

Density-functional theory

Trygve Helgaker

Centre for Theoretical and Computational Chemistry
Department of Chemistry, University of Oslo, Norway

The 10th Sostrup Summer School
Quantum Chemistry and Molecular Properties
June 29 – July 11 2008

Density-functional theory

- ▶ The solution of the **Schrödinger equation** is a horrendously difficult task

$$H\Psi = E\Psi$$

- ▶ the wave function depends on $3N$ spatial and N spin coordinates

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad \mathbf{x}_i = \{\mathbf{r}_i, \sigma_i\}$$

- ▶ It is possible to build a theory based on the **one-electron density**

$$\rho(\mathbf{r}) = N \int \dots \int |\Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\sigma d\mathbf{x}_2 \dots d\mathbf{x}_N$$

- ▶ the density depends on only **three spatial coordinates**, for all systems

$$N = \int \rho(\mathbf{r}) d\mathbf{r}, \quad \rho(\mathbf{r}) \geq 0$$

- ▶ In **density-functional theory (DFT)**, this approach is taken

- ▶ DFT combines **good accuracy** with **low cost**

- ▶ Literature:

- ▶ H. Eschrig, "The Fundamentals of Density Functional Theory" (Teubner 1996)

1 Hohenberg–Kohn theory

- ▶ the external potential
- ▶ the Hohenberg–Kohn theorem
- ▶ the Hohenberg–Kohn functional
- ▶ the Hohenberg–Kohn variation principle
- ▶ v -representable densities and ground-state potentials

2 Levy–Lieb constrained-search theory

- ▶ N -representable densities
- ▶ the Levy–Lieb constrained-search functional

3 Lieb convex-conjugate theory

- ▶ convex functions
- ▶ Legendre–Fenchel transform
- ▶ conjugate and biconjugate functions
- ▶ the Lieb convex-conjugate functional

The external potential

- ▶ Consider the **electronic Hamiltonian**

$$H[v] = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v(\mathbf{r}_i) + \sum_{i>j} r_{ij}^{-1}$$

where we have introduced the **external potential** $v(\mathbf{r})$

- ▶ the Hamiltonian $H[v]$ depends functionally on the potential v
 - ▶ the potential v specifies the system uniquely
- ▶ Typically, we are interested in **attractive Coulomb potentials**

$$v(\mathbf{r}) = - \sum_A \frac{Z_A}{r_A}$$

- ▶ More generally, we consider **all potentials that can bind N electrons**

$$\mathcal{V}_N = \{ v \mid H[v] \text{ has an } N\text{-electron ground state} \}$$

- ▶ attractive Coulomb potentials
- ▶ spatially uniform positive background potentials
- ▶ and many others ...

The interaction with the external potential

- ▶ Consider a system represented by the external potential v :

$$H[v] = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} r_{ij}^{-1} + \sum_i v(\mathbf{r}_i) = T + W + \sum_i v(\mathbf{r}_i)$$

- ▶ The Schrödinger equation is given by

$$H[v]\Psi = E[v]\Psi$$

- ▶ Taking the **expectation value** of the Hamiltonian, we obtain

$$\begin{aligned} E &= \langle \Psi | H[v] | \Psi \rangle = \langle \Psi | T + W | \Psi \rangle + \langle \Psi | \sum_i v(\mathbf{r}_i) | \Psi \rangle \\ &= \langle \Psi | T + W | \Psi \rangle + (v|\rho) \end{aligned}$$

where the **interaction with the external potential** v is given by

$$(v|\rho) = \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \quad \leftarrow \text{interaction or pairing}$$

- ▶ the relationship between v and ρ is at the heart of DFT

Different potentials have different wave functions

- ▶ The Hamiltonian is a functional of the external potential:

$$H[v] = T + W + \sum_i v(\mathbf{r}_i), \quad v \in \mathcal{V}_N$$

- ▶ Let us assume that two potentials v_1 and v_2 share the **same** wave function:

$$H[v_1]\Psi = E[v_1]\Psi \quad \& \quad H[v_2]\Psi = E[v_2]\Psi$$

- ▶ Subtracting the two Schrödinger equations, we obtain

$$(H[v_1] - H[v_2])\Psi = \sum_i [v_1(\mathbf{r}_i) - v_2(\mathbf{r}_i)]\Psi = (E[v_1] - E[v_2])\Psi$$

- ▶ Eliminating Ψ from both sides of last equation, we conclude that potentials with the same wave function **differ by at most an additive constant**:

$$v_1(\mathbf{r}) - v_2(\mathbf{r}) = c$$

Different potentials have different wave functions

$$v_1(\mathbf{r}) \neq v_2(\mathbf{r}) + c \quad \Rightarrow \quad \Psi[v_1] \neq \gamma \Psi[v_2]$$

The Hohenberg–Kohn theorem

- ▶ Consider two different systems $v_1(\mathbf{r}) \neq v_2(\mathbf{r}) + c$, $v_i \in \mathcal{V}_N$
 - ▶ these systems have different ground states $\Psi[v_1] \neq \gamma \Psi[v_2]$
- ▶ Invoking the variation principle for the ground state, we obtain

$$E[v_1] < \langle \Psi[v_2] | H[v_1] | \Psi[v_2] \rangle = E[v_2] + (v_1 - v_2 | \rho_2)$$

$$E[v_2] < \langle \Psi[v_1] | H[v_2] | \Psi[v_1] \rangle = E[v_1] - (v_1 - v_2 | \rho_1)$$

- ▶ Adding the two inequalities, we obtain

$$E[v_1] + E[v_2] < E[v_1] + E[v_2] + (v_1 - v_2 | \rho_2 - \rho_1)$$

- ▶ this gives a contradiction unless the two densities are different

$$v_1(\mathbf{r}) \neq v_2(\mathbf{r}) + c \quad \Rightarrow \quad \rho_1(\mathbf{r}) \neq \rho_2(\mathbf{r})$$

- ▶ two different potentials cannot give rise to the same density

The Hohenberg–Kohn (HK) theorem

Each N -electron density ρ is the ground-state density of at most one external potential $v[\rho] + c$, which is uniquely determined up to an additive constant c .

The HK mapping between potentials and densities

v -representable densities

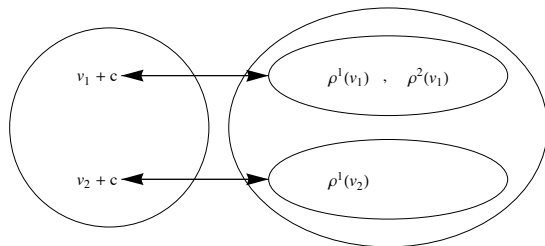
Each density ρ is the ground-state density of at most one external potential $v[\rho]$.

- ▶ those that arise from some potential $v[\rho]$ are said to be **v -representable**
- ▶ those that do not are said to be **non- v -representable**

- ▶ HK theory thus sets up a mapping between the following two sets:

$$v \in \mathcal{V}_N = \{ v \mid H[v] \text{ has an } N\text{-electron ground state} \}$$

$$\rho \in \mathcal{A}_N = \{ \rho \mid \rho \text{ comes from an } N\text{-electron ground state} \}$$



The Hohenberg–Kohn functional

- ▶ In HK theory, we may in principle determine the energy from the density

$$\rho \in \mathcal{A}_N \rightarrow v[\rho] \rightarrow \Psi[\rho] \rightarrow E[\rho]$$

- ▶ we shall often use the more compact notation $v_\rho = v[\rho]$ and $\Psi_\rho = \Psi[\rho]$.
- ▶ For a given $\rho \in \mathcal{A}_N$, the electronic energy is then calculated as

$$\begin{aligned} E[\rho] &= \left\langle \Psi_\rho \left| -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} r_{ij}^{-1} + \sum_i v_\rho(\mathbf{r}_i) \right| \Psi_\rho \right\rangle \\ &= \langle \Psi_\rho | T + W | \Psi_\rho \rangle + (v_\rho | \rho), \quad \rho \in \mathcal{A}_N \end{aligned}$$

The Hohenberg–Kohn universal density functional

$$F_{\text{HK}}[\rho] = \langle \Psi_\rho | T + W | \Psi_\rho \rangle, \quad \rho \in \mathcal{A}_N$$

- ▶ In terms of this functional, we may calculate the energy as

$$E[\rho] = F_{\text{HK}}[\rho] + (v_\rho | \rho), \quad \rho \in \mathcal{A}_N$$

The Hohenberg–Kohn variation principle

- ▶ For a **given density** $\rho \in \mathcal{A}_N$, the energy may be calculated as

$$E[\rho] = F_{\text{HK}}[\rho] + (v_\rho | \rho), \quad \rho \in \mathcal{A}_N \rightarrow v_\rho$$

- ▶ To calculate the energy for a **given potential** $u \in \mathcal{V}_N$, consider

$$E[\rho, u] = F_{\text{HK}}[\rho] + (u | \rho), \quad \rho \in \mathcal{A}_N, u \in \mathcal{V}_N, u \neq v_\rho$$

- ▶ From the **variation principle**, we now obtain

$$\begin{aligned} E[\rho, u] &= \langle \Psi_\rho | T + W | \Psi_\rho \rangle + \langle \Psi_\rho | \sum_i u(\mathbf{r}_i) | \Psi_\rho \rangle \\ &= \langle \Psi_\rho | H[u] | \Psi_\rho \rangle \geq E[u] \end{aligned}$$

The Hohenberg–Kohn variation principle

$$E[u] = \min_{\rho \in \mathcal{A}_N} \{ F_{\text{HK}}[\rho] + (u | \rho) \}, \quad u \in \mathcal{V}_N$$

- ▶ for $u \in \mathcal{V}_N$, we search over all v -representable densities ρ until $v_\rho = u$
- ▶ the functional $F_{\text{HK}}[\rho]$ is the same for all systems, only $(u | \rho)$ differs

The Hohenberg–Kohn Euler equation

- ▶ The Hohenberg–Kohn variation principle is given by

$$E[v] = \min_{\rho} E_v[\rho], \quad E_v[\rho] = F_{\text{HK}}[\rho] + (\rho|v)$$

- ▶ To minimize $E_v[\rho]$ for a fixed electron number N , we construct a Lagrangian:

$$L_v[\rho, N] = F_{\text{HK}}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) \, d\mathbf{r} - \mu \left(\int \rho(\mathbf{r}) \, d\mathbf{r} - N \right)$$

- ▶ The stationary condition now yields the **Hohenberg–Kohn Euler equation**:

$$\delta E_v[\rho, N] = 0 \quad \Rightarrow \quad \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu$$

where μ is the **chemical potential** and we have used the relation:

$$\frac{\delta}{\delta \rho(\mathbf{r})} \int f(\rho) \, d\mathbf{r} = \frac{\partial f(\rho)}{\partial \rho(\mathbf{r})}$$

- ▶ are the derivatives well defined?
- ▶ does the Euler equation have a (unique) solution?

