}\right] \end{aligned}$$

dRPA plasmon formula

- The form of the eigenvectors at $\boldsymbol{\lambda} = 0$ for positive eigenvalues, $\mathbf{C}_n^{\boldsymbol{\lambda}=0} =$

$$\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \\ -- \\ 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \end{pmatrix} \longleftarrow n^{\text{th}}$$

  leads to

$$\sum_{n>0} (\mathbf{C}_n^{\boldsymbol{\lambda}=0})^{\mathsf{T}} \boldsymbol{\Lambda}^{\boldsymbol{\lambda}=1} \mathbf{C}_n^{\boldsymbol{\lambda}=0} = \mathrm{tr}[\mathbf{A}^{\boldsymbol{\lambda}=1}] = \sum_{n>0} \omega_{n,\mathrm{dTDA}}^{\boldsymbol{\lambda}=1}$$

  where $\omega_{n,\mathrm{dTDA}}^{\boldsymbol{\lambda}=1}$ are the eigenvalues at $\boldsymbol{\lambda} = 1$ in the **direct Tamm-Dancoff approximation (dTDA)**:

$$\mathbf{A}^{\boldsymbol{\lambda}} \mathbf{X}_{n,\mathrm{dTDA}}^{\boldsymbol{\lambda}} = \omega_{n,\mathrm{dTDA}}^{\boldsymbol{\lambda}} \mathbf{X}_{n,\mathrm{dTDA}}^{\boldsymbol{\lambda}}$$

- We arrive at the **plasmon formula for the dRPA correlation energy**:

$$E_{\mathrm{c,dRPA}} = \frac{1}{2} \sum_{n>0} \left[\omega_{n,\mathrm{dRPA}}^{\boldsymbol{\lambda}=1} - \omega_{n,\mathrm{dTDA}}^{\boldsymbol{\lambda}=1} \right]$$

- There is a similar plasmon formula for RPAx-II, but not for RPAx-I and dRPA-II.

Outline

RPA as ring coupled-cluster doubles (CCD)

- Let us rewrite the **dRPA eigenvalue equation at $\lambda = 1$** as

$$\begin{cases} \mathbf{A}\,\mathbf{X} + \mathbf{B}\,\mathbf{Y} &= \mathbf{X}\,\boldsymbol{\omega} \\ \mathbf{B}\,\mathbf{X} + \mathbf{A}\,\mathbf{Y} &= -\mathbf{Y}\,\boldsymbol{\omega} \end{cases}$$

where $\boldsymbol{\omega}$ is the diagonal matrix containing the positive eigenvalues ω_n, $\mathbf{X}$ is the matrix containing all the eigenvectors $\mathbf{X}_n$ associated to positive eigenvalues, and similarly for $\mathbf{Y}$

- Let us multiply on the right by $\mathbf{X}^{-1}$ and introduce the **amplitude matrix $\mathbf{T} = \mathbf{Y}\,\mathbf{X}^{-1}$**

$$\begin{cases} \mathbf{A} + \mathbf{B}\,\mathbf{Y}\,\mathbf{X}^{-1} &= \mathbf{X}\,\boldsymbol{\omega}\,\mathbf{X}^{-1} \\ \mathbf{B} + \mathbf{A}\,\mathbf{Y}\,\mathbf{X}^{-1} &= -\mathbf{Y}\,\mathbf{X}^{-1}\,\mathbf{X}\,\boldsymbol{\omega}\,\mathbf{X}^{-1} \end{cases} \Leftrightarrow \begin{cases} \mathbf{A} + \mathbf{B}\,\mathbf{T} &= \mathbf{X}\,\boldsymbol{\omega}\,\mathbf{X}^{-1} \\ \mathbf{B} + \mathbf{A}\,\mathbf{T} &= -\mathbf{T}\,\mathbf{X}\,\boldsymbol{\omega}\,\mathbf{X}^{-1} \end{cases}$$

- We arrive at a **Riccati equation** for $\mathbf{T}$:

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

which is the **direct ring CCD equation for the double-excitation amplitudes** $T_{ia,jb}$.

