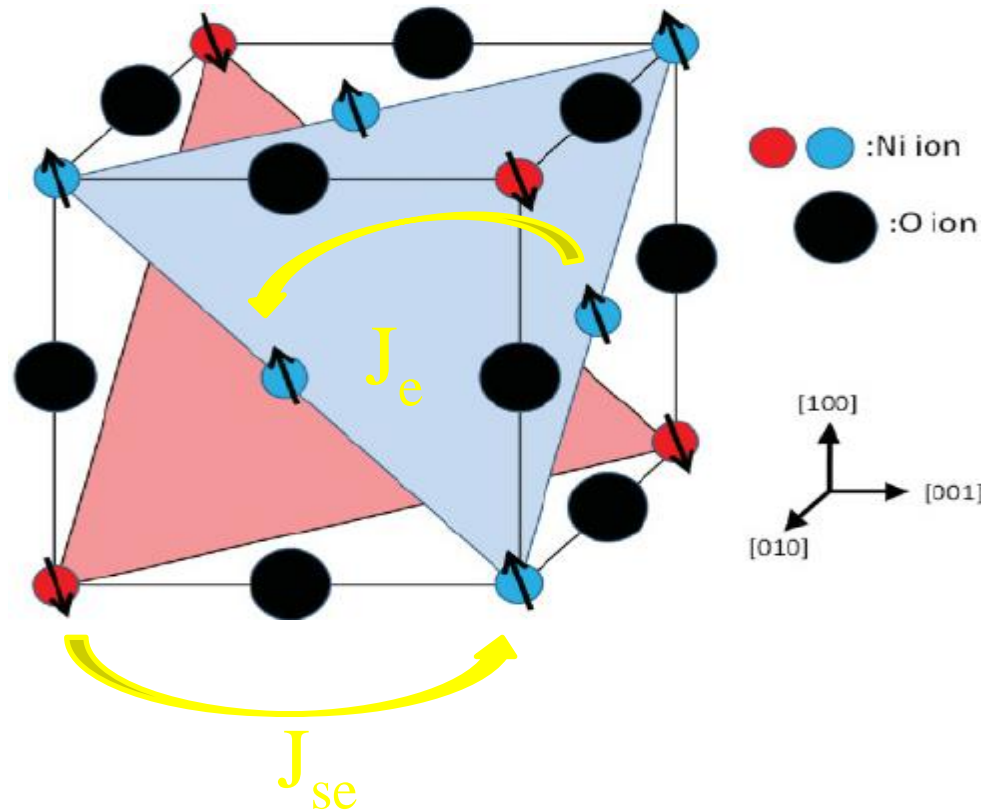


Strong correlation from the Random Phase Approximation and beyond

Thomas Olsen

Department of Physics, Technical University of Denmark

RPA workshop 3/5 - 2017



Static correlation denotes situation where the many-body wavefunction is poorly described by a Slater determinant



For a mean field Hydrogen molecule one gets

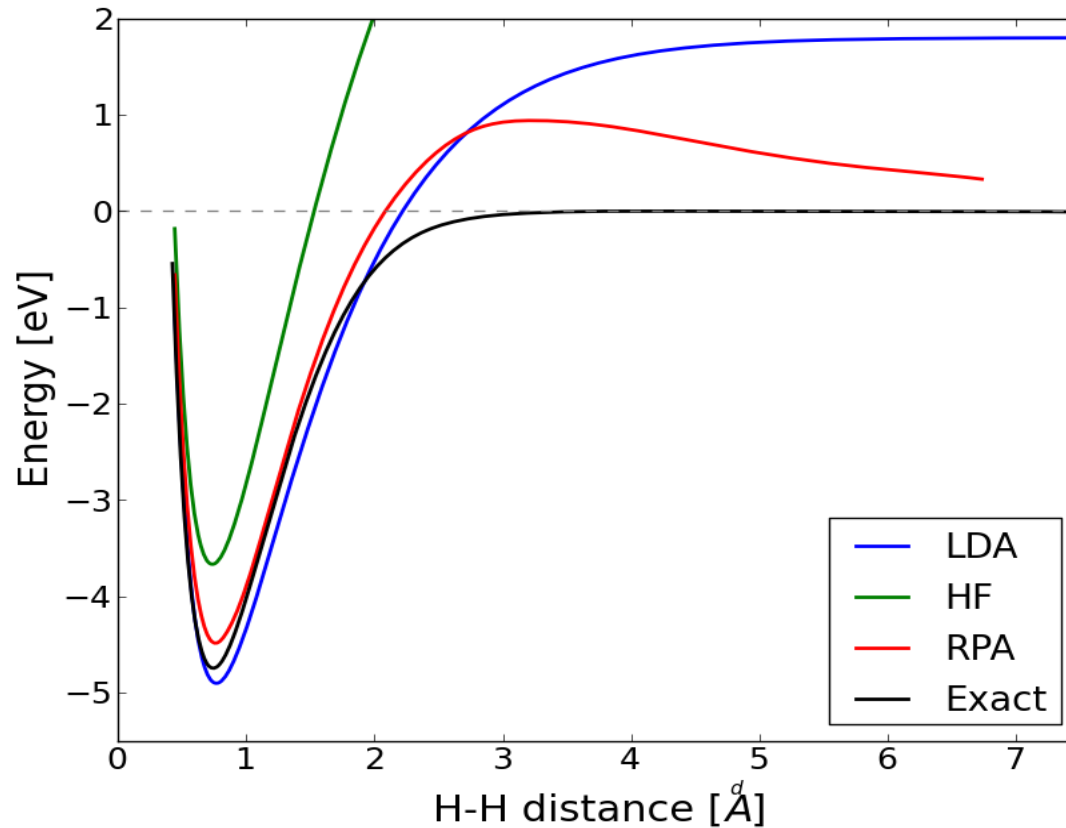
$$\varphi_{SL}(\mathbf{r}_1, \mathbf{r}_2) = \sigma_b(\mathbf{r}_1)\sigma_b(\mathbf{r}_2)(\alpha_1\beta_2 - \alpha_2\beta_1)$$

$$|\sigma_b\rangle = (|s_A\rangle + |s_B\rangle)/\sqrt{2}$$

In the dissociation limit a much better ansatz is the Heitler-London state

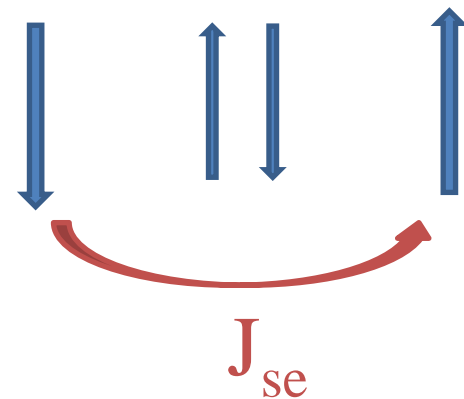
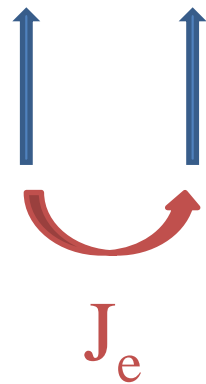
$$\varphi_{HL}(\mathbf{r}_1, \mathbf{r}_2) = [s_A(\mathbf{r}_1)s_B(\mathbf{r}_2) + s_A(\mathbf{r}_2)s_B(\mathbf{r}_1)](\alpha_1\beta_2 - \alpha_2\beta_1)$$