Hohenberg–Kohn theory summarized

The Hohenberg–Kohn functional and variation principle

$$F_{\text{HK}}[\rho] = \langle \Psi_\rho | T + W | \Psi_\rho \rangle, \quad \rho \in \mathcal{A}_N$$

$$E[v] = \min_{\rho \in \mathcal{A}_N} \{ F_{\text{HK}}[\rho] + (\rho|v) \}, \quad v \in \mathcal{V}_N$$

- ▶ We may obtain the ground-state energy by a **variation over densities**
 - ▶ there is no need to involve the wave function!
- ▶ However, certain **difficulties** remain
 - ▶ the explicit form of $F_{\text{HK}}[\rho]$ is unknown
 - ▶ the domain of $F_{\text{HK}}[\rho]$ is unknown
- ▶ Although the exact $F_{\text{HK}}[\rho]$ is unknown, good approximations are available
 - ▶ we shall consider in detail these later
- ▶ We shall first see how HK theory may be extended to an explicitly known set
 - ▶ the Levy–Lieb constrained-search functional
 - ▶ the Lieb convex-conjugate functional

The Levy–Lieb constrained-search functional

- ▶ From the usual variation principle, we obtain immediately

$$E[v] = \inf_{\Psi} \langle \Psi | T + W + \sum_i v(\mathbf{r}_i) | \Psi \rangle$$

- ▶ since $v \in \mathcal{V}_N$ is not assumed, there may not be a minimizing wave function
- ▶ we thus determine an **infimum** (greatest lower bound) rather than a **minimum**
- ▶ We now carry out the search in two separate steps

$$\begin{aligned} E[v] &= \inf_{\rho} \left[\inf_{\Psi \rightarrow \rho} \langle \Psi | T + W + \sum_i v(\mathbf{r}_i) | \Psi \rangle \right] \\ &= \inf_{\rho} \left[\inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle + (\rho|v) \right] \end{aligned}$$

- ▶ Introducing the **Levy–Lieb constrained-search functional**, we obtain

$$\begin{aligned} F_{LL}[\rho] &= \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle \\ E[v] &= \inf_{\rho} (F_{LL}[\rho] + (\rho|v)) \end{aligned}$$

- ▶ for the minimization to be exact, we must now search over all densities ρ that can be obtained from an N -electron wave function $\Psi \rightarrow \rho$

N -representable densities

- ▶ Consider the following two sets:

- ▶ all **square-integrable N -electron wave functions of finite kinetic energy**

$$\mathcal{W}_N = \{\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) \mid P_{ij}\Psi = -\Psi, \langle \Psi | \Psi \rangle < \infty, \langle \nabla_i \Psi | \nabla_i \Psi \rangle < \infty\}$$

- ▶ all **N -representable densities**

$$\mathcal{I}_N = \{\rho(\mathbf{r}) \mid \rho(\mathbf{r}) \geq 0, \int \rho(\mathbf{r}) \, d\mathbf{r} = N, \int |\nabla \rho^{1/2}(\mathbf{r})|^2 \, d\mathbf{r} < \infty\}$$

- ▶ It can be shown that:

$$\Psi \in \mathcal{W}_N \Leftrightarrow \rho \in \mathcal{I}_N, \quad \Psi \rightarrow \rho$$

- ▶ note that ρ can usually be obtained from **many different** $\Psi \rightarrow \rho$
 - ▶ among all $\Psi \rightarrow \rho$, there is always a **determinantal wave function** $\Psi_{\text{det}} \rightarrow \rho$
- ▶ We have previously considered the set of v -representable densities \mathcal{A}_N
 - ▶ it consists of all densities obtained from some ground state $\mathcal{A}_N \subset \mathcal{I}_N$
 - ▶ whereas \mathcal{A}_N is an unknown set, \mathcal{I}_N is a known set

The functionals $F_{\text{HK}}[\rho]$ and $F_{\text{LL}}[\rho]$ compared

- ▶ The Hohenberg–Kohn and Levy–Lieb functionals are given by

$$F_{\text{HK}}[\rho] = \langle \Psi_\rho | T + W | \Psi_\rho \rangle, \quad \rho \in \mathcal{A}_N$$

$$F_{\text{LL}}[\rho] = \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle, \quad \rho \in \mathcal{I}_N$$

where Ψ_ρ is the ground-state wave function associated with $\rho \in \mathcal{A}_N$

- ▶ By construction, they give the **same result** when used variationally:

$$E[v] = \min_{\rho \in \mathcal{A}_N} \{ F_{\text{HK}}[\rho] + (\rho|v) \} = \min_{\rho \in \mathcal{I}_N} \{ F_{\text{LL}}[\rho] + (\rho|v) \}, \quad v \in \mathcal{V}_N$$

- ▶ We can also demonstrate their **equivalence on \mathcal{A}_N** explicitly:

$$\begin{aligned} F_{\text{LL}}[\rho] &= \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle = \inf_{\Psi \rightarrow \rho} \langle \Psi | H[v] | \Psi \rangle - (\rho|v) \\ &= \langle \Psi_\rho | H[v] | \Psi_\rho \rangle - (\rho|v) = \langle \Psi_\rho | T + W | \Psi_\rho \rangle = F_{\text{HK}}[\rho] \end{aligned}$$

- ▶ F_{LL} is thus a **continuation** of F_{HK} from an **unknown** to a **known** domain
 - ▶ all “reasonable densities” are N -representable

Levy–Lieb constrained-search theory summarized

The Levy–Lieb functional and variation principle

$$F_{\text{LL}}[\rho] = \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle$$

$$E[v] = \inf_{\rho \in \mathcal{I}_N} (F_{\text{LL}}[\rho] + (\rho|v))$$

- ▶ We have avoided the unknown domain of Hohenberg–Kohn theory
 - ▶ search is over all “reasonable” N -representable densities
 - ▶ however, this theory is still not fully satisfactory
- ▶ We obtain the energy by a variational minimization of $F_{\text{LL}}[\rho] + (\rho|v)$
 - ▶ the functional to be minimized should then be as simple as possible
- ▶ In particular, we would like it to contain **at most one minimizer**
 - ▶ this would guarantee a unique solution of the Euler equation:

$$\frac{\delta F_{\text{LL}}[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu$$

- ▶ unfortunately, this cannot be proved for the Levy–Lieb functional

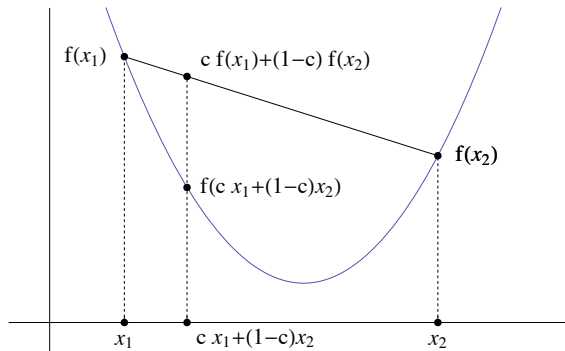
Lieb's convex-conjugate functional

- ▶ The **Hohenberg–Kohn functional** is defined only for v -representable densities
 - ▶ unfortunately, this domain is not explicitly known
- ▶ The **Levy–Lieb functional** is continuation to an explicitly known domain
 - ▶ these are the N -representable densities
 - ▶ unfortunately, it may give rise to several stationary points
- ▶ We shall now consider **Lieb's convex-conjugate functional**
 - ▶ it also has an explicitly known domain
 - ▶ it has only unique solutions
- ▶ Lieb's approach requires some understanding of **convex analysis**
 - ▶ we shall briefly review the theory of convex functions
- ▶ Particularly important are **Legendre–Fenchel (LF) transforms**
 - ▶ we shall obtain Lieb's functional by a LF transformation of the energy
 - ▶ the energy and density functional constitute a conjugate pair

Convex functions

- ▶ A function is said to be **convex** if it satisfies the inequality

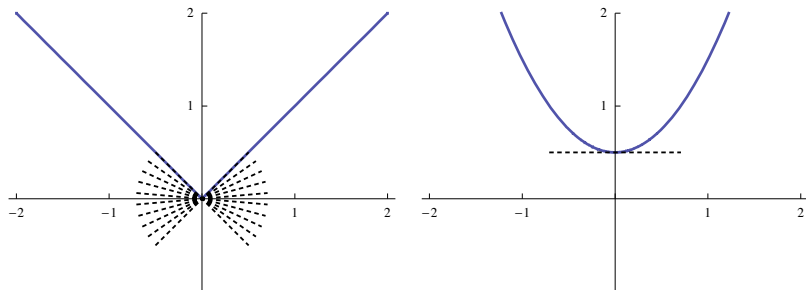
$$cf(x_1) + (1 - c)f(x_2) \geq f(cx_1 + (1 - c)x_2), \quad 0 \leq c \leq 1$$



