Introduction to density-functional theory

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`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_esqc_19.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`

Outline

1. Basic density-functional theory
   - The quantum many-electron problem
   - The universal density functional
   - The Kohn-Sham method

2. More advanced topics in density-functional theory
   - Exact expressions for the exchange and correlation functionals
   - Fractional electron numbers and frontier orbital energies

3. Usual approximations for the exchange-correlation energy
   - The local-density approximation
   - Semilocal approximations
   - Hybrid and double-hybrid approximations
   - Range-separated hybrid and double-hybrid approximations
   - Semiempirical dispersion corrections

4. Additional topics in density-functional theory
   - Time-dependent density-functional theory
   - Some less usual orbital-dependent exchange-correlation functionals
   - Uniform coordinate scaling

Outline

The quantum many-electron problem

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

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N} \nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ i\neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i)$$

  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**

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

  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 coordinates, and E is the associated energy.

- Using **Dirac notations** (representation-independent formalism):

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

  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**

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

where the minimization is over all N-electron antisymmetric wave functions Ψ, normalized to unity $\langle \Psi | \Psi \rangle = 1$.

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. $E_0 = \inf_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$.

- 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. $\int d\sigma = \sum_{\sigma=\uparrow,\downarrow}$.

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     - The Hohenberg-Kohn theorem
     - Levy's constrained-search formulation
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The Hohenberg-Kohn theorem

- Consider an electronic system with an arbitrary external local potential $v(\mathbf{r})$ 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 the associated **ground-state density** $n(\mathbf{r})$ can be deduced. Therefore, one has the mapping:

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

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

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

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 constant:

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

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,

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

   If $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) \neq 0$ for all $(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ and at least one fixed set of $(\sigma_1, \sigma_2, ..., \sigma_N)$, which is "true almost everywhere 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 share the same 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.

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

$$E_1 + E_2 < E_1 + E_2$$

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

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

The universal density functional and the variational property

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

$$n(\mathbf{r}) \longrightarrow v(\mathbf{r}) \longrightarrow \hat{H} \longrightarrow \text{everything}$$

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

- In particular, a **ground-state wave function** Ψ for a given potential $v(\mathbf{r})$ 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**

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

for the specific external potential $v_{\text{ne}}(\mathbf{r})$ of the system considered.

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

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

where the minimization is over N-electron densities n that are ground-state densities associated with some local potential (referred to as v-representable densities). The minimum is reached for an exact ground-state density $n_0(\mathbf{r})$ of the potential $v_{\text{ne}}(\mathbf{r})$.

Levy's constrained-search formulation

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

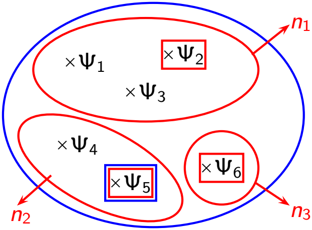
$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle = \langle \Psi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle$$

where "$\Psi \to n$" means that the minimization is done over normalized antisymmetric wave functions Ψ which yield the fixed density n.

Remark: This definition of $F[n]$ does not require the existence of a local potential associated with the density: it is defined on the larger set of N-electron densities coming from an antisymmetric wave function (referred to as N-representable densities).

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

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



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

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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**:

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

  where "$\Phi \to n$" means that the minimization is done over normalized **single-determinant** wave functions Φ which yield the fixed density n. The minimizing single-determinant wave function is called the **KS wave function** and is denoted by $\Phi[n]$.

  Remark: Introducing a single-determinant wave function is **not** *an approximation because any N-representable density n can be obtained from a single-determinant wave function.*

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

Kohn-Sham (KS) method: variational principle

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

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

  and the 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)

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

  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**

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

  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. 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** $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\delta_{\sigma_i,\sigma}$.
- The **total energy** to be minimized is

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

  and the **density** is

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

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

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

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

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

Interlude: Review on functional calculus

- For a **functional** $F[f]$ of the function $f(x)$, 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 $f(x)$: $\dfrac{\delta F[f]}{\delta f(x)}$

  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

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

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

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

  where we have used $\delta n(\mathbf{r}')/\delta \phi_i^*(\mathbf{r}) = \phi_i(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$ 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**

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

  The orbitals $\phi_i(\mathbf{r})$ 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

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

  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 $\{\phi_i(\mathbf{r})\}$ through the density.

