Introduction to density-functional theory

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`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_esqc_24.pdf`

Why and how learning density-functional theory?

Density-functional theory (DFT) is:

- a **practical electronic-structure computational method**, widely used in quantum chemistry and condensed-matter physics;
- an **exact and elegant reformulation of the quantum many-body problem**, which has led to new ways of thinking in the field.

Classical books:

- R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, 1989.
- R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem*, Springer-Verlag, 1990.
- W. Koch and M. C. Holthausen, *A Chemist's Guide To Density Functional Theory*, Wiley-VCH, 2001.

My lecture notes:

`http://www.lct.jussieu.fr/pagesperso/toulouse/enseignement/introduction_dft.pdf`

A book chapter:

J. Toulouse, in *Density Functional Theory*, edited by E. Cancès and G. Friesecke, Springer, 2023.

Outline

1. Basic density-functional theory
    - Quantum many-electron problem
    - Universal density functional
    - Kohn-Sham method
    - Generalized Kohn-Sham method

2. Exact constraints for the exchange-correlation functional
    - Exact expressions for the exchange and correlation functionals
    - Uniform coordinate scaling
    - One-orbital spatial regions and self-interaction
    - Lieb-Oxford lower bound
    - Frontier orbital energies

3. Usual approximations for the exchange-correlation energy
    - Local-density approximation
    - Semilocal approximations
    - Single-determinant hybrid approximations
    - Multideterminant hybrid approximations
    - Dispersion corrections

4. Additional topics in density-functional theory
    - Time-dependent density-functional theory
    - Some less usual orbital-dependent exchange-correlation functionals
    - Fractional electron numbers and frontier orbital energies

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   - Quantum many-electron problem
   - Universal density functional
     - The Hohenberg-Kohn theorem
     - Levy-Lieb constrained-search formulation
     - Density-matrix or Lieb density functional
   - Kohn-Sham method
     - Decomposition of the universal functional
     - The Kohn-Sham equations
     - Practical calculations in an atomic basis
     - Extension to spin density-functional theory
   - Generalized Kohn-Sham method

Quantum many-electron problem

- We consider an N-**electron system** in the Born-Oppenheimer and non-relativistic approximations.
- The **electronic Hamiltonian** in the position representation is, in atomic units,

$$H = -\frac{1}{2}\sum_{i=1}^{N} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ i\neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i)$$

  where $v_{\text{ne}}(\mathbf{r}_i) = -\sum_\alpha Z_\alpha/|\mathbf{r}_i - \mathbf{R}_\alpha|$ is the nuclei-electron interaction potential.
- Stationary states satisfy the **time-independent Schrödinger equation**

$$H\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

  where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a wave function written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i \in \{\uparrow, \downarrow\}$) which is antisymmetric with respect to the exchange of two space-spin coordinates, and E is the associated energy.
- We work on the **Hilbert space** $\mathcal{H} = \bigwedge^N L^2(\mathbb{R}^3 \times \{\uparrow, \downarrow\}, \mathbb{C})$.
- Using **Dirac notations** (representation-independent formalism):

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad \text{where} \qquad \hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}$$

  These operators can be conveniently expressed in (real-space) second quantization.

Wave-function variational principle

- The **ground-state electronic energy** E_0 can be expressed with the **wave-function variational principle**

  $$E_0 = \min_{\Psi \in \mathcal{W}} \langle \Psi | \hat{H} | \Psi \rangle$$

  where the minimization is done over the space of admissible normalized N-electron wave functions $\mathcal{W} = \{\Psi \in \bigwedge^N H^1(\mathbb{R}^3 \times \{\uparrow,\downarrow\},\mathbb{C}) \mid \langle \Psi | \Psi \rangle = 1\}$.

  Remark: If $\hat{H}$ *does not bind* N *electrons, then the minimum does not exist but the ground-state energy can still be defined as an infimum, i.e.* $E_0 = \inf_{\Psi \in \mathcal{W}} \langle \Psi | \hat{H} | \Psi \rangle$.

- DFT is based on a reformulation of this variational theorem in terms of the **one-electron density** defined as

  $$n(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{x}, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 \, \mathrm{d}\sigma \mathrm{d}\mathbf{x}_2 ... \mathrm{d}\mathbf{x}_N$$

  which is normalized to the electron number, $\int n(\mathbf{r}) \mathrm{d}\mathbf{r} = N$.

  Remark: Integration over a spin coordinate σ *means a sum over the two values of* σ*, i.e.* $\int d\sigma = \sum_{\sigma \in \{\uparrow,\downarrow\}}$.

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The Hohenberg-Kohn theorem

- Consider an electronic system with an arbitrary external local potential $v(\mathbf{r})$ (that bounds N electrons) in place of $v_{\text{ne}}(\mathbf{r})$.
- The corresponding ground-state wave function Ψ (or one of them if there are several) can be obtained by solving the Schrödinger equation, from which an associated **ground-state density** $n(\mathbf{r})$ can be deduced. Therefore, one has the (possibly multi-valued) mapping:

$$v(\mathbf{r}) \longrightarrow n(\mathbf{r})$$

- In 1964, Hohenberg and Kohn showed that this mapping can be inverted, i.e. a **ground-state density** $n(\mathbf{r})$ determines the potential $v(\mathbf{r})$ up to an arbitrary additive real-valued constant:

$$n(\mathbf{r}) \xrightarrow[\text{Hohenberg-Kohn}]{} v(\mathbf{r}) + \text{const}$$

Proof of the Hohenberg-Kohn theorem (1/2)

This is a two-step proof by contradiction.

Consider two local potentials differing by more than an additive real-valued constant:

$$\boxed{v_1(\mathbf{r}) \neq v_2(\mathbf{r}) + \text{const}}$$

We have two Hamiltonians:

$\hat{H}_1 = \hat{T} + \hat{W}_{ee} + \hat{V}_1$ with a ground state $\hat{H}_1|\Psi_1\rangle = E_1|\Psi_1\rangle$ and ground-state density $n_1(\mathbf{r})$

$\hat{H}_2 = \hat{T} + \hat{W}_{ee} + \hat{V}_2$ with a ground state $\hat{H}_2|\Psi_2\rangle = E_2|\Psi_2\rangle$ and ground-state density $n_2(\mathbf{r})$

1. We first show that $\Psi_1 \neq \Psi_2$:

   Assume $\Psi_1 = \Psi_2 = \Psi$. Then we have:

   $$(\hat{H}_1 - \hat{H}_2)|\Psi\rangle = (\hat{V}_1 - \hat{V}_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle$$

   or, in position representation,

   $$\left(\sum_{i=1}^{N}[v_1(\mathbf{r}_i) - v_2(\mathbf{r}_i)]\right)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = (E_1 - E_2)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

   If $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) \neq 0$ for at least one fixed set of $(\sigma_1, \sigma_2, ..., \sigma_N)$ and "almost" all $(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$, which is true for "reasonably well behaved potentials", then it implies that $v_1(\mathbf{r}) - v_2(\mathbf{r}) = \text{const}$, in contradiction with the initial hypothesis.

   $\Longrightarrow$ **Intermediate conclusion: two local potentials differing by more than an additive constant cannot have a common ground-state wave function.**

Proof of the Hohenberg-Kohn theorem (2/2)

② We now show than $n_1 \neq n_2$:

Assume $n_1 = n_2 = n$. Then, by the variational theorem, we have:

$$E_1 = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{H}_2 + \hat{V}_1 - \hat{V}_2 | \Psi_2 \rangle = E_2 + \int [v_1(\mathbf{r}) - v_2(\mathbf{r})]\, n(\mathbf{r}) \mathrm{d}\mathbf{r}$$

The strict inequality comes from the fact that Ψ_2 cannot be a ground-state wave function of $\hat{H}_1$, as shown in the first step of the proof.

So, we have shown

$$E_1 < E_2 + \int [v_1(\mathbf{r}) - v_2(\mathbf{r})]\, n(\mathbf{r}) \mathrm{d}\mathbf{r}$$

Symmetrically, by exchanging the role of system 1 and 2, we have the strict inequality

$$E_2 < E_1 + \int [v_2(\mathbf{r}) - v_1(\mathbf{r})]\, n(\mathbf{r}) \mathrm{d}\mathbf{r}$$

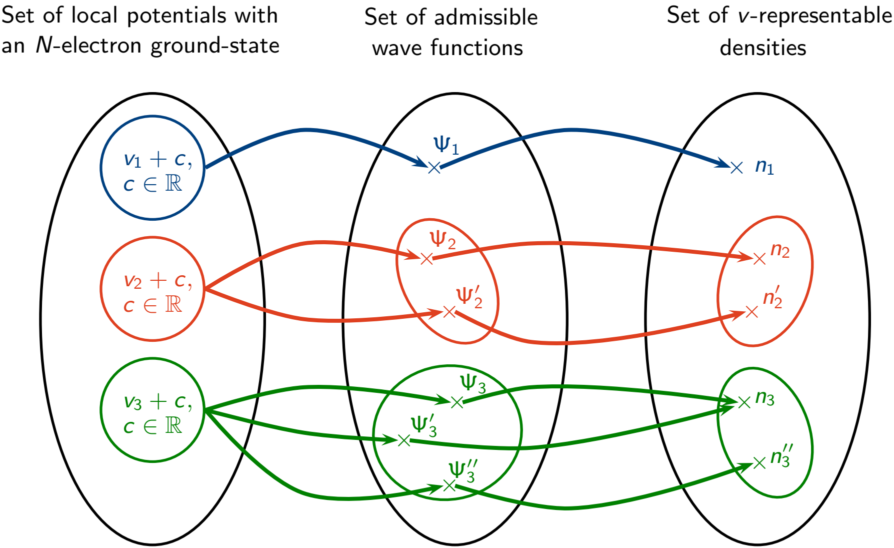
Adding the two inequalities gives the inconsistent result

$$E_1 + E_2 < E_2 + E_1$$

$\Longrightarrow$ **Conclusion: there cannot exist two local potentials differing by more than an additive constant which have a common ground-state density.**

Remark: This proof does not assume non-degenerate ground states (contrary to the original Hohenberg-Kohn proof).

Hohenberg-Kohn theorem: Schematic illustration



From any v-representable density n, we can always go back to the potential v (up to an additive constant) having n as ground-state density.

The universal density functional and the variational property

- **The Hohenberg-Kohn theorem can be summarized as**

$$n \longrightarrow v \longrightarrow \hat{H} \longrightarrow \text{everything}$$

v is a functional of the density n, i.e. $v[n]$, and all other quantities as well.

- For nondegenerate ground states, the **ground-state wave function** Ψ is a functional of n, denoted by $\Psi[n]$. Hohenberg and Kohn defined the **universal density functional**

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{\text{ee}} | \Psi[n] \rangle$$

and the **total electronic energy functional**

$$E[n] = F[n] + \int v_{\text{ne}}(\mathbf{r}) n(\mathbf{r}) \text{d}\mathbf{r}$$

Remark: In case of degeneracies, $\Psi[n]$ *stands for any degenerate ground-state wave function having the density* n*. Still,* $F[n]$ *remains unique.*

- The Hohenberg-Kohn universal functional is only defined for N-electron densities n that are ground-state densities associated with some local potential, the so-called set of v-**representable densities** which we will denote by $\mathcal{A}$.

- Hohenberg and Kohn showed that we have a **variational property** giving the exact ground-state energy

$$E_0 = \min_{n \in \mathcal{A}} \left\{ F[n] + \int v_{\text{ne}}(\mathbf{r}) n(\mathbf{r}) \text{d}\mathbf{r} \right\}$$

The minimum is reached for an exact ground-state density $n_0(\mathbf{r})$ of the potential $v_{\text{ne}}(\mathbf{r})$.

Levy-Lieb constrained-search formulation (1/2)

- In 1979 Levy, and later in 1983 Lieb, proposed to redefine the **universal density functional** as

$$F[n] = \min_{\substack{\Psi \in \mathcal{W} \\ \Psi \to n}} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle = \langle \Psi[n] | \hat{T} + \hat{W}_{\text{ee}} | \Psi[n] \rangle$$

  where "$\Psi \to n$" means that the wave function Ψ is constrained to yield the fixed density n.

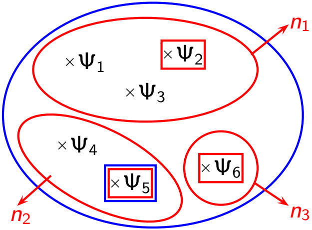
- This so-called Levy-Lieb functional $F[n]$ does not require the existence of a local potential associated with the density.

- It is an extension of the Hohenberg-Kohn functional: it is defined on the larger set of N-electron densities coming from a wave function $\Psi \in \mathcal{W}$, the so-called set of N-**representable densities** $\mathcal{D} = \{n \in L^1(\mathbb{R}^3) \mid n \geq 0, \int n(\mathbf{r})\mathrm{d}\mathbf{r} = N, \sqrt{n} \in H^1(\mathbb{R}^3)\}$.

Levy-Lieb constrained-search formulation (2/2)

- The **variational property** is easily obtained using the constrained-search formulation:

$$
\begin{aligned}
E_0 &= \min_{\Psi\in\mathcal{W}} \langle\Psi|\hat{T}+\hat{W}_{\text{ee}}+\hat{V}_{\text{ne}}|\Psi\rangle \\
&= \min_{n\in\mathcal{D}} \min_{\substack{\Psi\in\mathcal{W}\\ \Psi\to n}} \langle\Psi|\hat{T}+\hat{W}_{\text{ee}}+\hat{V}_{\text{ne}}|\Psi\rangle \\
&= \min_{n\in\mathcal{D}} \left\{ \min_{\substack{\Psi\in\mathcal{W}\\ \Psi\to n}} \langle\Psi|\hat{T}+\hat{W}_{\text{ee}}|\Psi\rangle + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right\} \\
&= \min_{n\in\mathcal{D}} \left\{ F[n] + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right\}
\end{aligned}
$$



- Hence, in DFT, we replace "$\min_{\Psi}$" by "$\min_{n}$" which is a **tremendous simplification**! However, $F[n] = T[n] + W_{\text{ee}}[n]$ is **very difficult to approximate**, in particular the kinetic energy part $T[n]$.

Density-matrix or Lieb density functional

- In 1980 Valone and in 1983 Lieb generalized the constrained-search approach from pure states to ensemble density matrices $\hat{\Gamma}$, resulting in the **density-matrix (DM) or Lieb universal density functional**

$$\boxed{F_{\text{DM}}[n] = \min_{\substack{\hat{\Gamma}\in\mathcal{D}_{\text{DM}} \\ \hat{\Gamma}\to n}} \text{Tr}[(\hat{T} + \hat{W}_{\text{ee}})\hat{\Gamma}]}$$

  where the minimization is done over admissible N-electron ensemble density matrices $\hat{\Gamma} \in \mathcal{D}_{\text{DM}} = \{\hat{\Gamma} = \sum_i w_i |\Psi_i\rangle\langle\Psi_i|, 0 \leq w_i \leq 1, \sum_i w_i = 1, \Psi_i \in \mathcal{W}, \langle\Psi_i|\Psi_j\rangle = \delta_{i,j}\}$ yielding the density n.

