Solved and Unsolved Problems in the Theory of Model Kohn–Sham Potentials

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Key ingredient of Kohn–Sham density-functional theory

Density-functional approximation		Kohn–Sham potential
$E_{XC}[\rho]$	→ functional differentiation	$v_{XC}([\rho];\mathbf{r})$

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

Functional derivatives

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

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

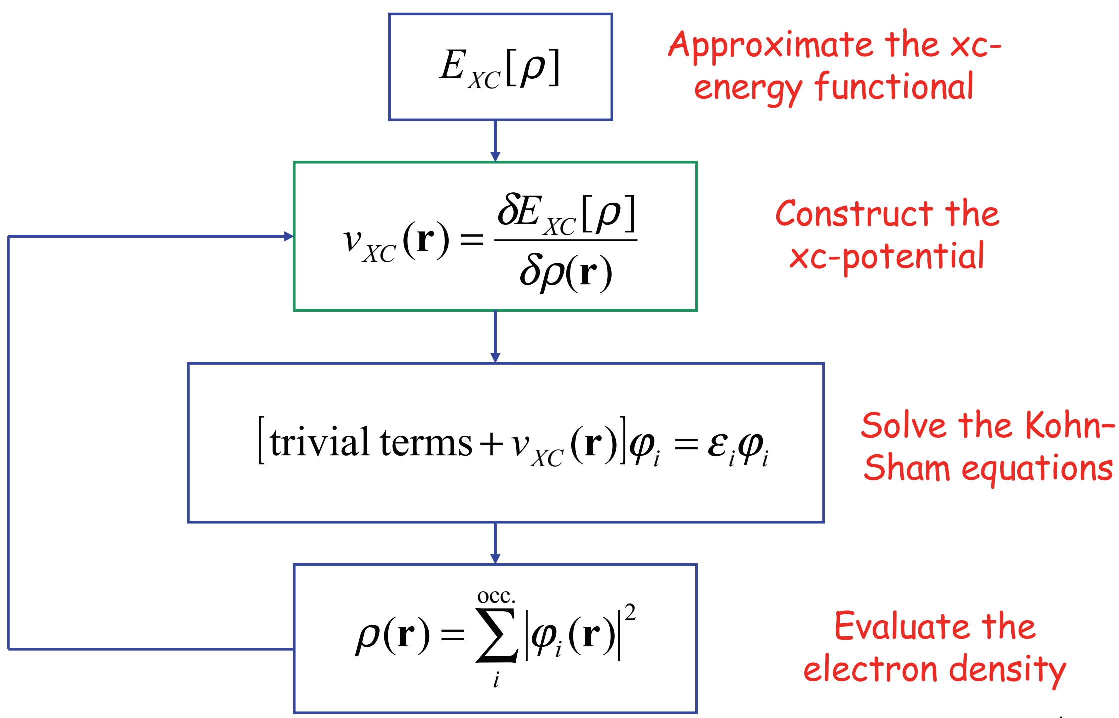
For density-functional approximations of the type

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

the **functional derivative** is given by

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

Conventional Kohn–Sham scheme



Potential-driven Kohn–Sham scheme

$$v_{XC}([\rho];\mathbf{r})$$

Approximate the xc-potential from $\rho(\mathbf{r})$

$$\left[\text{trivial terms} + v_{XC}(\mathbf{r})\right]\varphi_i = \varepsilon_i \varphi_i$$

Solve the Kohn-Sham equations

$$\rho(\mathbf{r}) = \sum_i^{\text{occ.}} \left|\varphi_i(\mathbf{r})\right|^2$$

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 $v_{XC}(\mathbf{r})$ is a relatively simple function of $\mathbf{r}$, so it is an appealing target for approximation.