- Physically, $h_\mathrm{s}(\mathbf{r})$ 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 $\{\phi_a(\mathbf{r})\}$ which together with the occupied KS orbitals form a complete basis since $h_\mathrm{s}(\mathbf{r})$ is a self-adjoint operator.

The Hartree-exchange-correlation potential

- *Remark: The existence of the functional derivative* $v_{Hxc}(\mathbf{r}) = \delta E_{Hxc}[n]/\delta n(\mathbf{r})$ *has been assumed. This is in fact not true for all densities but only for* v_s*-representable densities, i.e. densities that are the ground-state densities of a non-interacting system with some local potential.*
- *Remark: The KS potential is defined only up to an additive constant. For finite systems, we choose the constant so that the potential vanishes at infinity:* $\lim_{|\mathbf{r}|\to\infty} v_s(\mathbf{r}) = 0$
- Following the decomposition of $E_{\text{Hxc}}[n]$, the potential $v_{\text{Hxc}}(\mathbf{r})$ is also decomposed as

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

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

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

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

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

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

- *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** $\{\chi_\nu(\mathbf{r})\}$, e.g. GTO basis functions. The orbitals are expanded as

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

- Inserting this expansion in the KS equations

$$h_\mathrm{s}(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

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

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

  where $F_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) h_\mathrm{s}(\mathbf{r}) \chi_\nu(\mathbf{r}) \mathrm{d}\mathbf{r}$ are the elements of the KS Fock matrix and $S_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) \mathrm{d}\mathbf{r}$ 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: $h_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \chi_\nu(\mathbf{r}) \text{d}\mathbf{r}$
- $J_{\mu\nu}$ is the Hartree potential matrix:

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

where $(\chi_\mu \chi_\nu | \chi_\lambda \chi_\gamma) = \iint \frac{\chi_\mu^*(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\chi_\lambda^*(\mathbf{r}_2)\chi_\gamma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \text{d}\mathbf{r}_1 \text{d}\mathbf{r}_2$ 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: $V_{\text{xc},\mu\nu} = \int \chi_\mu^*(\mathbf{r}) v_{\text{xc}}(\mathbf{r}) \chi_\nu(\mathbf{r}) \text{d}\mathbf{r}$
- 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

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

  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

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

  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 polyatomic 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)

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

- Without external magnetic fields, this is **in principle not necessary**, even for open-shell systems. However, in practice, the dependence on the spin densities allows one to construct **more accurate approximate exchange-correlation functionals** and is therefore **almost always used for open-shell systems**.

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

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

  where the search is over normalized antisymmetric wave functions Ψ which yield fixed spin densities integrating to the numbers of σ-spin electrons, i.e. $\int n_\sigma(\mathbf{r})\mathrm{d}\mathbf{r} = N_\sigma$.

- 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

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

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

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

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

  with the spin-dependent exchange-correlation potentials

  $$v_{\text{xc},\sigma}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})}$$

  and the spin densities

  $$n_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\phi_{i\sigma}(\mathbf{r})|^2$$

- 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

1. Basic density-functional theory
   - The quantum many-electron problem
   - The universal density functional
   - The Kohn-Sham method

2. More advanced topics in density-functional theory
   - Exact expressions for the exchange and correlation functionals
   - Fractional electron numbers and frontier orbital energies

3. Usual approximations for the exchange-correlation energy
   - The local-density approximation
   - Semilocal approximations
   - Hybrid and double-hybrid approximations
   - Range-separated hybrid and double-hybrid approximations
   - Semiempirical dispersion corrections

4. Additional topics in density-functional theory
   - Time-dependent density-functional theory
   - Some less usual orbital-dependent exchange-correlation functionals
   - Uniform coordinate scaling

Outline

2 More advanced topics in density-functional theory

- Exact expressions for the exchange and correlation functionals
  - The exchange and correlation holes
  - The adiabatic connection
- 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
  - 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 $\Phi[n]$

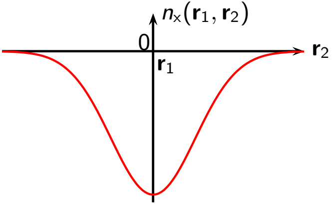
$$n_{2,\mathrm{KS}}(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)\int\cdots\int |\Phi[n](\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)|^2\, \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \mathrm{d}\mathbf{x}_3 ... \mathrm{d}\mathbf{x}_N$$