- $F_{\text{DM}}[n]$ is defined over the same set of N-representable densities $\mathcal{D}$ and it is always lower than the Levy-Lieb density functional, i.e. $\boxed{F_{\text{DM}}[n] \leq F[n]}$, with equality in the absence of degeneracies.

- Introducing the ground-state energy $E_0[v]$ as a functional of the external potential v, Lieb showed that $F_{\text{DM}}[n]$ is the **Legendre-Fenchel transform** of $E_0[v]$

$$\boxed{F_{\text{DM}}[n] = \sup_{v\in\mathcal{V}} \left(E_0[v] - \int v(\mathbf{r})n(\mathbf{r})\text{d}\mathbf{r} \right)}$$

  where the space of potentials is $\mathcal{V} = L^{3/2}(\mathbb{R}^3) + L^{\infty}(\mathbb{R}^3)$.

- $F_{\text{DM}}[n]$ has the mathematical advantage of being convex. However, in the remaining, we will only use the Levy-Lieb density functional.

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Kohn-Sham (KS) method: decomposition of the universal functional

- In 1965, Kohn and Sham proposed to decompose $F[n]$ as

$$F[n] = T_{\mathrm{s}}[n] + E_{\mathrm{Hxc}}[n]$$

- $T_{\mathrm{s}}[n]$ is the **non-interacting kinetic-energy functional**:

$$T_{\mathrm{s}}[n] = \min_{\substack{\Phi \in \mathcal{S} \\ \Phi \to n}} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle$$

  where the minimization is done over **single-determinant** wave functions $\Phi \in \mathcal{S} = \{\Phi = \psi_1 \wedge \psi_2 \wedge \cdots \wedge \psi_N \mid \psi_i \in H^1(\mathbb{R}^3 \times \{\uparrow,\downarrow\}, \mathbb{C}), \langle \psi_i | \psi_j \rangle = \delta_{i,j}\}$ yielding the fixed density n. A minimizing single-determinant wave function is called a **KS wave function** and is denoted by $\Phi[n]$.

- The remaining functional $E_{\mathrm{Hxc}}[n]$ is called the **Hartree-exchange-correlation functional**.

- $T_{\mathrm{s}}[n]$ is still defined over the **entire set of N-representable densities** $\mathcal{D}$ because any N-representable density can be obtained from a single-determinant wave function. Therefore, the **Kohn-Sham decomposition does not introduce any approximation**.

Kohn-Sham (KS) method: variational principle

- The **exact ground-state energy** can then be expressed as

$$
\begin{aligned}
E_0 &= \min_{n\in\mathcal{D}} \left\{ F[n] + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{r})\text{d}\mathbf{r} \right\} \\
&= \min_{n\in\mathcal{D}} \left\{ \min_{\substack{\Phi\in\mathcal{S}\\ \Phi\to n}} \langle\Phi|\hat{T}|\Phi\rangle + E_{\text{Hxc}}[n] + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{r})\text{d}\mathbf{r} \right\} \\
&= \min_{n\in\mathcal{D}} \min_{\substack{\Phi\in\mathcal{S}\\ \Phi\to n}} \left\{ \langle\Phi|\hat{T} + \hat{V}_{\text{ne}}|\Phi\rangle + E_{\text{Hxc}}[n_\Phi] \right\} \\
&= \min_{\Phi\in\mathcal{S}} \left\{ \langle\Phi|\hat{T} + \hat{V}_{\text{ne}}|\Phi\rangle + E_{\text{Hxc}}[n_\Phi] \right\}
\end{aligned}
$$

  and a minimizing single-determinant KS wave function gives an exact ground-state density $n_0(\mathbf{r})$.

- Hence, in KS DFT, we replace "$\min_{\Psi}$" by "$\min_{\Phi}$" which is still a **tremendous simplification**! The advantage of KS DFT over pure DFT is that a major part of the kinetic energy is treated explicitly with the single-determinant wave function Φ.

- KS DFT is similar to Hartree-Fock (HF)

$$
E_{\text{HF}} = \min_{\Phi\in\mathcal{S}} \langle\Phi|\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}|\Phi\rangle
$$

  but in KS DFT the exact ground-state energy and density are in principle obtained!

Kohn-Sham (KS) method: the Hartree-exchange-correlation functional

- $E_{\mathrm{Hxc}}[n]$ is decomposed as

$$E_{\mathrm{Hxc}}[n] = E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n]$$

- $E_{\mathrm{H}}[n]$ is the **Hartree energy functional**

$$E_{\mathrm{H}}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

  representing the classical electrostatic repulsion energy for the charge distribution $n(\mathbf{r})$ and which is calculated exactly.

- $E_{\mathrm{xc}}[n]$ is the **exchange-correlation energy functional** that remains to approximate. Assuming $\Phi[n]$ is unique (up to a phase factor), this functional is often decomposed as

$$E_{\mathrm{xc}}[n] = E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n]$$

  where $E_{\mathrm{x}}[n]$ is the **exchange energy functional**

$$E_{\mathrm{x}}[n] = \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle - E_{\mathrm{H}}[n]$$

  and $E_{\mathrm{c}}[n]$ is the **correlation energy functional**

$$E_{\mathrm{c}}[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle = T_{\mathrm{c}}[n] + U_{\mathrm{c}}[n]$$

  containing a kinetic contribution $T_{\mathrm{c}}[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} | \Phi[n] \rangle$
  and a potential contribution $U_{\mathrm{c}}[n] = \langle \Psi[n] | \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle - \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle$.

The Kohn-Sham equations (1/2)

- The single determinant Φ is constructed from a set of N **orthonormal occupied spin-orbitals** $\psi_i(\mathbf{x}) = \varphi_i(\mathbf{r})\delta_{\sigma_i,\sigma}$.
- The **total energy** to be minimized is

$$E[\{\varphi_i\}] = \sum_{i=1}^{N} \int \varphi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) d\mathbf{r} + E_{\text{Hxc}}[n]$$

  and the **density** is

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

- For minimizing over the orbitals $\{\varphi_i\}$ with the constraint of keeping the orbitals orthonormalized, we introduce the **Lagrangian**

$$\mathcal{L}[\{\varphi_i\}] = E[\{\varphi_i\}] - \sum_{i=1}^{N} \varepsilon_i \left(\int \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) d\mathbf{r} - 1 \right)$$

  where ε_i is the Lagrange multiplier associated with the normalization condition of $\varphi_i(\mathbf{r})$.
- The Lagrangian must be **stationary** with respect to variations of the orbitals $\varphi_i(\mathbf{r})$

$$\frac{\delta \mathcal{L}}{\delta \varphi_i^*(\mathbf{r})} = 0$$

Interlude: Review on functional derivatives

- For a **functional** $F : f \mapsto F[f]$ of the function $f : x \mapsto f(x)$, an infinitesimal variation δf of f leads to an infinitesimal variation of F which can be expressed as

$$\boxed{\delta F[f] = \int \frac{\delta F[f]}{\delta f(x)} \delta f(x) \mathrm{d}x}$$

This defines the **functional derivative** of $F[f]$ with respect to $f(x)$: $\dfrac{\delta F[f]}{\delta f(x)}$

Remark: For a function $F(f_1, f_2, ...)$ *of several variables* f_1, f_2, ..., *we have*

$$dF = \sum_i \frac{\partial F}{\partial f_i}\, df_i$$

$\delta F[f]/\delta f(x)$ *is the analog of* $\partial F/\partial f_i$ *for the case of an infinite continuous number of variables.*

- For a functional $F[f]$ of a function $f[g](x)$ which is itself a functional of another function $g(x)$, we have the **chain rule**

$$\boxed{\frac{\delta F}{\delta g(x)} = \int \frac{\delta F}{\delta f(x')} \frac{\delta f(x')}{\delta g(x)} \mathrm{d}x'}$$

Remark: It is the analog of the chain rule for a function $F(f_1, f_2, ...)$ *of several variables* $f_j(g_1, g_2, ...)$ *which are themselves functions of other variables* $g_1, g_2, ...$

$$\frac{\partial F}{\partial g_i} = \sum_j \frac{\partial F}{\partial f_j} \frac{\partial f_j}{\partial g_i}$$

The Kohn-Sham equations (2/2)

- We find for the functional derivative of the Lagrangian

$$0 = \frac{\delta \mathcal{L}}{\delta \varphi_i^*(\mathbf{r})} = \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) + \frac{\delta E_{\text{Hxc}}[n]}{\delta \varphi_i^*(\mathbf{r})} - \varepsilon_i \varphi_i(\mathbf{r})$$

- We calculate the term $\delta E_{\text{Hxc}}[n]/\delta \varphi_i^*(\mathbf{r})$ using the chain rule

$$\frac{\delta E_{\text{Hxc}}[n]}{\delta \varphi_i^*(\mathbf{r})} = \int \frac{\delta E_{\text{Hxc}}[n]}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta \varphi_i^*(\mathbf{r})} \mathrm{d}\mathbf{r}' = v_{\text{Hxc}}(\mathbf{r}) \varphi_i(\mathbf{r})$$

  where we have used $\delta n(\mathbf{r}')/\delta \varphi_i^*(\mathbf{r}) = \varphi_i(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$ and we have introduced the **Hartree-exchange-correlation potential** $v_{\text{Hxc}}(\mathbf{r})$

$$\boxed{v_{\text{Hxc}}(\mathbf{r}) = \frac{\delta E_{\text{Hxc}}[n]}{\delta n(\mathbf{r})}}$$

  which is itself a functional of the density.

- We arrive at the **KS equations**

$$\boxed{\left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})}$$

  The orbitals $\varphi_i(\mathbf{r})$ are called the KS orbitals and ε_i are the KS orbital energies.

The Kohn-Sham equations and the Kohn-Sham Hamiltonian

- The KS orbitals are eigenfunctions of the KS one-electron Hamiltonian

  $$h_{\mathrm{s}} = -\frac{1}{2}\nabla^2 + v_{\mathrm{s}}(\mathbf{r})$$

  where $v_{\mathrm{s}}(\mathbf{r}) = v_{\mathrm{ne}}(\mathbf{r}) + v_{\mathrm{Hxc}}(\mathbf{r})$ is the KS potential.

- Mathematically, the KS equations are a set of coupled self-consistent equations since the potential $v_{\mathrm{Hxc}}(\mathbf{r})$ depends on all the occupied orbitals $\{\varphi_i\}_{i=1,\ldots N}$ through the density.

- Physically, h_{s} defines the KS system which is a system of N non-interacting electrons in an effective external potential $v_{\mathrm{s}}(\mathbf{r})$ ensuring that its ground-state density $n(\mathbf{r})$ is the same as the exact ground-state density $n_0(\mathbf{r})$ of the physical system of N interacting electrons.

- The KS equations also defines virtual KS orbitals $\{\varphi_a\}_{a\geq N+1}$.

- $h_{\mathrm{s}}(\mathbf{r})$ is a self-adjoint operator and thus the set of KS orbitals can be chosen as orthonormal.

The Hartree-exchange-correlation potential

- To define $v_{\mathrm{Hxc}}(\mathbf{r}) = \delta E_{\mathrm{Hxc}}[n]/\delta n(\mathbf{r})$, we have assumed a form of differentiability of $E_{\mathrm{Hxc}}[n]$. This can in fact only hold on a restricted set of densities. This is known as the ***v*-representability problem**.
- The KS potential is defined only up to an additive constant. For atomic and molecular ground-state densities, we choose the constant so that the potential vanishes at infinity:

$$\lim_{|\mathbf{r}|\to\infty} v_{\mathrm{s}}(\mathbf{r}) = 0$$

- Following the decomposition of $E_{\mathrm{Hxc}}[n]$, the potential $v_{\mathrm{Hxc}}(\mathbf{r})$ is also decomposed as

$$v_{\mathrm{Hxc}}(\mathbf{r}) = v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r})$$

  with the **Hartree potential** $v_{\mathrm{H}}(\mathbf{r}) = \dfrac{\delta E_{\mathrm{H}}[n]}{\delta n(\mathbf{r})} = \displaystyle\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'$

  and the **exchange-correlation potential** $v_{\mathrm{xc}}(\mathbf{r}) = \delta E_{\mathrm{xc}}[n]/\delta n(\mathbf{r})$

- The potential $v_{\mathrm{xc}}(\mathbf{r})$ can be decomposed as $v_{\mathrm{xc}}(\mathbf{r}) = v_{\mathrm{x}}(\mathbf{r}) + v_{\mathrm{c}}(\mathbf{r})$

  with the **exchange potential** $v_{\mathrm{x}}(\mathbf{r}) = \delta E_{\mathrm{x}}[n]/\delta n(\mathbf{r})$

  and the **correlation potential** $v_{\mathrm{c}}(\mathbf{r}) = \delta E_{\mathrm{c}}[n]/\delta n(\mathbf{r})$

- Remark: Contrary to Hartree-Fock, the KS exchange potential is local.

Practical calculations in an atomic basis (1/3)

- We consider a **basis of M atom-centered functions** $\{\chi_\nu\}$, e.g. GTO basis functions. The orbitals are expanded as

$$\boxed{\varphi_i(\mathbf{r}) = \sum_{\nu=1}^{M} c_{\nu i}\; \chi_\nu(\mathbf{r})}$$

- Inserting this expansion in the KS equations

$$h_s \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

and multiplying on the left by $\chi_\mu^*(\mathbf{r})$ and integrating over $\mathbf{r}$, we arrive at the familiar **SCF generalized eigenvalue equation**

$$\boxed{\sum_{\nu=1}^{M} F_{\mu\nu}\; c_{\nu i} = \varepsilon_i \sum_{\nu=1}^{M} S_{\mu\nu}\; c_{\nu i}}$$

where $F_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) h_s \chi_\nu(\mathbf{r}) d\mathbf{r}$ are the elements of the KS Fock matrix and $S_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r}$ are the elements of the overlap matrix.

Practical calculations in an atomic basis (2/3)

- The Fock matrix is calculated as $F_{\mu\nu} = h_{\mu\nu} + J_{\mu\nu} + V_{\text{xc},\mu\nu}$
- $h_{\mu\nu}$ are the one-electron integrals: $h_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \chi_\nu(\mathbf{r}) d\mathbf{r}$
- $J_{\mu\nu}$ is the Hartree potential matrix:

$$J_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) v_{\text{H}}(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} = \sum_{\lambda=1}^{M} \sum_{\gamma=1}^{M} P_{\gamma\lambda} (\chi_\mu \chi_\nu | \chi_\lambda \chi_\gamma)$$

where $(\chi_\mu \chi_\nu | \chi_\lambda \chi_\gamma) = \iint \frac{\chi_\mu^*(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\chi_\lambda^*(\mathbf{r}_2)\chi_\gamma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ are the two-electron integrals (in chemists' notation) and $P_{\gamma\lambda} = \sum_{i=1}^{N} c_{\gamma i} c_{\lambda i}^*$ is the density matrix.