Ring CCD variants

- Starting from the plasmon formula, the dRPA correlation energy can be written as

$$E_{\mathrm{c,dRPA}} = \frac{1}{2}\,\mathrm{tr}[\boldsymbol{\omega} - \mathbf{A}] = \frac{1}{2}\,\mathrm{tr}[\mathbf{X}\,\boldsymbol{\omega}\,\mathbf{X}^{-1} - \mathbf{A}]$$

and, since $\mathbf{X}\,\boldsymbol{\omega}\,\mathbf{X}^{-1} = \mathbf{A} + \mathbf{B}\,\mathbf{T}$ and $\mathbf{B} = \mathbf{W}$, we arrive at the **ring-CCD formulation of the dRPA correlation energy**:

$$E_{\mathrm{c,dRPA}} = \frac{1}{2}\,\mathrm{tr}[\mathbf{W}\,\mathbf{T}]$$

(Scuseria *et al.* JCP 2008)

- Similarly, using the **ring CCD amplitude equation with exchange terms**

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

we arrive at the **RPAx-SO2 correlation energy**:

$$E_{\mathrm{c,RPAx\text{-}SO2}} = \frac{1}{2}\,\mathrm{tr}[\mathbf{W}\,\overline{\mathbf{T}}]$$

(Szabo & Ostlund JCP 1977)

- One can also construct other variants:

$$E_{\mathrm{c,RPAx\text{-}II}} = \frac{1}{4}\,\mathrm{tr}[\overline{\mathbf{W}}\,\overline{\mathbf{T}}]$$

(Szabo & Ostlund IJQC 1977)

$$E_{\mathrm{c,SOSEX}} = \frac{1}{2}\,\mathrm{tr}[\overline{\mathbf{W}}\,\mathbf{T}]$$

(Grüneis *et al.* JCP 2009)

Outline

dRPA in the dielectric-matrix formulation

- Let us come back to the adiabatic-connection fluctuation-dissipation expression for the dRPA correlation energy:

$$E_{\text{c,dRPA}} = -\frac{1}{2}\int_0^1 \mathrm{d}\boldsymbol{\lambda} \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{-i\omega 0^+} \, \mathrm{tr}[\mathbf{W}\,(\chi^{\boldsymbol{\lambda}}_{\text{dRPA}}(\omega) - \chi^{\boldsymbol{\lambda}=0}(\omega))]$$

- The dRPA response equation

$$\chi^{\boldsymbol{\lambda}}_{\text{dRPA}}(\omega)^{-1} = \chi^{\boldsymbol{\lambda}=0}(\omega)^{-1} - \boldsymbol{\lambda}\mathbf{W}$$

has the formal solution

$$\chi^{\boldsymbol{\lambda}}_{\text{dRPA}}(\omega) = \left[\mathbf{1} - \chi^{\boldsymbol{\lambda}=0}(\omega)\,\boldsymbol{\lambda}\mathbf{W}\right]^{-1} \chi^{\boldsymbol{\lambda}=0}(\omega)$$

- The integral over λ can be done analytically, leading to the **dielectric-matrix formulation of the dRPA correlation energy**:

$$E_{\text{c,dRPA}} = \frac{1}{2}\int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{-i\omega 0^+} \, \mathrm{tr}[\,\ln\left(1 - \chi^{\boldsymbol{\lambda}=0}(\omega)\,\mathbf{W}\right) - \chi^{\boldsymbol{\lambda}=0}(\omega)\,\mathbf{W}]$$

where $\epsilon(\omega) = 1 - \chi^{\boldsymbol{\lambda}=0}(\omega)\,\mathbf{W}$ is the **dielectric-function matrix**.

