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Two faces of RPA : density functional theory and many-body perturbation theory

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Outline

A. The two faces :

- *RPA from Density Functional Theory (DFT) Adiabatic Connection + FDT*
- *RPA from Many-Body Perturbation Theory*
- *the RPA correlation potential*

B. The RPA band gap

C. Static correlation in the RPA dissociation of H dimer.

- [1] Y.-M. Niquet, M. Fuchs, X. Gonze, J. Chem. Phys. 118, 9504 (2003)
- [2] Y.-M. Niquet, M. Fuchs, X. Gonze, Phys. Rev. A 68, 032507 (2003)
- [3] Y.-M. Niquet, X. Gonze, Phys. Rev. B 70, 245115 (2004)
- [4] M. Fuchs, Y.-M. Niquet, X. Gonze, K. Burke, J. Chem. Phys. 122, 094116 (2005)
- [5] M. Fuchs, X. Gonze, Phys. Rev. B 65, 235109 (2002)
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Density Functional Theory

Hohenberg & Kohn + Kohn & Sham (*Phys. Rev.* 136, B864 (1964); *Phys. Rev.* 140, A1133 (1965))

Mapping the interacting system on a non-interacting system

$$F[\rho] = \min_{\Psi \rightarrow \rho} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \right\}$$

If one considers a non-interacting electronic system :

$$T_0[\rho] = \min_{\Psi \rightarrow \rho} \left\{ \langle \Psi | \hat{T} | \Psi \rangle \right\} \quad \text{Kinetic energy functional of the density}$$

Exchange-correlation functional of the density :

$$E_{xc}[\rho] = F[\rho] - T_0[\rho] - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad \text{Not known explicitly !}$$

Approximated : LDA ...

$$E_{DFT}[V_{ext}] = \min_{\rho} \left\{ T_0[\rho] + \int \rho(\mathbf{r})V_{ext}(\mathbf{r})d^3\mathbf{r} + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] \right\}$$

The Kohn-Sham potential, orbitals and eigenvalues

Variational property of the DFT energy functional

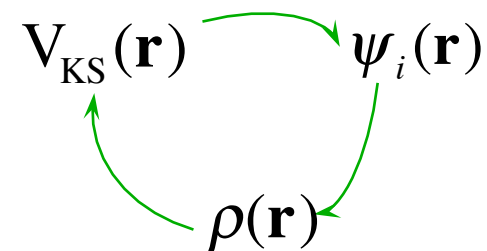
$$\left(-\frac{1}{2} \nabla^2 + V_{\text{KS}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad H_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_{\text{KS}}(\mathbf{r})$$

$$\text{Density } \rho(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}$$

Hartree potential Exchange-correlation potential

To be solved self-consistently !
Converges to the true density ...



The adiabatic connection (1)

- ✓ Consider the set of Hamiltonians $H(\lambda)$ with a scaled Coulomb interaction λV_{ee} giving the **same** ground-state (GS) density

$$H(\lambda) = T + \lambda V_{ee} + V_{eff}(\lambda)$$

- ✓ The coupling constant varying between 0 and 1 connects :
 - $H(\lambda = 1)$ the physical many-body Hamiltonian,
with $V_{eff}(\lambda = 1) = V_{ext}$
- to :
- $H(\lambda = 0)$ the non-interacting Kohn-Sham (KS) Hamiltonian,
with $V_{eff}(\lambda = 0) = V_{KS} = V_{ext} + V_H + V_{xc}$



The adiabatic connection (2)

✓ Let $|\Phi_0(\lambda)\rangle$ and $E_0(\lambda) = \langle \Phi_0(\lambda) | H(\lambda) | \Phi_0(\lambda) \rangle$

be the GS wavefunction [with density $\rho(\mathbf{r})$] and the mean of $H(\lambda)$:

- $E_0(\lambda = 1) = T_0[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} + E_{hxc}[\rho]$ is the GS energy of the physical interacting system,
- $E_0(\lambda = 0) = T_0[\rho] + \int V_{KS}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r}$ is the expectation value of the KS determinant.

✓ From the Hellman-Feynman theorem :

$$\frac{dE_0(\lambda)}{d\lambda} = \langle \Phi_0(\lambda) | \frac{dH(\lambda)}{d\lambda} | \Phi_0(\lambda) \rangle = \langle \Phi_0(\lambda) | V_{ee} | \Phi_0(\lambda) \rangle + \int \frac{\partial V_{eff}}{\partial \lambda}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r}$$

we get, since $E_0(\lambda = 1) = E_0(\lambda = 0) + \int_0^1 \frac{dE_0(\lambda)}{d\lambda} d\lambda$:

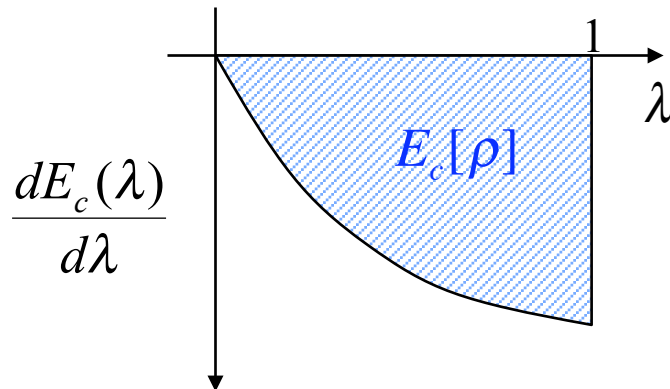
$$E_{hxc}[\rho] = \int_0^1 \langle \Phi_0(\lambda) | V_{ee} | \Phi_0(\lambda) \rangle d\lambda$$



Separating correlation from exchange + Hartree

- ✓ Since $|\Phi_0(\lambda=0)\rangle$ is the KS determinant with density $\rho(\mathbf{r})$,
 $\langle\Phi_0(\lambda=0)|V_{ee}|\Phi_0(\lambda=0)\rangle$ is the sum of Hartree and exchange energies.
The correlation energy can thus be written :

$$E_c[\rho] = \int_0^1 \underbrace{[\langle\Psi_0(\lambda)|V_{ee}|\Psi_0(\lambda)\rangle - \langle\Psi_0(0)|V_{ee}|\Psi_0(0)\rangle]}_{\frac{dE_c(\lambda)}{d\lambda}} d\lambda$$



Integrand is linear at small λ ,
then takes upward curvature.



The exact-exchange approximation

- ✓ **Exact exchange** : Explicit functional of the occupied wavefunctions
Implicit functional of the density.

$$E_x[\rho] \equiv E_x[\{\varphi_i\}_{i=1}^{N/2}] = - \sum_{j=1}^{N/2} \sum_{k=1}^{N/2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- ✓ $V_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})}$ satisfies an integral equation,

the **x-Optimized Effective Potential equation**, from the chain rule :

$$V_x(\mathbf{r}) = \int \frac{\delta E_x[\{\varphi_i\}_{i=1}^{N/2}]}{\delta V_{KS}(\mathbf{r}')} \frac{\delta V_{KS}(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}'$$

Connection with the non-int. susceptibility : $\frac{\delta \rho(\mathbf{r})}{\delta V_{KS}(\mathbf{r}'')} = \chi_0(\mathbf{r}, \mathbf{r}'')$

$$\int \chi_0(\mathbf{r}, \mathbf{r}') V_x(\mathbf{r}') d\mathbf{r}' = \rho_x(\mathbf{r}) \triangleq \frac{\delta E_x[\{\varphi_i\}_{i=1}^{N/2}]}{\delta V_{KS}(\mathbf{r})}$$



The fluctuation-dissipation (FD) theorem

- ✓ Introduce the imaginary frequency density-density response function (or susceptibility) at coupling strength λ :

$$\chi_\lambda(\mathbf{r}, \mathbf{r}'; iu) = 2\Re \sum_s \frac{\langle \Phi_0(\lambda) | \hat{\rho}(\mathbf{r}) | \Phi_s(\lambda) \rangle \langle \Phi_s(\lambda) | \hat{\rho}(\mathbf{r}') | \Phi_0(\lambda) \rangle}{E_0(\lambda) - E_s(\lambda) + iu}$$

- ✓ + Integration along the imaginary axis yields (FD theorem) :

$$\langle \Phi_0(\lambda) | V_{ee} | \Phi_0(\lambda) \rangle = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left[\langle \Phi_0(\lambda) | \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') | \Phi_0(\lambda) \rangle - \rho(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right]$$

$$\Rightarrow = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left[-\frac{1}{\pi} \int_0^{+\infty} \chi_\lambda(\mathbf{r}, \mathbf{r}'; iu) du + \rho(\mathbf{r}) \rho(\mathbf{r}') - \rho(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right]$$

- ✓ Giving the **exact** expression :

$$\begin{aligned} E_c[\rho] &= -\int_0^1 d\lambda \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_0^{+\infty} \frac{du}{2\pi} [\chi_\lambda(\mathbf{r}, \mathbf{r}'; iu) - \chi_0(\mathbf{r}, \mathbf{r}'; iu)] \\ &= -\int_0^1 d\lambda \int_0^{+\infty} \frac{du}{2\pi} \text{Tr} \left\{ v_C [\chi_\lambda(iu) - \chi_0(iu)] \right\} \end{aligned}$$



Computing the susceptibilities

- ✓ The expression of $\chi_0(\mathbf{r}, \mathbf{r}'; iu)$ as a function of the KS spin orbitals and KS energies is :

$$\chi_0(\mathbf{r}, \mathbf{r}'; iu) = 2\Re e \sum_{\sigma} \sum_n^{\text{occ.}} \sum_m^{\text{empty}} \frac{\varphi_{n\sigma}^*(\mathbf{r})\varphi_{m\sigma}(\mathbf{r})\varphi_{m\sigma}^*(\mathbf{r}')\varphi_{n\sigma}(\mathbf{r}')}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} + iu}$$