- $V_{\text{xc},\mu\nu}$ is the exchange-correlation potential matrix: $V_{\text{xc},\mu\nu} = \int \chi_\mu^*(\mathbf{r}) v_{\text{xc}}(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r}$
- The total electronic energy is calculated as

$$E = \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\nu\mu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\nu\mu} J_{\mu\nu} + E_{\text{xc}}$$

- The density is calculated as $n(\mathbf{r}) = \sum_{\gamma=1}^{M} \sum_{\lambda=1}^{M} P_{\gamma\lambda} \chi_\gamma(\mathbf{r}) \chi_\lambda^*(\mathbf{r})$

Practical calculations in an atomic basis (3/3)

- In the simplest approximation, the exchange-correlation energy functional has a local form

$$E_{\mathrm{xc}}^{\mathrm{local}} = \int f(n(\mathbf{r}))d\mathbf{r}$$

  where $f(n(\mathbf{r}))$ has a complicated nonlinear dependence on the density $n(\mathbf{r})$.

- For example, in the local-density approximation (LDA), the exchange energy is

$$E_{\mathrm{x}}^{\mathrm{LDA}} = C_{\mathrm{x}} \int n(\mathbf{r})^{4/3}d\mathbf{r}$$

  where C_{x} is a constant, and the exchange potential is

$$v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r}) = \frac{4}{3}C_{\mathrm{x}}n(\mathbf{r})^{1/3}$$

- Therefore, the integrals cannot be calculated analytically, but are instead evaluated by **numerical integration on a grid**

$$V_{\mathrm{xc},\mu\nu} \approx \sum_k w_k\, \chi_\mu^*(\mathbf{r}_k)v_{\mathrm{xc}}(\mathbf{r}_k)\chi_\nu(\mathbf{r}_k) \qquad \text{and} \qquad E_{\mathrm{xc}}^{\mathrm{local}} \approx \sum_k w_k\, f(n(\mathbf{r}_k))$$

  where $\mathbf{r}_k$ and w_k are quadrature points and weights. For molecules, the multicenter numerical integration scheme of Becke (1988) is generally used.

Extension to spin density-functional theory (1/2)

- For dealing with an external magnetic field, DFT has been extended from the total density to **spin-resolved densities** (von Barth and Hedin, 1972)

$$n_\sigma(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r}\sigma, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 \, \mathrm{d}\mathbf{x}_2 ... \mathrm{d}\mathbf{x}_N \quad \text{with} \quad \sigma \in \{\uparrow, \downarrow\}$$

  which integrate to the numbers of σ-spin electrons, i.e. $\int n_\sigma(\mathbf{r})\mathrm{d}\mathbf{r} = N_\sigma$.

- Without magnetic fields, this is **in principle not necessary**. In practice, the dependence on the spin densities allows one to construct **more accurate approximate exchange-correlation functionals** for **open-shell systems**.

- The **universal density functional** is now defined as

$$F[n_\uparrow, n_\downarrow] = \min_{\substack{\Psi \in \mathcal{W} \\ \Psi \to n_\uparrow, n_\downarrow}} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle$$

  where the search is over wave functions $\Psi \in \mathcal{W}$ with $N = N_\uparrow + N_\downarrow$ electrons and which yield fixed spin densities.

- A **KS method** is obtained by decomposing $F[n_\uparrow, n_\downarrow]$ as

$$F[n_\uparrow, n_\downarrow] = T_{\text{s}}[n_\uparrow, n_\downarrow] + E_{\text{H}}[n] + E_{\text{xc}}[n_\uparrow, n_\downarrow]$$

  where $T_{\text{s}}[n_\uparrow, n_\downarrow]$ is defined with a constrained search over (spin-unrestricted) Slater determinants Φ

$$T_{\text{s}}[n_\uparrow, n_\downarrow] = \min_{\substack{\Phi \in \mathcal{S} \\ \Phi \to n_\uparrow, n_\downarrow}} \langle \Phi | \hat{T} | \Phi \rangle$$

Extension to spin density-functional theory (2/2)

- The **exact ground-state energy** is expressed as

$$E_0 = \min_{\Phi \in \mathcal{S}} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{H}}[n_{\Phi}] + E_{\text{xc}}[n_{\uparrow,\Phi}, n_{\downarrow,\Phi}] \right\}$$

- Writing the spatial orbitals of the determinant as $\varphi_{i\sigma}(\mathbf{r})$ (with indices explicitly including spin now), we have now the **spin-dependent KS equations**

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc},\sigma}(\mathbf{r}) \right) \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma}\varphi_{i\sigma}(\mathbf{r})$$

with the spin-dependent exchange-correlation potential and density

$$v_{\text{xc},\sigma}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}(\mathbf{r})} \quad \text{and} \quad n_{\sigma}(\mathbf{r}) = \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r})|^2$$

- The spin-dependent exchange functional $E_{\text{x}}[n_{\uparrow}, n_{\downarrow}]$ can be obtained from the spin-independent exchange functional $E_{\text{x}}[n]$ with the **spin-scaling relation**

$$E_{\text{x}}[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2}\left(E_{\text{x}}[2n_{\uparrow}] + E_{\text{x}}[2n_{\downarrow}] \right)$$

Therefore, any approximation for the spin-independent exchange functional $E_{\text{x}}[n]$ can be easily extended to an approximation for the spin-dependent exchange functional $E_{\text{x}}[n_{\uparrow}, n_{\downarrow}]$. Unfortunately, there is no such relation for the correlation functional.

Outline

Generalized Kohn-Sham method

- An important extension of the KS method is the **generalized Kohn-Sham** (GKS) method (1996) in which the universal density functional $F[n]$ is decomposed as

$$F[n] = \min_{\substack{\Phi \in \mathcal{S} \\ \Phi \to n}} \left\{ \langle \Phi | \hat{T} | \Phi \rangle + E_{\mathrm{H}}[n_{\Phi}] + S[\Phi] \right\} + \bar{S}[n]$$

  where $S[\Phi]$ is any (reasonable) functional of a single-determinant wave function $\Phi \in \mathcal{S}$ and $\bar{S}[n]$ is the complementary density functional. E.g., in hybrids, $S[\Phi] = a E_{\mathrm{x}}^{\mathrm{HF}}[\Phi]$.

- Defining the **GKS exchange-correlation functional**, $E_{\mathrm{xc}}^{S}[\Phi] = S[\Phi] + \bar{S}[n_{\Phi}]$, we can express the **exact ground-state energy** as

$$E_0 = \min_{\Phi \in \mathcal{S}} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{H}}[n_{\Phi}] + E_{\mathrm{xc}}^{S}[\Phi] \right\}$$

  and any minimizing single-determinant wave function gives a ground-state density $n_0(\mathbf{r})$.

- The corresponding **GKS equations** are

$$\left(-\frac{1}{2} \nabla^2 + v_{\mathrm{ne}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\bar{S}}(\mathbf{r}) \right) \varphi_{i\sigma}(\mathbf{r}) + \frac{\delta S[\Phi]}{\delta \varphi_{i\sigma}^{*}(\mathbf{r})} = \varepsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r})$$

  where $v_{\bar{S}}(\mathbf{r}) = \delta \bar{S}[n] / \delta n(\mathbf{r})$ is a local potential and $\delta S[\Phi] / \delta \varphi_{i\sigma}^{*}(\mathbf{r})$ generates a one-electron (possibly nonlocal) operator.

- The GKS method gives **much more freedom** than the KS method (which corresponds to the special case $S[\Phi] = 0$).

Outline

1. Basic density-functional theory
    - Quantum many-electron problem
    - Universal density functional
    - Kohn-Sham method
    - Generalized Kohn-Sham method

2. Exact constraints for the exchange-correlation functional
    - Exact expressions for the exchange and correlation functionals
    - Uniform coordinate scaling
    - One-orbital spatial regions and self-interaction
    - Lieb-Oxford lower bound
    - Frontier orbital energies

3. Usual approximations for the exchange-correlation energy
    - Local-density approximation
    - Semilocal approximations
    - Single-determinant hybrid approximations
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    - Dispersion corrections

4. Additional topics in density-functional theory
    - Time-dependent density-functional theory
    - Some less usual orbital-dependent exchange-correlation functionals
    - Fractional electron numbers and frontier orbital energies

Outline

2 Exact constraints for the exchange-correlation functional

- Exact expressions for the exchange and correlation functionals
    - The exchange and correlation holes
    - The adiabatic connection
- Uniform coordinate scaling
- One-orbital spatial regions and self-interaction
- Lieb-Oxford lower bound
- Frontier orbital energies
    - HOMO and LUMO energies
    - Fundamental gap

The exchange-correlation hole

- The **pair density** associated with the wave function $\Psi[n]$ is

$$n_2(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)\int\cdots\int |\Psi[n](\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)|^2\, \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \mathrm{d}\mathbf{x}_3 ... \mathrm{d}\mathbf{x}_N$$

  which is a functional of the density. It is normalized to the number of electron pairs: $\iint n_2(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = N(N-1)$. It is proportional to the probability density of finding two electrons at positions $(\mathbf{r}_1,\mathbf{r}_2)$ with all the other electrons anywhere.

- It can be used to express the electron-electron interaction energy

$$\langle\Psi[n]|\hat{W}_{\mathrm{ee}}|\Psi[n]\rangle = \frac{1}{2}\iint \frac{n_2(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

- Mirroring the decomposition of $E_{\mathrm{Hxc}}[n]$, the pair density can be decomposed as

$$n_2(\mathbf{r}_1,\mathbf{r}_2) = \underbrace{n(\mathbf{r}_1)n(\mathbf{r}_2)}_{\substack{\text{independent}\\ \text{electrons}}} + \underbrace{n_{2,\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2)}_{\substack{\text{exchange and}\\ \text{correlation effects}}}$$

- We also introduce the **exchange-correlation hole** $n_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2)$ by

$$n_{2,\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2) = n(\mathbf{r}_1)n_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2)$$

  It can be interpreted as the modification due to exchange and correlation effects of the conditional probability of finding an electron at $\mathbf{r}_2$ knowing that one has been found at $\mathbf{r}_1$.

- We have the exact constraints: $n_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2) \geq -n(\mathbf{r}_2)$ and $\int n_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -1$

The exchange hole

- Similarly, we define the **KS pair density** associated with the KS single determinant $\Phi[n]$

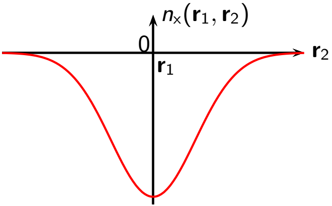
$$n_{2,\mathrm{KS}}(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)\int\cdots\int |\Phi[n](\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)|^2\, \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \mathrm{d}\mathbf{x}_3 ... \mathrm{d}\mathbf{x}_N$$

- It can be decomposed as

$$n_{2,\mathrm{KS}}(\mathbf{r}_1,\mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2) + n_{2,\mathrm{x}}(\mathbf{r}_1,\mathbf{r}_2)$$

and we introduce the **exchange hole** $n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2)$ by

$$n_{2,\mathrm{x}}(\mathbf{r}_1,\mathbf{r}_2) = n(\mathbf{r}_1)n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2)$$



which satisfies the exact constraints:

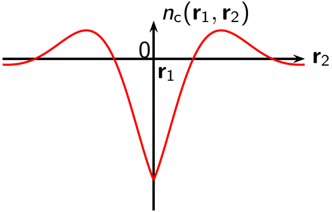
$$n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2) \geq -n(\mathbf{r}_2) \quad \text{and} \quad \int n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -1 \quad \text{and} \quad n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2) \leq 0$$

- The exchange energy functional is the electrostatic interaction energy between an electron and its exchange hole:

$$E_\mathrm{x}[n] = \frac{1}{2}\iint \frac{n(\mathbf{r}_1)n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = \int n(\mathbf{r}_1)\varepsilon_\mathrm{x}[n](\mathbf{r}_1)\mathrm{d}\mathbf{r}_1$$

where $\varepsilon_\mathrm{x}[n](\mathbf{r}_1)$ is the exchange energy per particle. In approximate exchange density functionals, the quantity $\varepsilon_\mathrm{x}[n](\mathbf{r}_1)$ is usually what is approximated.

The correlation hole



- The **correlation hole** is defined as the difference

  $$n_c(\mathbf{r}_1,\mathbf{r}_2) = n_{xc}(\mathbf{r}_1,\mathbf{r}_2) - n_x(\mathbf{r}_1,\mathbf{r}_2)$$

  and satisfies the sum rule

  $$\int n_c(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = 0$$

  which implies that the correlation hole has negative and positive contributions.

- The potential contribution to the correlation energy can be written in terms of the correlation hole

  $$U_c[n] = \frac{1}{2}\iint \frac{n(\mathbf{r}_1)n_c(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

  But in order to express the total correlation energy $E_c[n] = T_c[n] + U_c[n]$ in a similar form, we need to introduce the adiabatic-connection formalism.

The adiabatic connection (1/3)

- The idea of the **adiabatic connection** is to have a continuous path between the non-interacting KS system and the physical system while keeping the ground-state density constant.

- For this, we introduce a Hamiltonian depending on a **coupling constant** λ which switches on the electron-electron interaction

$$\boxed{\hat{H}^{\lambda} = \hat{T} + \lambda \hat{W}_{\text{ee}} + \hat{V}^{\lambda}}$$

where $\hat{V}^{\lambda}$ is the external local potential imposing that the ground-state density is the same as the ground-state density of the physical system for all λ, i.e. $n^{\lambda}(\mathbf{r}) = n_0(\mathbf{r}), \forall \lambda$.