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

model potential: a Kohn–Sham potential that is approximated directly using Kohn–Sham orbitals

Slater's exchange potential approximation

Hartree–Fock exchange energy:

$$E_X = -\sum_{i,j}^{\text{occ.}} \int d\mathbf{r} \int d\mathbf{r}' \frac{\varphi_i^*(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r})\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

The functional derivative:

Definition of the nonlocal Hartree-Fock potential

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

Averaged Hartree–Fock potential (Slater, 1951):

$$v_X^S(\mathbf{r}) = \frac{\sum_i \varphi_i^*(\mathbf{r})\hat{v}_X\varphi_i(\mathbf{r})}{\sum_k \varphi_k^*(\mathbf{r})\varphi_k(\mathbf{r})} = -\frac{2}{\rho(\mathbf{r})}\sum_{i,j}\varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})\int \frac{\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

Examples of model Kohn–Sham potentials

van Leeuwen and Baerends (1994)

$$v_{XC}^{\text{LB94}} = v_X^{\text{LDA}} - \rho^{1/3}\frac{\beta s^2}{1+3\beta s \sinh^{-1} s}, \qquad s = \frac{|\nabla\rho|}{\rho^{4/3}}$$

$\beta = 0.05$ is an empirical parameter

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

$$v_X^{\text{ELP}}(\mathbf{r}) = v_X^S(\mathbf{r}) + \frac{2}{\rho(\mathbf{r})}\sum_{i,j}^{\text{occ.}}\varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})\langle\varphi_j|v_X^{\text{ELP}} - \hat{v}_X|\varphi_i\rangle$$

Becke and Johnson (2006)

$$v_X^{\text{BJ}}(\mathbf{r}) = v_X^S(\mathbf{r}) + \frac{1}{\pi}\sqrt{\frac{5\tau}{6\rho}}, \quad \text{where} \quad \tau(\mathbf{r}) = \frac{1}{2}\sum_i^{\text{occ.}}|\nabla\varphi_i(\mathbf{r})|^2$$

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 $\rho_t(\mathbf{r})$ be the density parametrized in some way.

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

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

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

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

Here $$v([\rho_t];\mathbf{r}) \equiv v([\rho];\mathbf{r})\,\Big|_{\rho=\rho_t}$$

Reconstruction of density functionals

Let $\rho_t(\mathbf{r})$ be such that for $0 \le t \le 1$,

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

The line integration “reconstructs” the functional:

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

The integral over t can be evaluated analytically or numerically

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

Three convenient integration paths

Linear density scaling (Q-path):

$$0 \le q \le 1 \qquad \rho_q(\mathbf{r}) = q\rho(\mathbf{r}) \qquad \frac{\partial \rho_q(\mathbf{r})}{\partial q} = \rho(\mathbf{r})$$

Uniform density scaling (Λ-path):

$$0 \le \lambda \le 1 \qquad \rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r})$$

ζ-Scaling (Z-path):

$$0 \le \zeta \le 1 \qquad \rho_\varsigma(\mathbf{r}) = \varsigma^2 \rho(\varsigma^{1/3}\mathbf{r})$$

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:

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

Reconstructions of the LDA exchange functional

Q-path reconstruction:

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

original expression

Λ-path reconstruction:

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

Levy–Perdew relation

Z-path reconstruction:

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

linear combination of the Q- and Λ-reconstructions

A. P. Gaiduk, S. K. Chulkov, and VNS,
J. Chem. Theory Comput. **5**, 699 (2009).

EXAMPLE 2

Reconstruction of a correlation functional

Original functional (Wigner):

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

where a and b are parameters.

Functional derivative:

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

Reconstructions of the Wigner correlation functional

Q-path reconstruction:

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

original expression

Λ-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:

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

A. P. Gaiduk, S. K. Chulkov, and VNS,
J. Chem. Theory Comput. **5**, 699 (2009)

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 λ 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 ρ explicitly, this is possible using many density transformations, e.g.,

$$\rho_q(\mathbf{r}) = q\rho(\mathbf{r}), \qquad \rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r})$$

For orbital-dependent potentials, only one is known

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

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.