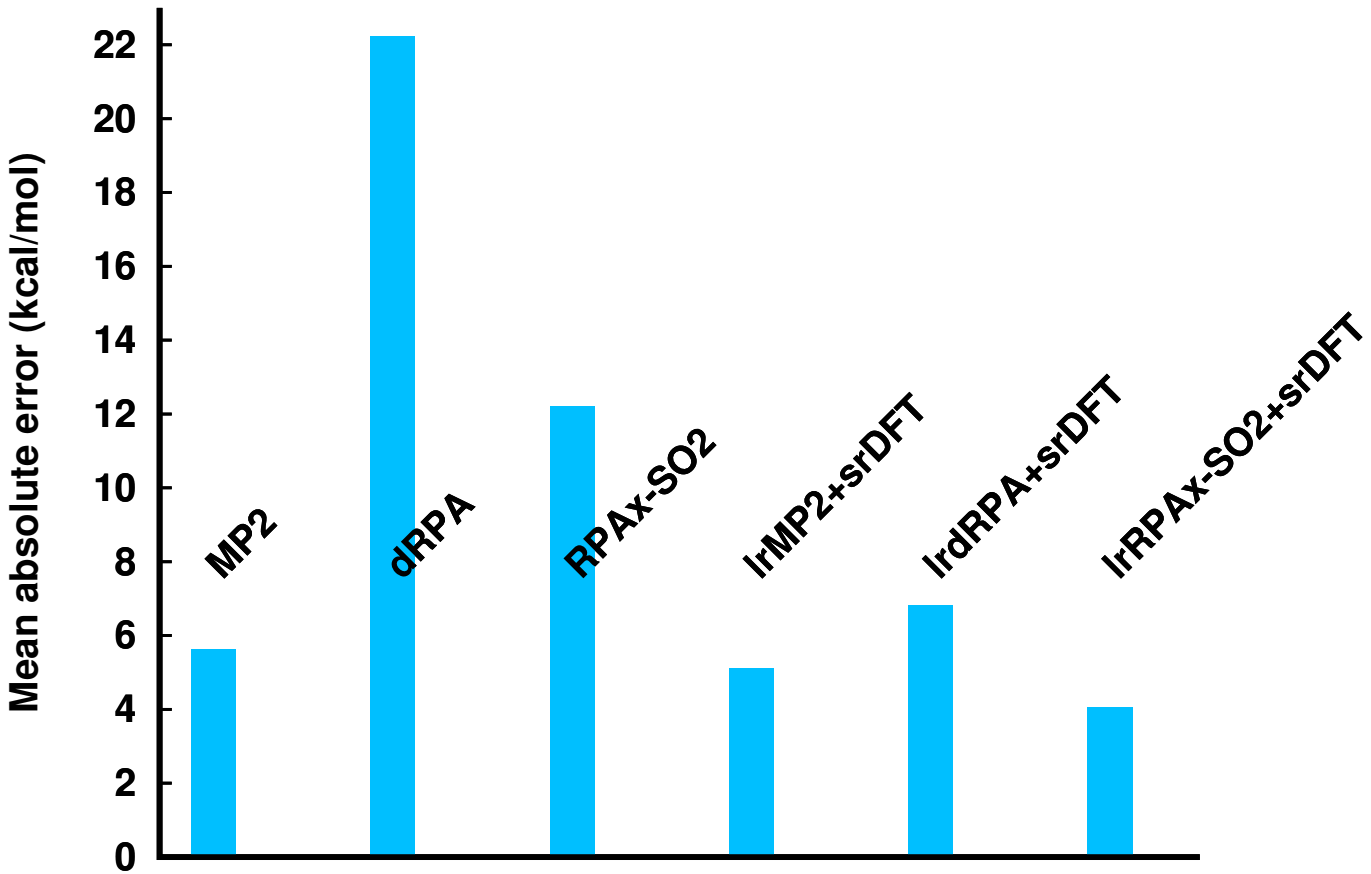
- Some RPAx variants can also be defined in this formulation.

Outline

Calculation of atomization energies

A set of **49 atomization energies** of small molecules (using cc-pVQZ basis).

