Why beyond RPA and GW?
DFT-based exchange vertex
Excited states from $GW\Gamma_x$
GS energy for molecules and solids
Conclusions

# DFT-based exchange vertex for the correlation energy and excited states

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## Outline

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DFT-based exchange vertex

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## Why beyond RPA and GW?

- RPA (DFT propagators), GW (dressed many-body propagators)

- Energy differences often good but correlation energies are too large

- van der Waals forces are underestimated

- Strong correlation

- Solution: a proper vertex correction

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## DFT-based exchange vertex

Adiabatic connection formula for the total energy with density fixed ($H = T + V_{ext} + V_{Hxc} + \lambda W - V^\lambda$)

$$E = T_s + \int n v_{ext} + E_{Hx} - \frac{i}{2} \int d\lambda \mathrm{Tr}\{v\chi^\lambda(\omega) - v\chi_s(\omega)\}$$

The scaled response function can be obtained from TDDFT (or MBPT)

$$\chi^\lambda = \chi_s + \chi_s(\lambda v + f_{xc}^\lambda[n])\chi^\lambda$$
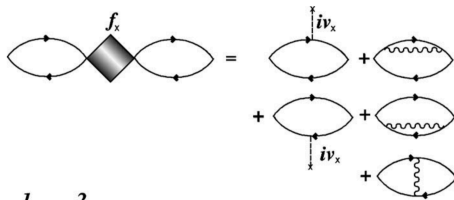
The level of approximation is determined by $f_{xc}^\lambda$:

$$f_{xc}^\lambda = \frac{\delta v_{xc}^\lambda}{\delta n}, \quad f_{xc}^\lambda = 0 \Rightarrow RPA$$

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## DFT-based exchange vertex

The exact-exchange (EXX) kernel $f_x$

$$f_x = \frac{\delta v_x}{\delta n} \ \Rightarrow \ \chi_s f_x \chi_s = H$$

Diagrammatic structure:



$$\underset{\sim\sim\sim\sim}{1 \quad 2} = -iv\,(1,2)$$

$$\chi^\lambda = \chi_s + \chi_s(\lambda v + f_x^\lambda[n])\chi^\lambda \rightarrow \text{RPAx}$$

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## DFT-based exchange vertex

Apply a local approximation to the self-energy

$$\Gamma = 1 + \frac{\delta\Sigma}{\delta V} \approx 1 + \frac{\delta v_{xc}}{\delta V} = 1 + f_{xc}\chi_s + f_{xc}\chi_s f_{xc}\chi_s + ...$$

With $f_x \leftrightarrow \Gamma_x$ the total energy can be re-written as

$$E = T_s + \int n v_{ext} + E_H - \frac{i}{2} \int \frac{d\lambda}{\lambda} \mathrm{Tr}\{\Sigma_s^\lambda(\omega) G_s(\omega)\}$$

where

$$\Sigma_s = G_s W \Gamma_x, \quad W = v + v P W, \quad P = -i G_s G_s \Gamma_x$$

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# DFT-based exchange vertex

- RPAx: $\Gamma_x = 1 + f_x \chi_s \Gamma_x$

$$E_c = E_c^{\mathrm{RPA}} + \tfrac{i}{4}\left(\!\!\!\text{⬡}\!\!\!\right) + \tfrac{i}{2}\left(\!\!\!\text{⬡}\!\!\!\right) + \tfrac{i}{2}\left(\!\!\!\overset{iv_x}{\text{⬡}}\!\!\!\right) + \cdots$$
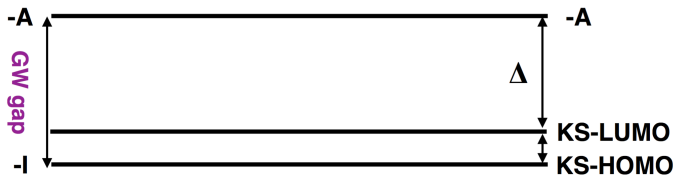
- SOSEX: $\Gamma_x = 1 + f_x \chi_s$ but keep $W = W^{RPA}$

- RPAx(1): $\Gamma_x = 1 + f_x \chi_s$

- $N^4$ scaling as RPA

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# Excited states from $GW\Gamma_x$



$$-A = \varepsilon_{\mathrm{L}} + \Delta_{\mathrm{xc}} = \varepsilon_{\mathrm{L}} + \langle \varphi_{\mathrm{L}} | \Sigma_{\mathrm{xc}}(\varepsilon_{\mathrm{L}}) - v_{\mathrm{xc}} | \varphi_{\mathrm{L}} \rangle$$

