

# Exchange and correlation functionals from the integration of density and wave-function theories

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## Micro-summary

- **Kohn-Sham (KS)** potential derived using a **wave-function** approach
- Use **perturbative expansion** for the interacting wavefunction
- Minimize an **energy difference** to obtain expansions of the KS potential
- **Exact-exchange (EXX)** potential obtained
- New KS potential with **exchange** and **correlation** character derived

## The energy difference

Central to our work is the following **energy difference**:

$$T_{\Psi}[v] = \langle \Psi | H_v | \Psi \rangle - E_v$$

local potential (mimics  $V_{ee}$ )    interacting state     $\langle \Phi_v | H_v | \Phi_v \rangle$

This energy difference has some key properties:

- 1 The potential  $v_s$  which **minimizes**  $T_{\Psi}[v]$  is the **KS potential**
- 2 The energy difference is **strictly positive**, even when the fully-interacting state  $\Psi$  is approximated
- 3 The above properties allow us to derive approximations for the KS potential, for example using **perturbation theory**

## New xc-functional

- The **energetically best** choice for  $u$  minimizes  $|E_u^c[u + v']| = T_u[w]$  ( $w = u + v'$ )
- We can **decouple** and hence **simplify** this minimization by splitting  $T_u[w]$  into single and double excitations:

$$T_u[w] = S_u[w] + D[u]$$

$$0 < S_u[w_0[u]] \ll D[u].$$

- The **double** excitation  $D[u]$  **dominates** and depends on  $u$  only
- The minimization procedure therefore proceeds as follows:

$$\frac{\delta}{\delta u} D[u] \Big|_{u=u_0} = 0$$

$$\downarrow u_0$$

$$\frac{\delta}{\delta w} S_{u_0}[w] \Big|_{w=w_0} = 0$$

$$\downarrow w_0$$

$$v_s = w_0[u_0]$$

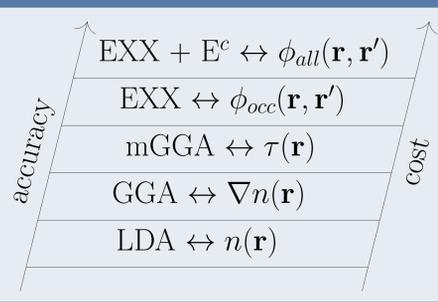
- $v_s$  has both **exchange** and **correlation** character

## Introduction

In DFT we strive to develop **accurate** and **reliable** approximations for the **exchange-correlation (xc)** functional.

To improve functional accuracy, we can ascend the so-called ‘Jacob’s Ladder’ of DFT functionals [1]:

## Jacob’s Ladder



**Perturbative** methods have been developed to model correlation energy in the top rung [2,3]; however, these methods are prone to **variational collapse** due to the minimization of unbound expressions.

In our work, we first prove a theorem which shows that the KS potential emerges from the minimization of an **energy difference**.

Crucially, the energy difference we minimize is **strictly positive**; this means we are **guaranteed against** variational collapse.

## Perturbative expansions

We **approximate** the interacting state  $\Psi$  using the following **perturbative** expansion,

$$H_u(\alpha)\Psi_u(\alpha) = E_u(\alpha)\Psi_u(\alpha),$$

$$H_u(\alpha) = H_u + \alpha \left[ V_{ee} - \sum_i u(\mathbf{r}_i) \right].$$

$u$  is a **local** potential which mimics  $V_{ee}$  but is **different** to  $v$ .

Setting  $v = u + \alpha v'$ , the leading term in the energy difference is **2nd order**:

$$T_{\Psi_u(\alpha)}[u + \alpha v'] = \alpha^2 T_u[u + v'].$$

Optimizing  $T_u[u + v']$  over  $v'$  only yields the following **1st order** expansion for  $v_s$ :

$$v_s[u] = v_{en} + u + \alpha v'[u].$$

We note the following:

- $v_s[u]$  is a functional of  $u$ ; for **each choice** of  $u$  there is a **corresponding**  $v_s[u]$
- We seek potentials  $u$  which lead to the **fastest-converging** expansions for  $v_s[u]$
- $u + v'[u]$  contains Hartree, exchange and correlation

## Optimal choices for $u$

Intuitively, we expect that minimizing **correlation energy** will ensure fast convergence of  $v_s[u]$ . In fact there is a **formal link** to correlation energy in the expressions we have derived.

**Lemma.** *The KS potential  $v_s[u]$  is that effective potential with weakest correlation energy from its ground-state.*

**Proof.** Up to 2nd order in  $\alpha$ , the correlation energy between  $\Psi_u(\alpha)$  and  $\Phi_v$  is equal to minus the energy difference:

$$E_{H_u(\alpha)}^c[u + \alpha v'] = -T_{\Psi_u(\alpha)}[u + \alpha v']$$

Since  $v_s[u]$  minimizes  $T_{\Psi_u(\alpha)}[u + \alpha v']$ , it must then also minimize  $|E^c|$ .

This strengthens our intuitive argument that the **best choice** of  $u$  is that which **minimizes**  $|E^c|$ .

- **Exact exchange:** The potential  $u$  which minimizes  $|E_u^c[u]|$  is  $u = v_s[u]$ , ie  $v'[u] = 0$ , which is in fact the exact exchange potential [4].
- **Local Fock exchange:** A different choice for  $\Psi$  is a 1st order **Møller-Plesset** expansion. This yields the LFX potential [5].

## Future work

- Ultimate goal is to implement the functional computationally
- Currently working on issues associated with the OEP method in finite basis set applications
- We expect good results for strongly-correlated (non-metallic) materials

## References

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