- ▶ For a **strictly convex function**, we may replace \geq by $>$ above
- ▶ A function $f(x)$ is **concave** if $-f(x)$ is convex

Some properties of convex functions

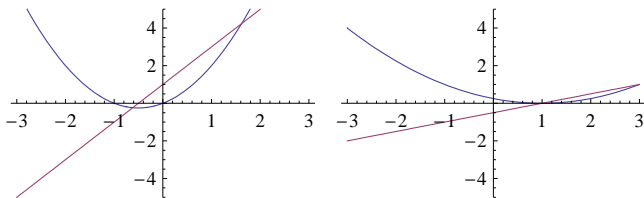
- ▶ A convex function has at most one stationary point: the global minimum



- ▶ A convex function is **continuous** except where it goes to infinity
 - ▶ however, it may be **nondifferentiable**
- ▶ At each point, there is an associated set of **tangents of support**
 - ▶ the slope of such a tangent of support is called a **subgradient**
- ▶ The condition for a (global) minimum is a zero subgradient

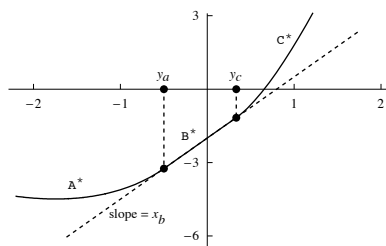
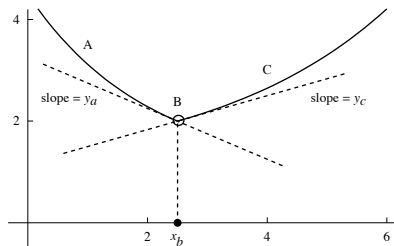
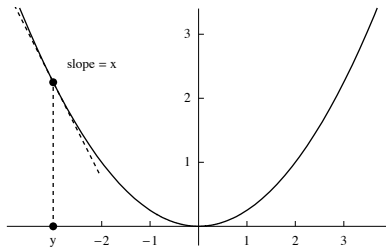
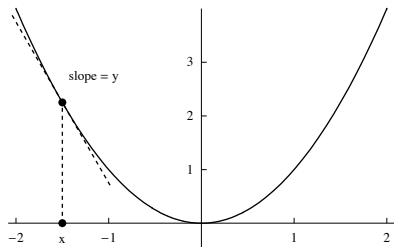
Convex conjugate functions

- ▶ Functions often come in **natural pairs**
 - ▶ knowledge of one function then implies knowledge of the other
 - ▶ inverse functions $g(f(x)) = x$ constitute such a pair
- ▶ A convex function is in general not invertible and has no inverse
- ▶ However, consider a strictly convex and differentiable function $f(x)$
 - 1 $f(x)$ has a monotonically increasing gradient $f'(x)$
 - 2 $f'(x)$ has a monotonically increasing inverse $g'(x) = f'^{-1}(x)$
 - 3 $g'(x)$ integrates to yield a new convex function $g(x) + c$

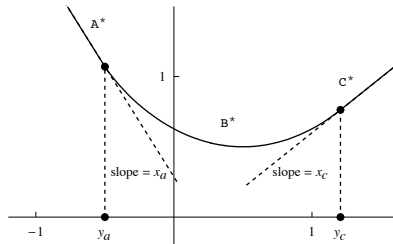
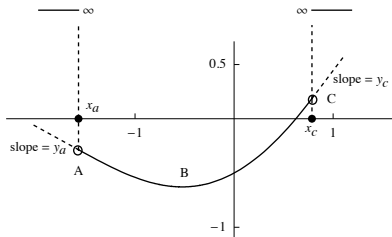
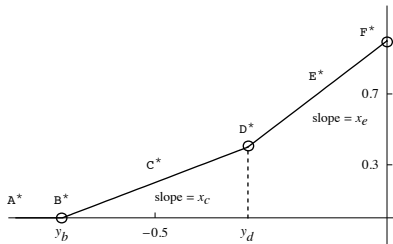
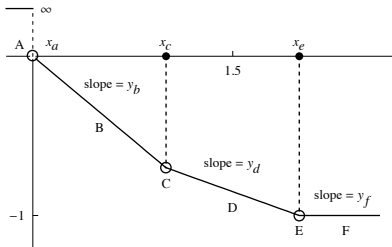


- ▶ The functions $f(x)$ and $g(x)$ are **convex conjugate** functions
 - ▶ they satisfy the **reciprocal relation** $g'(f'(x)) = x$

Examples of convex conjugate functions



More examples of convex conjugate functions



The Legendre–Fenchel transform

- ▶ We need a precise definition of conjugate functions

The Legendre–Fenchel transform (convex conjugate function)

$$f^*(y) = \sup_x \{yx - f(x)\}$$

- ▶ supremum (least upper bound) is used since a maximum may not exist
- ▶ in general, $f(x)$ need not be convex nor differentiable
- ▶ however, $f^*(y)$ itself is always convex

- ▶ Let us now assume that $f(x)$ is strictly convex and differentiable
 - ▶ there is then a unique stationary point (a maximum), for all y :

$$d(yx - f(x)) / dx = 0 \Rightarrow y = f'(x)$$

- ▶ we now differentiate $f^*(y)$ under the assumption $y = f'(x)$:

$$f^{*'}(y) = x + yx'(y) - f'(x)x'(y) = x \Rightarrow f^{*'}(f'(x)) = x$$

- ▶ this is the reciprocal relation of the previous slide

Legendre transform in classical mechanics

- ▶ If f is strictly convex and differentiable, f^* is called a **Legendre transform**
 - ▶ Legendre transforms are ubiquitous in physics
- ▶ The **Lagrangian** of classical mechanics is convex in the **velocity** \dot{x}

$$L(\dot{x}) = \frac{1}{2}m\dot{x}^2 - V_{\text{pot}}$$

- ▶ Its Legendre transform is the **Hamiltonian**:

$$H(p) = L^*(p) = \max_{\dot{x}} \left(p\dot{x} - \frac{1}{2}m\dot{x}^2 + V_{\text{pot}} \right)$$

- ▶ the stationary condition identifies the **momentum**

$$p = m\dot{x} \Leftrightarrow \dot{x} = p/m$$

- ▶ substituting $\dot{x} = p/m$ into $H(p)$, we obtain

$$H(p) = p^2/2m + V_{\text{pot}}$$

- ▶ The reciprocal relation is satisfied:

$$L'(\dot{x}) = m\dot{x} = p \quad \& \quad H'(p) = p/m = \dot{x}$$

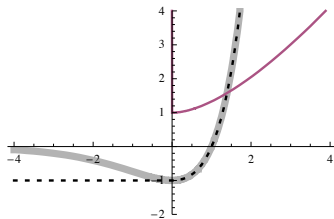
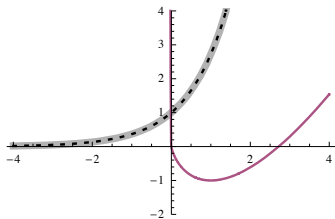
- ▶ Legendre transforms are used in thermodynamics

The double Legendre–Fenchel transform (convex biconjugate)

$$f^{**}(x) = \sup_y (xy - f^*(y))$$

- ▶ Conjugation relationships

$$f(x) \rightarrow f^*(y) \leftrightarrow f^{**}(x)$$



- ▶ The **biconjugate** is the largest convex function smaller than $f(x)$

$$f^{**}(x) \leq f(x) \quad (\text{arbitrary } f)$$

$$f^{**}(x) = f(x) \quad (\text{convex } f)$$

- ▶ f^{**} is said to be the **convex envelope** to $f(x)$

Legendre–Fenchel functional transforms

The single Legendre–Fenchel transform (convex conjugate)

$$F^*[g] = \sup_f ((g|f) - F[f]), \quad (g|f) = \int g(x)f(x)dx$$

- ▶ A functional and its conjugate satisfies the Fenchel–Young inequality

$$F^*[g] + F[f] \geq (f|g)$$

The double Legendre–Fenchel transform (convex biconjugate)

$$F^{**}[f] = \sup_y ((f|g) - F^*[g])$$

- ▶ The biconjugate is the maximal convex minorant to a functional

$$F^{**}[f] \leq F[f] \quad (\text{arbitrary } F)$$

$$F^{**}[f] = F[f] \quad (\text{convex } F)$$

- ▶ Conjugation relations

$$F[f] \rightarrow F^*[g] \leftrightarrow F^{**}[f]$$

The LF transform of the ground-state electronic energy

- ▶ Consider the variationally optimized ground-state electronic energy

$$E[v] = \inf_{\Psi} \langle \Psi | H[v] | \Psi \rangle$$

- ▶ concavity of $E[v]$ follows from the variation principle ($0 \leq c \leq 1$)

$$\begin{aligned} E[cv_1 + (1-c)v_2] &= \inf_{\Psi} (c \langle \Psi | H[v_1] | \Psi \rangle + (1-c) \langle \Psi | H[v_2] | \Psi \rangle) \\ &\geq c \inf_{\Psi} \langle \Psi | H[v_1] | \Psi \rangle + (1-c) \inf_{\Psi} \langle \Psi | H[v_2] | \Psi \rangle \\ &= cE[v_1] + (1-c)E[v_2] \end{aligned}$$

- ▶ the convex functional $-E[v]$ therefore has a conjugate partner
- ▶ Following the **standard LF procedure** (generalized to functionals), we obtain

$$F[\rho] = \sup_v \left(E[v] - (v|\rho) \right) \quad \leftarrow \text{density functional by LF transformation}$$

$$E[v] = \inf_{\rho} \left(F[\rho] + (v|\rho) \right) \quad \leftarrow \text{energy by LF back transformation}$$

- ▶ $E[v]$ and $F[\rho]$ are conjugate pairs, just like $L(\dot{x})$ and $H(p)$
- ▶ we must consider the domains of the functionals and other technicalities ...