Static correlation in H₂ dissociation not captured by LDA or HF

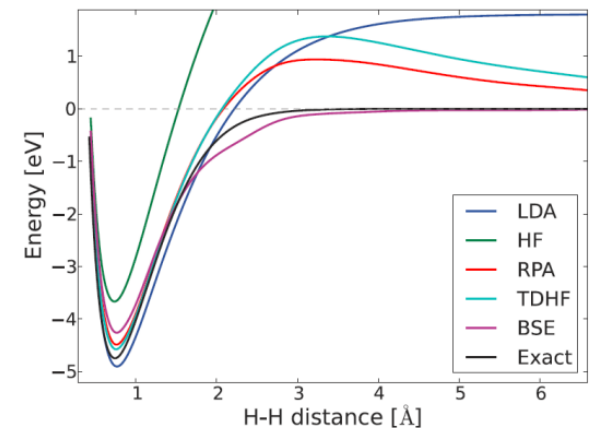


RPA does get it right, but performs poorly at intermediate distances

Exchange and superexchange from RPA

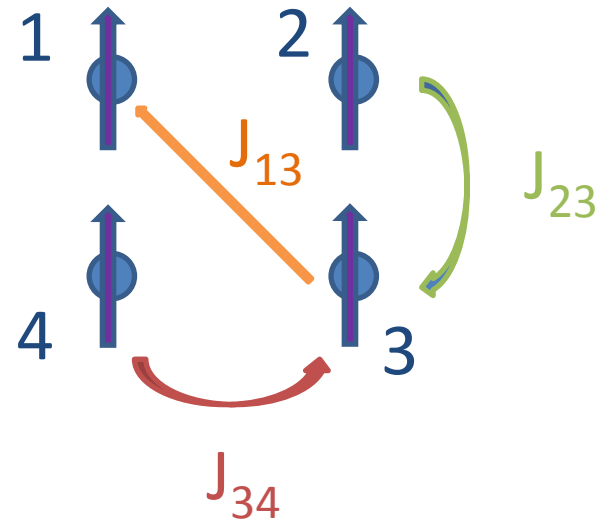


Dissociating H_2 with RPA and beyond



Magnetic interactions are modelled in terms of Heisenberg Hamiltonians:

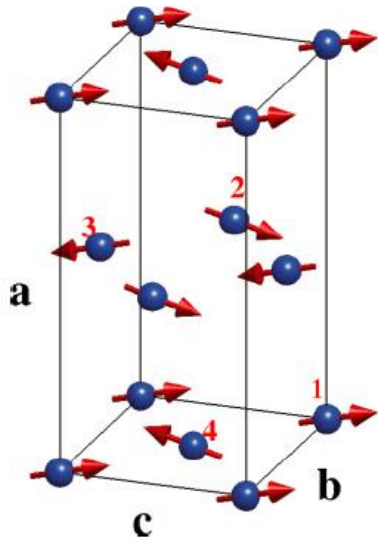
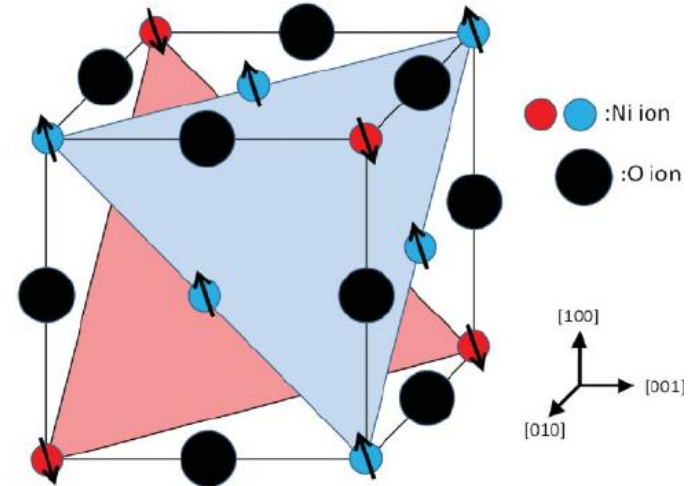
$$H = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$



Typically, magnetic coupling constants are determined experimentally from spin-wave dispersions or susceptibility.

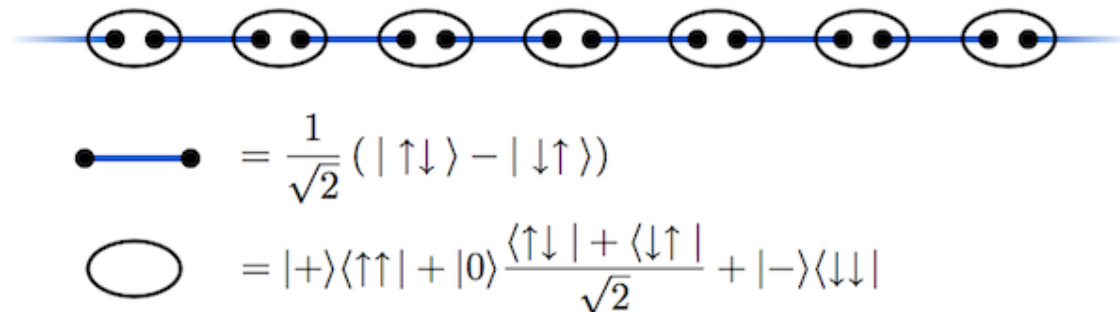
Different combinations of J_{ij} result in very different magnetic properties!

NiO: Antiferromagnetic coupling of ferromagnetic planes



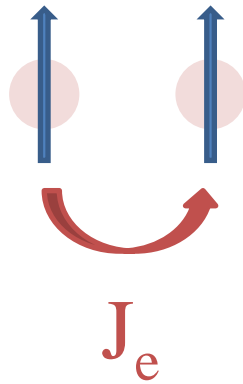
LiNiPO₄: Magnetolectric coupling from non-collinear spin configuration

Haldane phase:
S=1 chain exhibiting a topological gap



The microscopic origin of magnetic interactions may contain very different physics

Exchange

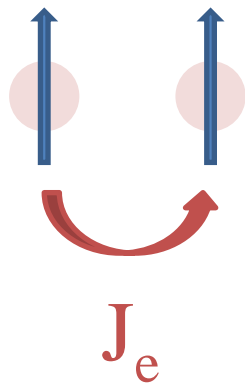


$$\Delta E \sim \langle \psi_0 | v_c | \psi_0 \rangle \sim -\frac{U}{2}$$

First order perturbation theory
in Coulomb interaction

The microscopic origin of magnetic interactions may contain very different physics

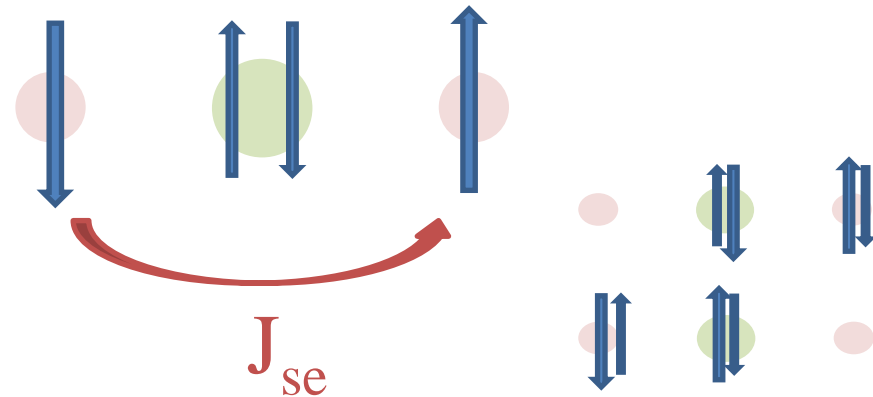
Exchange



$$\Delta E \sim \langle \psi_0 | v_c | \psi_0 \rangle \sim -\frac{U}{2}$$

First order perturbation theory
in Coulomb interaction

Superexchange



$$\Delta E \sim \frac{|\langle \psi_1 | V_{ion} | \psi_2 \rangle|^2}{\Delta \epsilon_{12}} \sim -\frac{4t^2}{U}$$

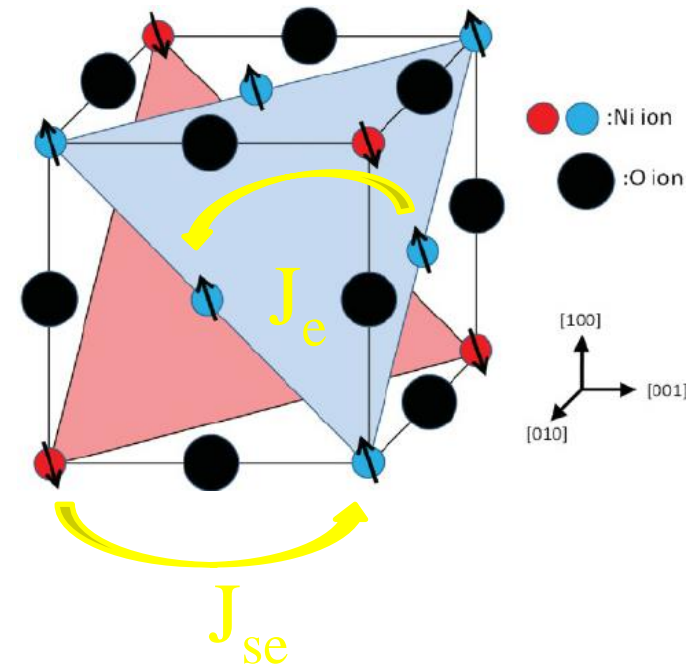
Second order in interatomic
Coupling: Non-perturbative in U

