

Objectives

- ▶ vocabulary :
Schrödinger's equation , wavefunction, *etc.*...
- ▶ what is the problem ? many body problem
- ▶ first steps toward resolution :
Hartree-Fock , Density Functional Theory , ...
- ▶ what "we" do : Range Separated Hybrid
- ▶ what "I" do : Random Phase Approximation

What is it all about ?

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- a molecule is a collection of M nuclei and N electrons

nuclei : charges $Z_{1 \rightarrow M}$, masses $M_{1 \rightarrow M}$, positions $\mathbf{R}_{1 \rightarrow M} \in \mathbb{R}^3$

electrons : spins $s_{1 \rightarrow N} \in \mathbb{S} = \{-\frac{1}{2}, \frac{1}{2}\}$, positions $\mathbf{r}_{1 \rightarrow N} \in \mathbb{R}^3$

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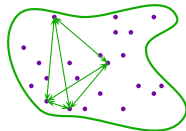
$|\Psi_{\text{elec}}(\mathbf{x}^N)\rangle$ is a function of
the Hilbert space $\mathcal{L}^2(\mathbb{X}^N, \mathbb{C})$

$|\Psi_{\text{elec}}(\mathbf{x}^N)\rangle$ is an
antisymmetric function

Hamiltonian

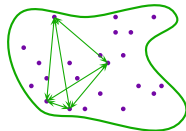
$$\hat{H}_{\text{elec}} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} = \sum_i \hat{h}_i + \sum_{ij} \hat{g}_{ij}$$

N body with *instantaneous* Coulombic interaction
(literally) infinitely complex problem



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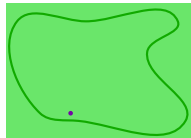


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THE approximation : mean field

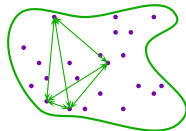
N -body problem \rightarrow superposition of N 1-body problems
interaction of each pair \rightarrow sum of interactions of $1e^-$ with the mean field

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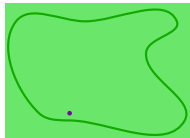


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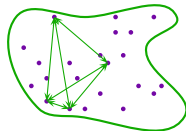


What do we gain ?

wavefunction factorisable

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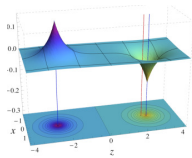
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What do we lose ?

the **correlation** between the electrons

fluctuating repulsion/ **correlation hole** missing



Remember ? "Hilbert space"

one particule	$\mathcal{L}^2(\mathbb{X}, \mathbb{C})$	set of <i>spin-orbitals</i> $\{ \psi_i\rangle\}_\infty$
N particules	$\mathcal{L}^2(\mathbb{X}^N, \mathbb{C})$	set of all <i>Hartree products</i> $\{ \psi_a\psi_b\cdots\psi_c\rangle\}_\infty$
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$$\langle \psi_i \psi_j | \hat{g}_{ij} | \psi_i \psi_j \rangle = \iint \psi_i^*(\mathbf{x}_1) \psi_i(\mathbf{x}_1) \hat{g}_{ij} \psi_j^*(\mathbf{x}_2) \psi_j(\mathbf{x}_2)$$

Hartree term E_H

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Exchange term E_x

$|\Psi(\mathbf{x}^N)\rangle$: $4N$ coordinates

Density Functional Theory

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$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle = T_e[n] + V_{ee}[n] \text{ is the universal functionnal}$$

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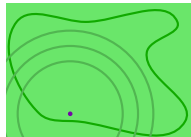
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$$E_0 = \min_{n \in \mathbb{N}} \left\{ T_s[n] + E_H[n] + E_{xc}[n] + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$

$E_{xc}[n]$ is the exchange-correlation functionnal

This is where we talk about DFAs
(LDA,GGA,PBE,PBE0,...)

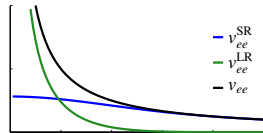


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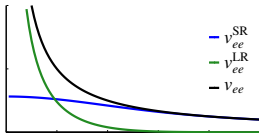
Range Separated Hybrid

$$\frac{1}{r} = v_{ee}^{lr}(\mathbf{r}) + v_{ee}^{sr}(\mathbf{r})$$



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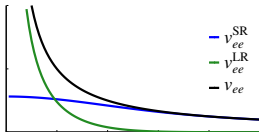
$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T}_e + \hat{V}_{ee}^{lr} | \Psi \rangle + E_{Hxc}^{sr}[n]$$

and :

$$E_0 = \min_{\Psi \rightarrow N} \left\{ \langle \Psi | \hat{T}_e + \hat{V}_{ee}^{lr} | \Psi \rangle + E_{Hxc}^{sr}[n_{\Psi}] + \int n_{\Psi}(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$

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RSH scheme :

$$E_{\text{RSH}} = \min_{\Phi} \left\{ \langle \Phi | \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}^{lr} | \Phi \rangle + E_{\text{Hxc}}^{sr}[n_{\Phi}] \right\}$$

total energy : $E = E_{\text{RSH}} + E_c^{lr}$

Random Phase Approximation

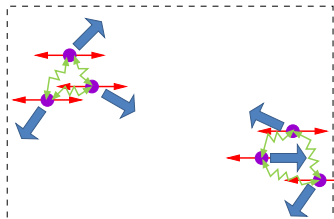
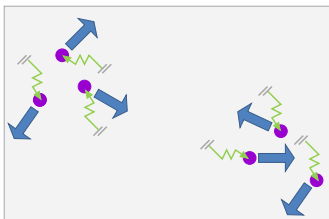
- ▶ Dispersion
 - mutual dynamical polarization of electron cloud
 - fluctuations of the electronic density correlating
 - need a good description of the long-range correlations
- ▶ RPA
 - treating the long-range
 - exchange in the response function
 - polarizability yields the correct long-range behaviour (C_6/R^6)
- ▶ Performances
 - average, due to the quality of the short-range correlation
 - considerably better in a range separation context

The origin/The way it was thought

In a gaz of electron : organized oscillations
(LR collective behavior) and (SR screened interaction)

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$$\begin{aligned}\hat{H} &= \hat{H}_{\text{particules}} \\ &+ \hat{H}_{\text{champ}} \\ &+ \hat{H}_{\text{interaction particules/champ}}\end{aligned}$$

$$\begin{aligned}\hat{H}^{\text{RPA}} &= \hat{H}_{\text{particules}} \\ &+ \hat{H}_{\text{oscillations}} \\ &+ \hat{H}_{\text{interaction particules/particules}}^{\text{sr}}\end{aligned}$$

contribution from particules in phase with the oscillation
the rest, which have random phases , are zeroed out

$$E_c^{\text{AC-FDT}} = \frac{1}{2} \int_0^1 d\alpha \int_{1,2;1',2'} \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} w(1,2;1',2') \left[\chi_\alpha(1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) \right]$$

