Key ingredient of Kohn–Sham density-functional theory

Density-functional approximation  \( E_{XC}[\rho] \)  

Kohn–Sham potential  \( v_{XC}([\rho]; \mathbf{r}) \)  

Functional differentiation  

\[ v_{XC}([\rho]; \mathbf{r}) = \frac{\delta E_{XC}}{\delta \rho(\mathbf{r})} \]
Functional derivatives

The functional derivative is to a functional what the gradient is to a scalar function of many variables.

\[ E(\rho_1, \rho_2, \ldots) \rightarrow \nabla E = \left( \frac{\partial E}{\partial \rho_1}, \frac{\partial E}{\partial \rho_2}, \ldots \right) \]

For density-functional approximations of the type

\[ E[\rho] = \int f(\mathbf{r}, \rho, \nabla \rho, \nabla^2 \rho, \ldots) d\mathbf{r} \]

the functional derivative is given by

\[ \nu([\rho]; \mathbf{r}) = \frac{\delta E}{\delta \rho} = \frac{\partial f}{\partial \rho} - \nabla \cdot \left( \frac{\partial f}{\partial \nabla \rho} \right) + \nabla^2 \left( \frac{\partial f}{\partial \nabla^2 \rho} \right) + \ldots \]

Conventional Kohn–Sham scheme

Approximate the xc-energy functional

\[ E_{XC}[\rho] \]

Construct the xc-potential

\[ \nu_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})} \]

Solve the Kohn-Sham equations

\[ \left[ \text{trivial terms} + \nu_{XC}(\mathbf{r}) \right] \varphi_i = \epsilon_i \varphi_i \]

Evaluate the electron density

\[ \rho(\mathbf{r}) = \sum_{i}^{\text{occ.}} |\varphi_i(\mathbf{r})|^2 \]
Potential-driven Kohn–Sham scheme

\[ v_{xc}(\rho; r) \]

Approximate the xc-potential from \( \rho(r) \)

\[ [\text{trivial terms} + v_{xc}(r)] \phi_i = \varepsilon_i \phi_i \]

Solve the Kohn-Sham equations

\[ \rho(r) = \sum_{i}^{\text{occ}} |\phi_i(r)|^2 \]

Evaluate the electron density

\[ E_{xc}[\rho] \]

Calculate the xc-energy (if needed)

Motivation for potential-driven DFT

1. The Kohn–Sham potential is a more fundamental quantity than the corresponding density functional.

2. The potential \( v_{xc}(r) \) is a relatively simple function of \( r \), so it is an appealing target for approximation.

3. With direct control over \( v_{xc}(r) \), it may be easier to achieve accurate description of physical properties that are sensitive to the quality of \( v_{xc}(r) \)

model potential: a Kohn–Sham potential that is approximated directly using Kohn–Sham orbitals
Slater’s exchange potential approximation

Hartree–Fock exchange energy:

\[
E_X = -\sum_{i,j}^{\text{occ}} \int dr \int dr' \frac{\varphi_i^*(r)\varphi_j^*(r')\varphi_j(r)\varphi_i(r')}{|r-r'|}
\]

The functional derivative:  
Definition of the nonlocal Hartree–Fock potential

\[
\frac{\delta E_X}{\delta \varphi_i^*(r)} = -2 \sum_j \varphi_j(r) \int \frac{\varphi_j^*(r')\varphi_i(r')}{|r-r'|} dr' \equiv \hat{v}_X \varphi_i(r)
\]

Averaged Hartree–Fock potential (Slater, 1951):

\[
v^S_X(r) = \frac{\sum_i \varphi_i^*(r)\hat{v}_X \varphi_i(r)}{\sum_k \varphi_k^*(r)\varphi_k(r)} = -\frac{2}{\rho(r)} \sum_{i,j}^{\text{occ}} \varphi_i^*(r)\varphi_j^*(r') \varphi_j(r) \int \frac{\varphi_j^*(r')\varphi_i(r')}{|r-r'|} dr'
\]