Lieb's conjugate density functional

- ▶ The ground-state energy may be represented in two alternative forms:

$$F[\rho] = \sup_v \{ E[v] - (v|\rho) \} \quad \leftarrow \text{energy as a functional of density}$$

$$E[v] = \inf_\rho \{ F[\rho] + (v|\rho) \} \quad \leftarrow \text{energy as a functional of potential}$$

- ▶ The potential v and the density ρ are **conjugate variables**
 - ▶ they belong to **dual linear spaces** such that $(v|\rho) = \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}$ is finite
 - ▶ they satisfy the reciprocal relations (assuming well defined derivatives)

$$\frac{\delta E[v]}{\delta v(\mathbf{r})} = \rho(\mathbf{r}) \quad \leftarrow \text{determines } v \text{ when calculating } F[\rho] \text{ from } E[v]$$

$$\frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} = -v(\mathbf{r}) \quad \leftarrow \text{determines } \rho \text{ when calculating } E[v] \text{ from } F[\rho]$$

- ▶ these are the Euler equations for $F[\rho]$ and $E[v]$
 - ▶ since the functionals are either convex or concave, their solutions are unique
- ▶ The LF approach highlights the symmetry between ρ and v
 - ▶ sometimes it is best to work with $F[\rho]$ (DFT), other times with $E[v]$ (MM)

Linear spaces of wave functions, densities and potentials

Banach space

- ▶ a Banach space is a complete normed vector space
- ▶ an important special case: Lebesgue space of p -integrable functions L^p

$$\|f\|_p = \left(\int |f(\mathbf{r})|^p d\mathbf{r} \right)^{1/p} < +\infty \quad \leftarrow \text{norm in } L^p$$

Hilbert space

- ▶ a Hilbert space is a Banach space equipped with an inner product $\langle f|g \rangle$
- ▶ an important special case: L^2 with norm $\|f\| = \sqrt{\langle f|f \rangle}$

To what spaces do wave functions, densities and potentials belong?

- ▶ wave functions belong to the Hilbert space $\psi \in L^2$
- ▶ densities belong to the Banach space $\rho \in X = L^1 \cap L^3$
- ▶ potentials belong to the dual Banach space $v \in X^* = L^\infty + L^{3/2}$
- ▶ the duality of X and X^* guarantees finite interactions $\langle v|\rho \rangle < +\infty$

The dual spaces of densities and potentials

- ▶ We first identify the Banach space densities, next the space of potentials.

The Banach space of densities X

- ▶ The density must be **integrable** $\int \rho(\mathbf{r}) \, d\mathbf{r} = N$
 - ▶ as a consequence, we require $\rho \in L^1$
- ▶ Next, we require a **finite kinetic energy**
 - ▶ it can be shown that this gives $\rho \in L^3$
- ▶ We conclude that $\rho \in X = L^1 \cap L^3$

The Banach space of potentials X^*

- ▶ We identify the space of potentials by requiring a **finite interaction** $(\rho|v)$.
 - ▶ this leads us to the dual space X^* of X
- ▶ We conclude that $v \in X^* = L^\infty + L^{3/2}$
- ▶ Finally, we confirm that X^* contains all Coulomb potentials.

A comparison of all density functionals

We have introduced three universal density functionals

$$F_{\text{HK}}[\rho] = \langle \Psi_\rho | T + W | \Psi_\rho \rangle, \quad \rho \in \mathcal{A}_N$$

$$F_{\text{LL}}[\rho] = \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle, \quad \rho \in \mathcal{I}_N$$

$$F[\rho] = \sup_{v \in X} \{ E[v] - (v|\rho) \}, \quad \rho \in X$$

- ▶ These functionals give the same results for ground-state densities:

$$F[\rho] = F_{\text{LL}}[\rho] = F_{\text{HK}}[\rho], \quad \rho \in \mathcal{A}_N$$

- ▶ Only the Levy–Lieb and Lieb functionals are defined for other densities

$$F[\rho] = F_{\text{LL}}^{**}[\rho] \leq F_{\text{LL}}[\rho], \quad \rho \in \mathcal{I}_N$$

- ▶ note: the Lieb functional is the convex envelope to the Levy–Lieb functional
- ▶ The Lieb functional is the preferred functional
 - ▶ it is convex, yielding at most one minimum
 - ▶ it is defined on a whole linear space of densities
 - ▶ it reflects the fundamental symmetry between densities and potentials

Review and preview

We have done the following:

- ▶ proved the Hohenberg–Kohn theorem
- ▶ introduced the Hohenberg–Kohn functional
- ▶ established the Hohenberg–Kohn variation principle
- ▶ introduced the Levy–Lieb constrained-search functional
- ▶ introduced the Lieb convex-conjugate functional

$$F[\rho] = \sup_v \{ E[v] - (v|\rho) \} \quad \leftarrow \text{energy as a functional of density}$$

$$E[v] = \inf_\rho \{ F[\rho] + (v|\rho) \} \quad \leftarrow \text{energy as a functional of potential}$$

We shall now discuss the following topics:

- ▶ the uniform electron gas
- ▶ Thomas–Fermi theory
- ▶ the noninteracting reference system and Kohn–Sham theory
- ▶ the exchange–correlation functional and potential
- ▶ review standard approximations

Review and preview

We have done the following:

- ▶ proved the Hohenberg–Kohn theorem
- ▶ introduced the Hohenberg–Kohn functional
- ▶ established the Hohenberg–Kohn variation principle
- ▶ introduced the Levy–Lieb constrained-search functional
- ▶ introduced the Lieb convex-conjugate functional

We shall now discuss the following topics:

- ▶ ensemble-state DFT
- ▶ the uniform electron gas
- ▶ Thomas–Fermi theory
- ▶ the noninteracting reference system and Kohn–Sham theory
- ▶ the exchange–correlation functional and potential
- ▶ standard approximations

Pure states

- ▶ Our discussion up to now has been for pure N -electron states

$$H[v]\Psi = E_N[v]\Psi \quad \leftarrow \quad \text{ground-state of an } N\text{-electron system}$$

- ▶ The energy is continuous and concave in v and has a conjugate partner:

$$F_N[\rho] = \sup_v \{E_N[v] - (v|\rho)\} \quad \leftarrow \quad \text{the Lieb convex-conjugate functional}$$

$$E_N[v] = \inf_\rho \{F_N[\rho] + (v|\rho)\} \quad \leftarrow \quad \text{the Hohenberg-Kohn variation principle}$$

- ▶ It can be shown that

$$F_N[\rho] = +\infty \quad \Leftarrow \quad \rho \notin \mathcal{I}_N$$

- ▶ For $v \in \mathcal{V}_N$, the N -electron ground-state energy is given by

$$E_N[v] = F_N[\rho] + (v|\rho), \quad \frac{\delta F_N[\rho]}{\delta \rho(\mathbf{r})} = -v(\mathbf{r})$$

- ▶ the functional derivative exists for all $\delta\rho$ within \mathcal{I}_N

Ensemble states

- ▶ For a more general DFT, we consider ensemble states
- ▶ To describe such states, we introduce the ensemble density operator

$$\hat{\gamma} = \sum_{N_i} p_{N_i} |\Psi_{N_i}\rangle \langle \Psi_{N_i}|, \quad p_{N_i} \geq 0, \quad \sum_{N_i} p_{N_i} = 1$$

- ▶ Here p_{N_i} is the probability that the system is found in state Ψ_{N_i} satisfying

$$\hat{H}[v]\Psi_{N_i} = E_{N_i}[v]\Psi_{N_i} \leftarrow \text{eigenfunction of the Hamiltonian}$$

$$\hat{N}\Psi_{N_i} = N\Psi_{N_i} \leftarrow \text{eigenfunction of the number operator}$$

- ▶ The expectation values may be expressed in terms of traces

$$\langle \hat{H}[v] \rangle = \text{tr} \hat{\gamma} \hat{H}[v] = \sum_{N_i} p_{N_i} E_{N_i}[v]$$

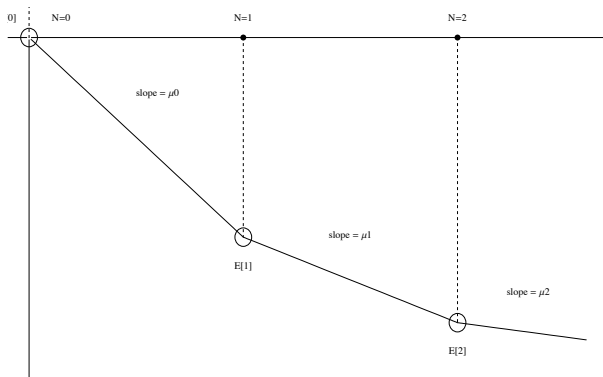
$$\langle \hat{N} \rangle = \text{tr} \hat{\gamma} \hat{N} = \sum_{N_i} p_{N_i} N$$

- ▶ For given v and N , we may calculate the ground-state energy as

$$E[v, N] = \inf_{\hat{\gamma} \rightarrow N} \text{tr} \hat{\gamma} \hat{H}[v]$$

The energy as a function of the particle number

- ▶ It can be shown that the ensemble-state energy is convex in N



- ▶ $E[v, N]$ consists of straight line segments between integer N
 - ▶ it is a conjecture that the pure-state energies $E_N[v]$ are also convex in N

$$E_N[v] = E[v, N] \quad (\text{integer } N)$$

The particle-independent density-functional $F[\rho]$

- ▶ For pure states, we have previously constructed $F_N[\rho]$ conjugate to $E_N[v]$
- ▶ For mixed states, we can likewise define

$$F[\rho, N] = \sup_v \{ E[v, N] - (v|\rho) \} \quad \leftarrow \text{energy as a functional of density}$$

$$E[v, N] = \inf_\rho \{ F[\rho, N] + (v|\rho) \} \quad \leftarrow \text{energy as a functional of potential}$$