- By varying λ, we connect the KS non-interacting system ($\lambda = 0$) to the physical interacting system ($\lambda = 1$):

$$\underbrace{\hat{H}^{\lambda=0}}_{\substack{\text{KS non-interacting} \\ \text{system}}} \xleftrightarrow{\quad 0\leq\lambda\leq1 \quad} \underbrace{\hat{H}^{\lambda=1}}_{\substack{\text{Physical interacting} \\ \text{system}}}$$

- We define a universal functional for each value of the parameter λ

$$\boxed{F^{\lambda}[n] = \min_{\substack{\Psi \in \mathcal{W} \\ \Psi \to n}} \langle \Psi | \hat{T} + \lambda \hat{W}_{\text{ee}} | \Psi \rangle = \langle \Psi^{\lambda}[n] | \hat{T} + \lambda \hat{W}_{\text{ee}} | \Psi^{\lambda}[n] \rangle}$$

The adiabatic connection (2/3)

- The functional $F^{\lambda}[n]$ can be decomposed as

$$F^{\lambda}[n] = T_{\mathrm{s}}[n] + E_{\mathrm{H}}^{\lambda}[n] + E_{\mathrm{x}}^{\lambda}[n] + E_{\mathrm{c}}^{\lambda}[n]$$

- $E_{\mathrm{H}}^{\lambda}[n]$ and $E_{\mathrm{x}}^{\lambda}[n]$ are the Hartree and exchange functionals associated with the interaction $\lambda\hat{W}_{\mathrm{ee}}$ and are simply linear in λ

$$E_{\mathrm{H}}^{\lambda}[n] = \lambda E_{\mathrm{H}}[n] \qquad \text{and} \qquad E_{\mathrm{x}}^{\lambda}[n] = \lambda E_{\mathrm{x}}[n]$$

- The correlation functional $E_{\mathrm{c}}^{\lambda}[n]$ is nonlinear in λ

$$E_{\mathrm{c}}^{\lambda}[n] = \langle \Psi^{\lambda}[n] | \hat{T} + \lambda \hat{W}_{\mathrm{ee}} | \Psi^{\lambda}[n] \rangle - \langle \Phi[n] | \hat{T} + \lambda \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle$$

- We can get rid of $\hat{T}$ by taking the derivative with respect to λ and using the Hellmann-Feynman theorem for the wave function $\Psi^{\lambda}[n]$

$$\frac{\partial E_{\mathrm{c}}^{\lambda}[n]}{\partial \lambda} = \langle \Psi^{\lambda}[n] | \hat{W}_{\mathrm{ee}} | \Psi^{\lambda}[n] \rangle - \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle$$

The adiabatic connection (3/3)

- Reintegrating over λ from 0 to 1, and using $E_c^{\lambda=1}[n] = E_c[n]$ and $E_c^{\lambda=0}[n] = 0$ (assuming no degeneracies at $\lambda = 0$), we arrive at the **adiabatic-connection formula**

$$\boxed{E_c[n] = \int_0^1 d\lambda \, \langle \Psi^{\lambda}[n] | \hat{W}_{ee} | \Psi^{\lambda}[n] \rangle - \langle \Phi[n] | \hat{W}_{ee} | \Phi[n] \rangle}$$

- Introducing the correlation hole $n_c^{\lambda}(\mathbf{r}_1, \mathbf{r}_2)$ associated with the wave function $\Psi^{\lambda}[n]$, the adiabatic-connection formula can also be written as

$$\boxed{E_c[n] = \frac{1}{2} \int_0^1 d\lambda \iint \frac{n(\mathbf{r}_1) n_c^{\lambda}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2}$$

- Introducing the λ-integrated correlation hole $\bar{n}_c(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 d\lambda \; n_c^{\lambda}(\mathbf{r}_1, \mathbf{r}_2)$, we finally write

$$\boxed{E_c[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1) \bar{n}_c(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \int n(\mathbf{r}_1) \varepsilon_c[n](\mathbf{r}_1) d\mathbf{r}_1}$$

where $\varepsilon_c[n](\mathbf{r}_1)$ is the correlation energy per particle, which is the quantity usually approximated in practice.

Outline

2 Exact constraints for the exchange-correlation functional

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Uniform coordinate scaling (1/2)

- We consider a **norm-preserving uniform coordinate scaling** in the N-electron wave function along the adiabatic connection $\Psi^{\lambda}[n]$ (ignoring untouched spin variables)

$$\boxed{\Psi_{\gamma}^{\lambda}[n](\mathbf{r}_1, ..., \mathbf{r}_N) = \gamma^{3N/2}\Psi^{\lambda}[n](\gamma\mathbf{r}_1, ..., \gamma\mathbf{r}_N)}$$

where $\gamma > 0$ is a scaling factor.

- The scaled wave function $\Psi_{\gamma}^{\lambda}[n]$ yields the **scaled density**

$$\boxed{n_{\gamma}(\mathbf{r}) = \gamma^{3}n(\gamma\mathbf{r})} \qquad \left(\text{with } \int n_{\gamma}(\mathbf{r})d\mathbf{r} = \int n(\mathbf{r})d\mathbf{r} = N\right)$$

and minimizes $\langle\Psi|\hat{T} + \lambda\gamma\hat{W}_{\text{ee}}|\Psi\rangle$ since it can be shown that

$$\langle\Psi_{\gamma}^{\lambda}[n]|\hat{T} + \lambda\gamma\hat{W}_{\text{ee}}|\Psi_{\gamma}^{\lambda}[n]\rangle = \gamma^{2}\langle\Psi^{\lambda}[n]|\hat{T} + \lambda\hat{W}_{\text{ee}}|\Psi^{\lambda}[n]\rangle$$

- We thus conclude

$$\boxed{\Psi_{\gamma}^{\lambda}[n] = \Psi^{\lambda\gamma}[n_{\gamma}]} \qquad \text{or, equivalently,} \qquad \boxed{\Psi_{\gamma}^{\lambda/\gamma}[n] = \Psi^{\lambda}[n_{\gamma}]}$$

- and for the **universal density functional**

$$\boxed{F^{\lambda\gamma}[n_{\gamma}] = \gamma^{2}F^{\lambda}[n]} \qquad \text{or, equivalently,} \qquad \boxed{F^{\lambda}[n_{\gamma}] = \gamma^{2}F^{\lambda/\gamma}[n]}$$

Uniform coordinate scaling (2/2)

- At $\lambda = 0$, we find the scaling relation of the **KS single-determinant wave function**

$$\Phi[n_\gamma] = \Phi_\gamma[n]$$

- This directly leads to the scaling relations for $T_s[n]$, $E_H[n]$, and $E_x[n]$

$$T_s[n_\gamma] = \gamma^2 T_s[n] \quad \text{and} \quad E_H[n_\gamma] = \gamma E_H[n] \quad \text{and} \quad E_x[n_\gamma] = \gamma E_x[n]$$

- However, $E_c[n]$ has the more complicated scaling (as $F[n]$)

$$E_c^\lambda[n_\gamma] = \gamma^2 E_c^{\lambda/\gamma}[n]$$

and, in particular for $\lambda = 1$,

$$E_c[n_\gamma] = \gamma^2 E_c^{1/\gamma}[n]$$

High- and low-density limits

- In the **high-density limit** ($\gamma \to \infty$), the correlation functional goes to a constant, for nondegenerate KS systems,

$$\boxed{\lim_{\gamma \to \infty} E_{\mathrm{c}}[n_\gamma] = E_{\mathrm{c}}^{\mathrm{GL2}}[n]}$$

  where $E_{\mathrm{c}}^{\mathrm{GL2}}[n]$ is the second-order Görling-Levy (GL2) correlation energy.

    - This is also called the **weak-correlation limit** since $E_{\mathrm{c}}[n] \ll E_x[n]$.
    - Atomic and molecular systems are often close to the high-density limit. E.g., for the ground-state density of He, $E_{\mathrm{c}}[n] = -0.0421$ a.u. and $\lim_{\gamma \to \infty} E_{\mathrm{c}}[n_\gamma] = -0.0467$ a.u..

- In the **low-density limit** ($\gamma \to 0$), the Hartree-exchange-correlation functional goes to zero linearly in γ

$$\boxed{E_{\mathrm{Hxc}}[n_\gamma] \underset{\gamma \to 0}{\sim} \gamma \, W_{\mathrm{ee}}^{\mathrm{SCE}}[n]}$$

  where $W_{\mathrm{ee}}^{\mathrm{SCE}}[n] = \inf\limits_{\substack{\Psi \in \mathcal{W} \\ \Psi \to n}} \langle \Psi | \hat{W}_{\mathrm{ee}} | \Psi \rangle$ is the strictly-correlated-electron (SCE) functional.

    - This limit corresponds to a Wigner crystallization.
    - This is also called the **strong-correlation limit** because $E_{\mathrm{c}}[n] \sim E_x[n]$.
    - Calculation of $W_{\mathrm{ee}}^{\mathrm{SCE}}[n]$ is computationally involved but has been done for a few systems (Seidl, Gori-Giorgi, ...).

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     - Fundamental gap

One-orbital spatial regions and self-interaction

- For **one-electron densities** $n_{1\mathrm{e}}(\mathbf{r}) = |\varphi_1(\mathbf{r})|^2$ where φ_1 is the unique occupied KS orbital, we have

$$\boxed{E_\mathrm{x}[n_{1\mathrm{e}}] = -E_\mathrm{H}[n_{1\mathrm{e}}]} \quad \text{and} \quad \boxed{E_\mathrm{c}[n_{1\mathrm{e}}] = 0}$$

- For **opposite-spin two-electron densities** $n_{2\mathrm{e}}^{\uparrow\downarrow}(\mathbf{r}) = 2|\varphi_1(\mathbf{r})|^2$ where φ_1 is the unique doubly occupied KS orbital, we have

$$\boxed{E_\mathrm{x}[n_{2\mathrm{e}}^{\uparrow\downarrow}] = -\frac{1}{2} E_\mathrm{H}[n_{2\mathrm{e}}^{\uparrow\downarrow}]}$$

- For systems with more electrons, **similar relations apply locally in one-orbital spatial regions**, i.e. in regions where only one occupied KS orbital is not zero. This situation can be approximately realized in chemical systems (unpaired electron in a radical, and electron pair in a single covalent bond, in a lone pair, or in a core orbital).

- If approximate exchange and correlation density functionals do not satisfy these constraints, we say that they introduce a **self-interaction error**.

Outline

2 Exact constraints for the exchange-correlation functional

- Exact expressions for the exchange and correlation functionals
  - The exchange and correlation holes
  - The adiabatic connection
- Uniform coordinate scaling
- One-orbital spatial regions and self-interaction
- **Lieb-Oxford lower bound**
- Frontier orbital energies
  - HOMO and LUMO energies
  - Fundamental gap

Lieb-Oxford lower bound

- Lieb and Oxford derived a useful **lower bound** which can be expressed as

$$E_{\mathrm{x}}[n] \geq E_{\mathrm{xc}}[n] \geq -C_{\mathrm{LO}} \int n(\mathbf{r})^{4/3} \mathrm{d}\mathbf{r}$$

  where the optimal (i.e., smallest) constant C_{LO} (independent of the electron number N) has been narrowed to $1.4442 \leq C_{\mathrm{LO}} \leq 1.5765$.

- This bound is approached in the low-density limit.

- For one-electron densities and opposite-spin two-electron densities, specific tigher bounds (i.e., with smaller C_{LO}) are known.

Outline

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The HOMO energy and the ionization energy

- For clarity, we will explicitly indicate the dependence on the electron number N in this section.
- For finite systems, the exact ground-state density of a N-electron system decays exponentially for $r = |\mathbf{r}| \to \infty$ with an exponent related to the **ionization energy** $I_N = E_0^{N-1} - E_0^N$

$$\boxed{n^N(\mathbf{r}) \underset{r\to\infty}{\propto} e^{-2\sqrt{2I_N}\, r}}$$

- Choosing the constant in the KS potential so that it goes to zero at infinity, i.e. $\lim_{|\mathbf{r}|\to\infty} v_s^N(\mathbf{r}) = 0$, it can be shown the density calculated from the KS orbitals decays exponentially with an exponent related to the **HOMO energy** ε_H^N

$$\boxed{n^N(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2 \underset{r\to\infty}{\propto} e^{-2\sqrt{-2\varepsilon_H^N}\, r}}$$

- This implies that the **KS HOMO energy is the opposite of the exact ionization energy**

$$\boxed{\varepsilon_H^N = -I_N}$$

- It is similar to Koopmans' theorem for HF, except that here it is exact (no neglect of correlation or orbital relaxation).

The LUMO energy, the electron affinity, the derivative discontinuity

- Contrary to what one could have expected, the **KS LUMO energy $\varepsilon_{\mathrm{L}}^{N}$ is not the opposite of the exact electron affinity $A_N = E_0^N - E_0^{N+1}$** but instead

  $$\varepsilon_{\mathrm{L}}^{N} = -A_N - \Delta_{\mathrm{xc}}^{N}$$

  where $\Delta_{\mathrm{xc}}^{N} \geq 0$ is a constant.

- For the $(N+1)$-electron system (with the same external potential v_{ne}), we have $\varepsilon_{\mathrm{H}}^{N+1} = -I_{N+1} = -A_N$, so it means that

  $$\Delta_{\mathrm{xc}}^{N} = \varepsilon_{\mathrm{H}}^{N+1} - \varepsilon_{\mathrm{L}}^{N}$$

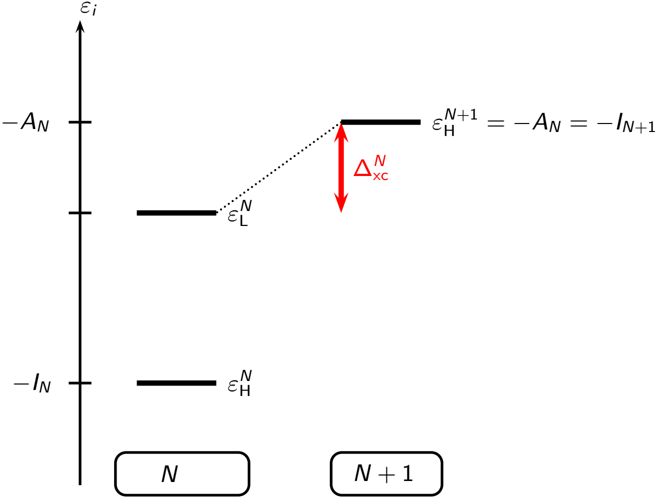
  i.e., the constant Δ_{xc}^{N} corresponds to the **"jump" of the LUMO energy** of the N-electron system upon adding an electron so that the HOMO energy of the $(N+1)$-electron system correctly gives $-I_{N+1}$.

- In the extension of DFT to fractional electron numbers, it can be shown that the constant Δ_{xc}^{N} corresponds to the **uniform jump** that the **exchange-correlation potential** makes when going from $N-\delta$ electrons to $N+\delta$ electrons with $\delta \to 0^+$

  $$\Delta_{\mathrm{xc}}^{N} = v_{\mathrm{xc}}^{N+\delta}(\mathbf{r}) - v_{\mathrm{xc}}^{N-\delta}(\mathbf{r}) = \left(\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}\right)_{N+\delta} - \left(\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}\right)_{N-\delta}$$

  i.e. Δ_{xc}^{N} is the **derivative discontinuity** in the exchange-correlation energy functional $E_{\mathrm{xc}}[n]$.

Kohn-Sham frontier orbital energies: Graphical summary



Fundamental gap

- The **fundamental gap** of the N-electron system is defined as

$$\boxed{E_{\text{gap}}^{N} = I_N - A_N}$$

- In KS DFT, it can thus be expressed as

$$\boxed{E_{\text{gap}}^{N} = \underbrace{\varepsilon_{\text{L}}^{N} - \varepsilon_{\text{H}}^{N}}_{\text{KS gap}} + \Delta_{\text{xc}}^{N}}$$

  So **the KS gap is not equal to the exact fundamental gap** of the system, the difference coming from the derivative discontinuity Δ_{xc}^{N}.

- The derivative discontinuity Δ_{xc}^{N} can represent an important contribution to the fundamental gap. In the special case of open-shell systems, we have $\varepsilon_{\text{L}}^{N} = \varepsilon_{\text{H}}^{N}$, and thus if the fundamental gap of an open-shell system is not zero (Mott insulator), it is entirely given by Δ_{xc}^{N}.