Examples of model Kohn–Sham potentials

van Leeuwen and Baerends (1994)

\[
v^{LB94}_{XC} = v^{LDA}_{X} - \rho^{1/3} \frac{\beta s^2}{1 + 3\beta s \sinh^{-1}s}, \quad s = \frac{|\nabla \rho|}{\rho^{4/3}}
\]

\[\beta = 0.05\] is an empirical parameter

Effective local potential (ELP=CEDA=LHF, 2001–2006)

\[
v^{ELP}_X(r) = v^S_X(r) + \frac{2}{\rho(r)} \sum_{i,j}^{\text{occ}} \varphi_i^*(r)\varphi_j(r) \langle \varphi_j | v^{ELP}_X - \hat{v}_X | \varphi_i \rangle
\]

Becke and Johnson (2006)

\[
v^{BJ}_X(r) = v^S_X(r) + \frac{1}{\pi} \sqrt{\frac{5\tau}{6\rho}}, \quad \text{where} \quad \tau(r) = \frac{1}{2} \sum_i^{\text{occ}} |\nabla \varphi_i(r)|^2
\]
Challenges of potential-driven DFT

1. How to recover the energy from a given model potential.

2. How to ensure that a model potential is a functional derivative of some density functional.

Inversion of functional differentiation

Let $\rho_i(r)$ be the density parametrized in some way.

Consider the integral (van Leeuwen and Baerends, 1995):

$$E[\rho_B] - E[\rho_A] = \int_A^B dt \frac{dE[\rho_t]}{dt}$$

$$= \int_A^B dt \int d\mathbf{r} \frac{\delta E[\rho_t]}{\delta \rho_t(\mathbf{r})} \frac{\partial \rho_t(\mathbf{r})}{\partial t}$$

$$= \int d\mathbf{r} \int_A^B dt \nu([\rho_t]; \mathbf{r}) \left. \frac{\partial \rho_t(\mathbf{r})}{\partial t} \right|_{\rho=\rho_t}$$

Here

$$\nu([\rho_t]; \mathbf{r}) \equiv \nu([\rho]; \mathbf{r}) \big|_{\rho=\rho_t}$$
Reconstruction of density functionals

Let \( \rho_t(r) \) be such that for \( 0 \leq t \leq 1 \),

\[
E[\rho_0] = 0 \quad \text{and} \quad \rho_1(r) = \rho(r)
\]

The line integration “reconstructs” the functional:

\[
E[\rho] = \int dr \int_0^1 dt \, v([\rho_t]; r) \frac{\partial \rho_t(r)}{\partial t}
\]

The integral over \( t \) can be evaluated analytically or numerically.

If \( v_{xc}(r) \) is a functional derivative of some functional, then the line integral is path-independent.

Three convenient integration paths

Linear density scaling (Q-path):

\( 0 \leq q \leq 1 \quad \rho_q(r) = q \rho(r) \quad \frac{\partial \rho_q(r)}{\partial q} = \rho(r) \)

Uniform density scaling (\( \Lambda \)-path):

\( 0 \leq \lambda \leq 1 \quad \rho_\lambda(r) = \lambda^3 \rho(\lambda r) \)

\( \zeta \)-Scaling (Z-path):

\( 0 \leq \zeta \leq 1 \quad \rho_\zeta(r) = \zeta^2 \rho(\zeta^{1/3} r) \)
EXAMPLE 1

Reconstruction of an exchange functional

Original functional (xLDA):

\[ E_X = -C_X \int \rho^{4/3}(\mathbf{r}) \, d\mathbf{r} \]

where \( C_X \) is a constant.