- ▶ note: like $F_N[\rho]$, $F[\rho, N] = +\infty$ for $\rho_N \neq N$
- ▶ We may combine these functionals into a single entity as

$$F[\rho] = F[\rho, \int \rho(\mathbf{r}) d\mathbf{r}] = \inf_N F[\rho, N]$$

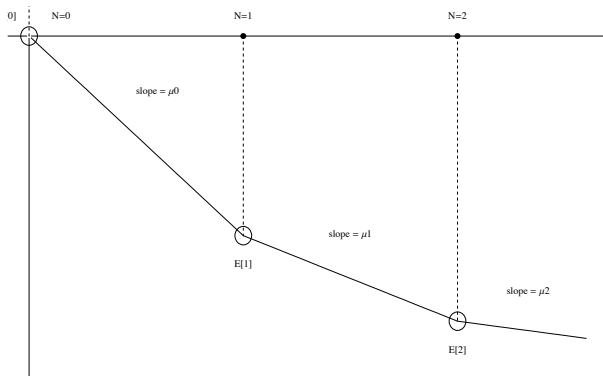
- ▶ this is our universal density-functional, valid for all particle numbers
- ▶ the functional is **convex** in ρ , without restrictions on the particle number
- ▶ From $F[\rho]$, we may now calculate energies for arbitrary N

$$E[v, N] = \inf_{\rho \in \mathcal{I}_N} \{ F[\rho] + (\rho|v) \}$$

- ▶ the constraint to \mathcal{I}_N is essential since $F[\rho]$ is now finite for all particle numbers

The chemical potential

- ▶ The ensemble energy $E[v, N]$ is piecewise linear in N



- ▶ The variable conjugate to N is the chemical potential μ_N
 - ▶ the potential is related to the ionization potential

$$\mu_N = E[v, N + 1] - E[v, N] = -I_{N+1} \quad \leftarrow \text{ionization potential}$$

- ▶ μ is constant between integers but jumps discontinuously at integers

Derivative discontinuity at integral particle numbers

- ▶ Energy from universal density functional

$$E[v, N] = \inf_{\rho \in \mathcal{I}_N} \{F[\rho] + (\rho|v)\}$$

- ▶ $E[v, N]$ is piecewise linear between integer N
- ▶ $E[v, N]$ is nondifferentiable with respect to N at integral N
- ▶ We must therefore have a **derivative discontinuity** in $F[\rho]$ at integral N
 - ▶ The variations in ρ can be decomposed as

$$\delta\rho(\mathbf{r}) = \delta\rho_N(\mathbf{r}) + \delta n \quad \text{such that} \quad \int \delta\rho(\mathbf{r})d\mathbf{r} = \delta n$$

- ▶ $F[\rho]$ is differentiable except in the direction of δn at integral N
- ▶ The slope in $E[v, N]$ between integral N is given by
$$\mu_N = E[v, N + 1] - E[v, N] = -I_{N+1} \quad \leftarrow \text{ionization potential}$$
- ▶ The derivative discontinuity in $F[\rho]$ at N is therefore

$$\left. \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} \right|_{N+\delta} - \left. \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} \right|_{N-\delta} = \Delta_N = I_N - I_{N+1} \geq 0, \quad \delta > 0$$

- ▶ can this be modelled?

The uniform electron gas (UEG)

- ▶ An important reference system for DFT is the **uniform electron gas (UEG)**
 - ▶ we assume **no interactions** among the electrons
 - ▶ we shall consider the interacting case (uniform electron liquid) later
- ▶ The Schrödinger equation for a free electron

$$-\frac{1}{2}\nabla^2\varphi(\mathbf{r}) = E\varphi(\mathbf{r})$$

- ▶ in a cubic box of length ℓ with periodic boundary conditions
- ▶ It has the normalized eigenfunctions and energies

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \ell^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad E_{\mathbf{k}} = k^2/2, \quad \mathbf{k} = 2\pi\ell^{-1}(n_x, n_y, n_z)$$

- ▶ We minimize energy by doubly occupying orbitals up to the **Fermi radius k_F** :

$$\rho(\mathbf{r}) = 2 \sum_{k \leq k_F} |\varphi_k|^2 = 2 \sum_{k \leq k_F} \ell^{-3}$$

- ▶ **uniform distribution of density in space**, dependent only upon k_F

The UEG one-electron density and energy density

- ▶ The **one-electron density** and **energy density** are given by

$$\rho = 2 \sum_{k \leq k_F} \frac{1}{\ell^3} = \frac{1}{4\pi^3} \int d\mathbf{k} = \frac{1}{\pi^2} \int_0^{k_F} k^2 dk = \frac{k_F^3}{3\pi^2}$$
$$\mathcal{E} = 2 \sum_{k \leq k_F} \frac{k^2}{2\ell^3} = \frac{1}{8\pi^3} \int k^2 d\mathbf{k} = \frac{1}{2\pi^2} \int_0^{k_F} k^4 dk = \frac{k_F^5}{10\pi^2}$$

- ▶ we have here replaced summations by integration with the volume element

$$d\mathbf{n} = (\ell/2\pi)^3 d\mathbf{k}$$

obtained from $(k_x, k_y, k_z) = 2\pi\ell^{-1}(n_x, n_y, n_z)$

- ▶ We may now express the energy density in terms of the electron density as

$$\mathcal{E} = C_F \rho^{5/3}, \quad C_F = \frac{3}{10} (3\pi^2)^{2/3} \approx 2.8712$$

- ▶ we shall later use this simple relationship between ρ and \mathcal{E} to construct an explicit density functional for the kinetic energy

The UEG two-electron density

- ▶ In DFT, it is useful to decompose the two-electron density in the form

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)h_x(\mathbf{r}_1; \mathbf{r}_2)$$

- ▶ the first term represents an uncorrelated description
 - ▶ the second term is an exchange correction
- ▶ Integrating over all space on both sides of this equation, we obtain

$$(N - 1)\rho(\mathbf{r}_1) = N\rho(\mathbf{r}_1) + \rho(\mathbf{r}_1) \int h_x(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2$$

and therefore

$$\int h_x(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1$$

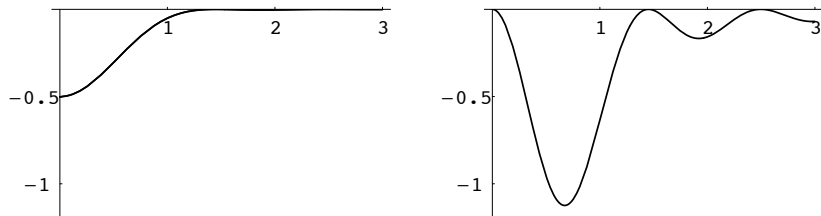
- ▶ For each \mathbf{r}_1 , $h_x(\mathbf{r}_1, \mathbf{r}_2)$, contains exactly one missing electron
 - ▶ it is called **exchange hole** or **Fermi hole**
- ▶ The one-electron density is uniform but the two-electron density nonuniform

The Fermi hole

- ▶ For the UEG, the Fermi hole has the shape

$$h_x(\mathbf{r}_1; \mathbf{r}_2) = -\frac{1}{2}\gamma^2(k_F r_{12})\rho(\bar{\mathbf{r}}), \quad \gamma(x) = 3x^{-3}(\sin x - x \cos x)$$

- ▶ The Fermi hole (to the left) and its radial distribution (to the right)



- ▶ the exchange hole is centered around $r_{12} = 0$, with depth $-1/2$
- ▶ this occurs since only same-spin electrons participate in exchange
- ▶ the hole decays in an oscillatory manner
- ▶ at large r_{12} , the frequency is π/k_F

The Thomas–Fermi (TF) model

- ▶ Let us now consider an explicit density functional for atoms and molecules
 - ▶ point-charge potentials rather than a spatially uniform charge distribution
- ▶ Independently, **Thomas and Fermi** (1927) suggested the following model

$$E_{\text{TF}}[\rho] = T_{\text{TF}}[\rho] + J[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) \, d\mathbf{r}$$

- ▶ it precedes the Hartree–Fock model by three years
- ▶ Apart from the external interaction, it contains two terms:
 - 1 the **Thomas–Fermi kinetic energy**

$$T_{\text{TF}}[\rho] = C_{\text{F}} \int \rho^{5/3}(\mathbf{r}) \, d\mathbf{r}, \quad C_{\text{F}} = \frac{3}{10} (3\pi^2)^{2/3} \approx 2.8712$$

obtained by applying locally the UEG expression for kinetic energy

- 2 the **Hartree energy**

$$J = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 d\mathbf{r}_2$$

which represents the classical interaction of the density with itself

- ▶ Thomas and Fermi ignored correlation and were unaware of exchange

Performance of the TF model

- ▶ The TF energy expression for an atom

$$E_{\text{TF}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 - Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r}$$

gives the following Euler equation (with undetermined multiplier μ)

$$\frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{Z}{r} = \mu$$

- ▶ Two problems are immediately obvious:
 - ▶ the density becomes infinite at the nucleus, as $r \rightarrow 0$
 - ▶ the density decays as a power law (not exponentially), as $r \rightarrow \infty$
- ▶ The total atomic energy is given by

$$E_{\text{TF}}(Z) = -0.7687 Z^{7/3}$$

- ▶ too low by 54% for H, 35% for He, and 10%–15% for heavy elements
 - ▶ no shell structure
- ▶ For molecules, there is **no binding!** (Teller nonbinding theorem)