- 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:

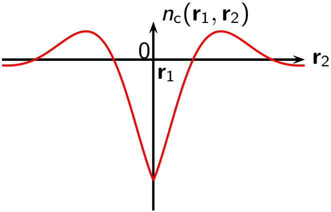
$$n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2) \geq -n(\mathbf{r}_2) \quad \text{and} \quad \int n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -1 \quad \text{and} \quad n_\mathrm{x}(\mathbf{r}_1,\mathbf{r}_2) \leq 0$$

- 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

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

  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

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

  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

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

  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

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

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 $E_c^{\lambda=0}[n] = 0$, we arrive at the **adiabatic-connection formula**

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

- 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

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

- 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

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

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

Outline

2. More advanced topics in density-functional theory
   - Exact expressions for the exchange and correlation functionals
     - The exchange and correlation holes
     - The adiabatic connection
   - 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
     - Fundamental gap

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

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

  where the minimization is over **ensemble density matrices** $\hat{\Gamma}$ of the form

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

  where f is fixed, and Ψ^{N-1} and Ψ^{N} are $(N-1)$- and N-electron normalized wave functions to be varied.

- 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

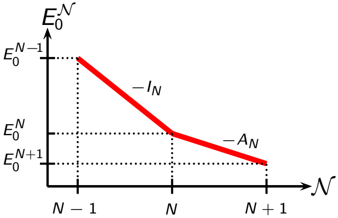
$$E_0^{N-1+f} = (1-f)\,E_0^{N-1} + f\,E_0^{N}$$

  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

$$F[n] = \min_{\hat{\Gamma}\to n} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \hat{W}_{\mathrm{ee}}\right)\right]$$

- As usual, to set up a KS method, $F[n]$ is decomposed as

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

where $T_{\mathrm{s}}[n] = \min_{\hat{\Gamma}_{\mathrm{s}}\to n} \mathrm{Tr}[\hat{\Gamma}_{\mathrm{s}}\hat{T}]$ is the KS non-interacting kinetic-energy functional and the minimization is over ensemble non-interacting density matrices $\hat{\Gamma}_{\mathrm{s}}$ of the form

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

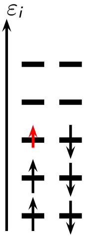
where $\Phi^{N-1,f}$ and $\Phi^{N,f}$ are $(N-1)$- and N-electron single-determinant wave functions, constructed from a **common set of orbitals** $\{\phi_i\}$ depending on the fixed f.

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

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

DFT with fractional electron numbers (2/2)

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



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

with the density $n(\mathbf{r}) = \sum_{i=1}^{N} n_i \left|\phi_i(\mathbf{r})\right|^2$ 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

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

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

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

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 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

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

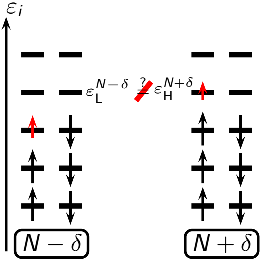
where $\varepsilon_{\mathrm{H}}^{N+\delta}$ is the HOMO energy from the right side of the discontinuity.

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 $\varepsilon_{\mathrm{L}}^{N-\delta}$:

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

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

- 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 $v_\text{s}^{N+\delta}(\mathbf{r})$ and $v_\text{s}^{N-\delta}(\mathbf{r})$ do differ by a uniform constant Δ_xc^N

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

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

$$\varepsilon_\text{H}^{N+\delta} = \varepsilon_\text{L}^{N-\delta} + \Delta_\text{xc}^N$$