Functional derivative:

\[ \nu_X ([\rho]; \mathbf{r}) = -\frac{4}{3} C_X \rho^{1/3}(\mathbf{r}) \]

Reconstructions of the LDA exchange functional

Q-path reconstruction:

\[ E_X[\rho] = \frac{3}{4} \int \rho \nu_X \, d\mathbf{r} = -C_X \int \rho^{4/3} \, d\mathbf{r} \]

\textit{original expression}

\( \Lambda \)-path reconstruction:

\[ E_X[\rho] = \int \nu_X (3\rho + \mathbf{r} \cdot \nabla \rho) \, d\mathbf{r} \]

\textit{Levy-Perdew relation}

Z-path reconstruction:

\[ E_X[\rho] = \frac{3}{5} \int \nu_X \left( 2\rho + \frac{\mathbf{r}}{3} \cdot \nabla \rho \right) \, d\mathbf{r} \]

\textit{linear combination of the Q- and \( \Lambda \)-reconstructions}

A. P. Gaiduk, S. K. Chulkov, and VNS, 
EXAMPLE 2

Reconstruction of a correlation functional

Original functional (Wigner):

$$E_C[\rho] = -a \int \frac{\rho}{b + r_s} \, d\mathbf{r} \quad r_s = \left( \frac{3}{4\pi \rho} \right)^{1/3}$$

where $a$ and $b$ are parameters.

Functional derivative:

$$\nu_C(\rho; \mathbf{r}) = -a \frac{b + (4/3)r_s}{(b + r_s)^2}$$

Reconstructions of the Wigner correlation functional

Q-path reconstruction:

$$E_C[\rho] = -a \int \frac{\rho}{b + r_s} \, d\mathbf{r}$$

$\Lambda$-path reconstruction:

$$E_C[\rho] = -a \int \left[ \frac{1}{b} \ln \frac{b + r_s}{r_s} + \frac{1}{3(b + r_s)} \right] \left( 3\rho + \mathbf{r} \cdot \nabla \rho \right) \, d\mathbf{r}$$

Z-path reconstruction:

$$E_C[\rho] = -a \int \left[ \frac{1 - \frac{r_s}{b} - \frac{3}{2} \left( \frac{r_s}{b} \right)^2}{b + r_s} + \frac{3r_s^{3/2} \tan^{-1} \sqrt{b/r_s}}{2b^{5/2}} \right] \left( 2\rho + \frac{\mathbf{r}}{3} \cdot \nabla \rho \right) \, d\mathbf{r}$$

Line integral of exchange potentials

Under uniform density scaling, all exchange-only potentials behave as follows:

\[ v_x ([\rho_{\lambda}]; \mathbf{r}) = \lambda v_x ([\rho]; \lambda \mathbf{r}) \]

In the line integral, analytic integration over \( \lambda \) yields

\[ E_x [\rho] = \int v_x (\mathbf{r}) [3 \rho (\mathbf{r}) + \mathbf{r} \cdot \nabla \rho (\mathbf{r})] \, d\mathbf{r} \]

which is the Levy–Perdew formula.

Unsolved problems

The line integral formula is sometimes used to assign energy values to model potentials that are not functional derivatives.

For potentials that depend on \( \rho \) explicitly, this is possible using many density transformations, e.g.,

\[ \rho_q (\mathbf{r}) = q \rho (\mathbf{r}), \quad \rho_{\lambda} (\mathbf{r}) = \lambda^3 \rho (\lambda \mathbf{r}) \]

For orbital-dependent potentials, only one is known

\[ \phi_i ([\rho_{\lambda}]; \mathbf{r}) = \lambda^{3/2} \phi_i ([\rho]; \lambda \mathbf{r}) \]

Q: Are there any other practical integration paths for orbital-dependent potentials?
The problem of stray potentials

Model potentials may not be functional derivatives of any functional. Such potentials are called stray.

Examples: All existing model potentials except those that depend only on \( \rho \).

Tests for stray potentials:

1) Path-independence of the line integral
2) Integrability conditions
3) Tests for spurious forces on the density
4) Behavior of the energy during the SCF convergence

SCF convergence for stray potentials

Artifacts of stray model potentials

- Energy assigned to a model potential may depend on the choice of coordinate axes:

  Example: \( \text{H}_2\text{O} \) molecule, HF/cc-pVQZ density  
  Model potential: Becke–Johnson

  Total energy calculated using  
  \[
  E_X[\rho] = \int v_X(r)[3\rho(r) + r \cdot \nabla \rho(r)] \, dr
  \]

  Initial orientation: \(-75.517\) hartree  
  After translation by 0.1 Å: \(-75.470\) hartree  
  \(\Delta E = 29.5\) kcal/mol

- Different energy formulas give different results even for a fixed orientation of the molecule.