For example: $CO_2 \rightarrow C + 2\ O$



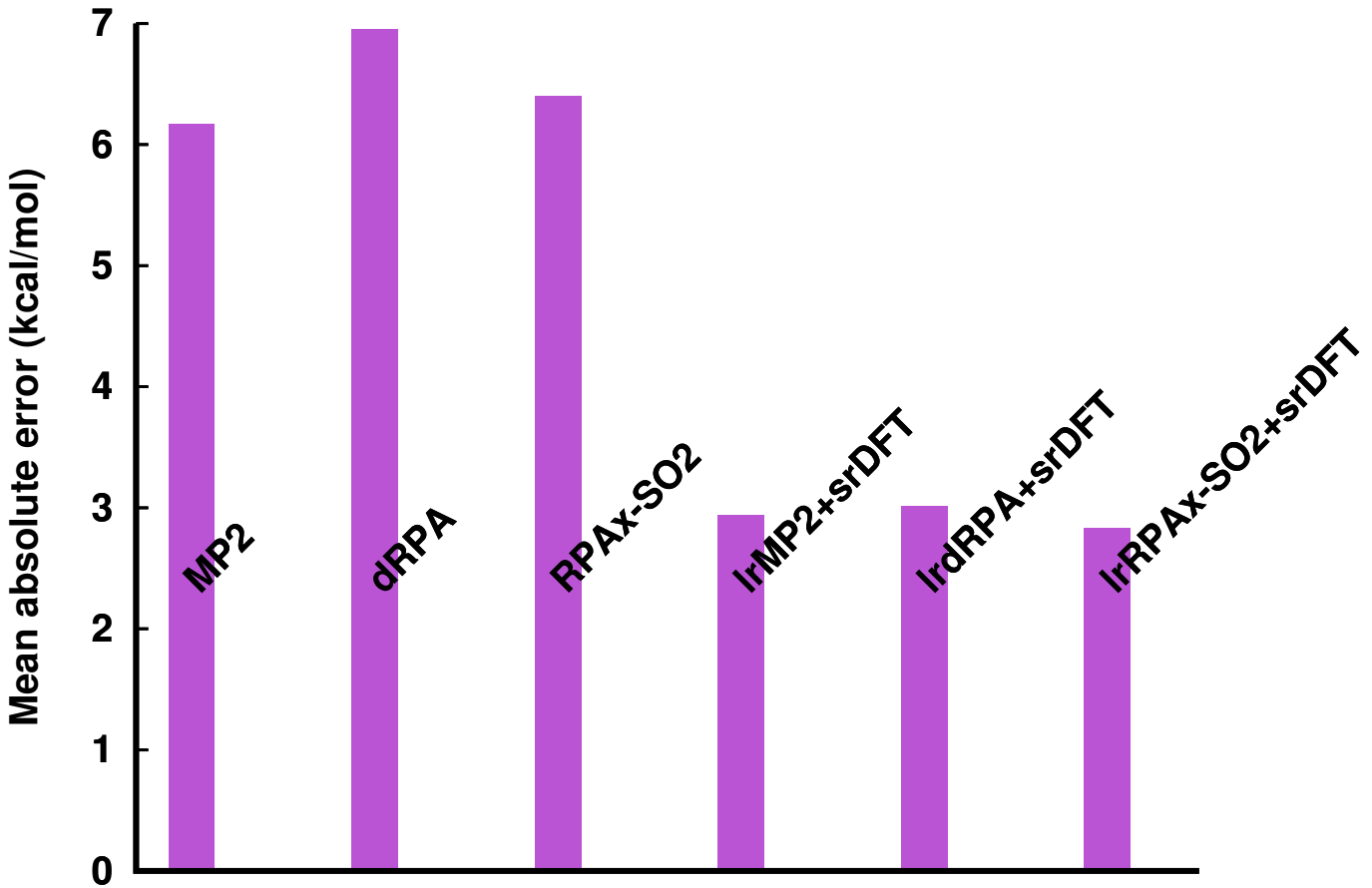
Mussard, Reinhardt, Ángyán, Toulouse, JCP, 2015

▸ See appendix for explanation on lrWFT+srDFT

Calculation of reaction barrier heights

A set of **24 barrier heights of reactions** with small molecules (using aug-cc-pVQZ basis).