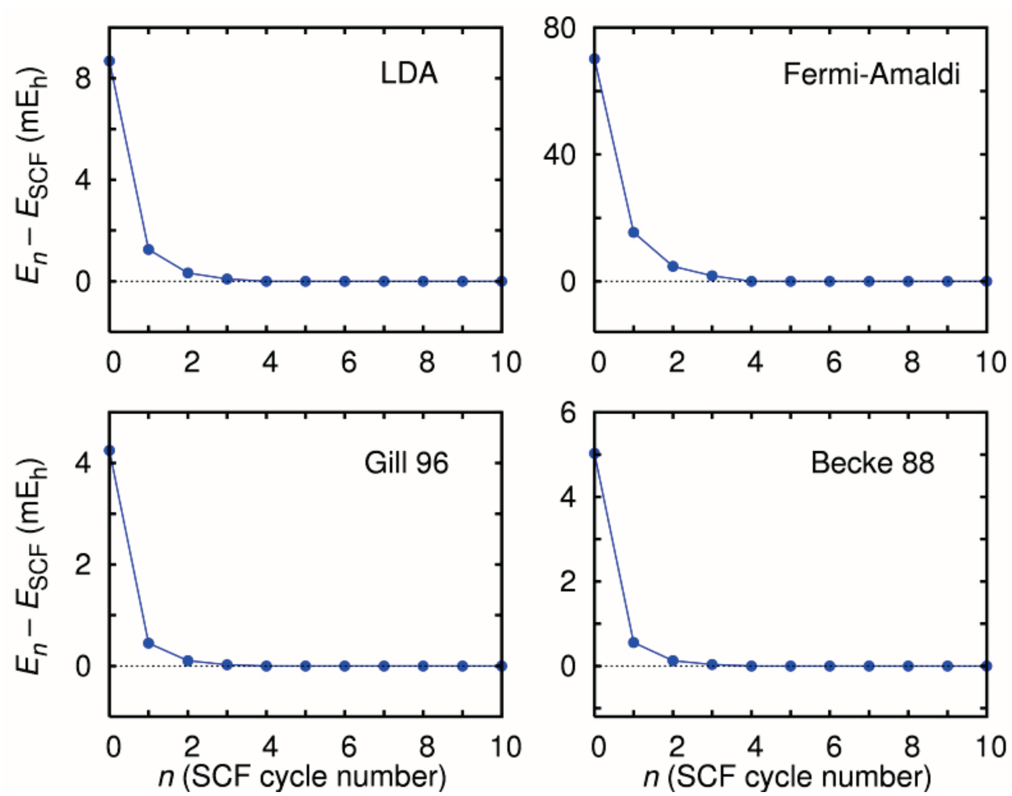
Examples: All existing model potentials except those that depend only on ρ.

Tests for stray potentials:

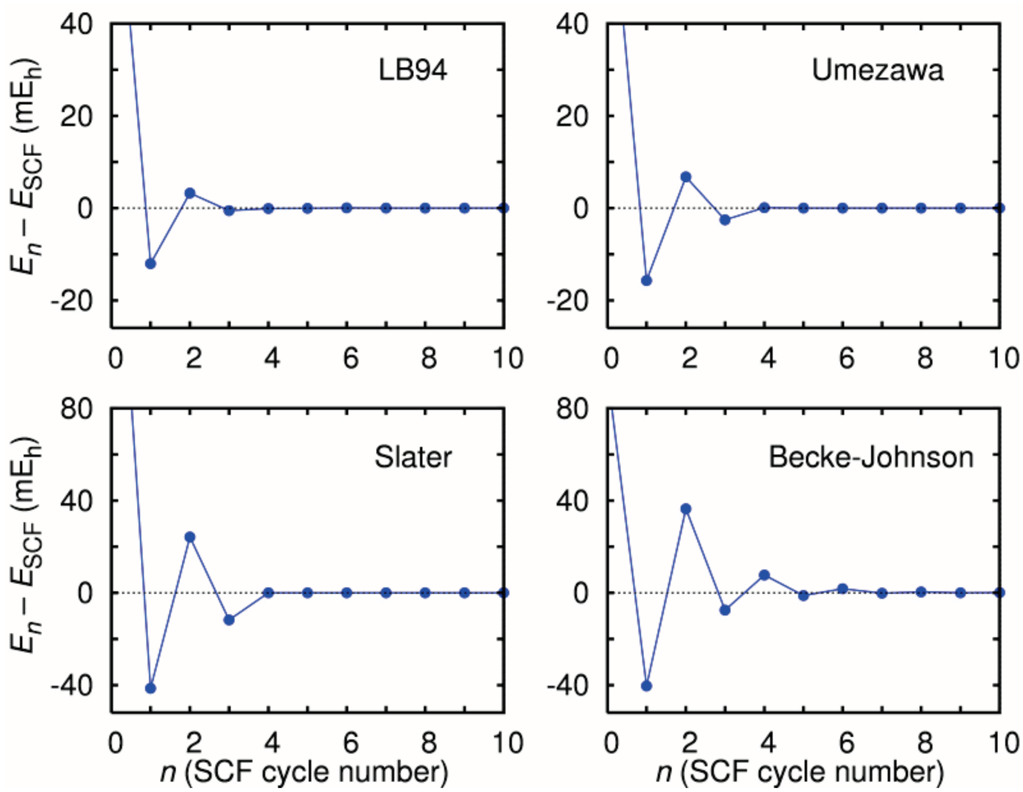
1) Path-independence of the line integral
2) Integrability conditions
3) Tests for spurious forces on the density
4) Behavior of the energy during the SCF convergence

A. P. Gaiduk and VNS, *J. Chem. Phys.* **131**, 044107 (2009)

SCF convergence for functional derivatives



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: H_2O molecule, HF/cc-pVQZ density
Model potential: Becke–Johnson

Total energy calculated using $E_X[\rho] = \int v_X(\mathbf{r})[3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})]\, d\mathbf{r}$

Initial orientation:	–75.517 hartree	$\Delta E = 29.5$ kcal/mol
After translation by 0.1 Å:	–75.470 hartree	

- 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:

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

H. Ou-Yang & M. Levy, *Phys. Rev. A* **44**, 54 (1991)

Theory of integrability: Definitions

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

The **first differential** in the direction h is defined by

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

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

$$DE[\rho,h] = \int v([\rho];\mathbf{r})h(\mathbf{r})\,d\mathbf{r}$$

where $v([\rho];\mathbf{r})$ is the **functional derivative**

$$v([\rho];\mathbf{r}) \equiv \frac{\delta E}{\delta\rho(\mathbf{r})}$$

More definitions

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

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

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

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

The kernel is called the **second functional derivative**

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

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 $\mathbf{r}$ and $\mathbf{r}'$

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

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

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

Symmetry of the second differential

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

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

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

$$D^2E[\rho,h,k] = \int Dv([\rho,k];\mathbf{r})h(\mathbf{r})\,d\mathbf{r}$$

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

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

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:

Differential form	Integral form
$\frac{\delta v([\rho];\mathbf{r})}{\delta\rho(\mathbf{r}')} = \frac{\delta v([\rho];\mathbf{r}')}{\delta\rho(\mathbf{r})}$	$\int Dv([\rho,k];\mathbf{r})h(\mathbf{r})\,d\mathbf{r} = \int Dv([\rho,h];\mathbf{r})k(\mathbf{r})\,d\mathbf{r}$
symmetry in $\mathbf{r}$ and $\mathbf{r}'$	symmetry in h and k
Requires manipulations with Dirac delta functions	Does not involve Dirac delta functions

A. P. Gaiduk and VNS, *J. Chem. Phys.* **133**, 101104 (2010)

Potentials that depend only on ρ and ∇ρ

Consider a model potential of the type

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

For this v, the second differential is

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

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

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

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

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

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

and is always a function of at most 4 ingredients:

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

A. P. Gaiduk and VNS, *Phys. Rev. A* **83**, 012509 (2011)

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:

$$\begin{cases} \dfrac{1}{g}\dfrac{\partial v}{\partial g} - l \dfrac{\partial v}{\partial w} - \dfrac{\partial^2 v}{\partial \rho \partial l} - g^2 \dfrac{\partial^2 v}{\partial \rho \partial w} - \dfrac{w}{g}\dfrac{\partial^2 v}{\partial g \partial w} = 0, \\ g \dfrac{\partial v}{\partial w} - \dfrac{\partial^2 v}{\partial g \partial l} = 0 \end{cases}$$

Note: these conditions are entirely in the (ρ, 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

$$T_W = \int \frac{|\nabla\rho|^2}{8\rho} d\mathbf{r}$$

Construction of integrable exchange potentials

Model potentials are normally expressed in terms of the dimensionless variables

$$s = \frac{g}{\rho^{4/3}}, \qquad q = \frac{l}{\rho^{5/3}}, \qquad u = \frac{w}{\rho^{13/3}}$$

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)

$$v_X^{\mathrm{LB94}} = v_X^{\mathrm{LDA}} - \rho^{1/3} \frac{\beta s^2}{1 + 3\beta s \sinh^{-1} \xi s},$$

where $s = \dfrac{g}{\rho^{4/3}}$ and $\beta = 0.05$ and ξ are constants

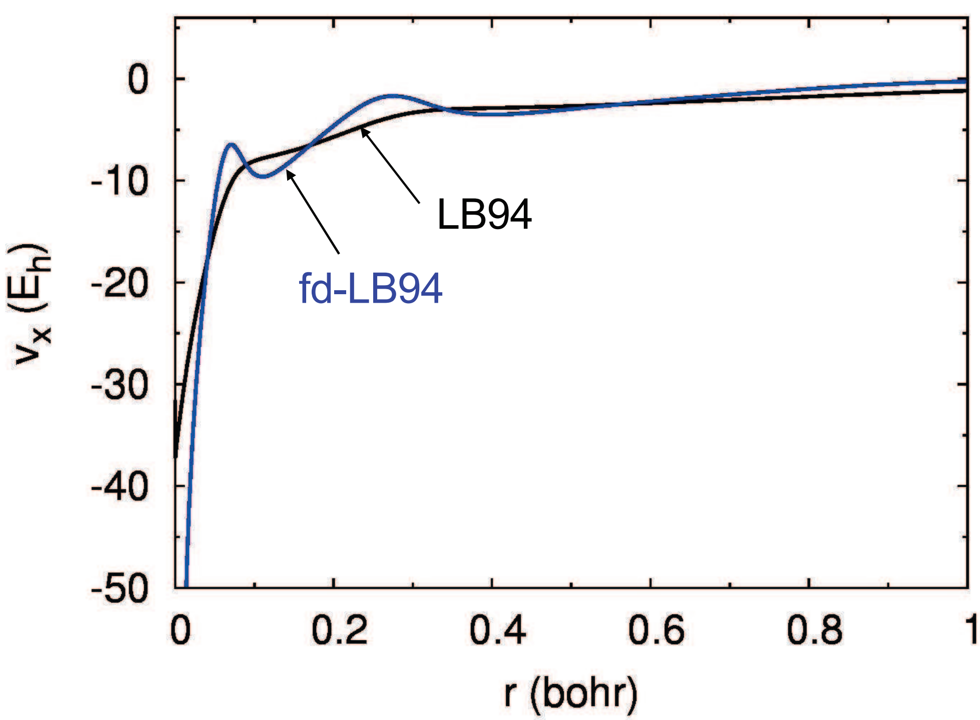
Functional derivative "grown" from LB94:

$$v_X = v_X^{\mathrm{LB94}} - \frac{\rho^{1/3}}{s}\left(I_0 \ln s - I_1 + I_0\right) q + \frac{\rho^{1/3}}{s^3}\left(I_0 \ln s - I_1 - s\frac{dI_0}{ds}\right) u$$