The Thomas–Fermi–Dirac (TFD) model

- ▶ Thomas and Fermi constructed their model, unaware of exchange
- ▶ The uniform-gas Fermi-hole expression leads to Dirac's exchange formula

$$K_D[\rho] = C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}, \quad C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \approx 0.7386$$

- ▶ Bloch (1929), Dirac (1930)
- ▶ As a refinement of the TF model, we now include Dirac's functional

$$E_{\text{TFD}}[\rho] = T_{\text{TF}}[\rho] + J[\rho] - K[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}$$

- ▶ The Thomas–Fermi–Dirac (TFD) model does not improve on the TF model
 - ▶ energy is lowered further
 - ▶ still no binding predicted
- ▶ The main error in TF theory is in the description of kinetic energy
 - ▶ The TF functional gives a too low kinetic energy
- ▶ Unlike the TF functional, the Dirac functional is still used

Scaling relations

- ▶ Consider the electron **coordinate scaling**:

$$\Psi(\mathbf{r}_i) \rightarrow \Psi_\alpha(\mathbf{r}_i) = \alpha^{3N/2} \Psi(\alpha \mathbf{r}_i), \quad \langle \Psi_\alpha | \Psi_\alpha \rangle = \langle \Psi | \Psi \rangle$$

- ▶ It may be shown that

$$\langle \Psi_\alpha | T | \Psi_\alpha \rangle = \alpha^2 \langle \Psi | T | \Psi \rangle$$

$$\langle \Psi_\alpha | W | \Psi_\alpha \rangle = \alpha \langle \Psi | W | \Psi \rangle$$

- ▶ The corresponding scaling of the electron density gives

$$\rho(\mathbf{r}) \rightarrow \rho_\alpha(\mathbf{r}) = \alpha^3 \rho(\alpha \mathbf{r})$$

- ▶ Consider the integral:

$$\int \rho_\alpha^\lambda(\mathbf{r}) \, d\mathbf{r} = \alpha^{3\lambda} \int \rho^\lambda(\alpha \mathbf{r}) \, d\mathbf{r} = \alpha^{3(\lambda-1)} \int \rho^\lambda(\mathbf{r}) \, d\mathbf{r}$$

- ▶ We then obtain **scaling relations** in agreement with **the TFD model**:

$$\int \rho_\alpha(\mathbf{r}) \, d\mathbf{r} = \int \rho(\mathbf{r}) \, d\mathbf{r} = N$$

$$T_{\text{TF}}[\rho_\alpha] = C_F \int \rho_\alpha^{5/3}(\mathbf{r}) \, d\mathbf{r} = \alpha^2 T_{\text{TF}}[\rho]$$

$$K[\rho_\alpha] = C_x \int \rho_\alpha^{4/3}(\mathbf{r}) \, d\mathbf{r} = \alpha K[\rho]$$

The local-density approximation (LDA) and beyond

- ▶ The TF model is the first example of a **local-density approximation (LDA)**
 - 1 an inhomogeneous system is viewed as consisting of small boxes
 - 2 in each box, we approximate the density and potential as constant
 - 3 in each box, we apply the results for a homogeneous system
 - 4 finally, we make the boxes infinitely small

$$E[\rho] \approx E_{\text{LDA}}[\rho] = \int \mathcal{E}_{\text{hom}}(\rho(\mathbf{r})) \, d\mathbf{r}$$

- ▶ for example, the TF functional is obtained from the UEG energy density as

$$\mathcal{E}_{\text{UEG}}(\rho) = C_F \rho^{5/3} \rightarrow T_{\text{TF}}[\rho] \approx C_F \int \rho(\mathbf{r})^{5/3} \, d\mathbf{r}$$

- ▶ The LDA approximation is not always a good one
 - ▶ this is particularly true for the kinetic energy
- ▶ As a next step, it is natural to utilize information about the density gradient
 - ▶ this idea leads to the **gradient-expansion approximation (GEA)**
 - ▶ to improve the description, a power-type expansion is attempted
 - ▶ a large number of such functionals have been developed

The von Weizsäcker kinetic-energy functional

- ▶ To improve upon the poor TF(D) model, von Weizsäcker suggested a **gradient correction** to the energy

$$T_W[\rho] = \frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} > 0 \leftarrow \text{von Weizsäcker correction}$$

- ▶ Let us calculate the total energy, with **an adjustable parameter** λ

$$T_{TF\lambda W} = T_{TF}[\rho] + \lambda T_W[\rho]$$

- ▶ $\lambda = 1$ in von Weizsäcker's original work
- ▶ $\lambda = 1/9$ from gradient-expansion approach
- ▶ $\lambda = 1/5$ from fitting to hydrogenic atoms
- ▶ Density is now much improved and **binding is predicted**
- ▶ Atomic energies:

	TF	TFD	TFD $\frac{1}{9}$ W	TFD $\frac{1}{5}$ W	HF
Ne	-165.6	-176.3	-139.9	-128.8	-128.6
Ar	-652.7	-680.7	-562.0	-524.9	-526.8

The noninteracting kinetic-energy functional $T_s[\rho]$

- ▶ Let us examine a **fictitious system of noninteracting electrons**
- ▶ In DFT, this system is described by the functional

$$E^0[\rho] = T[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r}$$

- ▶ The universal density-functional $T[\rho]$ is now the **kinetic-energy functional**
 - ▶ use of $T_{\text{TF}}[\rho]$ gives very poor results
 - ▶ however, in this case, we can solve the Schrödinger equation exactly
- ▶ The exact kinetic energy can now be written in the **Levy–Lieb form**

$$T_s[\rho] = \min_{\sum n_I |\phi_I|^2 \rightarrow \rho} \sum_I n_I \langle \phi_I | -\frac{1}{2} \nabla^2 | \phi_I \rangle \leftarrow \text{single-electron kinetic energy}$$

where the density is expressed in terms of **orbitals**:

$$\rho(\mathbf{r}) = \sum_I n_I |\phi_I(\mathbf{r})|^2, \quad 0 \leq n_I \leq 1, \quad \langle \phi_I | \phi_J \rangle = \delta_{IJ}, \quad \sum_I n_I = N$$

- ▶ for full generality, we allow for **fractional occupation numbers** n_I

The exchange–correlation (XC) energy

- ▶ In the general case, the exact kinetic energy cannot be evaluated as

$$T_s[\rho] = \min \sum_I n_I \langle \phi_I | -\frac{1}{2} \nabla^2 | \phi_I \rangle$$

- ▶ we may nevertheless use $T_s[\rho]$ as a reasonable approximation to $T[\rho]$
- ▶ We therefore decompose the universal density functional

$$F[\rho] = T[\rho] + W[\rho]$$

as

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho], \quad \rho(\mathbf{r}) = \sum_I n_I |\phi_I(\mathbf{r})|^2$$

- ▶ We have here introduced the **exchange–correlation (xc)** functional

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + W[\rho] - J[\rho]$$

where

$$T[\rho] - T_s[\rho] = \text{kinetic-energy correlation correction}$$

$$W[\rho] - J[\rho] = \begin{cases} \text{two-electron exchange and correlation energy} \\ \text{self-interaction correction} \end{cases}$$

Kohn–Sham theory

- ▶ In the **Kohn–Sham (KS) method**, the energy is calculated as

$$E[v] = \min_{\rho} \left(T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} + J[\rho] + E_{xc}[\rho] \right)$$

subject to the constraints

$$\rho(\mathbf{r}) = \sum_I n_I |\phi_I(\mathbf{r})|^2, \quad 0 \leq n_I \leq 1, \quad \langle \phi_I | \phi_J \rangle = \delta_{IJ}, \quad \sum_I n_I = N$$

- ▶ This gives the **Kohn–Sham equations**

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r}) \right] \phi_I(\mathbf{r}) = \varepsilon_I \phi_I(\mathbf{r}), \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots$$

- ▶ the **Kohn–Sham potential** and the **exchange–correlation potential**:

$$v_{KS}(\mathbf{r}) = v(\mathbf{r}) + v_J(\mathbf{r}) + v_{xc}(\mathbf{r}), \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

- ▶ Orbitals are occupied following the **Aufbau principle**
 - ▶ highest occupied molecular orbital (HOMO) may be **fractionally** occupied

The fictitious non-interacting Kohn–Sham system

- ▶ The KS energy may be viewed as obtained in a two-step optimization

$$E[v] = \min_{\rho} \left(T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} + J[\rho] + E_{xc}[\rho] \right)$$

$$T_s[\rho] = \min_{\sum |\phi_I|^2 \rightarrow \rho} \sum_I \langle \phi_I | -\frac{1}{2} \nabla^2 | \phi_I \rangle$$

- ▶ an outer minimization over all densities
 - ▶ an inner constrained-search minimization of the noninteracting kinetic energy
 - ▶ the Levy–Lieb constrained search approach with only T in the search
- ▶ The KS solution provides us with the **exact density**
 - ▶ constructed from **orbitals that minimize the noninteracting kinetic energy**
 - ▶ **fictitious noninteracting electrons** with the density of the physical system
 - ▶ the KS wave function is a determinant constructed from ϕ_I
 - ▶ The KS wave function has the physical density and the least kinetic energy
 - ▶ Comparing kinetic energies, we find

$$T[\rho] \geq T_{\text{HF}} \geq T_{\text{KS}}[\rho]$$

KS and HF self-consistent field (SCF) theories compared

- ▶ There are obvious similarities between the KS and HF SCF theories
 - ▶ in both methods, a set of orbitals are determined self-consistently
 - ▶ both methods use an effective potential
 - ▶ the costs of the methods are similar
- ▶ The HF orbitals give an approximate wave function
 - ▶ they minimize the total energy of the determinant
 - ▶ they provide an approximate method by design
- ▶ The KS orbitals give the exact density
 - ▶ they minimize the noninteracting kinetic energy
 - ▶ they provide an exact method in principle
- ▶ Since $E_{xc}[\rho]$ is unknown, the KS description is in practice approximate
 - ▶ it is possible to provide explicit but approximate forms for $E_{xc}[\rho]$ that gives results broadly similar to those of MP2, CCSD and even CCSD(T) methods
 - ▶ no simple systematic procedure for improving $E_{xc}[\rho]$ exists