- Spurious self-excitations in TDDFT (Kümmel et al.), etc.
Model potentials should be functional derivatives

An integrable potential is a functional derivative of some density functional.

Existing model potentials lead to unphysical artifacts because they are not functional derivatives

A necessary and sufficient integrability condition:

\[
\frac{\delta v([\rho]; r)}{\delta \rho(r')} = \frac{\delta v([\rho]; r')}{\delta \rho(r)}
\]


Theory of integrability: Definitions

\(E[\rho]\) some density-functional approximation
\(h(r), k(r)\) arbitrary variations of the density

The first differential in the direction \(h\) is defined by

\[
DE[\rho, h] = \lim_{t \to 0} \frac{E[\rho + th] - E[\rho]}{t} = \frac{d}{dt} E[\rho + th] \bigg|_{t=0}
\]

\(DE[\rho, h]\) is linear in \(h\) and can be written as

\[
DE[\rho, h] = \int v([\rho]; r)h(r) \, dr
\]

where \(v([\rho]; r)\) is the functional derivative

\[
v([\rho]; r) \equiv \frac{\delta E}{\delta \rho(r)}
\]
More definitions

The second differential of $E[\rho]$ may be defined by:

$$D^2 E[\rho, h, k] = \frac{d}{dt} \left. D E[\rho + tk, h] \right|_{t=0}$$

It is a bilinear functional in $h$ and $k$, so it may be written as

$$D^2 E[\rho, h, k] = \int dr \int dr' K([\rho]; r, r') h(r) k(r')$$

The kernel is called the second functional derivative

$$K([\rho]; r, r') = \frac{\delta^2 E}{\delta \rho(r) \delta \rho(r')} = \frac{\delta^v([\rho]; r)}{\delta \rho(r')}$$

The symmetric kernel condition

The second differential is symmetric in $h$ and $k$:

$$D^2 E[\rho, h, k] = D^2 E[\rho, k, h]$$

This implies that the kernel is symmetric in $r$ and $r'$

$$K([\rho]; r, r') = K([\rho]; r', r)$$

$$\frac{\delta^2 E}{\delta \rho(r) \delta \rho(r')} = \frac{\delta^2 E}{\delta \rho(r') \delta \rho(r)}$$

$$\frac{\delta^v([\rho]; r)}{\delta \rho(r')} = \frac{\delta^v([\rho]; r')}{\delta \rho(r)}$$
Symmetry of the second differential

The functional derivative $v([\rho]; r)$ is itself a functional of $\rho$, so its first differential in the direction $k$ is

$$Dv([\rho, k]; r) = \frac{d}{dt} v([\rho + tk]; r) \bigg|_{t=0}$$

The second differential of $E[\rho]$ may be written as

$$D^2 E[\rho, h, k] = \int Dv([\rho, k]; r)h(r) \, dr$$

The symmetry condition for $D^2 E$ can be stated as:

$$\int Dv([\rho, k]; r)h(r) \, dr = \int Dv([\rho, h]; r)k(r) \, dr$$

Theory of integrability in a nutshell

The necessary and sufficient condition of integrability for a trial potential $v$ can be stated in two equivalent forms:

<table>
<thead>
<tr>
<th>Differential form</th>
<th>Integral form</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\delta v([\rho]; r)}{\delta \rho(r')} = \frac{\delta v([\rho]; r')}{\delta \rho(r)}$</td>
<td>$\int Dv([\rho, k]; r)h(r) , dr = \int Dv([\rho, h]; r)k(r) , dr$</td>
</tr>
<tr>
<td>symmetry in $r$ and $r'$</td>
<td>symmetry in $h$ and $k$</td>
</tr>
</tbody>
</table>