- ✓ The interacting density-density response function $\chi_{\lambda}(\mathbf{r}, \mathbf{r}'; iu)$ is related to the non-interacting susceptibility by the Dyson equation :

$$\chi_{\lambda}^{-1}(\mathbf{r}, \mathbf{r}'; iu) = \chi_0^{-1}(\mathbf{r}, \mathbf{r}'; iu) - K_{hxc, \lambda}(\mathbf{r}, \mathbf{r}'; iu)$$

where :

$$K_{hxc, \lambda}(\mathbf{r}, \mathbf{r}'; iu) = \frac{\lambda}{|\mathbf{r} - \mathbf{r}'|} + f_{xc, \lambda}[\rho](\mathbf{r}, \mathbf{r}'; iu)$$

and $f_{xc, \lambda}[\rho](\mathbf{r}, \mathbf{r}'; iu)$ is the

frequency-dependent exchange-correlation kernel.



Approximate ACFD functionals ...

$$\text{RPA} : f_{xc,\lambda}[\rho](\mathbf{r},\mathbf{r}';iu) = 0$$

$$K_{hxc,\lambda}(\mathbf{r},\mathbf{r}';iu) = \lambda v_c(\mathbf{r},\mathbf{r}') = \frac{\lambda}{|\mathbf{r} - \mathbf{r}'|}$$

Short-range (SR) correlations are expected too strong in RPA...

Either use more elaborate kernels... :

$$\text{ALDA} : K_{hxc,\lambda}(\mathbf{r},\mathbf{r}';iu) = \lambda v(\mathbf{r},\mathbf{r}') + f_{xc,\lambda}^{\text{ALDA}}[\rho](\mathbf{r},\mathbf{r}')$$

PGG (approx. exchange kernel) :

$$K_{hxc,\lambda}(\mathbf{r},\mathbf{r}';iu) = \frac{\lambda}{|\mathbf{r} - \mathbf{r}'|} \left[1 - \frac{1}{\rho(\mathbf{r})\rho(\mathbf{r}')} \sum_{\sigma} |\gamma(\mathbf{r},\sigma;\mathbf{r}',\sigma)|^2 \right]$$

PGG exactly cancels RPA's self-interaction in $1e^-$ systems.

...or correct SR correlations with a local density approximation :

$$\text{RPA+} : E_c^{\text{RPA+}}[\rho] = E_c^{\text{RPA}}[\rho] + \left(E_c^{\text{LDA}}[\rho] - E_c^{\text{LDA-RPA}}[\rho] \right)$$



The Random Phase Approximation (RPA)

- ✓ The RPA correlation energy reads:

$$E_c^{RPA}[\rho] = -\int_0^1 d\lambda \int_0^{+\infty} \frac{du}{2\pi} \text{Tr} \left\{ v_C \left[\left(\chi_0^{-1}(iu) - \lambda v_C \right)^{-1} - \chi_0(iu) \right] \right\}$$

where:

- ✓ $v_C(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$ is the Coulomb kernel.
- ✓ The symbol Tr stands for the trace: $\text{Tr}[AB] = \int d^3\mathbf{r} \int d^3\mathbf{r}' A(\mathbf{r}, \mathbf{r}') B(\mathbf{r}', \mathbf{r})$
- ✓ The integration over coupling constant can be performed analytically:

$$E_c^{RPA}[\rho] = \int_0^{+\infty} \frac{du}{2\pi} \text{Tr} \left\{ \ln [1 - \chi_0(iu)v_C] + \chi_0(iu)v_C \right\}$$



Many Body Perturbation Theory (MBPT)

- ✓ Basic ingredient = **The one particle Green's function** :

$$G(\mathbf{x}, t; \mathbf{x}', t') = -i \langle \Phi_0 | T[\Psi(\mathbf{x}, t) \Psi^\dagger(\mathbf{x}', t')] | \Phi_0 \rangle \quad \mathbf{x} = (\mathbf{r}, \sigma)$$

- ✓ On top of DFT :

The interacting Green's function $G(\mathbf{x}, t; \mathbf{x}', t')$

is related to the non-interacting KS Green's function $G_{KS}(\mathbf{x}, t; \mathbf{x}', t')$

$$\left[i \frac{\partial}{\partial t} + \frac{1}{2} \Delta_{\mathbf{r}} - V_{KS}(\mathbf{x}) \right] G_{KS}(\mathbf{x}, t; \mathbf{x}', t') = \delta(\mathbf{x} - \mathbf{x}') \delta(t - t')$$

by the following Dyson equation :

$$G^{-1}(\mathbf{x}, t; \mathbf{x}', t') = G_{KS}^{-1}(\mathbf{x}, t; \mathbf{x}', t') - [\Sigma_{xc}(\mathbf{x}, t; \mathbf{x}', t') - V_{xc}(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}') \delta(t - t')]$$

where $\Sigma_{xc}(\mathbf{x}, t; \mathbf{x}', t')$ is the exchange-correlation **self-energy**.