Outline

1. Basic density-functional theory
    - Quantum many-electron problem
    - Universal density functional
    - Kohn-Sham method
    - Generalized Kohn-Sham method

2. Exact constraints for the exchange-correlation functional
    - Exact expressions for the exchange and correlation functionals
    - Uniform coordinate scaling
    - One-orbital spatial regions and self-interaction
    - Lieb-Oxford lower bound
    - Frontier orbital energies

3. Usual approximations for the exchange-correlation energy
    - Local-density approximation
    - Semilocal approximations
    - Single-determinant hybrid approximations
    - Multideterminant hybrid approximations
    - Dispersion corrections

4. Additional topics in density-functional theory
    - Time-dependent density-functional theory
    - Some less usual orbital-dependent exchange-correlation functionals
    - Fractional electron numbers and frontier orbital energies

Outline

Local-density approximation

- In the **local-density approximation** (LDA), introduced by Kohn and Sham (1965), the exchange-correlation functional is approximated as

  $$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int n(\mathbf{r})\varepsilon_{\mathrm{xc}}^{\mathrm{UEG}}(n(\mathbf{r}))\mathrm{d}\mathbf{r}$$

  where $\varepsilon_{\mathrm{xc}}^{\mathrm{UEG}}(n)$ is the exchange-correlation energy per particle of the infinite **uniform electron gas (UEG)** with the density n.

- The exchange energy per particle of the UEG can be calculated analytically

  $$\varepsilon_{\mathrm{x}}^{\mathrm{UEG}}(n) = C_{\mathrm{x}}\, n^{1/3}$$ Dirac (1930) and Slater (1951)

- For the correlation energy per particle $\varepsilon_{\mathrm{c}}^{\mathrm{UEG}}(n)$ of the UEG, there are some parametrized functions of n fitted to QMC data and imposing the high- and low-density expansions (using the Wigner-Seitz radius $r_{\mathrm{s}} = (3/(4\pi n))^{1/3}$)

  $$\varepsilon_{\mathrm{c}}^{\mathrm{UEG}} \underset{r_{\mathrm{s}}\to 0}{=} A \ln r_{\mathrm{s}} + B + C\, r_{\mathrm{s}} \ln r_{\mathrm{s}} + O(r_{\mathrm{s}})$$ high-density limit or weak-correlation limit

  $$\varepsilon_{\mathrm{c}}^{\mathrm{UEG}} \underset{r_{\mathrm{s}}\to \infty}{=} \frac{a}{r_{\mathrm{s}}} + \frac{b}{r_{\mathrm{s}}^{3/2}} + \frac{c}{r_{\mathrm{s}}^{2}} + O\left(\frac{1}{r_{\mathrm{s}}^{5/2}}\right)$$ low-density limit or strong-correlation limit

  The two most used parametrizations are VWN and PW92. Generalization to spin densities $\varepsilon_{\mathrm{c}}^{\mathrm{UEG}}(n_{\uparrow}, n_{\downarrow})$ is sometimes referred to as local-spin-density (LSD) approximation.

Outline

The gradient-expansion approximation

- The next logical step beyond the LDA is the **gradient-expansion approximation** (GEA) which consists in a systematic expansion of $E_{\text{xc}}[n]$ in terms of the gradients of $n(\mathbf{r})$.
- To derive the GEA, one starts from the uniform electron gas, introduce a weak and slowly-varying external potential $v(\mathbf{r})$, and expand the exchange-correlation energy in terms of the gradients of the density. Alternatively, one can perform a semiclassical expansion of the exact $E_{\text{xc}}[n]$.
- At second order, the GEA has the form

$$E_{\text{xc}}^{\text{GEA}}[n] = E_{\text{xc}}^{\text{LDA}}[n] + \int n(\mathbf{r})^{4/3}\ C_{\text{xc}}^{(2)}(n(\mathbf{r}))\ \left(\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})^{4/3}}\right)^2 \mathrm{d}\mathbf{r}$$

  where $C_{\text{xc}}^{(2)}(n) = C_{\text{x}}^{(2)} + C_{\text{c}}^{(2)}(n)$ are known coefficients.
- We use the **reduced density gradient** $|\nabla n|/n^{4/3}$ which is a dimensionless quantity.
- The GEA should improve over the LDA provided that the reduced density gradient is small. Unfortunately, for real molecular systems, the reduced density gradient can be large in some regions of space, and the GEA turns out to be a worse approximation than the LDA.

Generalized-gradient approximations (1/4)

- The failure of the GEA lead to the development of **generalized-gradient approximations (GGAs)**, started in the 1980s, of the generic form

$$E_{\text{xc}}^{\text{GGA}}[n] = \int e_{\text{xc}}^{\text{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}))\text{d}\mathbf{r}$$

- The GGAs provide a big improvement over LDA for molecular systems.
- The GGAs are often called **semilocal** approximations, which means that they involve a single integral on $\mathbf{r}$ using "semilocal information" through $\nabla n(\mathbf{r})$.
- For simplicity, we consider here only the spin-independent form, but in practice GGA functionals are more generally formulated in terms of spin densities and their gradients

$$E_{\text{xc}}^{\text{GGA}}[n_\uparrow, n_\downarrow] = \int e_{\text{xc}}^{\text{GGA}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}), \nabla n_\uparrow(\mathbf{r}), \nabla n_\downarrow(\mathbf{r}))\text{d}\mathbf{r}$$

- (Too) Many GGA functionals have been proposed. We will review some of the most widely used ones.

Generalized-gradient approximations (2/4)

- **Becke 88 (B88 or B) exchange functional**

$$E_x^{\mathrm{B}}[n] = E_x^{\mathrm{LDA}}[n] + \int n(\mathbf{r})^{4/3}\, f\left(\frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})^{4/3}}\right) \mathrm{d}\mathbf{r}$$

  - This form ensures the fulfilment of the scaling relation $E_x^{\mathrm{B}}[n_\gamma] = \gamma E_x^{\mathrm{B}}[n]$.
  - Function f chosen so as to satisfy the exact asymptotic behavior of the exchange energy per particle:

$$\varepsilon_x(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{1}{2r}$$

  - It contains an empirical parameter fitted to Hartree-Fock exchange energies of rare-gas atoms.

- **Lee-Yang-Parr (LYP) correlation functional** (1988)
  - One of the rare functionals not constructed starting from LDA.
  - It originates from the Colle-Salvetti (1975) correlation-energy approximation depending on the curvature of Hartree-Fock hole and containing four parameters fitted to Helium data.
  - LYP introduced a further approximation to retain dependence on only n, ∇n, $\nabla^2 n$.
  - The density Laplacian $\nabla^2 n$ can be exactly eliminated by an integration by parts.

Generalized-gradient approximations (3/4)

- **Perdew-Wang 91 (PW91) exchange-correlation functional**
  - It is based on a model of exchange and correlation holes from which we express the exchange and correlation energies per particle:
    $$\varepsilon_x(\mathbf{r}_1) = \frac{1}{2}\int \frac{n_x(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_2 \qquad \text{and} \qquad \varepsilon_c(\mathbf{r}_1) = \frac{1}{2}\int \frac{\bar{n}_c(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_2$$
  - It starts from the GEA model of these holes and removes the unrealistic long-range parts of these holes to restore important conditions satisfied by the LDA.
    - For the GEA exchange hole: the spurious positive parts are removed to enforce $n_x(\mathbf{r}_1,\mathbf{r}_2) \leq 0$ and a cutoff in $|\mathbf{r}_1-\mathbf{r}_2|$ is applied to enforce $\int n_x(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = -1$.
    - For the GEA correlation hole: a cutoff is applied to enforce $\int \bar{n}_c(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = 0$.
  - The exchange and correlation energies per particle calculated from these numerical holes are then fitted to functions of n and $|\nabla n|$ chosen to satisfy a number of exact conditions.

Generalized-gradient approximations (4/4)

- **Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional** (1996)

  This is a simplification of the PW91 functional: ε_x and ε_c are simpler functions of n and $|\nabla n|$ enforcing fewer exact conditions and with no fitted parameters.

  For exchange, the conditions imposed are:

  - Second-order GEA expansion: $\varepsilon_\text{x} \underset{s\to 0}{\sim} \varepsilon_\text{x}^\text{LDA} + n^{1/3} C_\text{x}^{(2)}\ s^2$ where $s = |\nabla n|/n^{4/3}$ (with only approximate $C_\text{x}^{(2)} \approx -C_\text{c}^{(2)}$).
  - A local version of Lieb-Oxford bound, $E_\text{x} \geq -C_\text{LO} \int n(\mathbf{r})^{4/3} \text{d}\mathbf{r}$. It was chosen to reach the bound in the $s \to \infty$ limit.

  For correlation, the conditions imposed are:

  - High-density limit: $\varepsilon_\text{c} \xrightarrow[r_\text{s}\to 0]{}$ const (cancellation of diverging term $A \ln r_\text{s}$ from LDA).
  - Second-order GEA expansion: $\varepsilon_\text{c} \underset{s\to 0}{\sim} \varepsilon_\text{c}^\text{LDA} + n^{1/3} C_\text{c}^{(2)}\ s^2$ (with $C_\text{c}^{(2)}$ only in $r_\text{s} \to 0$ limit).
  - Large reduced-density-gradient limit: $\varepsilon_\text{c} \xrightarrow[s\to\infty]{} 0$ (exchange dominates).

Meta-generalized-gradient approximations (1/2)

- The **meta-generalized-gradient approximations (mGGAs)** are of the generic form

$$E_{\text{xc}}^{\text{mGGA}}[n,\tau] = \int e_{\text{xc}}^{\text{mGGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))\text{d}\mathbf{r}$$

  where $\nabla^2 n(\mathbf{r})$ is the Laplacian of the density and $\tau(\mathbf{r})$ is the **non-interacting positive kinetic energy density**

$$\tau(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N} |\nabla \varphi_i(\mathbf{r})|^2$$

  which, as we will see, contains useful information.

- A mGGA can be either considered as an implicit functional of the density in the KS method, i.e. $E_{\text{xc}}[n] = E_{\text{xc}}^{\text{mGGA}}[n, \tau_{\Phi[n]}]$, or more commonly as an explicit functional of a single-determinant Φ in the GKS method, i.e. $E_{\text{xc}}^{S}[\Phi] = E_{\text{xc}}^{\text{mGGA}}[n_\Phi, \tau_\Phi]$.

- In the GKS method, a mGGA functional generates a non-multiplicative potential. But don't worry, this is allowed in GKS!

- Nowadays, $\nabla^2 n(\mathbf{r})$ is rarely used to construct mGGAs because it contains similar information than $\tau(\mathbf{r})$.

- The mGGAs are considered as part of the family of semilocal approximations.

- The mGGAs provide a modest improvement over GGAs.

Meta-generalized-gradient approximations (2/2)

- Motivations for introducing the variable $\tau(\mathbf{r})$:
  - Short-range expansion of the spherically average exchange hole (for closed-shell systems):

$$\tilde{n}_{\mathrm{x}}(\mathbf{r}_1, r_{12}) = -\frac{n(\mathbf{r}_1)}{2} - \frac{1}{3}\left(\frac{1}{4}\nabla^2 n(\mathbf{r}_1) - 4\tau(\mathbf{r}_1) + \frac{|\nabla n(\mathbf{r}_1)|^2}{8n(\mathbf{r}_1)}\right) r_{12}^2 + O(r_{12}^4)$$

    Thus $\tau(\mathbf{r})$ is needed to describe the curvature of the exchange hole.

  - $\tau(\mathbf{r})$ can be used as an indicator of **one-orbital spatial regions** (regions containing one or two electrons in a single orbital).
    This is done by comparing $\tau(\mathbf{r})$ with the **von Weizsäcker kinetic energy density**

$$\tau^{\mathrm{W}}(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})}$$

    which is the exact $\tau(\mathbf{r})$ for one and two electrons in a single orbital.

- In practice, $\tau(\mathbf{r})$ is often used through the variables
  - $z(\mathbf{r}) = \tau^{\mathrm{W}}(\mathbf{r})/\tau(\mathbf{r})$
  - $\alpha(\mathbf{r}) = (\tau(\mathbf{r}) - \tau^{\mathrm{W}}(\mathbf{r}))/\tau^{\mathrm{UEG}}(\mathbf{r})$ where $\tau^{\mathrm{UEG}}(\mathbf{r}) = c\ n(\mathbf{r})^{5/3}$

- Examples of mGGAs: TPSS (2003), M06-L (2006), and SCAN (2015).

Outline

3. Usual approximations for the exchange-correlation energy
   - Local-density approximation
   - Semilocal approximations
     - The gradient-expansion approximation
     - Generalized-gradient approximations
     - Meta-generalized-gradient approximations
   - Single-determinant hybrid approximations
     - Hybrid approximations
     - Range-separated hybrid approximations
   - Multideterminant hybrid approximations
     - Double-hybrid approximations
     - Range-separated double-hybrid approximations
   - Dispersion corrections
     - Semiempirical dispersion corrections
     - Nonlocal van der Waals density functionals

Hybrid approximations

- In 1993, Becke proposed to **mix Hartree-Fock (HF) exchange** with GGA functionals in a three-parameter hybrid (3H) approximation

$$E_{\mathrm{xc}}^{\mathrm{3H}}[\Phi] = a\, E_{\mathrm{x}}^{\mathrm{HF}}[\Phi] + b\, E_{\mathrm{x}}^{\mathrm{GGA}}[n_\Phi] + (1-a-b)\, E_{\mathrm{x}}^{\mathrm{LDA}}[n_\Phi] + c\, E_{\mathrm{c}}^{\mathrm{GGA}}[n_\Phi] + (1-c)\, E_{\mathrm{c}}^{\mathrm{LDA}}[n_\Phi]$$

  where a, b, and c are empirical parameters. Example: B3LYP ($a = 0.20$)

- These hybrids are approximations within the **GKS method**. The term $S[\Phi] = aE_{\mathrm{x}}^{\mathrm{HF}}[\Phi]$ generates a **nonlocal HF exchange potential** $av_{\mathrm{x},\sigma}^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$. Again, this is perfectly allowed in the GKS method.

- Adding a fraction a of HF exchange decreases the **self-interaction error**, which tends to favor too much delocalized electron densities. However, a too large a tends to increase the **static-correlation error** (stretched chemical bonds, transition metal elements, ...).

- In 1996, Becke proposed a simpler **one-parameter hybrid (1H) approximation**

$$E_{\mathrm{xc}}^{\mathrm{1H}}[\Phi] = a\, E_{\mathrm{x}}^{\mathrm{HF}}[\Phi] + (1-a)\, E_{\mathrm{x}}^{\mathrm{DFA}}[n_\Phi] + E_{\mathrm{c}}^{\mathrm{DFA}}[n_\Phi]$$

  where $E_{\mathrm{x}}^{\mathrm{DFA}}$ and $E_{\mathrm{c}}^{\mathrm{DFA}}$ can be any semilocal density-functional approximations (DFAs).