The magnetic couplings are obtained from first principle by energy mapping to the Heisenberg model

For NiO we need three configurations to obtain J_e and J_{se}

Each Ni atom has:

- 12 direct nearest neighbors
- 6 next nearest neighbors connected by oxygen bridge



We have tested LDA+U, PBE+U, HSE06@PBE+U, EXX@PBE+U and RPA@PBE+U

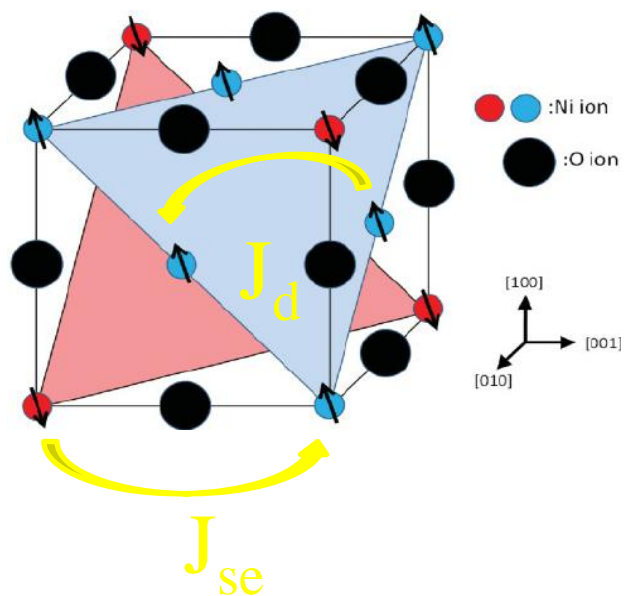
Due to the energy mapping scheme the J_{ij} can be written as

$$J^{\text{RPA}} = J_{\text{EXX}} + J_{\text{c}}^{\text{RPA}}$$

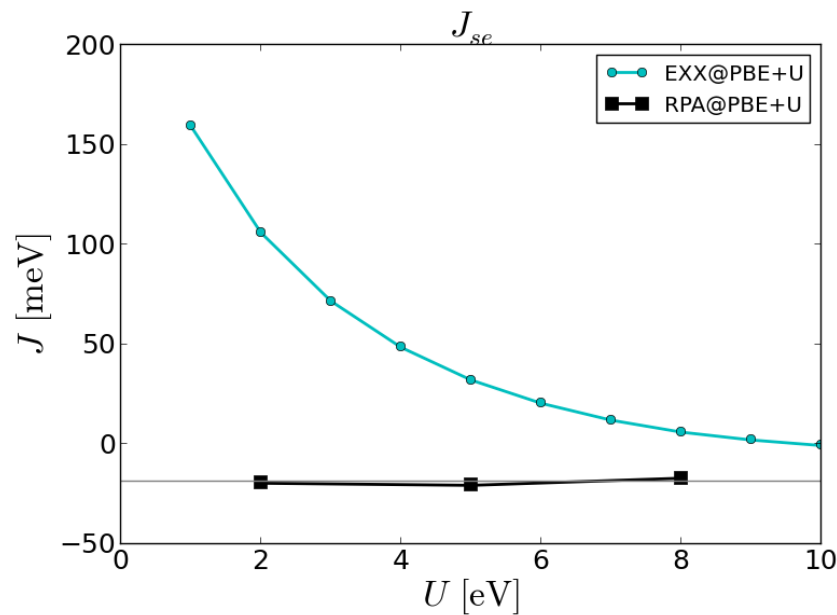
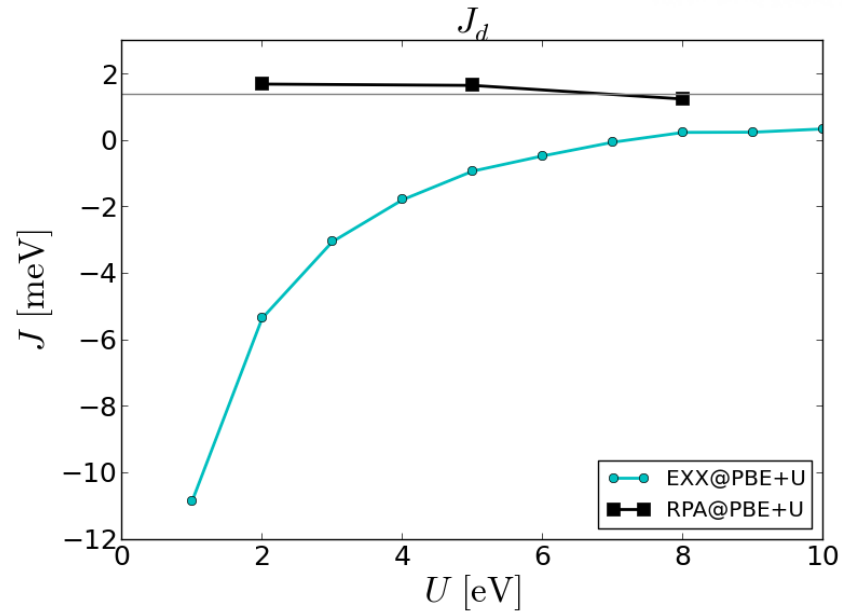
which allow us to separate the exchange and correlation parts of the magnetic couplings

All calculations performed with the electronic structure package GPAW using plane waves and PAW