The GW approximation

- ✓ The GW self-energy is the first term of an expansion of $\Sigma_{xc}(\mathbf{x},t;\mathbf{x}',t')$ in terms of a screened Coulomb interaction $W(\mathbf{x},t;\mathbf{x}',t')$:

$$\begin{cases} \Sigma_{xc}(\mathbf{x},t;\mathbf{x}',t') = iG(\mathbf{x},t;\mathbf{x}',t')W(\mathbf{x},t^+;\mathbf{x}',t') \\ W = v_C + v_C P W = [I - v_C P]^{-1} v_C \\ P(\mathbf{x},t;\mathbf{x}',t') = -iG(\mathbf{x},t;\mathbf{x}',t')G(\mathbf{x}',t';\mathbf{x},t) \end{cases}$$

- ✓ In principle, this set of equations should be solved self-consistently [since $\Sigma_{xc}(\mathbf{x},t;\mathbf{x}',t')$ and $G(\mathbf{x},t;\mathbf{x}',t')$ are related by the Dyson equation], but in most cases the KS Green's function $G_{KS}(\mathbf{x},t;\mathbf{x}',t')$ is used in P , W and Σ_{xc} when calculating quasi-particle energies. Then $P(\mathbf{x},\mathbf{x}';iu) = \chi_0(\mathbf{x},\mathbf{x}';iu)$ and $W(\mathbf{x},\mathbf{x}';iu)$ is the standard RPA screened Coulomb interaction.



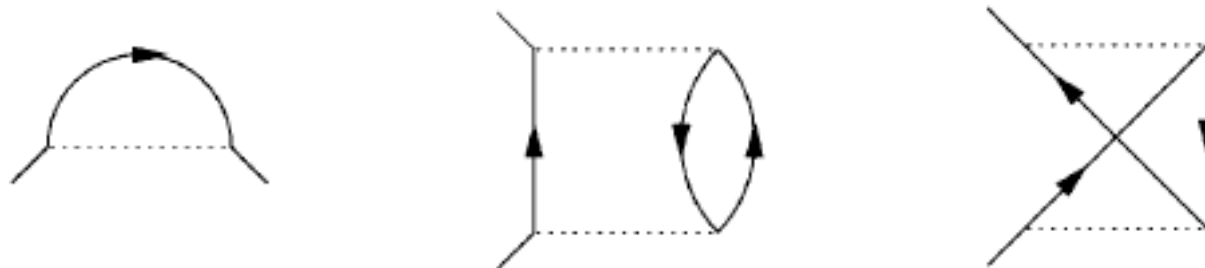
The total energy in MBPT

- ✓ Migdal-Galitskii (non-variational).
- ✓ Several variational formulation of the total energy (Luttinger-Ward, Klein, Nozières ...) among which :

$$E[G, G_0] = \int \frac{d\omega}{2\pi i} e^{i\eta\omega} \text{Tr} \left\{ \omega G_0(\omega) - G_0^{-1}(\omega) G(\omega) - \ln G_0(\omega) G^{-1}(\omega) \right\} \\ + \sum_{n=1}^{\infty} \frac{1}{2n} \int \frac{d\omega}{2\pi i} e^{i\eta\omega} \text{Tr} \left\{ \Sigma_{xc}^{(n)} [G] G \right\}$$

(P. Nozières, *Theory of Interacting Fermi Systems Benjamin, NY 1964*)

where $\Sigma_{xc}^{(n)} [G_{KS}]$ is the sum of all skeleton diagrams of order n





One link with the DFT-RPA

- ✓ By using $G = G_0 = G_{KS}$ one recovers the same total energy expression than with the RPA Adiabatic Connection – Fluctuation Dissipation

$$E_{xc}[G_{KS}, G_{KS}] = \sum_{n=1}^{\infty} \frac{1}{2n} \int \frac{d\omega}{2\pi i} e^{i\eta\omega} \text{Tr} \left\{ \Sigma_{xc}^{(n)}[G_{KS}] G_{KS} \right\} = E_x[\rho] + E_c^{RPA}[\rho]$$

(see M. Fuchs, K. Burke, Y.-M. Niquet, X.G. PRL, 90, 189701(2003))

- ✓ From Casida (PRA 51, 2005 (1995)), one can deduce that the RPA exchange-correlation potential

$$V_{xc}^{RPA}(\mathbf{r}) = \frac{\delta E_{xc}^{RPA}[\rho]}{\delta \rho(\mathbf{r})}$$

satisfies a linear-response Sham-Schlüter equation

$$\int \chi_0(\mathbf{r}, \mathbf{r}') V_{xc}^{RPA}(\mathbf{r}') d\mathbf{r}' = \rho_{xc}^{RPA}(\mathbf{r}) \triangleq \int \frac{du}{2\pi} G_{KS}(\mathbf{r}, \mathbf{r}'; iu) \Sigma_{xc, GW}(\mathbf{r}', \mathbf{r}''; iu) G_{KS}(\mathbf{r}'', \mathbf{r}; iu)$$

in which the GW self-energy operator appears.