- The optimal a is often around 0.25. Example: PBE0 = HF/PBE hybrid with $a = 0.25$.

- A strategy is to use flexible $E_{\mathrm{x}}^{\mathrm{DFA}}$ and $E_{\mathrm{c}}^{\mathrm{DFA}}$ in a hybrid approximation and optimize many parameters on molecular properties.
  Example: B97 (13 parameters) and M06 and M06-2X (36 parameters).

Range-separated hybrid approximations

- Based on ideas of Savin (1996), Hirao and coworkers (2001) proposed a **long-range correction (LC)** scheme

$$E_{\text{xc}}^{\text{LC}}[\Phi] = E_{\text{x}}^{\text{lr,HF}}[\Phi] + E_{\text{x}}^{\text{sr,DFA}}[n_\Phi] + E_{\text{c}}^{\text{DFA}}[n_\Phi]$$

  where

  - $E_{\text{x}}^{\text{lr,HF}}[\Phi]$ is the HF exchange energy for the **long-range electron-electron interaction** $\frac{\text{erf}(\mu r_{12})}{r_{12}}$ replacing the Coulomb interaction $\frac{1}{r_{12}}$,
  - $E_{\text{x}}^{\text{sr,DFA}}[n]$ is a semilocal DFA exchange energy for the complement **short-range electron-electron interaction** (semilocal DFAs are more accurate if limited to short-range interactions),
  - the range-separation parameter μ (also sometimes denoted as ω) is often taken as $\mu \approx 0.3 - 0.5$ bohr^{-1}.

  Example: LC-ωPBE

- In 2004, Yanai, Tew, and Handy introduced a more flexible decomposition called the **Coulomb-attenuating method (CAM)**

$$E_{\text{xc}}^{\text{CAM}}[\Phi] = a\, E_{\text{x}}^{\text{sr,HF}}[\Phi] + b\, E_{\text{x}}^{\text{lr,HF}}[\Phi] + (1-a)\, E_{\text{x}}^{\text{sr,DFA}}[n_\Phi] + (1-b)\, E_{\text{x}}^{\text{lr,DFA}}[n_\Phi] + E_{\text{c}}^{\text{DFA}}[n_\Phi]$$

  Examples: CAM-B3LYP, ωB97X
  A special case: HSE ($b = 0$)

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  - Semiempirical dispersion corrections
  - Nonlocal van der Waals density functionals

Double-hybrid approximations

- In 2006, Grimme introduced a **two-parameter double-hybrid (2DH) approximation**

  $$E_{\mathrm{xc}}^{\mathrm{2DH}} = a_{\mathrm{x}}\, E_{\mathrm{x}}^{\mathrm{HF}}[\Phi] + (1-a_{\mathrm{x}})\, E_{\mathrm{x}}^{\mathrm{DFA}}[n_\Phi] + (1-a_{\mathrm{c}}) E_{\mathrm{c}}^{\mathrm{DFA}}[n_\Phi] + a_{\mathrm{c}} E_{\mathrm{c}}^{\mathrm{MP2}}$$

  where the MP2-like correlation energy $E_{\mathrm{c}}^{\mathrm{MP2}}$ is added a posteriori with the previously calculated orbitals. Example: B2-PLYP ($a_{\mathrm{x}} = 0.53$ and $a_{\mathrm{c}} = 0.27$).

- The presence of nonlocal MP2 correlation allows one to use a larger fraction of nonlocal HF exchange.

- In 2011, Sharkas, Toulouse, and Savin showed that double hybrids can be understood as approximations of a **multideterminant extension of the KS method** based on the adiabatic-connection formalism in which the exact ground-state energy is written as

  $$E_0 = \min_{\Psi \in \mathcal{W}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \lambda \hat{W}_{\mathrm{ee}} | \Psi \rangle + \bar{E}_{\mathrm{Hxc}}^{\lambda}[n_\Psi] \right\}$$

  where $\bar{E}_{\mathrm{Hxc}}^{\lambda}[n] = (1-\lambda) E_{\mathrm{H}}[n] + (1-\lambda) E_{\mathrm{x}}[n] + \bar{E}_{\mathrm{c}}^{\lambda}[n]$ and $\bar{E}_{\mathrm{c}}^{\lambda}[n] = E_{\mathrm{c}}[n] - \lambda^2 E_{\mathrm{c}}[n_{1/\lambda}]$.

  - At second order of a non-linear Møller-Plesset-like perturbation theory, and using $E_{\mathrm{c}}[n_{1/\lambda}] \approx E_{\mathrm{c}}[n]$, we obtain a **one-parameter double-hybrid (1DH) approximation**

    $$E_{\mathrm{xc}}^{\mathrm{1DH}} = \lambda\, E_{\mathrm{x}}^{\mathrm{HF}}[\Phi] + (1-\lambda)\, E_{\mathrm{x}}^{\mathrm{DFA}}[n_\Phi] + (1-\lambda^2) E_{\mathrm{c}}^{\mathrm{DFA}}[n_\Phi] + \lambda^2 E_{\mathrm{c}}^{\mathrm{MP2}}$$

  - The multideterminant extension of the KS method can also be used to rigorously combine wave-function methods such as MCSCF with DFT.

Range-separated double-hybrid approximations

- In 1996, Savin introduced the **range-separated multideterminant extension of the KS scheme** in which the exact ground-state energy is written as

$$E_0 = \min_{\Psi \in \mathcal{W}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\text{sr}}[n_\Psi] \right\}$$

  where $\hat{W}_{\text{ee}}^{\text{lr}}$ is the long-range electron-electron operator for the pair potential $\text{erf}(\mu r_{12})/r_{12}$ and $\bar{E}_{\text{Hxc}}^{\text{sr}}[n]$ is the complementary short-range density functional.

- The approach can be used to rigorously combine any wave-function method with DFT.

- In 2005, Ángyán, Gerber, Savin, and Toulouse introduced a **range-separated double-hybrid (RSDH)** approximation (also called RSH+MP2)

$$E_{\text{xc}}^{\text{RSDH}} = E_{\text{x}}^{\text{lr,HF}}[\Phi] + E_{\text{x}}^{\text{sr,DFA}}[n_\Phi] + E_{\text{c}}^{\text{sr,DFA}}[n_\Phi] + E_{\text{c}}^{\text{lr,MP2}}$$

  - Obtained as second order of a non-linear Møller-Plesset-like perturbation theory.
  - Long-range MP2 is qualitatively correct for London dispersion interactions.
  - Long-range MP2 has a fast convergence with the one-electron basis size.

- Extensions of this scheme to a more flexible CAM decomposition have also been proposed.

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Semiempirical dispersion corrections

- To explicitly account for London dispersion interactions, it has been proposed in the 2000s to add to the standard approximate functionals a **semiempirical dispersion correction** of the form

$$E_{\text{disp}} = -s \sum_{\alpha<\beta} f(R_{\alpha\beta}) \frac{C_6^{\alpha\beta}}{R_{\alpha\beta}^6}$$

  where
  - $R_{\alpha\beta}$ is the distance between a pair of atoms,
  - $C_6^{\alpha\beta}$ is the dispersion coefficient between these atoms,
  - $f(R_{\alpha\beta})$ is a damping function which tends to 1 at large $R_{\alpha\beta}$ and tends to 0 at small $R_{\alpha\beta}$,
  - s is a scaling parameter that can be adjusted for each approximate functional.
- The dispersion coefficients $C_6^{\alpha\beta}$ are empirically obtained from tabulated data.
- The most recent versions also includes $C_8^{\alpha\beta}$ two-body terms and $C_9^{\alpha\beta\gamma}$ three-body terms.
- This approach was named "DFT-D" by Grimme. Examples of DFT-D functionals: PBE-D, B97-D, B3LYP-D, ωB97X-D, B2PLYP-D.
- There are also various proposals to make the determination of dispersion coefficients less empirical, e.g. Becke and Johnson (2007), Tkatchenko and Scheffler (2009), Sato and Nakai (2010).

Nonlocal van der Waals density functionals

- Another approach to describe dispersion interactions is to add to the standard approximate functionals a **nonlocal van der Waals density functional** of the form

  $$E_c^{\mathrm{nl}}[n] = \frac{1}{2} \iint n(\mathbf{r}_1) n(\mathbf{r}_2) \phi(\mathbf{r}_1, \mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

  where $\phi(\mathbf{r}_1, \mathbf{r}_2)$ is a correlation kernel.
- Two main families of such nonlocal correlation functionals exist: the "van der Waals density functionals" (vdW-DF) of Langreth, Lundqvist and coworkers and the Vydrov-Van Voorhis (VV) functionals.
- For example, the VV10 nonlocal correlation functional (2010) uses a theory-based kernel $\phi(\mathbf{r}_1, \mathbf{r}_2)$ with two adjustable parameters.
- Nonlocal van der Waals density functionals are less empirical but more computationally expensive than semiempirical dispersion corrections.
- Examples of functionals using VV10: ωB97X-V and ωB97M-V.

Outline

1. Basic density-functional theory
    - Quantum many-electron problem
    - Universal density functional
    - Kohn-Sham method
    - Generalized Kohn-Sham method
2. Exact constraints for the exchange-correlation functional
    - Exact expressions for the exchange and correlation functionals
    - Uniform coordinate scaling
    - One-orbital spatial regions and self-interaction
    - Lieb-Oxford lower bound
    - Frontier orbital energies
3. Usual approximations for the exchange-correlation energy
    - Local-density approximation
    - Semilocal approximations
    - Single-determinant hybrid approximations
    - Multideterminant hybrid approximations
    - Dispersion corrections
4. Additional topics in density-functional theory
    - Time-dependent density-functional theory
    - Some less usual orbital-dependent exchange-correlation functionals
    - Fractional electron numbers and frontier orbital energies

Outline

4 Additional topics in density-functional theory

Time-dependent density-functional theory (TDDFT)

- Consider the **time-dependent electronic Schrödinger equation** with an external **time-dependent potential** $\hat{V}(t)$

$$i\frac{\partial|\Psi(t)\rangle}{\partial t} = \left(\hat{T} + \hat{W}_{\text{ee}} + \hat{V}(t)\right)|\Psi(t)\rangle$$

- Similarly to the Hohenberg-Kohn theorem, **Runge and Gross** (1984) showed that, for a given initial wave function $\Psi(0)$, the time-dependent density $n(\mathbf{r},t)$ determines the time-dependent potential $v(\mathbf{r},t)$ up to an arbitrary additive time function:

$$n(\mathbf{r},t) \xrightarrow[\text{Runge-Gross}]{} v(\mathbf{r},t) + c(t)$$

- We can thus set up a **time-dependent non-interacting KS system**

$$i\frac{\partial\varphi_i(\mathbf{r},t)}{\partial t} = \left(-\frac{1}{2}\nabla^2 + v_{\text{s}}(\mathbf{r},t)\right)\varphi_i(\mathbf{r},t)$$

  where the time-dependent KS potential $v_{\text{s}}(\mathbf{r},t) = v(\mathbf{r},t) + v_{\text{Hxc}}(\mathbf{r},t)$ **reproduces the evolution of the exact density** as $n(\mathbf{r},t) = \sum_{i=1}^{N}|\varphi_i(\mathbf{r},t)|^2$.

- *Remark: The proof of the Runge-Gross theorem was later shown not to apply to Coulomb interactions! Also, Runge and Gross established a TDDFT variational theorem, but it was later shown to violate causality. Several different possible solutions to these problems have been proposed but they are not yet accepted as mathematically rigorous.*

Linear-response TDDFT

- Let us consider a time-periodic potential of frequency ω. In Fourier space, a variation of the KS potential $v_s(\mathbf{r}_1,\omega)$ caused by a variation of the density $n(\mathbf{r}_2,\omega)$ can be written as

$$\frac{\delta v_s(\mathbf{r}_1,\omega)}{\delta n(\mathbf{r}_2,\omega)} = \frac{\delta v(\mathbf{r}_1,\omega)}{\delta n(\mathbf{r}_2,\omega)} + \frac{\delta v_{\text{Hxc}}(\mathbf{r}_1,\omega)}{\delta n(\mathbf{r}_2,\omega)}$$

- This can be rewritten as

$$\chi_s^{-1}(\mathbf{r}_1,\mathbf{r}_2,\omega) = \chi^{-1}(\mathbf{r}_1,\mathbf{r}_2,\omega) + f_{\text{Hxc}}(\mathbf{r}_1,\mathbf{r}_2,\omega)$$

  where

  - $\chi_s(\mathbf{r}_1,\mathbf{r}_2,\omega) = \delta n(\mathbf{r}_1,\omega)/\delta v_s(\mathbf{r}_2,\omega)$ is the **KS non-interacting linear-response function**
  - $\chi(\mathbf{r}_1,\mathbf{r}_2,\omega) = \delta n(\mathbf{r}_1,\omega)/\delta v(\mathbf{r}_2,\omega)$ is the **interacting linear-response function**
  - $f_{\text{Hxc}}(\mathbf{r}_1,\mathbf{r}_2,\omega) = \delta v_{\text{Hxc}}(\mathbf{r}_1,\omega)/\delta n(\mathbf{r}_2,\omega)$ is the **Hartree-exchange-correlation kernel**

- The interacting linear-response function $\chi(\mathbf{r}_1,\mathbf{r}_2,\omega)$ is thus found from the **Dyson-like response equation**

$$\chi^{-1}(\mathbf{r}_1,\mathbf{r}_2,\omega) = \chi_s^{-1}(\mathbf{r}_1,\mathbf{r}_2,\omega) - f_{\text{Hxc}}(\mathbf{r}_1,\mathbf{r}_2,\omega)$$

  or, equivalently,

$$\chi(\mathbf{r}_1,\mathbf{r}_2,\omega) = \chi_s(\mathbf{r}_1,\mathbf{r}_2,\omega) + \iint d\mathbf{r}_3 d\mathbf{r}_4 \; \chi_s(\mathbf{r}_1,\mathbf{r}_3,\omega) \; f_{\text{Hxc}}(\mathbf{r}_3,\mathbf{r}_4,\omega) \; \chi(\mathbf{r}_4,\mathbf{r}_2,\omega)$$

Excitation energies from linear-response TDDFT

- The KS linear-response function has poles at the KS (de-)excitation energies

$$\chi_s(\mathbf{r}_1,\mathbf{r}_2,\omega) = \sum_{\sigma\in\{\uparrow,\downarrow\}} \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} \left[\frac{\varphi_{i\sigma}^*(\mathbf{r}_1)\varphi_{a\sigma}(\mathbf{r}_1)\varphi_{a\sigma}^*(\mathbf{r}_2)\varphi_{i\sigma}(\mathbf{r}_2)}{\omega-(\varepsilon_a-\varepsilon_i)+i0^+} - \frac{\varphi_{a\sigma}^*(\mathbf{r}_1)\varphi_{i\sigma}(\mathbf{r}_1)\varphi_{i\sigma}^*(\mathbf{r}_2)\varphi_{a\sigma}(\mathbf{r}_2)}{\omega+(\varepsilon_a-\varepsilon_i)+i0^+} \right]$$

- Similarly, $\chi(\mathbf{r}_1,\mathbf{r}_2,\omega)$ has poles at the exact excitation energies $\omega_n = E_n - E_0$.