The KS-LDA method

- ▶ We have set up a theory in which T is calculated to reasonable accuracy

$$T_c[\rho] = T[\rho] - T_s[\rho] \geq 0 \quad \leftarrow \text{positive correlation correction}$$

- ▶ The error is about as large as the correlation energy (but of opposite sign)

$$T_c[\rho_{\text{He}}] \approx 36 \text{ mH}, \quad E_c[\rho_{\text{He}}] \approx -42 \text{ mH}$$

- ▶ To apply Kohn–Sham theory, we must now approximate $E_{\text{xc}}[\rho]$
 - ▶ it is customary to divide this contribution into two parts

$$E_{\text{xc}}[\rho] = E_x[\rho] + E_c[\rho]$$

$$E_x[\rho] < 0 \quad \text{Fermi and static correlation}$$

$$E_c[\rho] < 0 \quad \text{dynamical correlation}$$

- ▶ By far the largest contribution is usually exchange
 - ▶ in Ne, exchange and correlation contribute -12.12 and -0.39 H, respectively
 - ▶ as a first approximation to exact Kohn–Sham theory, we apply LDA to $E_{\text{xc}}[\rho]$:

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int f(\rho) \, d\mathbf{r}$$

The X_α method

- ▶ In **Slater's X_α method**, we ignore correlation and approximate exchange by the scaled Dirac functional:

$$E_{X_\alpha}[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + J[\rho] - \frac{3\alpha}{2} C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

- ▶ The X_α method was proposed by Slater in 1951, as approximate HF theory
 - ▶ this was before KS theory was proposed in 1965
- ▶ The parameter α may be treated as an adjustable parameter
 - ▶ important special values

$$\alpha = 1 \quad \text{original value}$$

$$\alpha = 2/3 \quad \text{KS-LDA without correlation}$$

- ▶ The X_α method may thus be viewed as a special case of KS-LDA
- ▶ The X_α method differs from TFD theory only in the kinetic energy

LDA correlation: the electron liquid

- ▶ We have an explicit exchange functional from the UEG: Dirac's functional
- ▶ For correlation, we must consider interacting electrons: the **electron liquid**
 - ▶ no single explicit functional form exists
 - ▶ accurate **quantum Monte-Carlo simulations** by Ceperley and Alder (1980)
- ▶ The simulations are carried out for different total and spin densities

$$\rho = \rho_\alpha + \rho_\beta, \quad \zeta = \frac{\rho_\alpha - \rho_\beta}{\rho}, \quad \begin{cases} \zeta = 0 & \text{paramagnetic (lowest energy)} \\ \zeta = 1 & \text{ferromagnetic (highest energy)} \end{cases}$$

- ▶ The density is usually expressed in terms of the **Wigner-Seitz radius**:

$$r_s = \left(\frac{3}{4\pi\rho} \right)^{1/3} \quad \leftarrow \text{radius of sphere containing one electron}$$

- ▶ for $r_s < 1$ (high densities), manybody perturbation theory is accurate
 - ▶ for intermediate and large r_s , parameterization of simulations
- ▶ Popular functionals based on simulations:
 - ▶ **Perdew-Zunger (PZ81)**: popular in solid-state physics (1981)
 - ▶ **Vosko-Wilkes-Nusair (VWN)**: popular in quantum chemistry (1980)

KS-LDA: the SVWN functional

- ▶ In the KS-LDA method, the following XC functional is mostly used:

$$E_{xc}^{SVWN}[\rho] = E_x^{\text{Dirac}}[\rho] + E_c^{\text{VWN}}[\rho] \leftarrow \text{Slater-Vosko-Wilkes-Nusair}$$

- ▶ In LDA, the largest error is the overestimation of exchange by about 10%
 - ▶ this overestimation is larger than the whole correlation energy
 - ▶ electron correlation is underestimated, sometimes by a factor of two
 - ▶ systematic error cancellation
- ▶ Atomic energies:

	TF	TFD	$X_{2/3}$	LDA	HF	exp.
Ne	-165.6	-176.3	-127.5	-128.1	-128.6	-128.9
Ar	-652.7	-680.7	-524.5	-525.9	-526.8	-527.6

- ▶ For molecules LDA overbinds but produces reasonable structures
- ▶ LDA remains the workhorse of physics
- ▶ For DFT to have an impact on chemistry, an improvement was needed

Beyond LDA: GEAs and GGAs

- ▶ To improve upon the LDA model

$$E_{xc}^{\text{LDA}}[\rho] = \int f(\rho_\alpha, \rho_\beta) d\mathbf{r}$$

we must take into account the inhomogeneity in the electron density

- ▶ A natural first step is to include some dependence on the density gradient:

$$E_{xc}^{\text{GGA}}[\rho] = \int f(\rho_\alpha, \rho_\beta, \zeta_{\alpha\alpha}, \zeta_{\beta\beta}, \zeta_{\alpha\beta}) d\mathbf{r}$$

$$\zeta_{\sigma\tau} = \nabla\rho_\sigma \cdot \nabla\rho_\tau$$

- ▶ in **gradient-expansion approximations (GEAs)**, a systematic power-series expansion is attempted
- ▶ in **generalized-gradient approximations (GGAs)**, a more general dependence on density gradient is attempted
- ▶ While there is essentially only one LDA, many GGAs have been proposed
 - ▶ the functional form is guided by boundary conditions and exact relationships
 - ▶ adjustable parameters are typically introduced
 - ▶ these may be adjusted to experiment to satisfy exact relations

The Becke exchange correction

- ▶ In 1988, Becke proposed the following exchange functional:

$$E_x[\rho] = \sum_{\sigma} \int \rho_{\sigma} (\mathcal{E}_{x\sigma}^{\text{LDA}} + \Delta\mathcal{E}_{x\sigma}^{\text{B88}}) d\mathbf{r}$$

where the gradient correction is given by

$$\Delta\mathcal{E}_{x\sigma}^{\text{B88}} = -\beta\rho_{\sigma}^{1/3} \frac{s_{\sigma}^2}{1 + 6\beta s_{\sigma} \sinh^{-1} s_{\sigma}}, \quad s_{\sigma} = \frac{|\nabla\rho_{\sigma}|}{\rho_{\sigma}^{4/3}}$$

- ▶ The exchange energy density now has the correct r^{-1} asymptotic dependence
- ▶ The B88 correction contains one empirical parameter

$$\beta = 0.0042$$

obtained by a least-squares fit to the HF exchange of noble-gas atoms

- ▶ Used with VWN correlation, it gave a binding energy for N_2 within 5 kcal/mol
- ▶ This constitutes a remarkable improvement on LDA and made DFT a predictive tool of quantum chemistry

The LYP correlation functional

- ▶ In 1988, Lee, Yang and Parr proposed the following correlation energy density:

$$\mathcal{E}_c^{\text{LYP}} = -a(1 + d\rho^{-1/3})^{-1} - ab\omega\rho \left[C_F\rho^{8/3} + |\nabla\rho|^2\left(\frac{5}{12} - \delta\frac{7}{72}\right) - \frac{11}{24}\rho^2|\nabla\rho|^2 \right]$$
$$\omega = \frac{\exp(-c\rho^{-1/3})}{1 + d\rho^{-1/3}}\rho^{-11/3}, \quad \delta = c\rho^{-1/3} + \frac{d\rho^{-1/3}}{1 + d\rho^{-1/3}}$$

- ▶ form given above valid for closed-shell systems
- ▶ It is based on a correlation-energy formula for helium in terms of the second-order HF density matrix by Colle and Salvetti (1975)
- ▶ It contains four parameters (a, b, c, d), calculated by Colle and Salvetti in their fit to the helium atom.
- ▶ The LYP functional is often used in combination with the B88 exchange correction
- ▶ The resulting BLYP functional contains five adjustable parameters, all obtained from noble-gas atoms.

HF exchange and hybrid methods

- ▶ The B88 functional was adjusted to exact HF exchange in closed-shell atoms
- ▶ Why not always calculate exact HF exchange?

$$E_{xc} = E_x^{\text{HF}} + E_c$$

- ▶ Such a **hybrid approach** works well for atoms but fails for molecules
 - ▶ mean absolute errors for G2 atomization energies:
78, 5–7, and 32 kcal/mol for HF, GGA, and such hybrid methods, respectively
- ▶ What is the reason for the poor behaviour of this hybrid functional?
 - ▶ HF exchange becomes delocalized in molecules
 - ▶ the delocalized HF exchange must be compensated for by static correlation
 - ▶ GGA exchange is always localized
 - ▶ it corresponds to Fermi correlation plus static correlation
 - ▶ in noble-gas atoms, there is no static correlation

The adiabatic connection

- ▶ The XC energy contains apparently **unrelated** contributions

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + W[\rho] - J[\rho]$$

- ▶ Consider now the **Levy–Lieb constrained-search formula**

$$F_\lambda[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | T + \lambda W | \Psi \rangle = \langle \Psi_\rho^\lambda | T + \lambda W | \Psi_\rho^\lambda \rangle$$

- ▶ λ is the **coupling-strength parameter**
- ▶ We may now write the XC energy as

$$E_{xc}[\rho] = F_1[\rho] - F_0[\rho] - J[\rho] = \int_0^1 \frac{dF_\lambda[\rho]}{d\lambda} d\lambda - J[\rho]$$