Requires manipulations with Dirac delta functions | Does not involve Dirac delta functions

Potentials that depend only on $\rho$ and $\nabla \rho$

Consider a model potential of the type

$$v = v(\rho, \nabla \rho)$$

For this $v$, the second differential is

$$\int Dv([\rho, k]; \mathbf{r}) h(\mathbf{r}) \, d\mathbf{r} = \int \left( \frac{\partial v}{\partial \rho} k h + \frac{\partial v}{\partial \nabla \rho} \cdot h \nabla k \right) \, d\mathbf{r}$$

This integral is symmetric in $h$ and $k$ if and only if

$$\frac{\partial v}{\partial \nabla \rho} = 0$$

Consequence: A model potential of the type $v(\rho, \nabla \rho)$ can never be a functional derivative

New integrability conditions

Consider a model potential of the type

$$v = v(\rho, \nabla \rho, \nabla^2 \rho)$$

The second differential may be written as

$$\int Dv([\rho, k]; \mathbf{r}) h(\mathbf{r}) \, d\mathbf{r}$$

$$= \int \left[ \frac{\partial v}{\partial \rho} k h + \left( \frac{\partial v}{\partial \nabla \rho} - \nabla \frac{\partial v}{\partial \nabla^2 \rho} \right) \cdot h \nabla k - \frac{\partial v}{\partial \nabla^2 \rho} \nabla h \cdot \nabla k \right] \, d\mathbf{r}$$

This integral can be symmetric in $h$ and $k$ if and only if

$$\frac{\partial v}{\partial \nabla \rho} = \nabla \frac{\partial v}{\partial \nabla^2 \rho}$$
Generalized-gradient approximations (GGA)

GGA functionals:

\[ E[\rho] = \int f(\rho, g) \, d\mathbf{r} \]

The functional derivative of every GGA has the form

\[ v = \frac{\partial f}{\partial \rho} - \frac{\partial^2 f}{\partial \rho \partial g} \frac{g}{\partial g} \frac{\partial f}{\partial l} + \left( \frac{\partial f}{\partial g} - g \frac{\partial^2 f}{\partial g^2} \right) \frac{w}{g^3} \]

and is always a function of at most 4 ingredients:

\[ \rho, \quad g \equiv |\nabla \rho|, \quad l \equiv \nabla^2 \rho, \quad w = g \nabla g \cdot \nabla \rho \]


Integrability conditions for GGA potentials

One can show that for a trial potential of the type

\[ v = v(\rho, g, l, w) \]

the necessary and sufficient condition to be a functional derivative is:

\[
\begin{align*}
\frac{1}{g} \frac{\partial v}{\partial g} - l \frac{\partial v}{\partial w} - \frac{\partial^2 v}{\partial \rho \partial l} - g^2 \frac{\partial^2 v}{\partial \rho \partial w} - w \frac{\partial^2 v}{\partial g \partial w} = 0, \\
\frac{\partial v}{\partial w} - \frac{\partial^2 v}{\partial g \partial l} = 0
\end{align*}
\]

Note: these conditions are entirely in the \((\rho, g, l, w)\) space.
Construction of functional derivatives:

Example

Consider the expression

\[ v_0 = \frac{g^2}{8\rho^2} \]

not a functional derivative

Assume that \( v_0 \) is the first term of the functional derivative of some GGA:

\[ v = v_0(\rho, g) + X(\rho, g)l + Y(\rho, g)w \]

Solving for \( X \) and \( Y \) we obtain

\[ v = \frac{g^2}{8\rho^2} - \frac{l}{4\rho} \]

functional derivative of

\[ T_w = \int \frac{\nabla \rho^2}{8\rho} \, dr \]

Construction of integrable exchange potentials

Model potentials are normally expressed in terms of the dimensionless variables

\[ s = \frac{g}{\rho^{4/3}}, \quad q = \frac{l}{\rho^{5/3}}, \quad u = \frac{w}{\rho^{13/3}} \]

For reasons of dimensionality, every functional derivative of an exchange GGA can be written as

\[ v(\rho, s, q, u) = \rho^{1/3} \left[ R(s) + Q(s)q + U(s)u \right] \]

where \( R, Q \) and \( U \) are some functions.