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# Excited states from $GW\Gamma_x$

$$v_x^+ = v_x^- + \Delta$$

$$\Gamma_x = 1 + \frac{\delta v_x}{\delta V}$$

$$\Gamma_x^+ = \Gamma_x^- + G_x$$



$$- A = \varepsilon_L + \Delta_{xc} = \varepsilon_L + \langle \varphi_L | \Sigma_{xc}(\varepsilon_L) - v_{xc} | \varphi_L \rangle$$
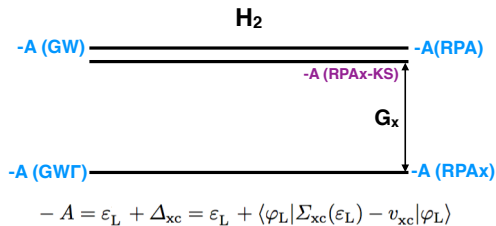
Spectral properties of strongly correlated systems relies on a
dynamical discontinuity in the DFT-vertex (beyond EXX)

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# GS energy for molecules and solids



$H_2$ dissociation

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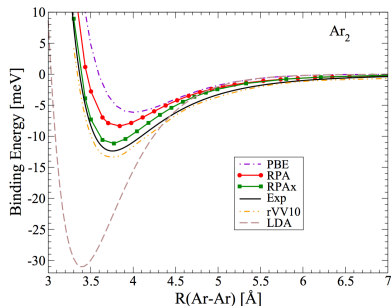Excited states from $GW\Gamma_x$
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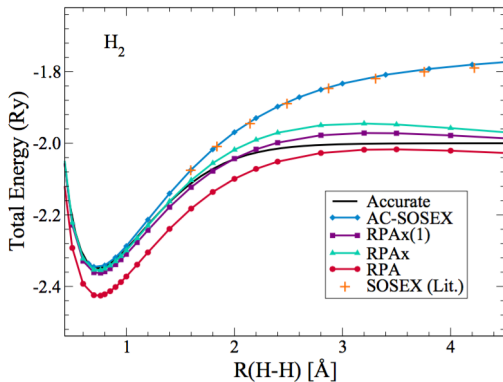
# GS energy for molecules and solids

✓ Improved van der Waals forces with RPAx



## Atomic $C_6$ coefficients
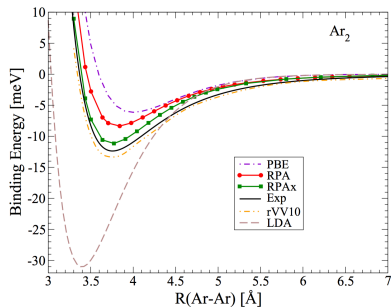
| Atom | RPA | RPAx | Litt. |
|------|-----|------|-------|
| He | 1.21 | 1.41 | 1.46 |
| Ne | 5.52 | 6.19 | 6.38 |
| Ar | 53.7 | 63.2 | 64.3 |
| Be | 142 | 235 | 214 |
| Mg | 386 | 634 | 627 |

Obtained with self-consistent
RPA/RPAx orbitals

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### Solid argon

|          | CE (meV) | AE |
|----------|----------|----|
| LDA      | 140      | 51 |
| RPA      | 68       | 21 |
| RPAx     | 87       | 2  |
| RPAx(1)  | 89       | 0  |
| AC-SOSEX | 93       | 4  |
| Exp.     | 89       |    |

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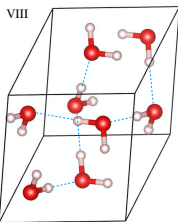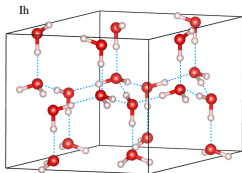GS energy for molecules and solids
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# GS energy for molecules and solids

Molecular test-set including hydrogen and van der Waals bonds
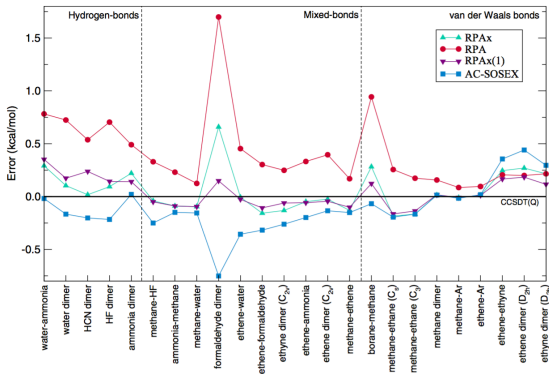


**RPA**: MA%E: 23% (0.44 kcal/mol)— **RPAx(1)**: MA%E: 8% (0.13 kcal/mol)

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# GS energy for molecules and solids



Lattice energies (kJ/mol)

| Method | Ih | VIII |
|--------|------|-----------|
| Exp. | 58.9 | 56.0(57.4) |
| RPAx | 58.7 | 56.4 |
| SOSEX | 61.0 | 59.2 |
| RPA | 51.9 | 49.1 |
| PBE-TS | 68.9 | 59.7 |

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## Conclusions

- The DFT-EXX kernel provides a systematic improvement on RPA and unifies different MBPT approximations

- RPAx gives very accurate total energies and van der Waals forces

- Excited states are accessible provided DFT-discontinuities are taken into account

- First efficient plane-wave implementation for solids

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## References

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Thank you for your attention!