Density Functional Theory for gaps

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Gaps

- HOMO-LUMO gap:

$$\boxed{\Omega_{\mathrm{HL}} = \epsilon_{\mathrm{L}} - \epsilon_{\mathrm{H}}}$$

- Kohn-Sham gap:

$$\boxed{\Omega_{\mathrm{KS}} = \epsilon_{\mathrm{L}}^{\mathrm{KS}} - \epsilon_{\mathrm{H}}^{\mathrm{KS}}}$$

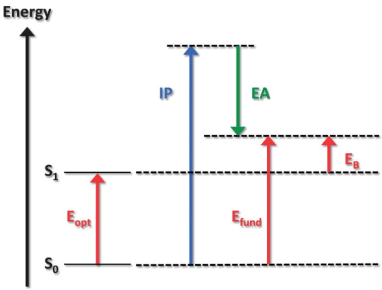
- Optical gap:

$$\boxed{\Omega_{\mathrm{opt}}^{N} = E_1^N - E_0^N};$$

- Fundamental gap:

$$\boxed{\Omega_{\mathrm{fund}}^{N} = I^N - A^N}$$

Bredas, Mater. Horiz. 1 (2014) 17



Piecewise linearity

Exact energy

The exact energy $E(N)$ is piecewise linear.

Hartree-Fock

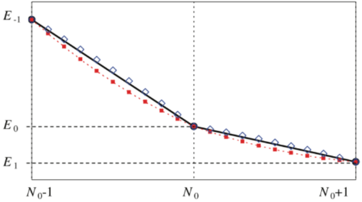
The Hartree-Fock energy is concave.

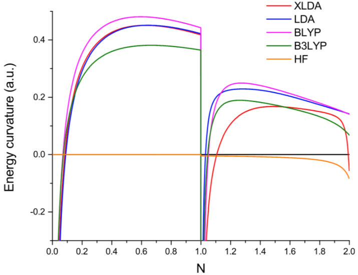
DFT

Semilocal functionals usualy lead to a piecewise convexe energy.

Kraisler E. & Kronik L., JCP 1 (2014) 140 18

Li C. & Yang W., JCP 146 (2017) 02

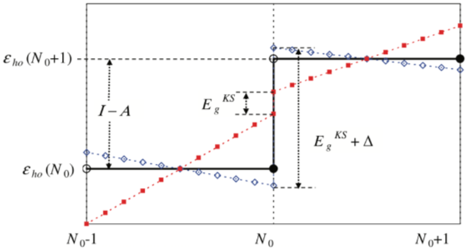




Derivative discontinuity

Important

There is a discontinuity of $E(N)$ curvature when N crosses an integer point.



Derivative discontinuity

The KS gap is not enough, something is missing!

$$\boxed{\Omega = \epsilon_{\mathrm{L}}^{\mathrm{KS}} - \epsilon_{\mathrm{H}}^{\mathrm{KS}} + \Delta}$$

eDFT

In ensemble DFT, the determination of the derivative discontinuity Δ can considerably improve gap estimates.

What is eDFT?

Take an ensemble of M pure state densities n_i, each associated with a weight w_i.
Then you get an ensemble density and an ensemble energy:

$$\boxed{n^{\{w_i\}} = \sum_{i=0}^{M-1} w_i n_i} \qquad \boxed{E^{\{w_i\}} = \sum_{i=0}^{M-1} w_i E_i} \quad .$$

The weights w_i must be chosen wisely according to some constraints/criteria:

$$\boxed{E_0 \leq E_1 \leq \dots \implies w_0 \geq w_1 \geq \dots \quad \text{and} \quad \sum_{i=0}^{M-1} w_i = 1} \quad .$$

Gross-Oliveira-Kohn principle

Similarly to the Rayleigh-Ritz principle in DFT, the GOK principle makes eDFT a variational method.

Deur K. & Fromager E., JCP 150 (2019)

Optical gap from eDFT?

Case 1: How to get the optical gap in eDFT?

First, construct the ensemble density

$$\boxed{n^{w,N}(\mathbf{r}) = (1-w)n_0^N(\mathbf{r}) + w n_1^N(\mathbf{r})}$$

Note that

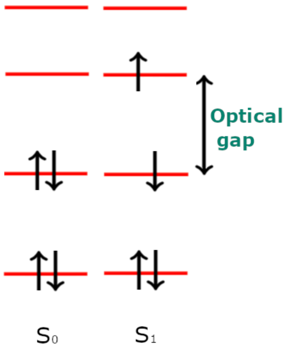
$$\int n^{w,N}(\mathbf{r})\mathrm{d}\mathbf{r} = N$$

then the ensemble energy is given by

$$\boxed{E^{w,N} = (1-w)E_0^N + wE_1^N}$$

We see that

$$\boxed{\frac{\partial E^{w,N}}{\partial w} = E_1^N - E_0^N = \Omega_{\mathrm{opt}}^N}$$



Senjean B. & Fromager E., Phys. Rev. A 2 98 (2018)

Fundamental gap from eDFT?

Case 2: How to get the fundamental gap in eDFT?

N-centered ensemble density

$$\boxed{n^{\xi}(\mathbf{r}) = \xi n_0^{N-1}(\mathbf{r}) + (1-2\xi) n_0^{N}(\mathbf{r}) + \xi n_0^{N+1}(\mathbf{r})}$$

Note that

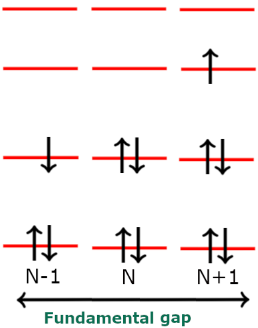
$$\int n^{\xi}(\mathbf{r})\mathrm{d}\mathbf{r} = N$$

leading to the ensemble energy

$$\boxed{E^{\xi} = \xi E_0^{N-1} + (1-2\xi) E_0^{N} + \xi E_0^{N+1}}$$

So that

$$\boxed{\frac{\partial E^{\xi}}{\partial \xi} = E_0^{N-1} - 2E_0^{N} + E_0^{N+1} = I^N - A^N = \Omega^N_{\text{fund}}}$$



Summary/Main issue/Highlights

What about the derivative discontinuity in eDFT?

$$\boxed{\frac{\partial E^{w,N}}{\partial w} = \Omega^N_{\text{opt}} = \underbrace{\epsilon^w_{\text{L}} - \epsilon^w_{\text{H}}}_{\Omega^w_{\text{KS}}} + \frac{\partial E^w_{\text{xc}}[n]}{\partial w}}$$

eDFT or DFT?

In eDFT, the weigh dependency of the ensemble energy can improve/compensate the failure of the KS gap.

Main issue

The weight dependency of the exchange-correlation functional is crucial when it comes to predicting gaps.

$\Longrightarrow$ How to construct the weight-dependent xc functional?