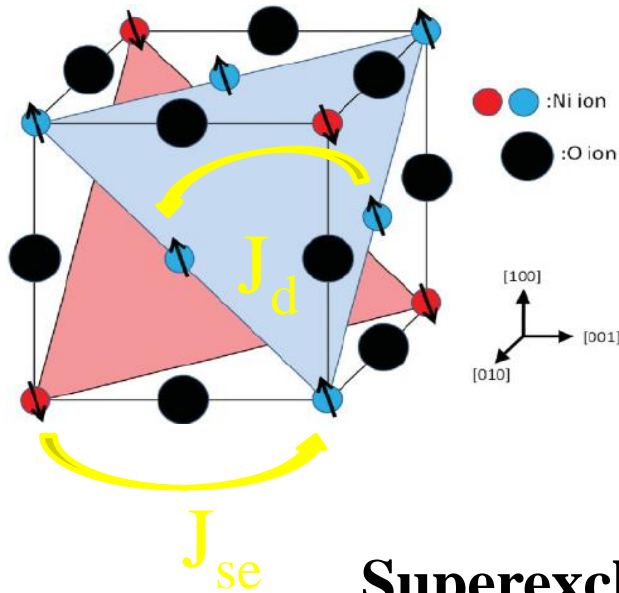
Direct exchange



Superexchange

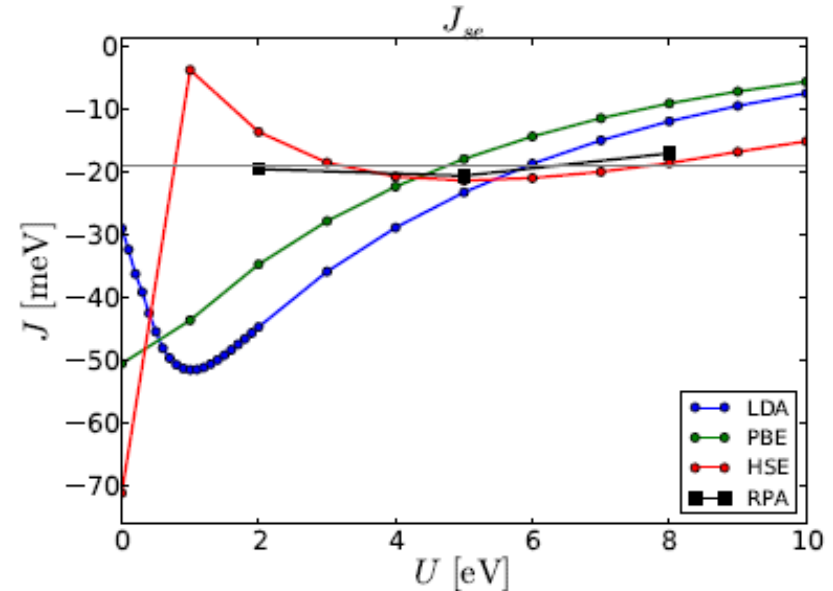
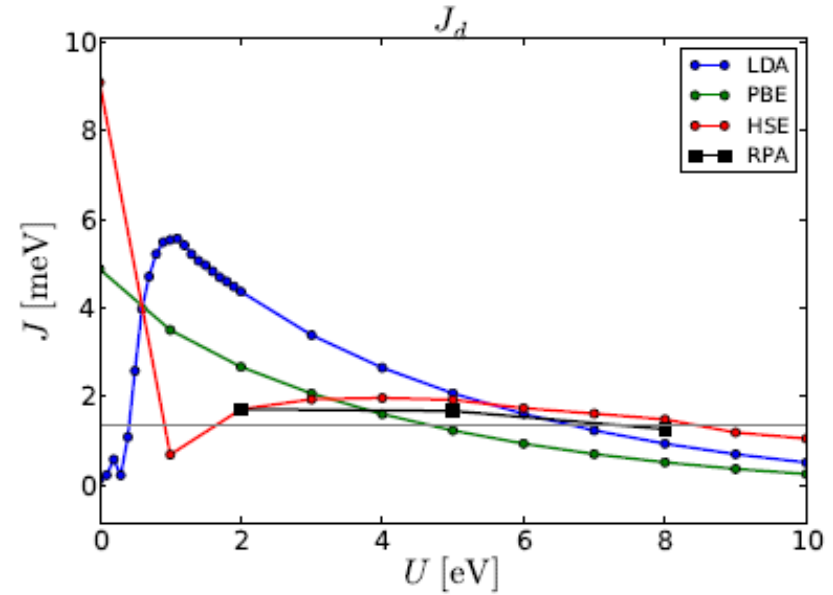


Direct exchange

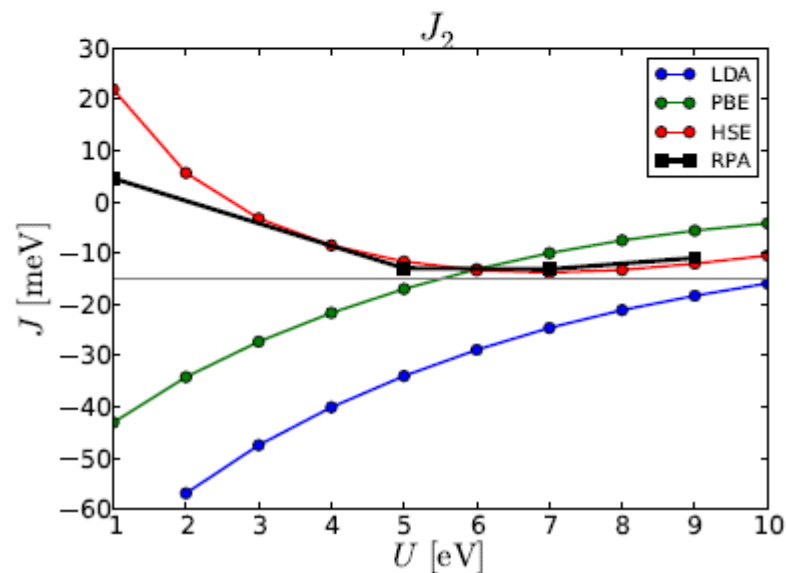
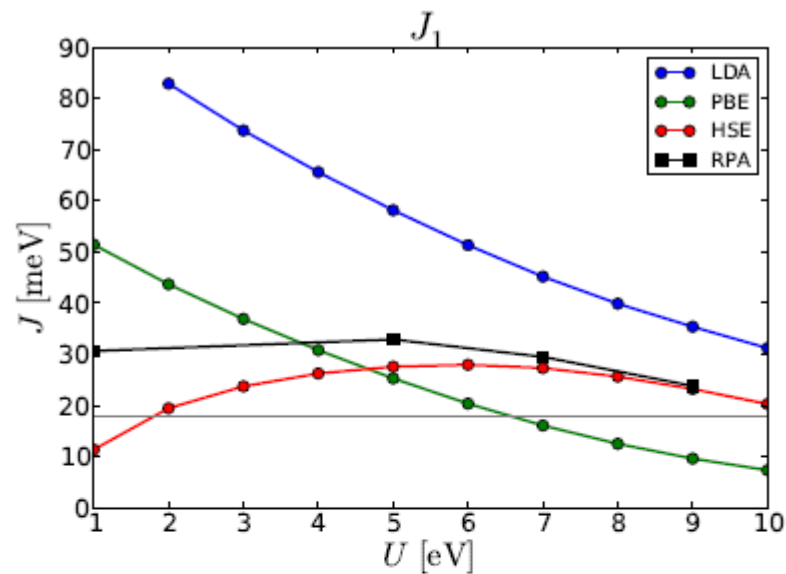
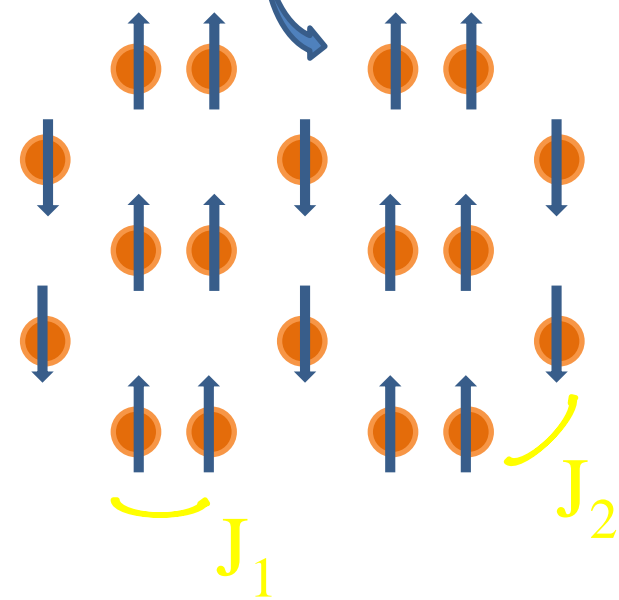
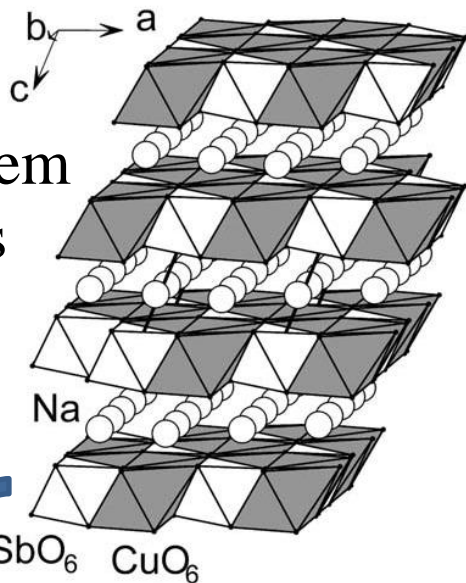