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

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

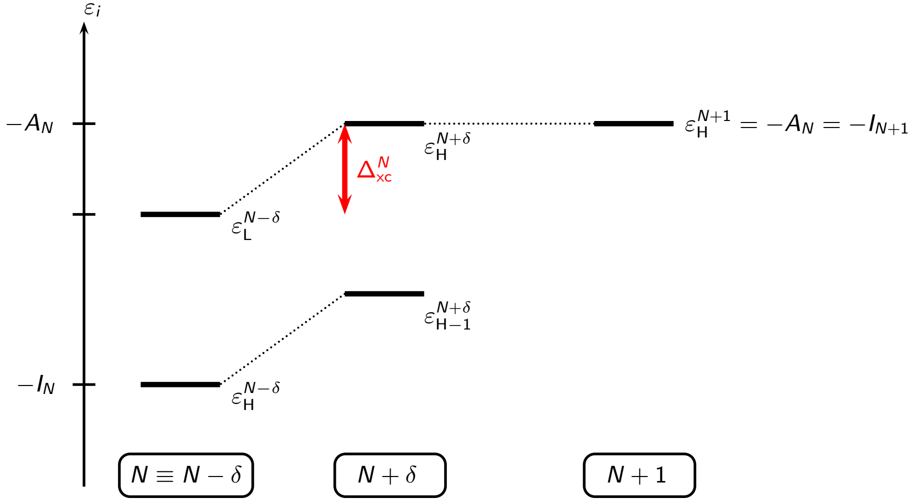
  due to the discontinuity Δ_xc^N in the KS potential.

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

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

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

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 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}.

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The local-density approximation

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

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

  where $\varepsilon_{\mathrm{xc}}^{\mathrm{unif}}(n)$ 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

$$\varepsilon_{\mathrm{x}}^{\mathrm{unif}}(n) = c_{\mathrm{x}}\ n^{1/3}$$

  Dirac (1930) and Slater (1951)

- For the correlation energy per particle $\varepsilon_{\mathrm{c}}^{\mathrm{unif}}(n)$ 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 $r_{\mathrm{s}} = (3/(4\pi n))^{1/3}$)

$$\varepsilon_{\mathrm{c}}^{\mathrm{unif}} \underset{r_{\mathrm{s}}\to 0}{=} A\ln r_{\mathrm{s}} + B + C\ r_{\mathrm{s}}\ln r_{\mathrm{s}} + O(r_{\mathrm{s}})$$

  high-density limit or
  weak-correlation limit

$$\varepsilon_{\mathrm{c}}^{\mathrm{unif}} \underset{r_{\mathrm{s}}\to \infty}{=} \frac{a}{r_{\mathrm{s}}} + \frac{b}{r_{\mathrm{s}}^{3/2}} + O\left(\frac{1}{r_{\mathrm{s}}^{2}}\right)$$

  low-density limit or
  strong-correlation limit

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

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  - Meta-generalized-gradient approximations
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  - Hybrid approximations
  - Double-hybrid approximations
- Range-separated hybrid and double-hybrid approximations
  - Range-separated hybrid approximations
  - Range-separated double-hybrid approximations
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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

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

where $C_{\text{xc}}(n) = C_{\text{x}} + C_{\text{c}}(n)$ 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

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

- 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

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

- (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**

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

  - 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:
$$\varepsilon_x(\mathbf{r}_1) = \frac{1}{2}\int \frac{n_x(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_2 \qquad \text{and} \qquad \varepsilon_c(\mathbf{r}_1) = \frac{1}{2}\int \frac{\bar{n}_c(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_2$$
  - 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 $\int n_x(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -1$.
    - For the GEA correlation hole: a cutoff is applied to enforce $\int \bar{n}_c(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = 0$.
  - 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 $s = |\nabla n|/n^{4/3}$ enforcing fewer exact conditions and with no fitted parameters.

  For correlation, the conditions imposed are:

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

  For exchange, the conditions imposed are:

  - Second-order GEA expansion: $\varepsilon_\mathrm{x} \underset{s\to 0}{\sim} \varepsilon_\mathrm{x}^\mathrm{LDA} + C_\mathrm{x}\, s^2$ (with only approximate $C_\mathrm{x} \approx -C_\mathrm{c}$).
  - Lieb-Oxford bound: $E_\mathrm{x} \geq -C \int n(\mathbf{r})^{4/3} \mathrm{d}\mathbf{r}$

    More precisely, it was chosen to impose the sufficient local condition $\varepsilon_\mathrm{x}(\mathbf{r}) \geq -C\, n(\mathbf{r})^{1/3}$ and to reach the bound in the $s \to \infty$ limit.