(see M. Fuchs, K. Burke, Y.-M. Niquet, X.G. PRA, 68, 032507(2003))



The DFT bandgap problem (I)

- DFT is a ground state theory

=> no direct interpretation of Kohn-Sham eigenenergies ϵ_i in

$$\left(-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + V_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

- However $\{\epsilon_i\}$ are similar to quasi-particle band structure :
LDA / GGA results for valence bands are accurate ... but

NOT for the band gap $E_g^{KS} = \epsilon_c - \epsilon_v$

- The band gap can alternatively be obtained from total energy differences (affinity/ionisation potential)

$$E_g = E(N+1) + E(N-1) - 2 E(N) = \{E(N+1) - E(N)\} - \{E(N) - E(N-1)\}$$

in the limit $N \rightarrow \infty$

(where $E(N)$ is the total energy of the N - electron system)

The DFT bandgap problem (II)

- For LDA & GGA, the XC potential is a continuous functional of the number of electrons

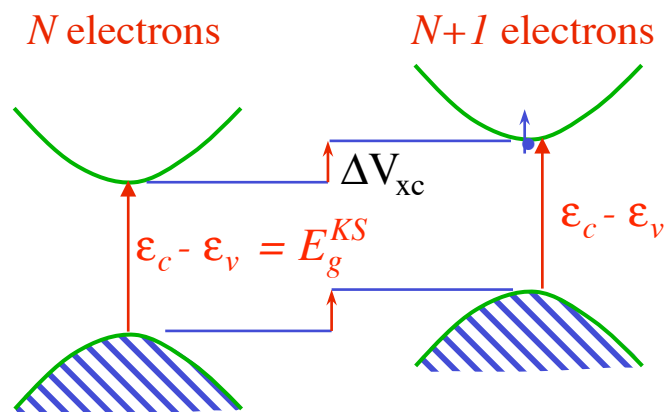
$$\epsilon_i = \frac{\partial E}{\partial f_i} \quad [\text{Janak's theorem}]$$

$$\Rightarrow E_g^{KS} = \epsilon_c - \epsilon_v \underset{N \rightarrow \infty}{=} E_g = E(N+1) + E(N-1) - 2E(N)$$

- In general, the XC potential might be discontinuous with the number of particle

e.g. *xOEP*

$$E_g^{KS} \neq E_g$$



How to compute ΔV_{xc} ?

Standard approach to band gap : GW approximation ...

- pseudopotentials
LDA, GGA
 $r - G_0W_0$ } $\rightarrow G_0, W_0 \rightarrow E_{n,k} = \epsilon_{n,k} + Z_{nk} \text{Re} \langle \Psi_{n,k} | \Sigma - V | \Psi_{n,k} \rangle$
gives excellent results (~ 0.2 eV of experiment)

Silicon	Exp.gap = 1.17 eV	$r - G_0W_0$ gap = 1.149 eV
Carbon diamond	Exp.gap = 5.48 eV	$r - G_0W_0$ gap = 5.603 eV

- But attempts to include full self-consistency [GW] shows it spoils the agreement !

Why should the self-consistency be avoided ?

Also : effect of pseudopotentials vs. all-electron ?
questions about the renormalisation factor ?

$$Z = \left[1 - \left\langle \Psi \left| \frac{\partial \Sigma}{\partial \epsilon} \right| \Psi \right\rangle \right]^{-1}$$

The band gap energy in DFT - RPA

- We compute analytically

$$E_g = \underbrace{\{E(N+1) - E(N)\}}_{\text{- electronic affinity } A} - \underbrace{\{E(N) - E(N-1)\}}_{\text{- ionisation energy } I}$$

in the limit $N, \Omega \Rightarrow \infty$ N/Ω constant

the volume

$$\Rightarrow -A = \epsilon_c + \left\langle \varphi_c \left| \sum_{xc} (\epsilon_c) - v_{xc}^{RPA} \right| \varphi_c \right\rangle + O(\Omega^{-1/4})$$

$$-I = \epsilon_v + \left\langle \varphi_v \left| \sum_{xc} (\epsilon_v) - v_{xc}^{RPA} \right| \varphi_v \right\rangle + O(\Omega^{-1/4})$$

where $\sum_{xc}(\vec{r}, \vec{r}'; \epsilon) = - \int \frac{du}{2\pi} e^{iu\delta} G_0(\vec{r}, \vec{r}'; \epsilon + iu) W_0(\vec{r}, \vec{r}'; iu)$

is the G_0W_0 self energy

$$E_g^{RPA} = E_g^{KS-RPA} + \left\langle \varphi_c \left| \sum_{xc} (\epsilon_c) - v_{xc}^{RPA} \right| \varphi_c \right\rangle - \left\langle \varphi_v \left| \sum_{xc} (\epsilon_v) - v_{xc}^{RPA} \right| \varphi_v \right\rangle$$