Suppose that \( R \) is known. Then \( Q \) and \( U \) can be obtained from the integrability conditions.
Model potential of van Leeuwen and Baerends (LB94)

\[ v_{X}^{\text{LB94}} = v_{X}^{\text{LDA}} - \rho^{1/3} \frac{\beta s^2}{1 + 3\beta s \sinh^{-1}(\xi s)}, \]

where \( s = \frac{g}{\rho^{4/3}} \) and \( \beta = 0.05 \) and \( \xi \) are constants

Functional derivative “grown” from LB94:

\[ v_{X} = v_{X}^{\text{LB94}} - \frac{\rho^{1/3}}{s} \left( I_0 \ln s - I_1 + I_0 \right) q + \frac{\rho^{1/3}}{s^3} \left( I_0 \ln s - I_1 - s \frac{dI_0}{ds} \right) u \]

where

\[ I_\alpha(s) = -\frac{3}{4} \int_{\psi}^{s} \frac{\beta \ln^\alpha s}{1 + 3\beta s \sinh^{-1}(\xi s)} ds, \quad \alpha = 0, 1 \]

LB94 and a “grown” functional derivative (fd)
LB94 and LB94-based functional derivatives

![Graph showing the comparison between LB94, fd-LB94, and fd-revLB94.]

Total energies from the LB94 potential and the reconstructed functional derivative

<table>
<thead>
<tr>
<th>Atom</th>
<th>original LB94</th>
<th>func. deriv. from LB94</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>−2.821</td>
<td>−4.275</td>
</tr>
<tr>
<td>Ne</td>
<td>−129.430</td>
<td>−138.597</td>
</tr>
<tr>
<td>Ar</td>
<td>−529.173</td>
<td>−547.017</td>
</tr>
<tr>
<td>Kr</td>
<td>−2761.921</td>
<td>−2797.106</td>
</tr>
</tbody>
</table>

*All values are obtained using the path of uniformly scaled densities (the Levy–Perdew formula).*
Total energies from model exchange potentials

<table>
<thead>
<tr>
<th>Atom</th>
<th>original LB94</th>
<th>func. deriv. from revised LB94</th>
<th>PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>-2.821</td>
<td>-2.896</td>
<td>-2.862</td>
</tr>
<tr>
<td>Ne</td>
<td>-129.430</td>
<td>-128.597</td>
<td>-128.547</td>
</tr>
<tr>
<td>Ar</td>
<td>-529.173</td>
<td>-526.691</td>
<td>-526.629</td>
</tr>
<tr>
<td>Kr</td>
<td>-2761.921</td>
<td>-2751.519</td>
<td>-2751.624</td>
</tr>
</tbody>
</table>

*All values are obtained using the path of uniformly scaled densities (the Levy–Perdew formula).*

Unsolved problems

Using the above method, one can construct integrable Kohn–Sham potentials from any explicitly density-dependent ingredients such as

\[
\rho, \quad g=\nabla \rho, \quad l=\nabla^2 \rho, \quad w=g\nabla g \cdot \nabla \rho
\]

Q: Can we construct integrable orbital-dependent potentials?

Q: In particular, can one make the Becke–Johnson model potential integrable?

\[
v_X^{BJ}(r) = v_X^S(r) + \frac{1}{\pi} \sqrt{\frac{5 \tau}{6 \rho}}, \quad \text{where} \quad \tau(r) = \frac{1}{2} \sum_{i} |\nabla \varphi_i(r)|^2
\]
Summary

1. It is not difficult to reconstruct a density functional from its functional derivative in more than one way.

2. It is always possible to assign an xc-energy to a stray model Kohn–Sham potential.

3. Model potentials should by construction be functional derivatives.

4. It is possible to construct a functional derivative without knowing the parent density functional.

5. Development of integrable model potentials reduces to construction of simple functions of a few variables.

Acknowledgments