Meta-generalized-gradient approximations (1/2)

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

$$E_{\text{xc}}^{\text{meta-GGA}} = \int f(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))\text{d}\mathbf{r}$$

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

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

- Usually, n and τ are taken as independent variables, i.e. $E_{\text{xc}}^{\text{meta-GGA}}[n, \tau]$. This tacitly implies a slight extension of the usual KS method.
- Nowadays, $\nabla^2 n(\mathbf{r})$ is rarely used to construct meta-GGAs because it contains similar information than $\tau(\mathbf{r})$.
- The meta-GGAs are considered as part of the family of semilocal approximations.
- The meta-GGAs 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 exchange hole (for closed-shell systems):

$$n_x(\mathbf{r},\mathbf{r}') = -\frac{n(\mathbf{r})}{2} - \frac{1}{3}\left(\nabla^2 n(\mathbf{r}) - 4\tau(\mathbf{r}) + \frac{|\nabla n(\mathbf{r})|^2}{2n(\mathbf{r})}\right)|\mathbf{r}-\mathbf{r}'|^2 + \cdots$$

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

  - $\tau(\mathbf{r})$ can be used as an indicator of spatial regions of **single-orbital character** (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 exact for one and two electrons in a single orbital.

- In practice, $\tau(\mathbf{r})$ is used through the variables
  - $\tau(\mathbf{r})/\tau^{\mathrm{W}}(\mathbf{r})$
  - or, $\alpha(\mathbf{r}) = (\tau(\mathbf{r}) - \tau^{\mathrm{W}}(\mathbf{r}))/\tau^{\mathrm{unif}}(\mathbf{r})$ where $\tau^{\mathrm{unif}}(\mathbf{r}) = c\ n(\mathbf{r})^{5/3}$
- Examples of meta-GGAs: TPSS (2003) and SCAN (2015).

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Hybrid approximations

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

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

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

- $E_{\mathrm{x}}^{\mathrm{HF}}[\{\phi_i\}]$ depends on the occupied orbitals. The orbitals are optimized using a nonlocal HF exchange potential $v_{\mathrm{x},\sigma}^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$ instead of a local one. This is a slight extension of the usual KS method, referred to as **generalized Kohn-Sham**.

- Adding a fraction of HF exchange decreases the **self-interaction error**, which tends to favor too much delocalized electron densities (problems with dissociation of charged fragments, reaction barriers, radicals,...).

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

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

  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 (36 parameters).

Double-hybrid approximations

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

  $$E_{\text{xc}}^{\text{2DH}} = a_{\text{x}}\, E_{\text{x}}^{\text{HF}} + (1 - a_{\text{x}})\, E_{\text{x}}^{\text{DFA}} + (1 - a_{\text{c}}) E_{\text{c}}^{\text{DFA}} + a_{\text{c}} E_{\text{c}}^{\text{MP2}}$$

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

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

- In 2011, Sharkas, Toulouse, and Savin provided a rigorous reformulation using the adiabatic-connection formalism, leading to a **one-parameter double-hybrid (1DH) approximation**

  $$E_{\text{xc}}^{\text{1DH}} = \lambda\, E_{\text{x}}^{\text{HF}} + (1 - \lambda)\, E_{\text{x}}^{\text{DFA}} + (1 - \lambda^2) E_{\text{c}}^{\text{DFA}} + \lambda^2 E_{\text{c}}^{\text{MP2}}$$

- Double-hybrid approximations are examples of correlation functionals depending on virtual orbitals. Another example is the random-phase approximation (RPA).

Outline

Range-separated hybrid approximations

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

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

  where

  - $E_{\text{x}}^{\text{lr,HF}}$ is the HF exchange energy for the **long-range electron-electron interaction** $\frac{\text{erf}(\mu r_{12})}{r_{12}}$ replacing the Coulomb interaction $\frac{1}{r_{12}}$,
  - $E_{\text{x}}^{\text{sr,DFA}}$ is a semilocal DFA exchange energy for the complement **short-range electron-electron interaction**,
  - 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)**

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

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

Range-separated double-hybrid approximations

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

$$E_{\mathrm{xc}}^{\mathrm{RSDH}} = E_{\mathrm{x}}^{\mathrm{lr,HF}} + E_{\mathrm{x}}^{\mathrm{sr,DFA}} + E_{\mathrm{c}}^{\mathrm{sr,DFA}} + E_{\mathrm{c}}^{\mathrm{lr,MP2}}$$

  - This is a well-defined approximation to a rigorous multideterminant extension of KS DFT called “range-separated DFT”.
  - Semilocal DFAs are more accurate if limited to short-range interactions.
  - Long-range MP2 is qualitatively correct for London dispersion interactions.
  - Long-range MP2 has a fast convergence with the 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

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

  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.
- This approach was named "DFT-D" by Grimme.
- 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.
- 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).