G_0W_0 without renormalization factor

Y.M. Niquet & X.G., *Phys. Rev. B* 70, 245115 (2004)



Sketch of the demonstration ... (I)

- The affinity $A = E(N) - E(N+1)$ in the limit $N, \Omega \Rightarrow \infty$ N/Ω constant

$$E^{RPA}[\rho] = E_0[\rho] + E_x[\rho] + E_c[\rho] \quad A^{RPA} = A_0 + A_x + A_c$$

What is the change in these terms due to the addition of one electron ?

$$-A_0 = \left\langle \varphi_c \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}} + v_h \right| \varphi_c \right\rangle + U_{\text{cc}}$$

$$-A_x = \left\langle \varphi_c \left| \Sigma_x \right| \varphi_c \right\rangle - U_{\text{cc}} \quad \Sigma_x(\mathbf{r}, \mathbf{r}') = - \sum_{j=1}^{N/2} \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

For the correlation contribution :

$$E_c[\rho] = \frac{1}{2} \int \frac{du}{2\pi} \text{Tr} \left\{ \ln[1 - v\chi_0(iu)] + v\chi_0(iu) \right\}$$

$$-A_c = \frac{1}{2} \int \frac{du}{2\pi} \text{Tr} \left\{ \ln[1 - v\chi_0(iu) - v\delta\chi_0(iu)] - \ln[1 - v\chi_0(iu)] + v\delta\chi_0(iu) \right\}$$

$$= \frac{1}{2} \int \frac{du}{2\pi} \text{Tr} \left\{ \ln[1 - W(iu)\delta\chi_0(iu)] + v\delta\chi_0(iu) \right\}$$

where $W(iu) = [1 - v\chi_0(iu)]^{-1} v$ is the RPA screened Coulomb interaction



Sketch of the demonstration ... (II)

$$-A_c = \frac{1}{2} \int \frac{du}{2\pi} \text{Tr} \left\{ \ln [1 - W(iu) \delta\chi_0(iu)] + v \delta\chi_0(iu) \right\}$$

The first-order term in $\delta\chi_0(iu)$ can be isolated from higher-order ones, that vanish in the macroscopic limit.

$$-A_c^{\text{qp}} = -\frac{1}{2} \int \frac{du}{2\pi} \text{Tr} \left\{ [W(iu) - v] \delta\chi_0(iu) \right\}$$

$\delta\chi_0(iu)$ is the change in $\chi_0(iu)$ when adding one electron of either spin to the lowest unoccupied KS orbital

$$\delta\chi_0(\mathbf{r}, \mathbf{r}'; iu) = \varphi_c^*(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}'; \varepsilon_c + iu) \varphi_c(\mathbf{r}') + \text{c.c.}$$

where the KS Green's function is defined as

$$G_0(\mathbf{r}, \mathbf{r}'; z) = \sum_j \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}')}{z - \varepsilon_j}$$



G_0W_0 versus $r\text{-}G_0W_0$ / GW

- G_0W_0 without renormalization is theoretically justified by DFT - RPA

	<i>Exp</i>	$r\text{-}G_0W_0$	$G_0W_0(\text{RPA})$	<i>KS-LDA</i>
<i>Si</i>	1.17 eV	1.149 eV	1.351 eV	0.481 eV
<i>C(diam)</i>	5.48 eV	5.603 eV	5.884 eV	4.150 eV

But $r\text{-}G_0W_0$ works better !

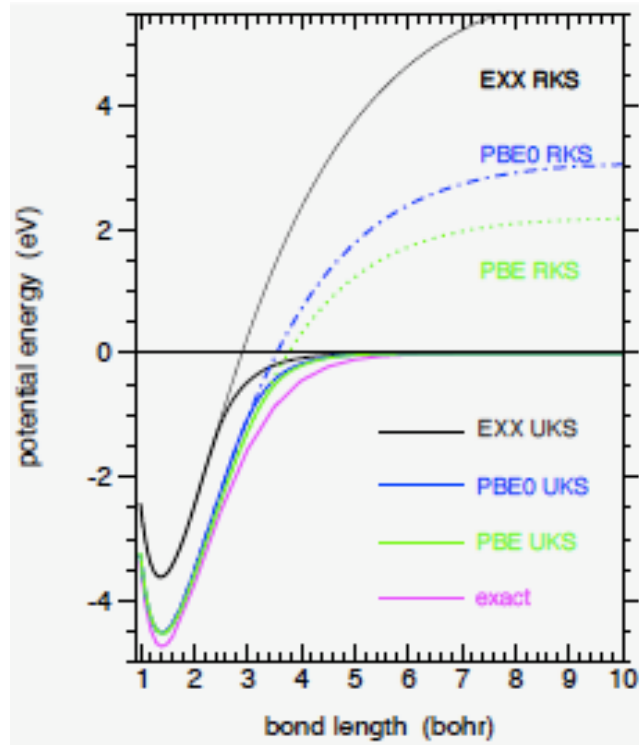
? Effect of pseudopotential approximation vs all-electron ?