- Writing $\chi^{-1}(\omega) = \chi_s^{-1}(\omega) - f_{\text{Hxc}}(\omega)$ in the spin-orbital tensor-product basis $\{\psi_i^*\psi_a, \psi_a^*\psi_i\}$

$$\boldsymbol{\chi}^{-1}(\omega) = -\left[\begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}(-\omega)^* & \mathbf{A}(-\omega)^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]$$

  where the matrices $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ are

$$[\mathbf{A}(\omega)]_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \langle aj|f_{\text{Hxc}}(\omega)|ib\rangle$$

$$[\mathbf{B}(\omega)]_{ia,jb} = \langle ab|f_{\text{Hxc}}(\omega)|ij\rangle$$

- The excitation energies ω_n can be calculated from the generalized eigenvalue equation

$$\begin{pmatrix} \mathbf{A}(\omega_n) & \mathbf{B}(\omega_n) \\ \mathbf{B}(-\omega_n)^* & \mathbf{A}(-\omega_n)^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}$$

The Hartree-exchange-correlation kernel

- In linear-response TDDFT, the key quantity to be approximated is the **Hartree-exchange-correlation kernel**

$$f_{\mathrm{Hxc}}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \frac{\delta v_{\mathrm{Hxc}}(\mathbf{r}_1, \omega)}{\delta n(\mathbf{r}_2, \omega)}$$

- It can be decomposed as

$$f_{\mathrm{Hxc}}(\mathbf{r}_1, \mathbf{r}_2, \omega) = f_{\mathrm{H}}(\mathbf{r}_1, \mathbf{r}_2) + f_{\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2, \omega)$$

  where the Hartree kernel is simply $f_{\mathrm{H}}(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$.

- In almost all TDDFT calculations, the frequency dependence of f_{xc} is neglected, which is called the **adiabatic approximation**

$$f_{\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2, \omega) \approx \frac{\delta v_{\mathrm{xc}}(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)} = \frac{\delta^2 E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)}$$

  with the notorious consequence that only single-electron excitations are taken into account (double excitations and higher are missing).

- To describe nonlocal excitations, such as charge-transfer excitations, range-separated hybrid approximations are often used. The kernel has then the expression

$$f_{\mathrm{xc}} = f_{\mathrm{x}}^{\mathrm{lr},\mathrm{HF}} + f_{\mathrm{x}}^{\mathrm{sr},\mathrm{DFA}} + f_{\mathrm{c}}^{\mathrm{DFA}}$$

  where $f_{\mathrm{x}}^{\mathrm{lr},\mathrm{HF}}$ is the long-range HF exchange kernel.

Outline

Orbital-dependent exchange-correlation functionals

- We discuss here some exchange-correlation energy functionals **depending explicitly on the KS orbitals and KS orbital energies**: $E_{\text{xc}}[\{\varphi_p\}, \{\varepsilon_p\}]$

- Since the KS orbitals and KS orbital energies are implicit functionals of the density, i.e. $\varphi_p[n](\mathbf{r})$ and $\varepsilon_p[n]$, these exchange-correlation expressions are **implicit functionals of the density**.

- In fact, the (range-separated) hybrid and double-hybrid approximations that we have seen already are sometimes considered to belong to this family, but they are more commonly considered within the GKS method, i.e. the orbitals are obtained with a **nonlocal** potential.

- Here, we are concerned with orbital-dependent exchange-correlation energy functionals within the KS method, i.e. with orbitals obtained with a **local potential**: $v_{\text{xc}}(\mathbf{r}) = \dfrac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}$

- Then, the calculation of the potential $v_{\text{xc}}(\mathbf{r})$ requires the **optimized-effective-potential (OEP) method**, which tends to be computationally involved.

Exact exchange

- The **exact exchange (EXX)** energy functional is

$$E_x = -\frac{1}{2} \sum_{\sigma \in \{\uparrow,\downarrow\}} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \iint \frac{\varphi_{i\sigma}^*(\mathbf{r}_1)\varphi_{j\sigma}(\mathbf{r}_1)\varphi_{j\sigma}^*(\mathbf{r}_2)\varphi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

  It has exactly the same form as the HF exchange energy, but the orbitals used in this expression are different.

- The associated EXX potential $v_x(\mathbf{r})$ is calculated using the chain rule via the total KS potential $v_s(\mathbf{r})$

$$\frac{\delta E_x}{\delta v_s(\mathbf{r})} = \int \frac{\delta E_x}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} \mathrm{d}\mathbf{r}'$$

- Introducing the non-interacting KS static linear-response function $\chi_s(\mathbf{r}', \mathbf{r}) = \delta n(\mathbf{r}')/\delta v_s(\mathbf{r})$, we find the **OEP equation for the EXX potential**

$$\int v_x(\mathbf{r}')\chi_s(\mathbf{r}', \mathbf{r})\mathrm{d}\mathbf{r}' = \frac{\delta E_x}{\delta v_s(\mathbf{r})}$$

  Explicit expressions in terms of the orbitals can be derived for $\delta E_x/\delta v_s(\mathbf{r})$ and $\chi_s(\mathbf{r}', \mathbf{r})$.

- The EXX occupied orbitals are very similar the HF ones, but the EXX virtual orbitals are much less diffuse than the HF ones ($v_x(\mathbf{r}) \underset{r\to\infty}{\sim} -1/r$ for all orbitals, contrary to HF).

Görling-Levy perturbation theory (1/2)

- In 1993, Görling and Levy developed a **perturbation theory in terms of the coupling constant λ of the adiabatic connection**.

- The Hamiltonian along the adiabatic connection (keeping the density constant) is

$$\hat{H}^{\lambda} = \hat{T} + \lambda \hat{W}_{\text{ee}} + \hat{V}^{\lambda} = \hat{H}_{\text{s}} + \lambda(\hat{W}_{\text{ee}} - \hat{V}_{\text{Hx}}) - \lambda^2 \hat{V}_{\text{c}}^{(2)} - \cdots$$

where we have used $\hat{V}^{\lambda} = \hat{V}_{\text{s}} - \lambda \hat{V}_{\text{Hx}} - \hat{V}_{\text{c}}^{\lambda} = \hat{V}_{\text{s}} - \lambda \hat{V}_{\text{Hx}} - \lambda^2 \hat{V}_{\text{c}}^{(2)} - \cdots$

- At $\lambda = 0$, we have the KS non-interacting reference Hamiltonian $\hat{H}_{\text{s}} = \hat{T} + \hat{V}_{\text{s}}$

$$\hat{H}_{\text{s}} |\Phi_n\rangle = \mathcal{E}_n |\Phi_n\rangle$$

where $\Phi_0 \equiv \Phi$ is the ground-state KS determinant.

- The intermediate-normalized ground-state wave function $\tilde{\Psi}^{\lambda} = \Psi^{\lambda} / \langle \Phi | \Psi^{\lambda} \rangle$ of $\hat{H}^{\lambda}$ is expanded in powers of λ

$$|\tilde{\Psi}^{\lambda}\rangle = |\Phi\rangle + \lambda |\tilde{\Psi}^{(1)}\rangle + \cdots \quad \text{with} \quad |\tilde{\Psi}^{(1)}\rangle = -\sum_{n \neq 0} \frac{\langle \Phi_n | \hat{W}_{\text{ee}} - \hat{V}_{\text{Hx}} | \Phi \rangle}{\mathcal{E}_n - \mathcal{E}_0} |\Phi_n\rangle$$

assuming a **nondegenerate KS ground state**.

Görling-Levy perturbation theory (2/2)

- The correlation energy is then expanded in powers of λ

$$E_c^\lambda = \langle \Psi^\lambda | \hat{T} + \lambda \hat{W}_{ee} | \Psi^\lambda \rangle - \langle \Phi | \hat{T} + \lambda \hat{W}_{ee} | \Phi \rangle = E_c^{(0)} + \lambda E_c^{(1)} + \lambda^2 E_c^{(2)} + \cdots$$

where the zeroth- and first-order terms vanish: $E_c^{(0)} = 0$ and $E_c^{(1)} = (\partial E_c^\lambda / \partial \lambda)_{\lambda=0} = 0$

- The second-order term is the **second-order Görling-Levy (GL2) correlation energy**

$$E_c^{\text{GL2}} \equiv E_c^{(2)} = \langle \Phi | \hat{W}_{ee} | \tilde{\Psi}^{(1)} \rangle = \langle \Phi | \hat{W}_{ee} - \hat{V}_{\text{Hx}} | \tilde{\Psi}^{(1)} \rangle$$

where we have used $\langle \Phi | \hat{V}_{\text{Hx}} | \tilde{\Psi}^{(1)} \rangle = 0$ since it is the derivative with respect to λ at $\lambda = 0$ of $\langle \Psi^\lambda | \hat{V}_{\text{Hx}} | \Psi^\lambda \rangle = \int v_{\text{Hx}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$ which does not depend on λ.

- The **GL2 correlation energy** is thus

$$E_c^{\text{GL2}} = - \sum_{n \neq 0} \frac{|\langle \Phi | \hat{W}_{ee} - \hat{V}_{\text{Hx}} | \Phi_n \rangle|^2}{\mathcal{E}_n - \mathcal{E}_0} = E_c^{\text{MP2}} + E_c^{\text{S}}$$

with a double-excitation MP2-like term E_c^{MP2} and single-excitation term E_c^{S}

$$E_c^{\text{MP2}} = -\frac{1}{4} \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

and

$$E_c^{\text{S}} = - \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{|\langle i | \hat{V}_x^{\text{HF}} - \hat{V}_x | a \rangle|^2}{\varepsilon_a - \varepsilon_i}$$

- In practice, results are often disappointing! It is preferable to go beyond second order with the random-phase approximation.

Adiabatic-connection fluctuation-dissipation approach (1/2)

- The **adiabatic-connection formula** for the correlation energy is

$$E_c = \frac{1}{2}\int_0^1 d\lambda \iint \frac{n_{2,c}^{\lambda}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- The correlation part of the pair density can be written

$$n_{2,c}^{\lambda}(\mathbf{r}_1,\mathbf{r}_2) = \langle \Psi^{\lambda}|\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)|\Psi^{\lambda}\rangle - \langle \Phi|\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)|\Phi\rangle$$

  where $\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)$ is the pair-density operator.

- We use the expression of the pair-density operator in terms of the density operator $\hat{n}(\mathbf{r})$

$$\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2) = \hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) - \delta(\mathbf{r}_1-\mathbf{r}_2)\hat{n}(\mathbf{r}_1)$$

  and the fact that the density is constant along the adiabatic connection

$$\langle \Psi^{\lambda}|\hat{n}(\mathbf{r}_1)|\Psi^{\lambda}\rangle = \langle \Phi|\hat{n}(\mathbf{r}_1)|\Phi\rangle$$

- We thus see that the correlation pair density can be written as

$$n_{2,c}^{\lambda}(\mathbf{r}_1,\mathbf{r}_2) = \langle \Psi^{\lambda}|\hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2)|\Psi^{\lambda}\rangle - \langle \Phi|\hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2)|\Phi\rangle$$

Adiabatic-connection fluctuation-dissipation approach (2/2)

- Let us consider the **linear-response function along the adiabatic connection**

$$\chi_\lambda(\mathbf{r}_1,\mathbf{r}_2,\omega) = \sum_{n\neq 0} \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_1)|\Psi_n^\lambda\rangle\langle \Psi_n^\lambda|\hat{n}(\mathbf{r}_2)|\Psi^\lambda\rangle}{\omega-\omega_n^\lambda+i0^+} - \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi_n^\lambda\rangle\langle \Psi_n^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle}{\omega+\omega_n^\lambda+i0^+}$$

  where the sum is over all eigenstates Ψ_n^λ of the Hamiltonian $\hat{H}^\lambda$, i.e. $\hat{H}^\lambda|\Psi_n^\lambda\rangle = E_n^\lambda|\Psi_n^\lambda\rangle$, except the ground state $\Psi^\lambda \equiv \Psi_0^\lambda$, and $\omega_n^\lambda = E_n^\lambda - E_0^\lambda$ are the excitation energies.

- By contour integrating $\chi_\lambda(\mathbf{r}_1,\mathbf{r}_2,\omega)$ around the right half ω-complex plane, we arrive at the **fluctuation-dissipation theorem**

$$n_{2,\mathrm{c}}^\lambda(\mathbf{r}_1,\mathbf{r}_2) = -\int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi} \left[\chi_\lambda(\mathbf{r}_1,\mathbf{r}_2,i\omega) - \chi_\mathrm{s}(\mathbf{r}_1,\mathbf{r}_2,i\omega)\right]$$

  which relates ground-state correlations in the time-independent system $n_{2,\mathrm{c}}^\lambda(\mathbf{r}_1,\mathbf{r}_2)$ to the linear response of the system $\chi_\lambda(\mathbf{r}_1,\mathbf{r}_2,\omega)$ due to a time-dependent external perturbation.

- We thus have the **adiabatic-connection fluctuation-dissipation** (ACFD) formula for the correlation energy

$$E_\mathrm{c} = -\frac{1}{2}\int_0^1 \mathrm{d}\lambda \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi} \iint \frac{\chi_\lambda(\mathbf{r}_1,\mathbf{r}_2,i\omega) - \chi_\mathrm{s}(\mathbf{r}_1,\mathbf{r}_2,i\omega)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

Random-phase approximation

- The ACFD formula involves $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2, i\omega)$ which can be obtained from linear-response TDDFT

$$\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \omega) = \chi_\mathrm{s}(\mathbf{r}_1, \mathbf{r}_2, \omega) + \iint \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4 \; \chi_\mathrm{s}(\mathbf{r}_1, \mathbf{r}_3, \omega) \; f_\mathrm{Hxc}^\lambda(\mathbf{r}_3, \mathbf{r}_4, \omega) \; \chi_\lambda(\mathbf{r}_4, \mathbf{r}_2, \omega)$$

- The simplest approximation is the (direct) **random-phase approximation (RPA)**

$$f_\mathrm{Hxc}^\lambda(\mathbf{r}_1, \mathbf{r}_2, \omega) \approx f_\mathrm{H}^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \lambda w_\mathrm{ee}(\mathbf{r}_1, \mathbf{r}_2)$$

where $w_\mathrm{ee}(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ is the Coulomb interaction.