Superexchange

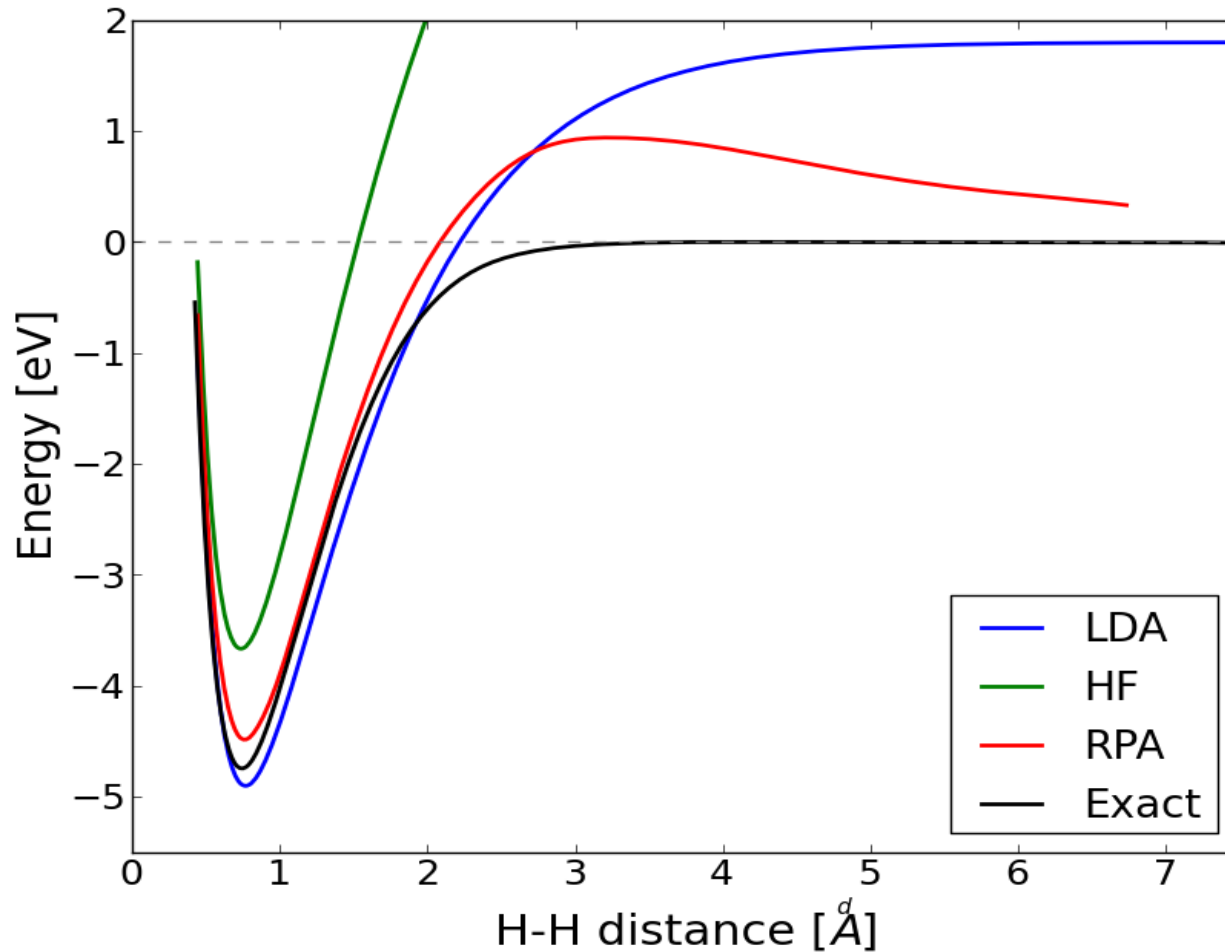
PBE+U is quite good for the "right" U.
 RPA is not very sensitive to U



Spin $\frac{1}{2}$ system
of Cu^{2+} ions



Can we improve the dissociation curve of H_2 by going beyond RPA?



Within the adiabatic connection – fluctuation dissipation theorem the correlation energy can be written as

$$E_c = \frac{-1}{2\pi} \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \int_0^\infty d\omega [\chi^\lambda(\mathbf{r}, \mathbf{r}'; i\omega) - \chi^0(\mathbf{r}, \mathbf{r}'; i\omega)]$$

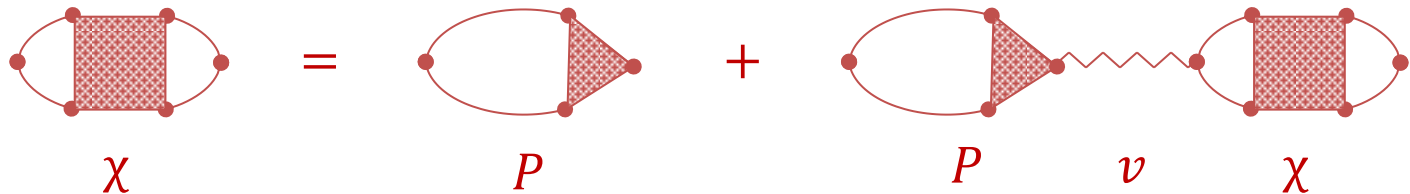
where $\chi^\lambda(r, r')$ is the (reducible) response function at coupling λ

Within the adiabatic connection – fluctuation dissipation theorem the correlation energy can be written as

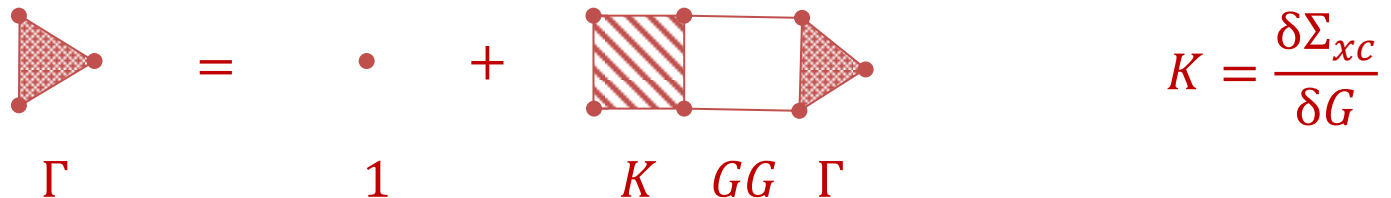
$$E_c = \frac{-1}{2\pi} \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \int_0^\infty d\omega [\chi^\lambda(\mathbf{r}, \mathbf{r}'; i\omega) - \chi^0(\mathbf{r}, \mathbf{r}'; i\omega)]$$

where $\chi^\lambda(r, r')$ is the (reducible) response function at coupling λ


In terms of diagrams (from Hedins formulation)



where




The RPA is simply obtained by

$$\Sigma_H = 0$$


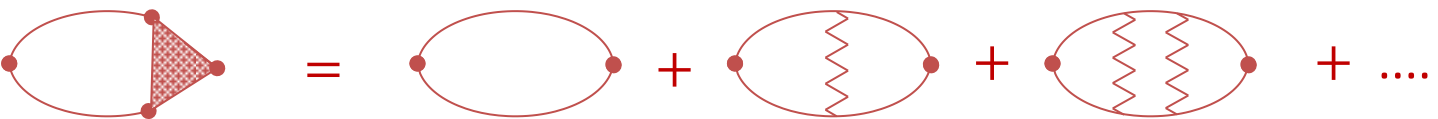
The diagrammatic equation shows the Hartree self-energy Σ_H is equal to zero. On the left, a red oval with two vertices is shown with a shaded triangular region attached to its right side, representing a self-energy correction. This is followed by an equals sign and a simple red oval with two vertices, representing the Hartree self-energy.

The RPA is simply obtained by

$$\Sigma_H = 0$$



The diagram shows a red bubble with two vertices on the left and two on the right. A shaded triangular region is attached to the right side, representing a self-energy insertion. This is set equal to a simple red bubble with two vertices on the left and two on the right.

If the Fock self-energy is used one obtains TDHF


$$\Sigma_F = Gv$$


The diagram shows a red bubble with two vertices on the left and two on the right. A shaded triangular region is attached to the right side, representing a self-energy insertion. This is set equal to a sum of three terms: a simple red bubble with two vertices on the left and two on the right; a red bubble with two vertices on the left and two on the right and one wavy interaction line inside; a red bubble with two vertices on the left and two on the right and two wavy interaction lines inside; and an ellipsis indicating further terms in the series.