- For further information & discussion, see
Y.M. Niquet & X. Gonze, *Phys. Rev. B* 70, 245115 (2004)



Molecular dissociation without the symmetry dilemma ?

H₂ Potential Energy Curve



- ✓ KS GS is a single determinant with MO's:

$$\sigma_g(r) \rightarrow \frac{1}{\sqrt{2}} \{s_a(r) + s_b(r)\} = \sqrt{\frac{n(r)}{2}}$$

- ✓ Heitler-London picture for dissociation

$$\psi_\infty \rightarrow \{H^\bullet + H^\bullet\} = \sqrt{\frac{1}{2}} \{s_a(1)s_b(2) + s_b(1)s_a(2)\}$$

- ✗ Dissociation incorrect, in spin-restricted HF, LDA, GGA :

$$\psi_\infty^{KS} \rightarrow H^\bullet + \frac{1}{2}(H^- + H^+)$$

- ... not enough left-right (static) correlation
- ... local correlation hole cannot 'localize' delocalized exchange hole

- ✗ Use spin unrestricted UHF, LSDA, GGA: inversion symmetry broken,

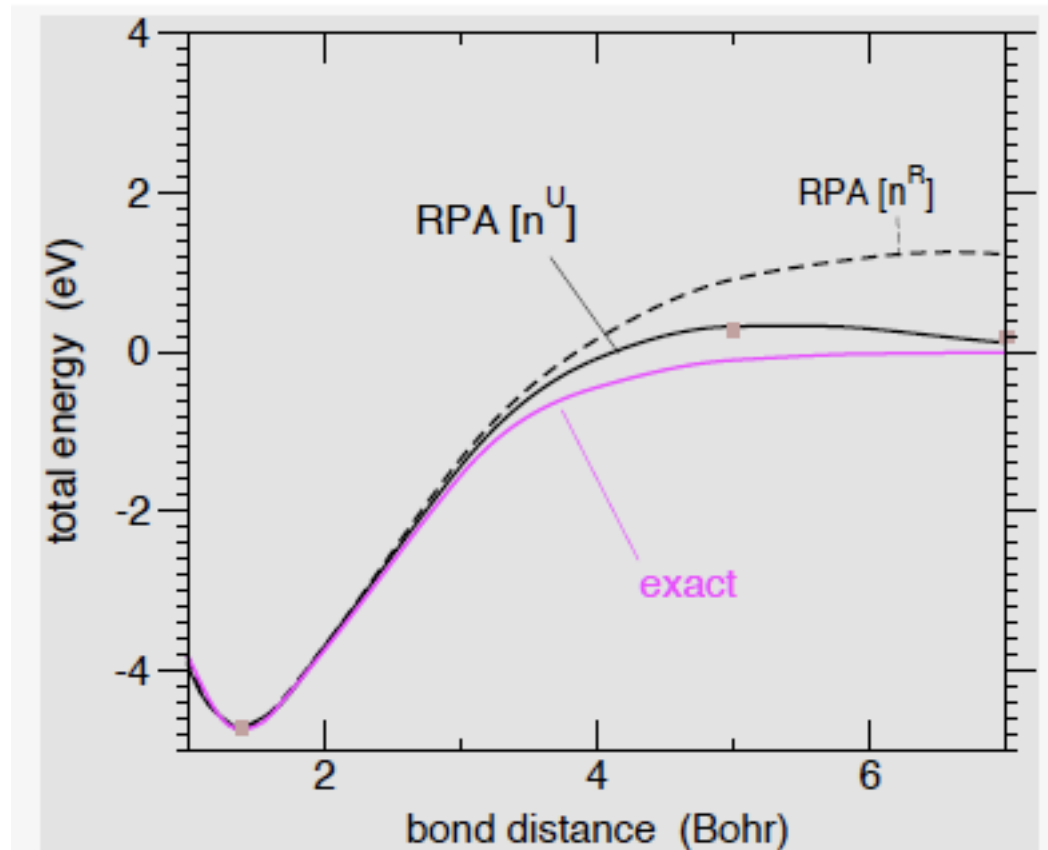
$$n_\uparrow(r) \neq n_\downarrow(r), \langle S^2 \rangle > 0$$

Task : Examine ACDFT XC functionals (RPA etc.)
... yielding proper dissociation ?



RPA : dissociation without the symmetry dilemma ...

RPA vs. exact potential energy curve



Perform RPA on $n^U(\mathbf{r}) = n_{\uparrow}^U(\mathbf{r}) + n_{\downarrow}^U(\mathbf{r})!$

Exact CI data from W Kolos, L Wolniewicz, *J Chem Phys* 43, 2429 (1965).

RPA: MF, YM Niquet, X Gonze, *Phys Rev Lett* 90, 189701 (2003).