- By iterating the TDDFT response equation, we find the RPA linear-response function

$$\boldsymbol{\chi}_\lambda^\mathrm{RPA}(\omega) = \boldsymbol{\chi}_\mathrm{s}(\omega) + \lambda \; \boldsymbol{\chi}_\mathrm{s}(\omega)\mathbf{w}_\mathrm{ee}\boldsymbol{\chi}_\mathrm{s}(\omega) + \lambda^2 \; \boldsymbol{\chi}_\mathrm{s}(\omega)\mathbf{w}_\mathrm{ee}\boldsymbol{\chi}_\mathrm{s}(\omega)\mathbf{w}_\mathrm{ee}\boldsymbol{\chi}_\mathrm{s}(\omega) + \cdots$$

- Finally, the **(direct) RPA correlation energy** is

$$E_\mathrm{c}^\mathrm{RPA} = -\frac{1}{2}\int_0^1 \mathrm{d}\lambda \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{Tr}\left[\mathbf{w}_\mathrm{ee}\left(\lambda\boldsymbol{\chi}_\mathrm{s}(i\omega)\mathbf{w}_\mathrm{ee}\boldsymbol{\chi}_\mathrm{s}(i\omega) + \lambda^2\boldsymbol{\chi}_\mathrm{s}(i\omega)\mathbf{w}_\mathrm{ee}\boldsymbol{\chi}_\mathrm{s}(i\omega)\mathbf{w}_\mathrm{ee}\boldsymbol{\chi}_\mathrm{s}(i\omega) + \cdots\right)\right]$$

which can be exactly summed.

- The (direct) RPA correlation energy corresponds to the sum of all **direct ring diagrams**. It accounts for long-range van der Waals dispersion interactions. However, it shows large self-interaction errors, which can be overcome by adding exchange diagrams.

Outline

4 Additional topics in density-functional theory

- Time-dependent density-functional theory
- Some less usual orbital-dependent exchange-correlation functionals
    - Exact exchange
    - Görling-Levy perturbation theory
    - Adiabatic-connection fluctuation-dissipation approach
- Fractional electron numbers and frontier orbital energies
    - Quantum mechanics with fractional electron numbers
    - Density-functional theory with fractional electron numbers
    - The HOMO energy and the ionization energy
    - The LUMO energy, the electron affinity, and the derivative discontinuity

Quantum mechanics with fractional electron numbers (1/2)

- The ground-state energy of a system with a **fractional number of electrons** $\mathcal{N} = N - 1 + f$ (where N is an integer and $0 \leq f \leq 1$) can be defined as

$$E_0^{N-1+f} = \min_{\hat{\Gamma} \in \mathcal{D}_{\text{DM}}^{N-1+f}} \text{Tr}\left[\left(\hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}\right)\hat{\Gamma}\right]$$

  where the minimization is over **ensemble density matrices** $\hat{\Gamma}$ in the set

$$\mathcal{D}_{\text{DM}}^{N-1+f} = \left\{\hat{\Gamma} = (1-f)|\Psi^{N-1}\rangle\langle\Psi^{N-1}| + f|\Psi^{N}\rangle\langle\Psi^{N}|,\ \Psi^{N-1} \in \mathcal{W}^{N-1}, \Psi^{N} \in \mathcal{W}^{N}\right\}$$

  where f is fixed, and Ψ^{N-1} and Ψ^{N} are arbitrary wave functions in the $(N-1)$- and N-electron admissible wave-function sets $\mathcal{W}^{N-1}$ and $\mathcal{W}^{N}$, respectively.

- The minimizing ensemble density matrix is

$$\hat{\Gamma}_0 = (1-f)\ |\Psi_0^{N-1}\rangle\langle\Psi_0^{N-1}| + f\ |\Psi_0^{N}\rangle\langle\Psi_0^{N}|$$

  where Ψ_0^{N-1} and Ψ_0^{N} are the $(N-1)$- and N-electron ground-state wave functions.

- The ground-state energy is **linear** in f between the integer numbers $N-1$ and N

$$E_0^{N-1+f} = (1-f)\ E_0^{N-1} + f\ E_0^{N}$$

  where E_0^{N-1} and E_0^{N} are the $(N-1)$- and N-electron ground-state energies.

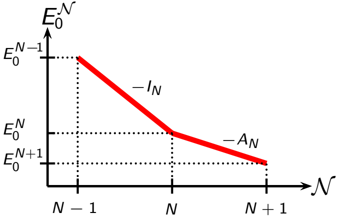
- Similarly, between the integer electron numbers N and $N+1$, we have

$$E_0^{N+f} = (1-f)\ E_0^{N} + f\ E_0^{N+1}$$

Quantum mechanics with fractional electron numbers (2/2)

- The ground-state energy is a **continuous piecewise linear function** of the fractional electron number $\mathcal{N}$.
- The derivative of $E_0^{\mathcal{N}}$ with respect to $\mathcal{N}$ defines the **electronic chemical potential**

$$\mu = \frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}}$$



- Taking the derivative with respect to $\mathcal{N}$ corresponds to taking the derivative with respect to f, we find for $N-1 < \mathcal{N} < N$

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}}\right)_{N-1<\mathcal{N}<N} = E_0^{N} - E_0^{N-1} = -I_N$$

  where I_N is the **ionization energy** of the N-electron system.

- Similarly for $N < \mathcal{N} < N+1$

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}}\right)_{N<\mathcal{N}<N+1} = E_0^{N+1} - E_0^{N} = -A_N$$

  where A_N is the **electron affinity** of the N-electron system.

- The electronic chemical potential μ has thus a **discontinuity** at the integer electron number N. So, the plot of $E_0^{\mathcal{N}}$ with respect to $\mathcal{N}$ is made of a series of straight lines between integer electron numbers, with derivative discontinuities at each integer.

DFT with fractional electron numbers (1/2)

- The universal density functional $F[n]$ is extended to densities integrating to a fractional electron number, $\int n(\mathbf{r})\mathrm{d}\mathbf{r} = \mathcal{N} = N - 1 + f$, as

$$F[n] = \min_{\substack{\hat{\Gamma} \in \mathcal{D}_{\mathrm{DM}}^{N-1+f} \\ \hat{\Gamma} \to n}} \mathrm{Tr}\left[\left(\hat{T} + \hat{W}_{\mathrm{ee}}\right)\hat{\Gamma}\right]$$

- To set up a KS method, we introduce the decomposition $F[n] = T_{\mathrm{s}}[n] + E_{\mathrm{Hxc}}[n]$ where

$$T_{\mathrm{s}}[n] = \min_{\substack{\hat{\Gamma}_{\mathrm{s}} \in \mathcal{D}_{\mathrm{DM,s}}^{N-1+f} \\ \hat{\Gamma}_{\mathrm{s}} \to n}} \mathrm{Tr}[\hat{T}\hat{\Gamma}_{\mathrm{s}}]$$

  is the KS non-interacting kinetic-energy functional and the minimization is over ensemble non-interacting density matrices $\hat{\Gamma}_{\mathrm{s}}$ in the set

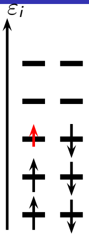
$$\mathcal{D}_{\mathrm{DM,s}}^{N-1+f} = \left\{ \hat{\Gamma}_{\mathrm{s}} = (1-f)\,|\Phi^{N-1,f}\rangle\langle\Phi^{N-1,f}| + f\,|\Phi^{N,f}\rangle\langle\Phi^{N,f}| \right\}$$

  where $\Phi^{N-1,f}$ and $\Phi^{N,f}$ are $(N-1)$- and N-electron single-determinant wave functions, constructed from a **common set of orbitals** $\{\varphi_i\}$ depending on the fixed f.

- The exact ground-state energy can then be expressed as

$$E_0^{N-1+f} = \min_{\hat{\Gamma}_{\mathrm{s}} \in \mathcal{D}_{\mathrm{DM,s}}^{N-1+f}} \left\{ \mathrm{Tr}\left[\left(\hat{T} + \hat{V}_{\mathrm{ne}}\right)\hat{\Gamma}_{\mathrm{s}}\right] + E_{\mathrm{Hxc}}[n_{\hat{\Gamma}_{\mathrm{s}}}] \right\}$$

DFT with fractional electron numbers (2/2)



- The total energy can be written in terms of **orbital occupation numbers** n_i

$$E^{N-1+f} = \sum_{i=1}^{N} n_i \int \varphi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) d\mathbf{r} + E_{\text{Hxc}}[n]$$

  with the density $n(\mathbf{r}) = \sum_{i=1}^{N} n_i \left|\varphi_i(\mathbf{r})\right|^2$ and the occupation numbers $n_i = 1$ for $i \leq N-1$ and $n_N = f$ for the HOMO (ignoring degeneracy for simplicity).

- The orbitals satisfy standard-looking KS equations

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{s}}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad \text{with} \quad v_{\text{s}}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \frac{\delta E_{\text{Hxc}}[n]}{\delta n(\mathbf{r})}$$

  with the important difference that we can now fix the arbitrary constant in $v_{\text{s}}(\mathbf{r})$. This is because we can now allow variations of $n(\mathbf{r})$ changing $\mathcal{N}$, i.e. $\int \delta n(\mathbf{r}) d\mathbf{r} \neq 0$

$$\delta E_{\text{Hxc}}[n] = \int \left(\frac{\delta E_{\text{Hxc}}[n]}{\delta n(\mathbf{r})} + \text{const} \right) \delta n(\mathbf{r}) d\mathbf{r}$$

  making the constant no longer arbitrary. This unambiguously fixes the values of the KS orbital energies ε_i.

- **Janak's theorem** (1978): After optimizing the orbitals with fixed occupation numbers, we have

$$\frac{\partial E^{\mathcal{N}}}{\partial n_i} = \varepsilon_i \qquad \text{for occupied orbitals}$$

The HOMO energy and the ionization energy

- For clarity in the discussion, we will now explicitly indicate the dependence on the electron number $\mathcal{N}$.
- Janak's theorem applied to the HOMO for $\mathcal{N} = N - \delta$ where $\delta \to 0^+$ gives

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}} \right)_{N-\delta} = \varepsilon_{\mathrm{H}}^{N-\delta} \equiv \varepsilon_{\mathrm{H}}^{N}$$

  where $\varepsilon_{\mathrm{H}}^{N}$ is the HOMO energy of the N-electron system (defined as the left side of discontinuity).
- This implies that the **KS HOMO energy is the opposite of the exact ionization energy**

$$\varepsilon_{\mathrm{H}}^{N} = -I_N$$

- Combining this result with the known asymptotic behavior of the exact ground-state density (for finite systems)

$$n^N(\mathbf{r}) \underset{r \to \infty}{\sim} e^{-2\sqrt{2I_N}\, r}$$

  it can be shown that it implies that the KS potential $v_{\mathrm{s}}^N(\mathbf{r}) \equiv v_{\mathrm{s}}^{N-\delta}(\mathbf{r})$ (defined as the limit from the left side) vanishes asymptotically

$$\lim_{r \to \infty} v_{\mathrm{s}}^N(\mathbf{r}) = 0$$

The LUMO energy, the electron affinity, the derivative discontinuity (1/2)

- Janak's theorem applied to the HOMO but now for $\mathcal{N} = N + \delta$ where $\delta \to 0^+$ gives

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}}\right)_{N+\delta} = \varepsilon_{\mathrm{H}}^{N+\delta} = -A_N$$

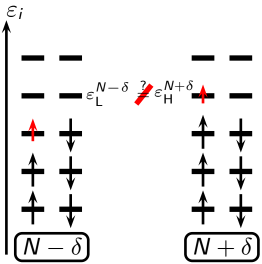
where $\varepsilon_{\mathrm{H}}^{N+\delta}$ is the HOMO energy from the right side of the discontinuity.

Remark: $\partial E_0^{\mathcal{N}}/\partial\mathcal{N}$ is constant for all $N < \mathcal{N} < N+1$, so: $\varepsilon_H^{N+\delta} = \varepsilon_H^{N+1-\delta} \equiv \varepsilon_H^{N+1}$

- One may think that $\varepsilon_{\mathrm{H}}^{N+\delta}$ is equal to the LUMO energy of the N-electron system $\varepsilon_{\mathrm{L}}^{N}$

$$\varepsilon_{\mathrm{H}}^{N+\delta} \cancel{\overset{?}{=}} \varepsilon_{\mathrm{L}}^{N} \equiv \varepsilon_{\mathrm{L}}^{N-\delta}$$

but this is WRONG!



- Let us compare $\varepsilon_{\mathrm{H}}^{N+\delta}$ and $\varepsilon_{\mathrm{L}}^{N-\delta}$:

$$\varepsilon_{\mathrm{H}}^{N+\delta} = \int \varphi_{\mathrm{H}}^{N+\delta}(\mathbf{r})^* \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}^{N+\delta}(\mathbf{r})\right) \varphi_{\mathrm{H}}^{N+\delta}(\mathbf{r})\mathrm{d}\mathbf{r}$$

$$\varepsilon_{\mathrm{L}}^{N-\delta} = \int \varphi_{\mathrm{L}}^{N-\delta}(\mathbf{r})^* \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}^{N-\delta}(\mathbf{r})\right) \varphi_{\mathrm{L}}^{N-\delta}(\mathbf{r})\mathrm{d}\mathbf{r}$$

- The density is continuous at the integer N, i.e. $n^{N+\delta}(\mathbf{r}) = n^{N-\delta}(\mathbf{r})$, but this only imposes that $v_{\mathrm{s}}^{N+\delta}(\mathbf{r})$ and $v_{\mathrm{s}}^{N-\delta}(\mathbf{r})$ be equal up to an **additive constant** (according to the Hohenberg-Kohn theorem).

The LUMO energy, the electron affinity, the derivative discontinuity (2/2)

- Indeed, it turns out that $v_s^{N+\delta}(\mathbf{r})$ and $v_s^{N-\delta}(\mathbf{r})$ do differ by a uniform constant Δ_{xc}^N

$$v_s^{N+\delta}(\mathbf{r}) - v_s^{N-\delta}(\mathbf{r}) = \Delta_{xc}^N$$

- The orbitals are continuous at the integer N, so $\varphi_H^{N+\delta}(\mathbf{r}) = \varphi_L^{N-\delta}(\mathbf{r})$, and we find

$$\varepsilon_H^{N+\delta} = \varepsilon_L^{N-\delta} + \Delta_{xc}^N$$

- In conclusion, the **KS LUMO energy is not the opposite of the exact electron affinity**

$$\varepsilon_L^N = -A_N - \Delta_{xc}^N$$

  due to the discontinuity Δ_{xc}^N in the KS potential.

- Such a discontinuity can only come from the exchange-correlation part of the potential $v_{xc}^{\mathcal{N}}(\mathbf{r})$ since $v_{ne}(\mathbf{r})$ is independent from $\mathcal{N}$ and the Hartree potential $v_H^{\mathcal{N}}(\mathbf{r}) = \int n^{\mathcal{N}}(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}'$ is a continuous function of $\mathcal{N}$. So, we have

$$\Delta_{xc}^N = v_{xc}^{N+\delta}(\mathbf{r}) - v_{xc}^{N-\delta}(\mathbf{r}) = \left(\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right)_{N+\delta} - \left(\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right)_{N-\delta}$$

  i.e. Δ_{xc}^N is the **derivative discontinuity** in the exchange-correlation energy functional $E_{xc}[n]$.

Kohn-Sham frontier orbital energies: Graphical summary