For example: $HO^- + CH_3F \rightarrow HOCH_3 + F^-$

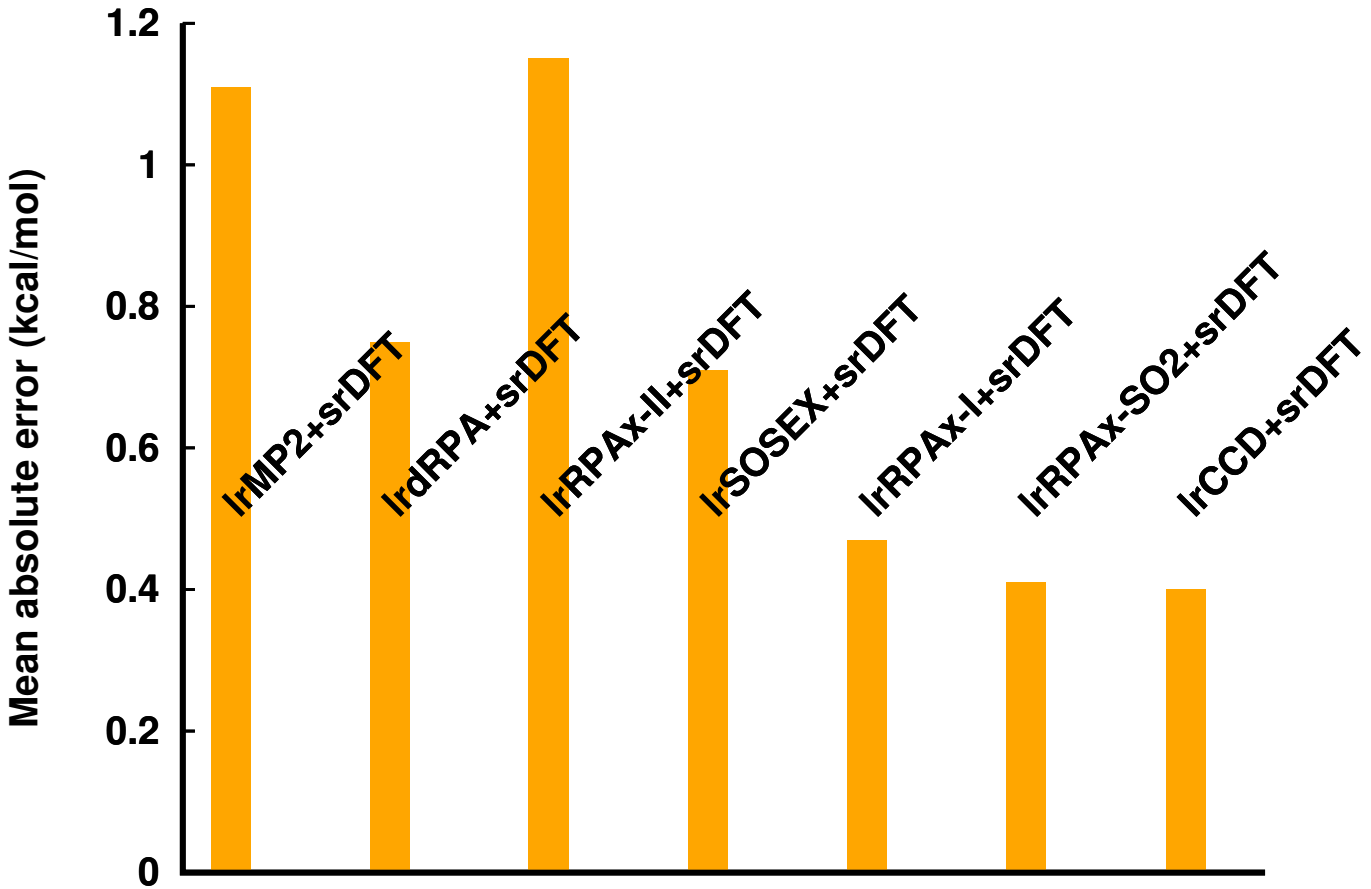


Mussard, Reinhardt, Ángyán, Toulouse, JCP, 2015

Calculation of intermolecular interaction energies

A set of **22 intermolecular interaction energies** from water dimer to DNA base pairs (using aug-cc-pVDZ basis).

For example: $C_6H_6 \cdots C_6H_6 \rightarrow C_6H_6 + C_6H_6$



Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

Outline

Other RPA variants

- **RPA-F12**: alternative to long-range RPA + short-range DFT for fast basis convergence (Hehn, Tew, Klopper JCP 2015)
- **Extensions of adiabatic-connection RPA with exchange-correlation response kernels** in the framework of time-dependent DFT or the Bethe-Salpeter equation.
- **Orbital-optimized RPA**: optimization of orbitals taking into account RPA correlation using either a local potential, a nonlocal potential, or a nonlocal dynamic potential
- **Self-consistent RPA**: matrices **A** and **B** are updated to take into account ground-state RPA correlation (e.g., Delion, Schuck, Tohyama EPJB 2016)
  A lot of variants: higher RPA, renormalized RPA, extended RPA, ...
- **Particle-particle RPA**, as opposed to particle-hole RPA: ground-state correlation energy extracted from particle-particle/hole-hole propagator (connected with ladder diagrams). A unifying generalization of ph-RPA and pp-RPA is given by quasiparticle RPA.
- **Second RPA**: addition of 2p-2h terms
- Very recently, **multireference adiabatic-connection RPA**: RPA starting from a multiconfiguration wave function (Pernal PRL 2018)

Conclusions and prospects

- RPA provides a simple way to **go beyond second-order perturbation theory**.
- There are **many formulations and variants** for defining a RPA ground-state correlation energy.
- There are **limitations in accuracy and robustness** (instability issues with RPAx variants).
- The combination of **long-range RPA and short-range DFT** alleviates some limitations of RPA.
- **Multireference RPA** might be a way forward.
- In nuclear physics, the RPA energy is normally defined as the **ground-state energy of a quadratic bosonic Hamiltonian** constructed with the matrices **A** and **B**.
  It seems that there is much less debate than in quantum chemistry about possible other definitions. Is this true and why?