- ▶ Invoking the **Hellmann–Feynman theorem**

$$dF_\lambda[\rho]/d\lambda = \langle \Psi_\rho^\lambda | W | \Psi_\rho^\lambda \rangle$$

we obtain a single, coherent expression for the XC energy

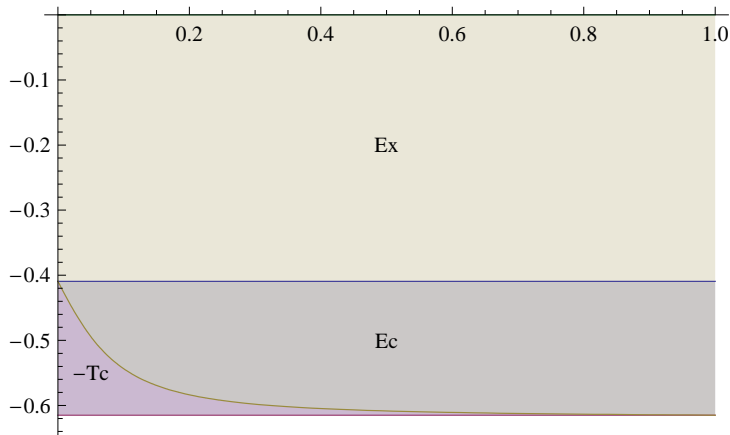
$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\rho^\lambda | W - J[\rho] | \Psi_\rho^\lambda \rangle d\lambda$$

- ▶ a **coupling-strength integrated nonclassical electron-repulsion energy**

The adiabatic connection

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\rho^\lambda | W - J[\rho] | \Psi_\rho^\lambda \rangle d\lambda$$

$$F_\lambda[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | T + \lambda W | \Psi \rangle = \langle \Psi_\rho^\lambda | T + \lambda W | \Psi_\rho^\lambda \rangle$$



Becke's half-and-half formula

- ▶ The adiabatic-connection formula

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\rho^\lambda | W - J[\rho] | \Psi_\rho^\lambda \rangle d\lambda$$

- ▶ the XC energy expressed as the λ -averaged nonclassical Coulomb energy
- ▶ There are two limiting cases:
 - $\lambda = 0$: exchange-only independent-particle limit, can be treated exactly
 - $\lambda = 1$: fully interacting system, can only be approximated
- ▶ Two-point quadrature gives **Becke's half-and-half formula** (1993):

$$E_{xc}^{HH} = \frac{1}{2} E_{xc}^{\lambda=0} + \frac{1}{2} E_{xc}^{\lambda=1}$$

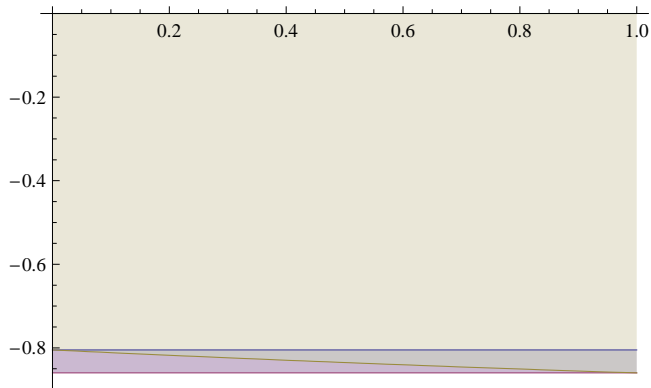
- ▶ the G2 mean absolute errors for atomization energies: 6.5 kcal/mol
- ▶ Some proportion of exact HF exchange may be a good thing

The adiabatic connection

- ▶ Adiabatic-connection formula:

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\rho^\lambda | W - J[\rho] | \Psi_\rho^\lambda \rangle d\lambda$$

- ▶ Adiabatic connection curve for H_2 at bond distance 0.70 bohr

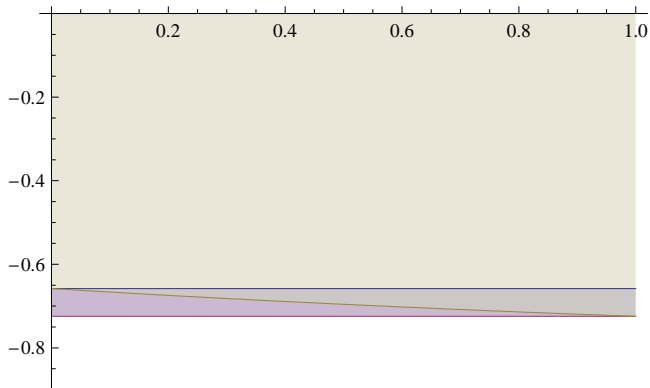


The adiabatic connection

- ▶ Adiabatic-connection formula:

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\rho^\lambda | W - J[\rho] | \Psi_\rho^\lambda \rangle d\lambda$$

- ▶ Adiabatic connection curve for H_2 at bond distance 1.40 bohr

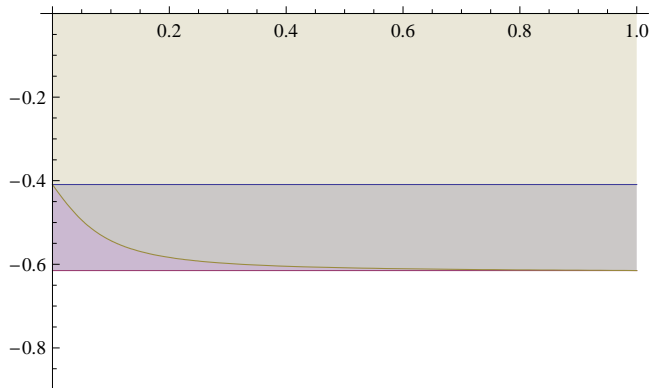


The adiabatic connection

- ▶ Adiabatic-connection formula:

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\rho^\lambda | W - J[\rho] | \Psi_\rho^\lambda \rangle d\lambda$$

- ▶ Adiabatic connection curve for H_2 at bond distance 5.00 bohr

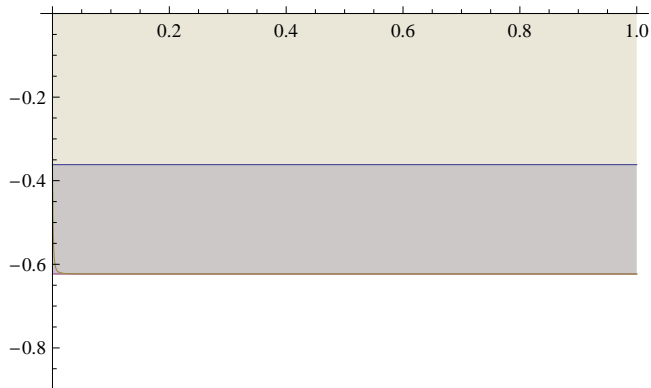


The adiabatic connection

- ▶ Adiabatic-connection formula:

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\rho^\lambda | W - J[\rho] | \Psi_\rho^\lambda \rangle d\lambda$$

- ▶ Adiabatic connection curve for H_2 at bond distance 10.0 bohr



Semi-empirical hybrid theories

- ▶ Motivated by the adiabatic-connection formula, we would like to introduce some proportion of exact exchange
 - ▶ this must be done semi-empirically
- ▶ Becke's B3 functional (1993):

$$E_{xc}^{B3} = (1 - a)E_{Dirac} + aE_x^{HF} + bE_x^{B8} + E_c^{VWN} + cE_c^{PW91}$$

- ▶ fitting to the G2 atomization and ionization energies gives

$$a = 0.20, \quad b = 0.71 \quad c = 0.81$$

- ▶ The B3LYP functional (1994) is a small modification to Becke's functional:

$$E_{xc}^{B3LYP} = (1 - a)E_{Dirac} + aE_x^{HF} + bE_x^{B8} + (1 - c)E_c^{VWN} + cE_c^{LYP}$$

- ▶ adjustable parameters from the B3 functional
- ▶ the most popular XC functional in chemistry

Derivative discontinuities

- ▶ The total energy is a piecewise linear curve between integral particle numbers
 - ▶ this implies a **derivative discontinuity** in $F[\rho]$ at integral N :

$$\left. \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \right|_{N+\delta} - \left. \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \right|_{N-\delta} = \Delta_N = I_N - I_{N+1} \geq 0, \quad \delta > 0$$

- ▶ In KS theory, we decompose the universal density functional in the manner

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

- ▶ a derivative discontinuity is introduced with $T_s[\rho]$:

$$\left. \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \right|_{N+\delta} - \left. \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \right|_{N-\delta} = \Delta_N^{\text{KS}} = \varepsilon_{N+1} - \varepsilon_N$$

- ▶ the rest must be supplied by $E_{xc}[\rho]$:

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

- ▶ The XC potential **jumps by a constant amount** at integer particle numbers
 - ▶ integer discontinuity cannot easily be achieved with continuum functionals
 - ▶ instead they average over the two limits

Self-interaction

- ▶ There are no electron repulsion interactions in a one-electron system
 - ▶ there should be a complete cancellation of $J[\rho]$ and $E_{xc}[\rho]$ in such systems
- ▶ However, current functionals achieve this cancellation only to within 1%
- ▶ The self-interaction problem exists also in many-electron systems
- ▶ How can this deficiency be amended?
- ▶ Perdew and Zunger (1981) proposed the **self-interaction correction (SIC)**:

$$E_{xc}^{\text{SIC}}[\rho_\alpha, \rho_\beta] = E_{xc}[\rho_\alpha, \rho_\beta] - \sum_{i\sigma} (J[\rho_{i\sigma}] + E_{xc}[\rho_{i\sigma}, 0])$$

- ▶ does not affect the exact functional
- ▶ leads to a difficult optimization with different potentials for different orbitals