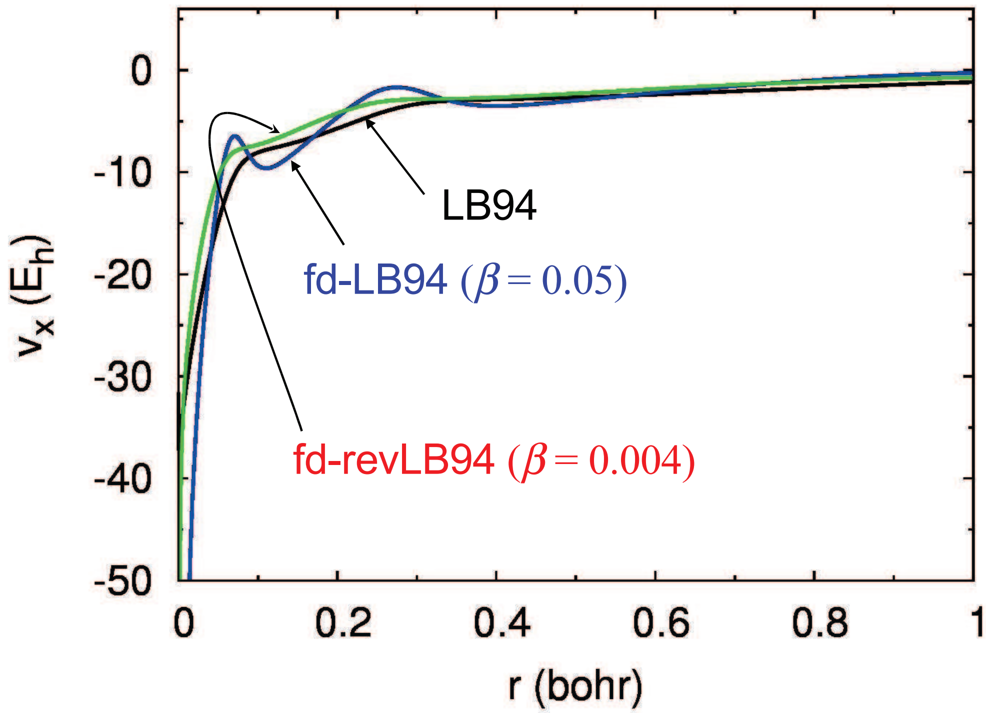
where

$$I_\alpha(s) = -\frac{3}{4}\int^{s} \frac{\beta \ln^\alpha s}{1 + 3\beta s \sinh^{-1} \xi s} ds, \qquad \alpha = 0, 1$$

LB94 and a "grown" functional derivative (fd)



LB94 and LB94-based functional derivatives



Total energies from the LB94 potential and the reconstructed functional derivative

Atom	original LB94	func. deriv. from LB94
He	− 2.821	− 4.275
Ne	− 129.430	− 138.597
Ar	− 529.173	− 547.017
Kr	−2761.921	−2797.106

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

Total energies from model exchange potentials

Atom	original LB94	func. deriv. from revised LB94	PBE
He	– 2.821	– 2.896	– 2.862
Ne	– 129.430	– 128.597	– 128.547
Ar	– 529.173	– 526.691	– 526.629
Kr	–2761.921	–2751.519	–2751.624

*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?

$$v_X^{\mathrm{BJ}}(\mathbf{r}) = v_X^S(\mathbf{r}) + \frac{1}{\pi}\sqrt{\frac{5\tau}{6\rho}}, \quad \text{where} \quad \tau(\mathbf{r}) = \frac{1}{2}\sum_i^{\mathrm{occ.}} \left|\nabla\varphi_i(\mathbf{r})\right|^2$$

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.

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