Acknowledgments

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www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_saclay_18.pdf

Outline

Long-range WFT + short-range DFT

- Derivation by constrained-search formalism (Savin, 1996)

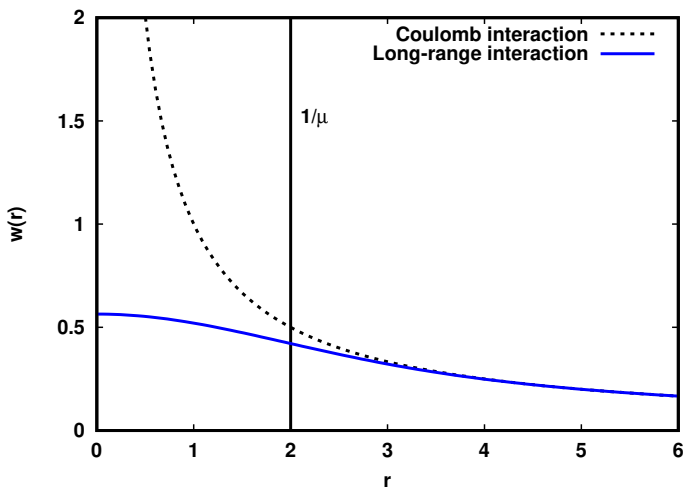
$$
\begin{aligned}
E &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W} | \Psi \rangle \\
&= \min_{n} \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W} | \Psi \rangle \\
&= \min_{n} \left\{ \min_{\Psi^{\text{lr}} \to n} \langle \Psi^{\text{lr}} | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}^{\text{lr}} | \Psi^{\text{lr}} \rangle + E_{\text{Hxc}}^{\text{sr}}[n] \right\}
\end{aligned}
$$

$$
E = \min_{\Psi^{\text{lr}}} \left\{ \langle \Psi^{\text{lr}} | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}^{\text{lr}} | \Psi^{\text{lr}} \rangle + E_{\text{Hxc}}^{\text{sr}}[n_{\Psi^{\text{lr}}}] \right\}
$$

- **Long-range e-e interaction**

$$
\hat{W}^{\text{lr}} = \sum_{i<j} \frac{\text{erf}(\mu r_{ij})}{r_{ij}}
$$

with $1/\mu$ acting as a cutoff radius



The short-range density functional

- Decomposition into Hartree and exchange-correlation contributions:

$$E_{\mathrm{Hxc}}^{\mathrm{sr}}[n] = E_{\mathrm{H}}^{\mathrm{sr}}[n] + E_{\mathrm{xc}}^{\mathrm{sr}}[n]$$

where $E_{\mathrm{H}}^{\mathrm{sr}}[n] = (1/2) \iint n(\mathbf{r}_1) n(\mathbf{r}_2) w^{\mathrm{sr}}(r_{12}) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$

- Semilocal density-functional approximations (srLDA, srGGAs) for $E_{\mathrm{xc}}^{\mathrm{sr}}[n]$:

$$E_{\mathrm{xc}}^{\mathrm{sr}}[n] \approx \int e_{\mathrm{xc}}^{\mathrm{sr}}(n(\mathbf{r}), \nabla n(\mathbf{r})) \, \mathrm{d}\mathbf{r}$$

- In the limit of a very short-range interaction, i.e. $\mu \to \infty$, the short-range exchange energy becomes a local functional of the density:

$$E_{\mathrm{x}}^{\mathrm{sr}}[n] = -\frac{\pi}{4\mu^2} \int n(\mathbf{r})^2 \mathrm{d}\mathbf{r} + \cdots$$

and the short-range correlation energy becomes a local functional of the on-top pair density:

$$E_{\mathrm{c}}^{\mathrm{sr}}[n] = \frac{\pi}{2\mu^2} \int P_{\mathrm{c}}(\mathbf{r}, \mathbf{r}) \mathrm{d}\mathbf{r} + \cdots$$