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4. Additional topics in density-functional theory
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    - Some less usual orbital-dependent exchange-correlation functionals
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        - Görling-Levy perturbation theory
        - Adiabatic-connection fluctuation-dissipation approach
    - Uniform coordinate scaling

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**

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

  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 $n(\mathbf{r}, t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}, t)|^2$.

- *Remark: Runge and Gross also established a TDDFT variational theorem, but it was later shown to violate causality. Several different possible solutions to this problem have then been proposed.*

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

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

- This can be rewritten as

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

  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**
  - $f_{Hxc}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \delta v_{Hxc}(\mathbf{r}_1, \omega)/\delta n(\mathbf{r}_2, \omega)$ 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**

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

  or, equivalently,

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

Excitation energies from linear-response TDDFT

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

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

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

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

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

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

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

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

- 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**

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

  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

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

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

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
   - Uniform coordinate scaling

Orbital-dependent exchange-correlation functionals

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

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

- In fact, the hybrid, double-hybrid, and range-separated approximations that we have seen already belong to this family, with the caveat that the orbitals are usually obtained with a **nonlocal** potential.

- Here, we are concerned with orbital-dependent exchange-correlation energy functionals 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 (at least for molecules).

Exact exchange

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

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

  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 ground-state wave function Ψ^{λ} of $\hat{H}^{\lambda}$ is expanded in powers of λ

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

  assuming a **nondegenerate KS system**.

Görling-Levy perturbation theory (2/2)

- The correlation energy is then expanded in powers of λ

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

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

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

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

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

- The **GL2 correlation energy** is thus

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

  with a double-excitation MP2-like term $E_\mathrm{c}^\mathrm{MP2}$ and single-excitation term E_c^S

$$E_\mathrm{c}^\mathrm{MP2} = -\frac{1}{4} \sum_{i,j}^{\mathrm{occ}} \sum_{a,b}^{\mathrm{vir}} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \quad \text{and} \quad E_\mathrm{c}^\mathrm{S} = -\sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{vir}} \frac{|\langle i | \hat{V}_\mathrm{x}^\mathrm{HF} - \hat{V}_\mathrm{x} | a \rangle|^2}{\varepsilon_a - \varepsilon_i}$$

- 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 due to a time-dependent external perturbation $\chi_\lambda(\mathbf{r}_1,\mathbf{r}_2,\omega)$.

- 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

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

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

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

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

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

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

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

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

  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
- Uniform coordinate scaling

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)

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

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

- The scaled wave function $\Psi^{\lambda}_{\gamma}[n]$ 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

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

- We thus conclude

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

- 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**

$$\boxed{\Phi[n_\gamma] = \Phi_\gamma[n]}$$

- This directly leads to the scaling relations for $T_\text{s}[n]$, $E_\text{H}[n]$, and $E_\text{x}[n]$

$$\boxed{T_\text{s}[n_\gamma] = \gamma^2 T_\text{s}[n]} \quad \text{and} \quad \boxed{E_\text{H}[n_\gamma] = \gamma E_\text{H}[n]} \quad \text{and} \quad \boxed{E_\text{x}[n_\gamma] = \gamma E_\text{x}[n]}$$

- However, $E_\text{c}[n]$ has the more complicated scaling (as $F[n]$)

$$\boxed{E_\text{c}^{\lambda}[n_\gamma] = \gamma^2 E_\text{c}^{\lambda/\gamma}[n]}$$

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

$$\boxed{E_\text{c}[n_\gamma] = \gamma^2 E_\text{c}^{1/\gamma}[n]}$$

High- and low-density limits

- The **high-density limit** of the correlation functional is, for nondegenerate KS systems,

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

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

  - This is also called the **weak-correlation limit** since $E_c[n] \ll E_x[n]$.
  - LDA does not satisfy this condition: $\varepsilon_c^{\mathrm{unif}}(r_s/\gamma) \underset{\gamma\to\infty}{\sim} A\ln(r_s/\gamma) \to -\infty$. GGAs such as PBE are constructed to cancel out this divergence.
  - Atomic and molecular systems are often close to the high-density limit.

- The **low-density limit** of the correlation functional is

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

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

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