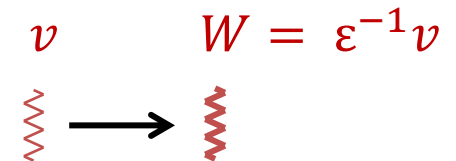
The RPA is simply obtained by

$$\Sigma_H = 0$$



If the Fock self-energy is used one obtains TDHF

$$\Sigma_F = Gv$$



Screened Coulomb interaction gives the BSE:



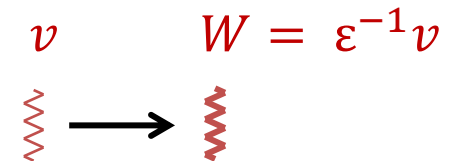
The RPA is simply obtained by

$$\Sigma_H = 0$$


If the Fock self-energy is used one obtains TDHF

$$\Sigma_F = Gv$$


Screened Coulomb interaction gives the BSE:

$$v \rightarrow W = \epsilon^{-1}v$$


$$\Sigma_{GW} = GW$$

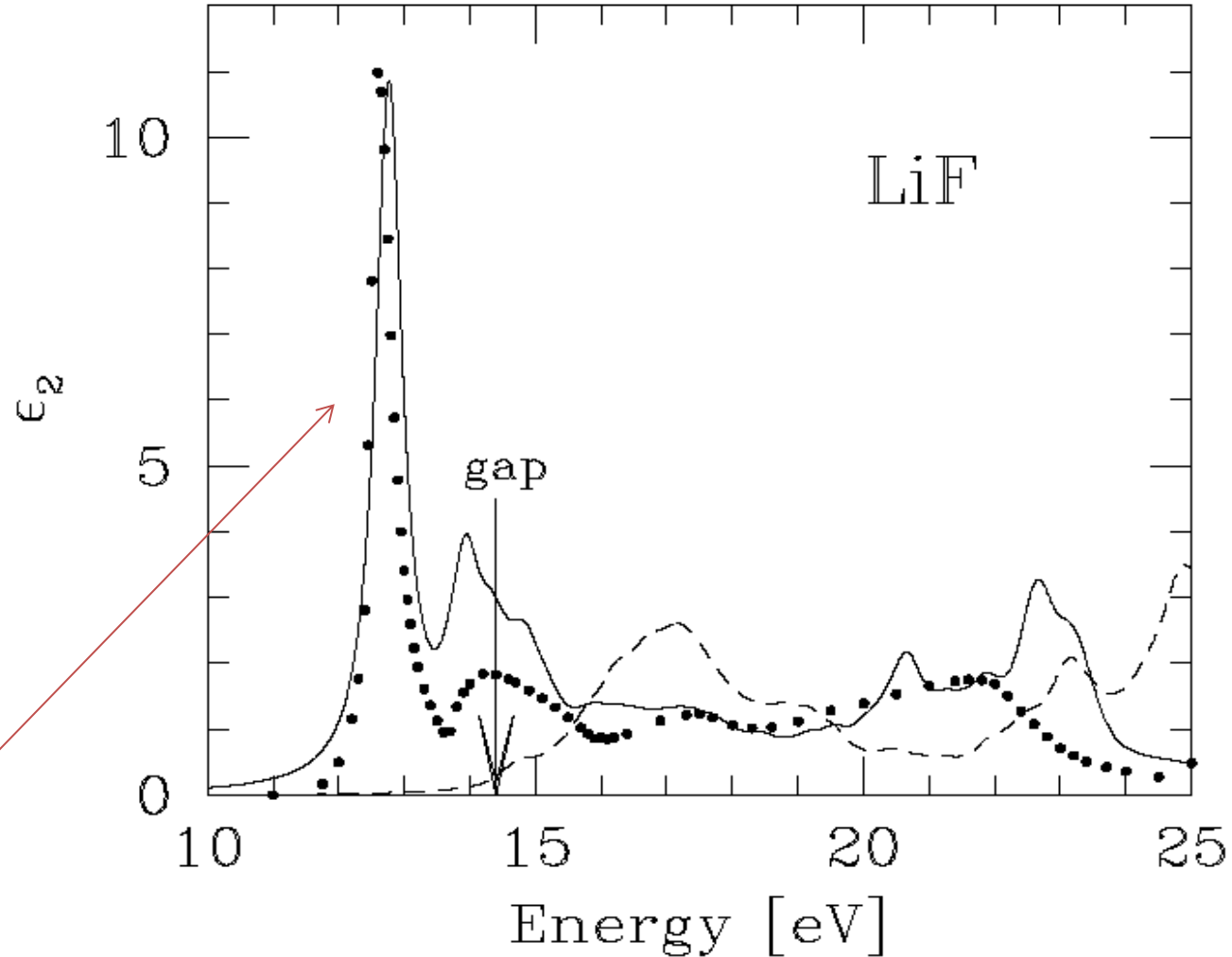
Full GW self-energy gives TDGW:



Only bands in the vicinity of the gap is needed to reproduce low energy spectrum

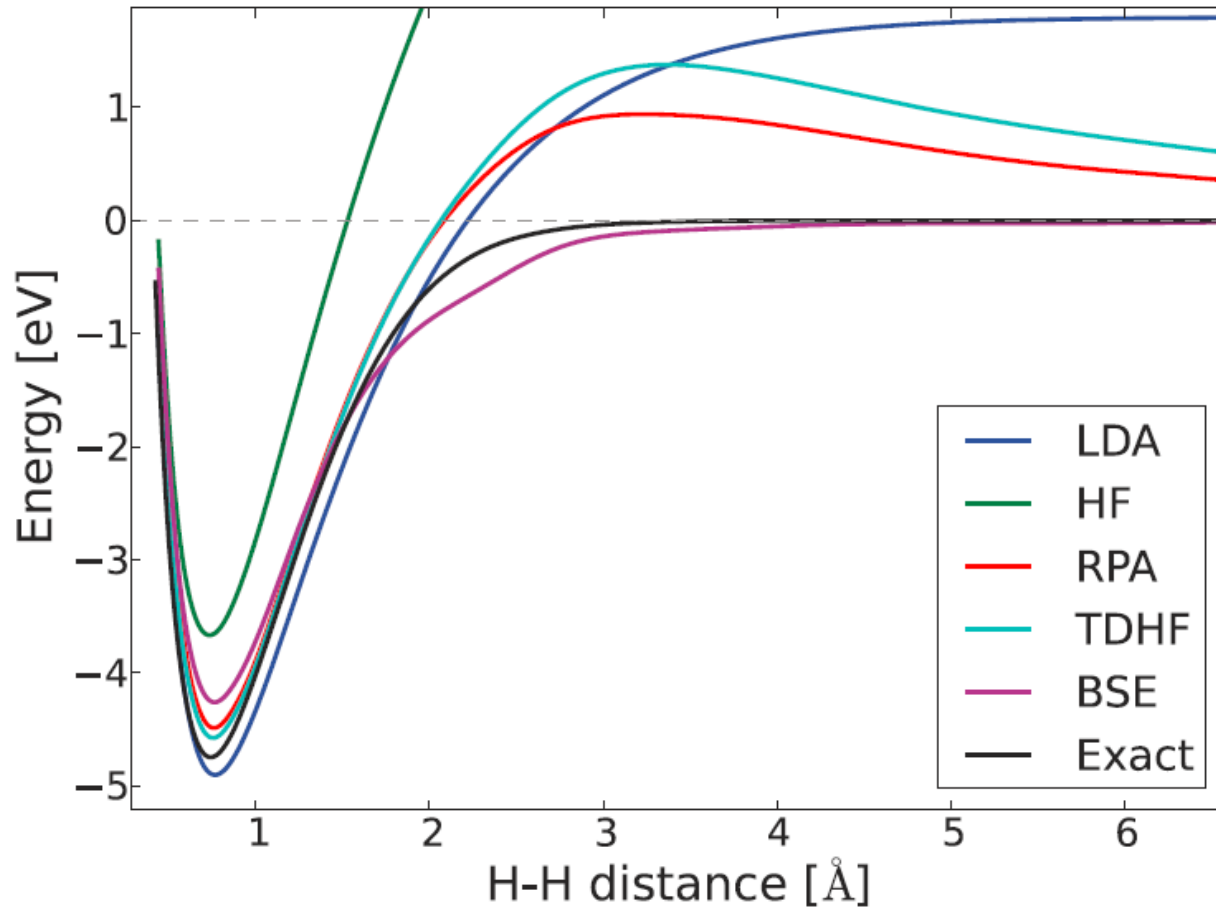
Problem mapped to a Hamiltonian

Exciton

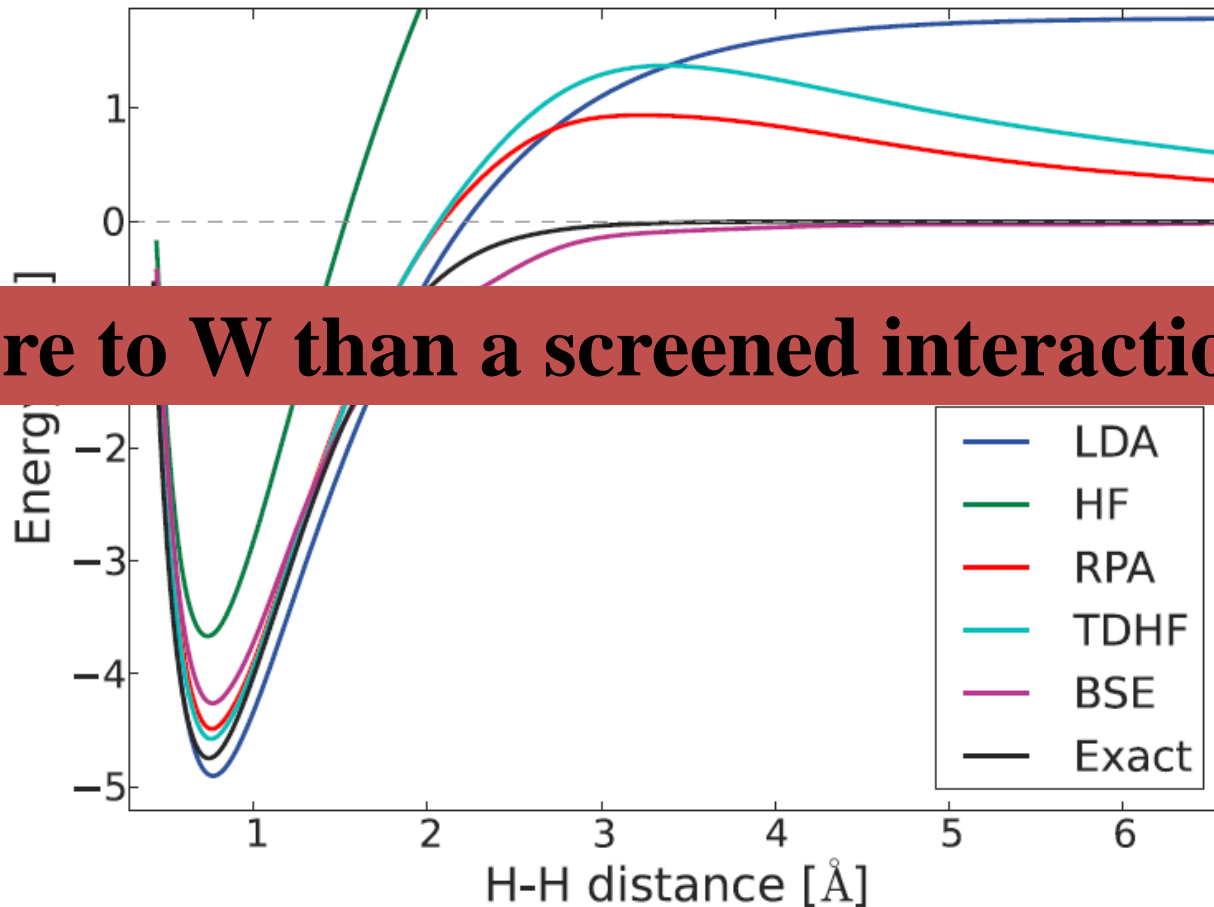


- We need all bands
- No Tamm-Dancoff approximation → non-Hermitian Hamiltonian
- The calculations is carried out at many point along the adiabatic path
- Analytical frequency integration → correlation energy is a sum of the residues

We have performed *ab initio* calculations with TDHF and BSE for the potential energy curve of H₂

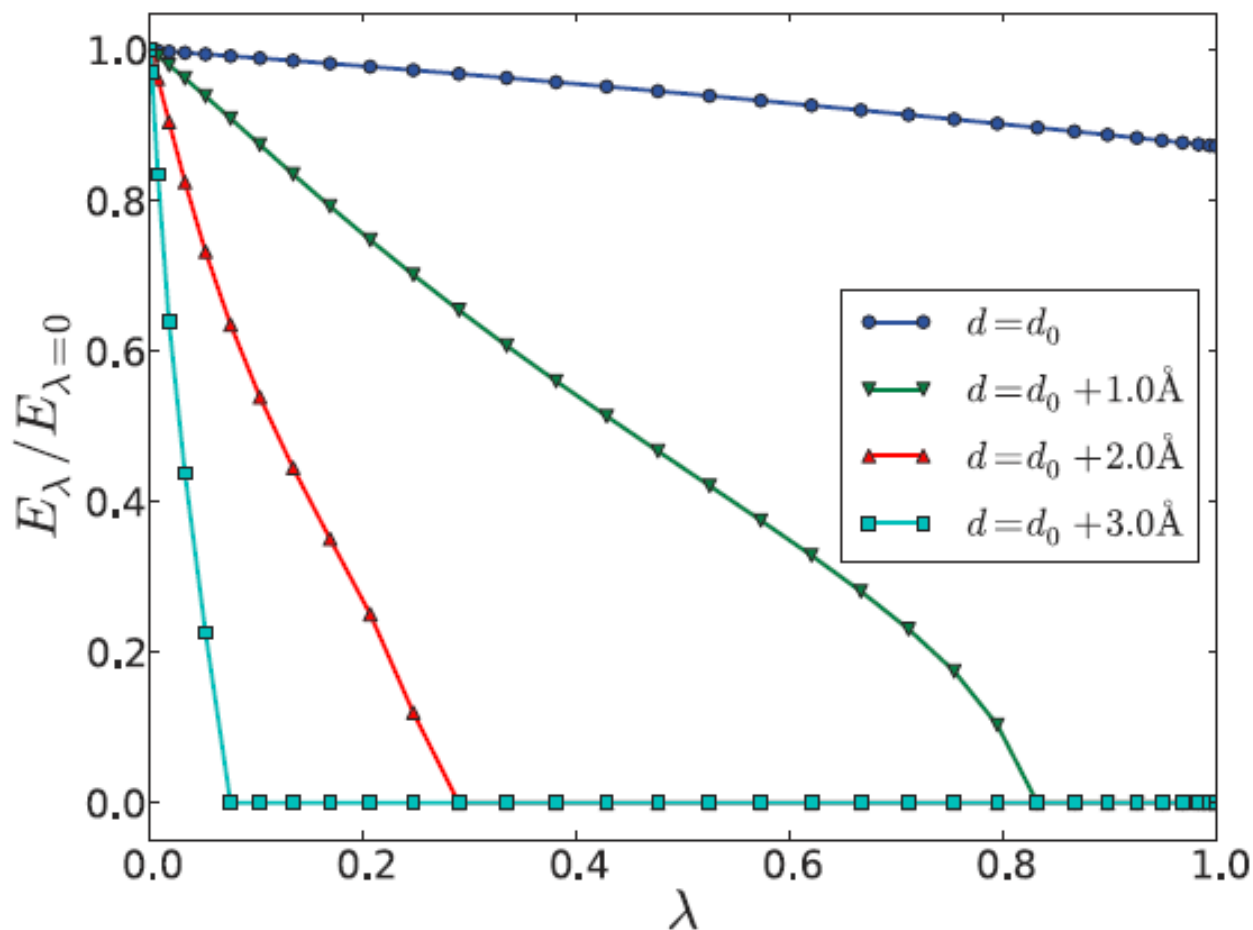


We have performed *ab initio* calculations with TDHF and BSE for the potential energy curve of H₂



More to W than a screened interaction!