Toulouse, Colonna, Savin, PRA, 2004

Long-range single-reference perturbation theory

- Single-determinant approximation: **lrHF+srDFT**

$$E_{\text{lrHF+srDFT}} = \min_{\Phi}\left\{\langle\Phi|\hat{T} + \hat{V}_{\text{ne}} + \hat{W}^{\text{lr}}|\Phi\rangle + E^{\text{sr}}_{\text{Hxc}}[n_\Phi]\right\}$$

with minimizing single-determinant Φ_0 given by

$$\left(\hat{T} + \hat{V}_{\text{ne}} + \hat{V}^{\text{lr}}_{\text{Hx,HF}} + \hat{V}^{\text{sr}}_{\text{Hxc}}\right)|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle$$

- **Adiabatic connection** between the single-determinant reference ($\lambda = 0$) and the exact energy ($\lambda = 1$):

$$E^{\lambda} = \min_{\Psi}\left\{\langle\Psi|\hat{T} + \hat{V}_{\text{ne}} + \hat{V}^{\text{lr}}_{\text{Hx,HF}} + \lambda\hat{\mathcal{W}}^{\text{lr}}|\Psi\rangle + E^{\text{sr}}_{\text{Hxc}}[n_\Psi]\right\}$$

with the long-range MP perturbation operator $\hat{\mathcal{W}}^{\text{lr}} = \hat{W}^{\text{lr}} - \hat{V}^{\text{lr}}_{\text{Hx,HF}}$

- Total energy by adding the **long-range correlation energy** E^{lr}_{c}

$$E = E_{\text{lrHF+srDFT}} + E^{\text{lr}}_{\text{c}} \quad \text{with} \quad E^{\text{lr}}_{\text{c}} = \sum_{n=2}^{\infty} E^{(n)}$$

E^{lr}_{c} can be approximated by lrMP2, lrRPA, lrCC, etc...

Ángyán, Gerber, Savin, Toulouse, PRA, 2005

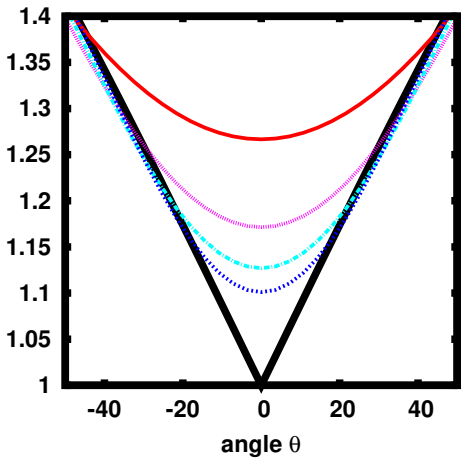
Fast basis convergence with long-range interaction

Behavior of the wave function at small interelectronic distance $r_{12} \to 0$:

Coulomb interaction

$$\frac{\Psi(r_{12})}{\Psi(0)} = 1 + \frac{r_{12}}{2} + \cdots$$

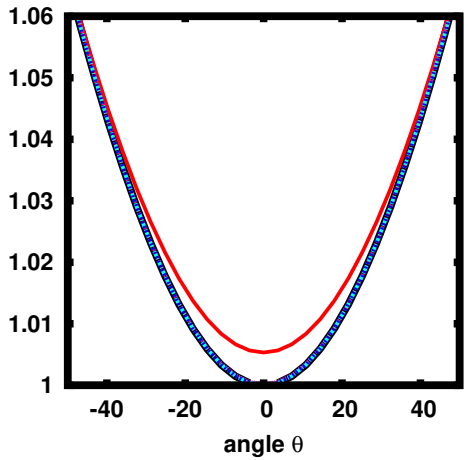
$$= \sum_{\ell=0}^{\infty} c_\ell P_\ell(\cos\theta) \text{ with } \mathbf{c_\ell} \sim \ell^{-2}$$



Long-range interaction

$$\frac{\Psi^{\text{lr}}(r_{12})}{\Psi^{\text{lr}}(0)} = 1 + \frac{\mu r_{12}^2}{3\sqrt{\pi}} + \cdots$$

$$= \sum_{\ell=0}^{\infty} c_\ell P_\ell(\cos\theta) \text{ with } \mathbf{c_\ell} \sim \mathbf{e}^{-\alpha\ell}$$