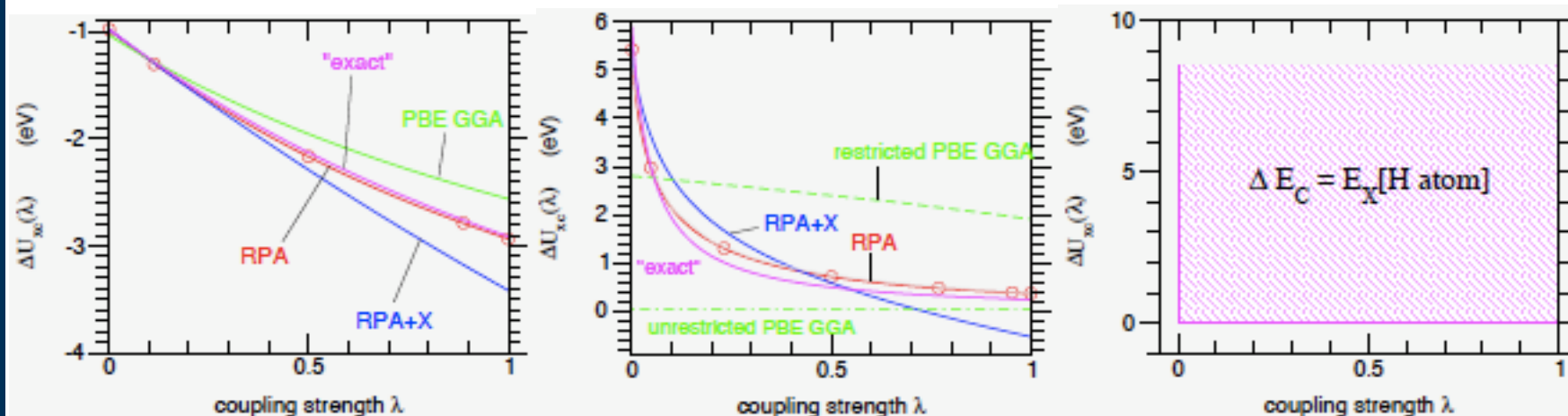
RPA: Stretching H_2

Adiabatic connection $\Delta U_{XC}(\lambda) = U_{XC}(\lambda)[H_2] - 2U_{XC}(\lambda)[H \text{ atom}]$ for ...

R=1.4 Bohr

R=5.0 Bohr

R= \Rightarrow infinity



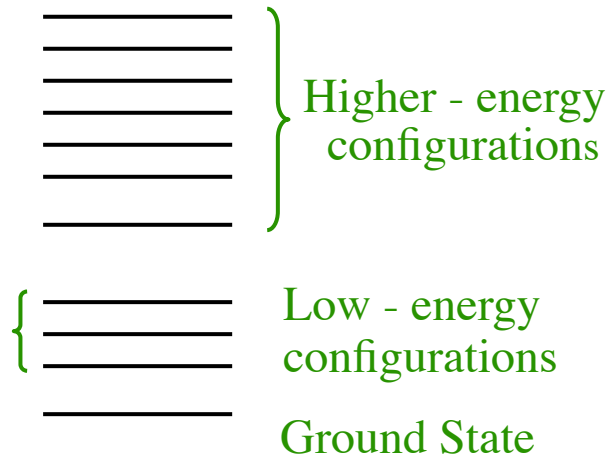
ACFDT functionals (RPA, RPA+X) capture strong static correlation
 ... with somewhat too little static correlation ?
 Accurate without error cancellation between exchange and correlation
 ... in contrast to standard functionals !

Exact curves based on data from: *R. van Leeuwen, PhD thesis, VU Amsterdam (1996).*



Static vs. dynamic correlation (Quantum Chemistry)

Hartree – Fock spectrum



When turning on configuration interaction, the lowering of energy can come from:

- few low-energy determinants
- numerous higher-energy determinants

The latter gives the correct behaviour close to zero electronic interdistance [cusp], and can be treated perturbatively

The low-energy determinants would better be treated in a multi-configuration framework at the very beginning.

In the RPA framework χ_0 feels the presence of low-energy configurations: transitions from occupied to unoccupied *KS* states. Then, it is "compared" with a typical Coulomb+XC energy in the Dyson equation.

$$\chi_0(r,r';iu) = 2 \Re e \sum_{\sigma} \sum_n^{occ} \sum_m^{unocc} \frac{\varphi_{n\sigma}^*(r) \varphi_{m\sigma}(r) \varphi_{m\sigma}^*(r') \varphi_{n\sigma}(r')}{\epsilon_{n\sigma} - \epsilon_{m\sigma} + iu}$$

Summary - Conclusions

ACFD xc functionals : a large class of functionals, among which the RPA is the simplest ...

RPA expression from ACFD – DFT and MPBT (Nozières)

Band-gap energy in ACFD - RPA

G_0W_0 without renormalization factor

Dissociation of H_2

RPA

- correctly dissociate H_2 in 2H atoms
- overcome symmetry dilemma of LDA, GGA & Co
- capture strong static correlation
- exhibit false repulsion at intermediate separations