As we approach the dissociation limit the BSE Hamiltonian acquire imaginary poles giving rise to vanishing $E_c(\lambda)$



$$E_c = \int_0^1 d\lambda E_\lambda$$

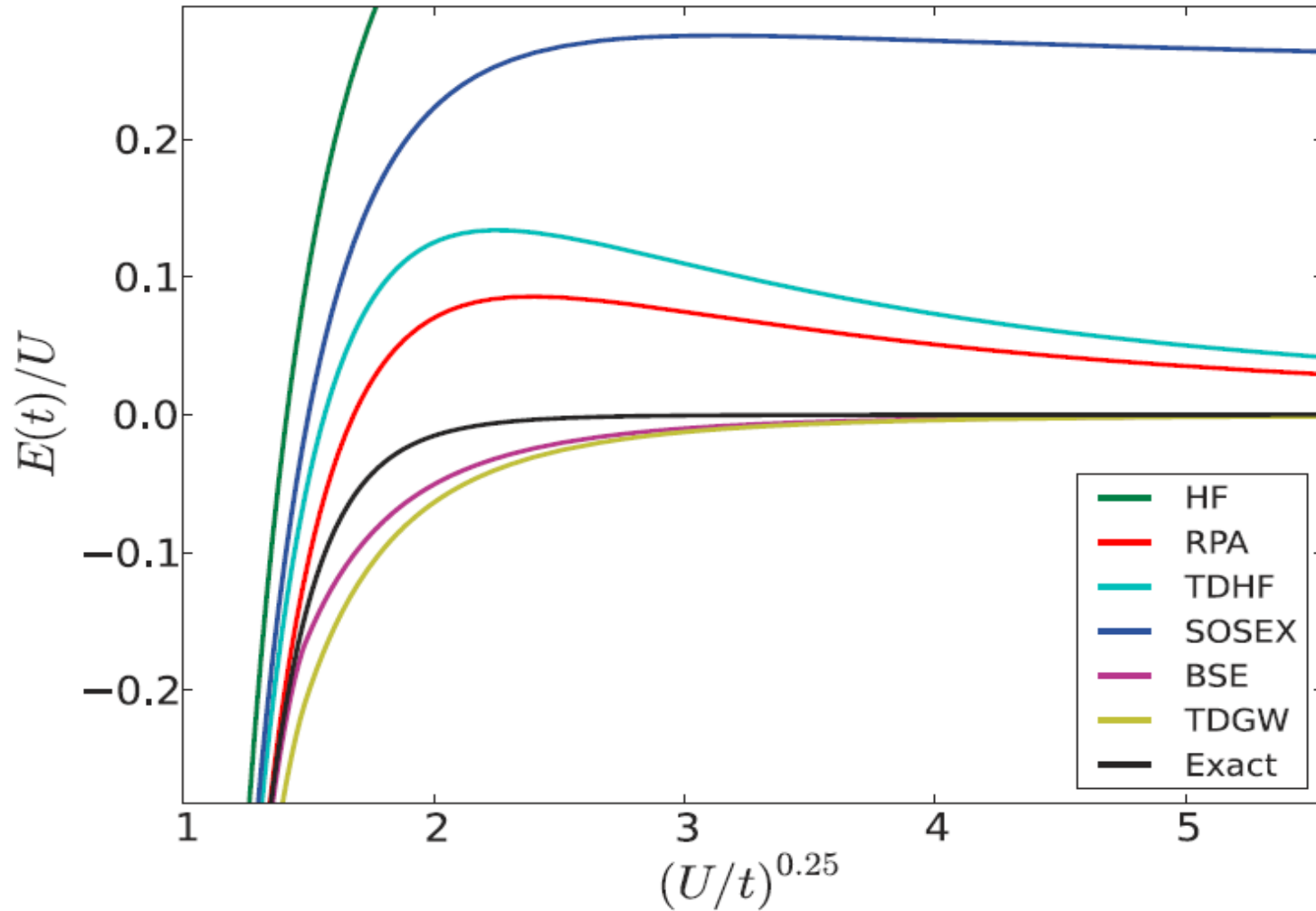
To assess the performance of TDGW we consider a Hubbard dimer

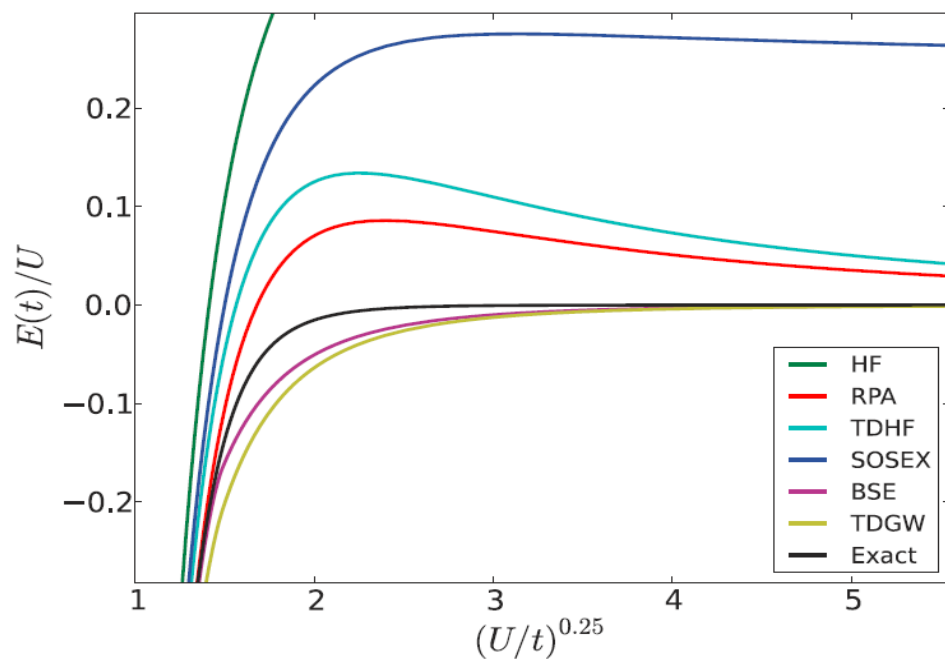
$$H = -t \sum_{i \neq j, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + \frac{U}{2} \sum_{i, \sigma \sigma'} c_{i\sigma}^\dagger c_{i\sigma'}^\dagger c_{i\sigma'} c_{i\sigma}$$

At half filling there is 6 Slater determinants and H can be diagonalized analytically

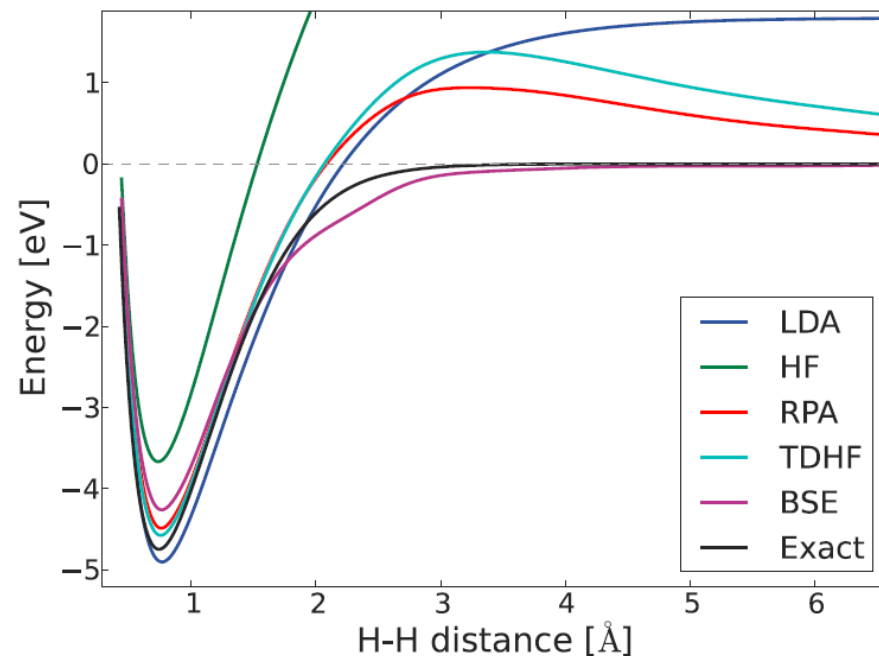
The correlation energy in various approximations can be obtained from

$$E_c = -\frac{U}{2} \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_{i\sigma\sigma'} \text{Im}[\chi_{i\sigma i\sigma'}(\omega) - \chi_{i\sigma i\sigma'}^0(\omega)]$$





Hubbard dimer



Ab initio H₂

- RPA performs well for exchange and superexchange magnetic interactions
- ... but so does PBE+U and HSE06 for the "right" value of U
- The dissociation curve for H₂ is significantly improved going to the BSE level – but calculations are intractable for realistic systems
- RPA and BSE fails dramatically for H₂⁺

Thank you for the attention