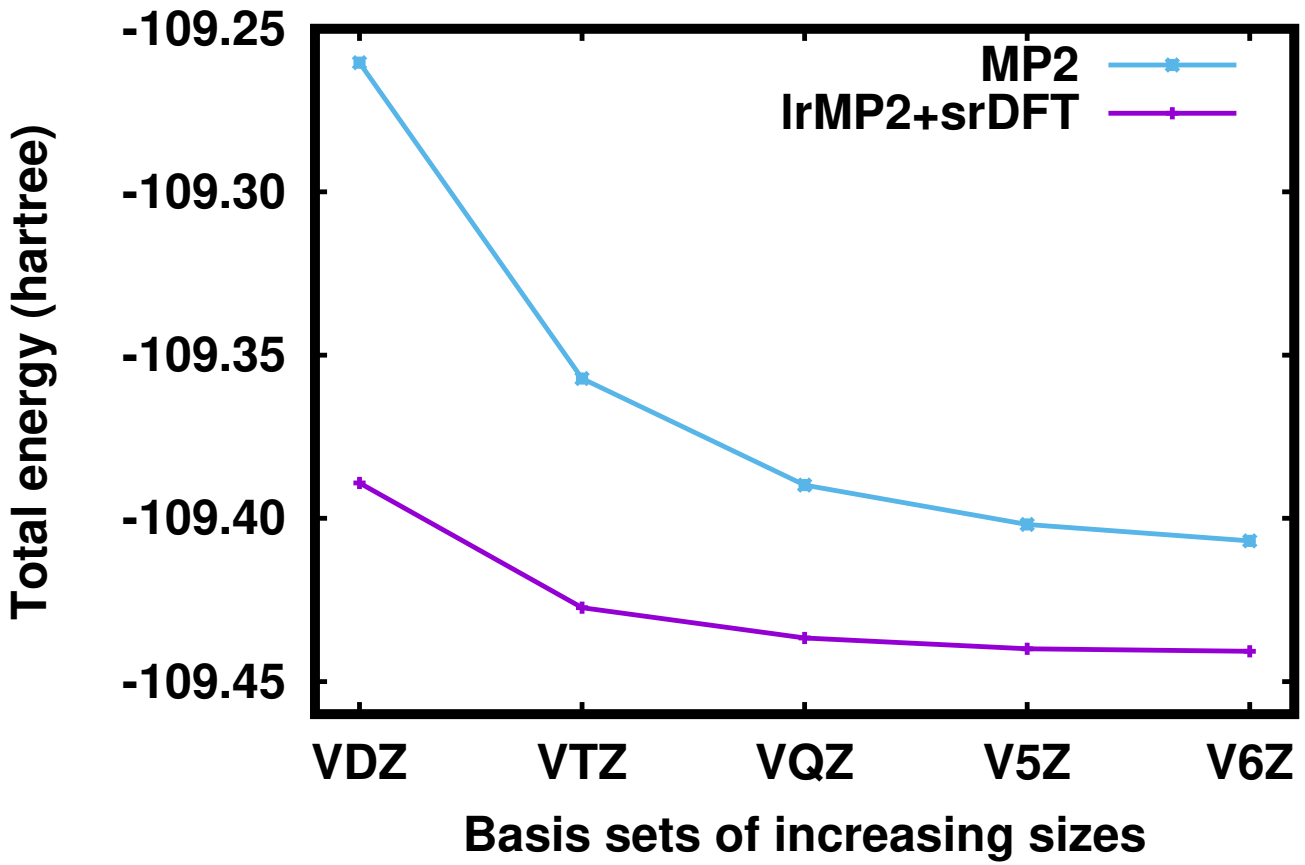


$\mu = 0.5$ bohr^{-1}

Gori-Giorgi, Savin, PRA, 2006; Franck, Mussard, Luppi, Toulouse, JCP, 2015

Fast basis convergence of long-range perturbation theory

Total energy of N_2 calculated with a series of **Gaussian basis sets**:
cc-pVXZ with $X = \mathrm{D}, \mathrm{T}, \mathrm{Q}, 5, 6$
with inverse cutoff parameter $\mu = 0.5$ bohr^{-1}



$\Longrightarrow$ **Exponential basis convergence of lrMP2+srDFT**

▸ Come back to results