TOTAL ENERGIES
OF ELECTRONIC SYSTEMS

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OUTLINE:
1. MANY ELECTRON THEORY
2. DFT theorems
3. LDA results
4. LDA inherent difficulties
5. GRADIENTS GEA
6. GRADIENTS GGA
7. LIMITATIONS band gaps, symmetry...
8. REAL SPACE orbital dep. func.s
Topics not covered:

Spin dependence
Current DFT
Relativistic DFT
Excited states
Time-dependent DFT
Temperature-dependent DFT
Multi-component DFT
DFT for superconductors
Fractional occupation numbers
A DIFFERENT APPROACH:
- Let us do without Density Functional Theory (DFT) as long as possible
- How far do we get?

THE HAMILTONIAN

\[ H = -\frac{1}{2} \sum_{i} N \nabla_i^2 + \sum_{i} w(\vec{r}_i) + \]
\[ \quad + \frac{1}{2} \sum_{i \neq j} u(\vec{r}_i - \vec{r}_j) \]

\[ u(\vec{r}) = 1/r \]
- units a.u.
- non-relativistic
- no spin-orbit
- no magnetic fields
- no time dependence

TYPICALLY \[ w(\vec{r}) = -\sum_{\mu} \varepsilon_{\mu} \cdot u(\vec{r} - \vec{R}_{\mu}) \]
\[ E = \langle \Psi | H | \Psi \rangle \quad \langle \Psi | \Psi \rangle = 1 \]

The simplest term in the energy
\[ W = \langle \Psi | \hat{V} | \Psi \rangle = \langle \Psi | \sum_{\xi} N_{\xi} \psi(\vec{r}_{\xi}) | \Psi \rangle = \int d\vec{r} w(\vec{r}) \langle \Psi | \sum_{\xi} \delta(\vec{r} - \vec{r}_{\xi}) | \Psi \rangle = \int d\vec{r} w(\vec{r}) \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle = \int d\vec{r} w(\vec{r}) \cdot n(\vec{r}) \]

a very intuitive and classical result!

We have above defined the density operator \( \hat{n}(\vec{r}) \)
\[ \hat{n}(\vec{r}) = \sum_{\xi} \delta(\vec{r} - \vec{r}_{\xi}) \]
and the density \( n(\vec{r}) \)
\[ n(\vec{r}) = \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle = \langle \Psi | \sum_{\xi} N_{\xi} \delta(\vec{r} - \vec{r}_{\xi}) | \Psi \rangle = \langle \Psi | \sum_{\xi} \delta(\vec{r} - \vec{r}_{\xi}) | \Psi \rangle = N \int \delta(\vec{r} - \vec{r}_{\xi}) | \Psi(\vec{r}_{1}, \vec{r}_{2}, \ldots, \vec{r}_{N}) \rangle^2 d^{3}r_{1} \ldots d^{3}r_{N} : d\sigma_{1} \ldots d\sigma_{N} \]
\[ n(\vec{r}) = N \int d\sigma_1 dx_2 \cdots dx_N |\psi(\vec{r}_1, x_2, \ldots, x_N)|^2 \]

\[(\vec{r}, \sigma) = x\]

We move to the next simplest term - the kinetic energy

\[ T = \langle \psi | \hat{T} | \psi \rangle = \langle \psi | -\frac{1}{2} \sum_i \nabla_i^2 | \psi \rangle = \]

\[ = -\frac{N}{2} \int d\sigma_1 d^3r_1 \psi^* (\vec{r}_1, \sigma_1, x_2, \ldots, x_N) \nabla_1^2 \psi +
\]

\[ - \psi^* (\vec{r}_1, \sigma_1, x_2, \ldots, x_N) dx_2 \cdots dx_N \]

Define:

\[ \Gamma^{(1)}_{\sigma_1}(\vec{r}, \vec{r}') \]

\[ \Gamma^{(1)}_{\sigma_1}(\vec{r}, \vec{r}') = N \int \psi^* (\vec{r}, \sigma_1, x_2, \ldots, x_N) \psi (\vec{r}', \sigma_1, x_2, \ldots, x_N) dx_2 \cdots dx_N \]

Then

\[ T = -\frac{1}{2} \sum_\sigma \int [\nabla^2 \Gamma^{(1)}_{\sigma, \sigma}(\vec{r}, \vec{r}')]_{\vec{r} = \vec{r}'} d^3r \]

\[ T = -\frac{1}{2} \Re [\nabla^2 \Gamma^{(1)}] \quad \text{abstract} \]
Lesson: Very little of the total information in the wave function is needed in order to calculate the energies.

Let's go to the most complicated term - the interaction energy $U$

$$U = \langle \Psi | 1 \hat{V} 1 \Psi \rangle = \langle \Psi | \frac{1}{2} \sum_{i,j}^{N} U(\vec{r}_i - \vec{r}_j) 1 \Psi \rangle =$$

$$= \frac{1}{2} N (N-1) \int U(\vec{r}_1 - \vec{r}_2) 1 \Psi (x_1, x_2, \ldots, x_N) |^2 dx_1 \ldots dx_N =$$

$$= \frac{1}{2} \sum_{\sigma \sigma'} \int \Gamma^{(2)}_{\sigma \sigma'} (\vec{r}, \vec{r}') U(\vec{r} - \vec{r}') d\vec{r} d\vec{r}'$$

Where we have defined the diagonal of the two-particle density matrix $\Gamma^{(2)}$

$$\Gamma^{(2)}_{\sigma \sigma'} (\vec{r}, \vec{r}') = N (N-1) \int \Psi (\vec{r}_1', \vec{r}_2', x_3, \ldots, x_N) |^2 \Psi (\vec{r}_1, \vec{r}_2, x_3, \ldots, x_N)$$

$$dx_3 \ldots dx_N$$

$\Gamma^{(2)}$ has many important properties.
\[ \Gamma_0^{(3)} (\mathbf{F}, \mathbf{F}') \geq 0 \]
\[ \Gamma_0^{(3)} (\mathbf{F}, \mathbf{F}) = 0 \quad \text{Pauli excl. princ.} \]
\[ \Gamma_0^{(3)} (\mathbf{F}, \mathbf{F'}) = \Gamma_0^{(3)} (\mathbf{F}', \mathbf{F}) \quad \text{symmetry} \]
\[ \Gamma_0^{(3)} (\mathbf{F}, \mathbf{F'}) \quad \text{is an observable} \]

Define the one-particle spin-density operator:
\[ \hat{n}_\sigma (\mathbf{r}) = \sum_{\mathbf{r}_i} \delta (\mathbf{r} - \mathbf{r}_i) \cdot \delta_{\sigma \sigma_i} \]
and the spin density
\[ n_\sigma (\mathbf{r}) = \langle 41 | \hat{n}_\sigma (\mathbf{r}) | 14 \rangle \]

The two-particle spin-density operator is
\[ \hat{n}_{\sigma \sigma'} (\mathbf{F}, \mathbf{F}') = \sum_{\mathbf{r}_i, \mathbf{r}'_j} \delta (\mathbf{r} - \mathbf{r}_i) \cdot \delta (\mathbf{r}' - \mathbf{r}'_j) \delta_{\sigma \sigma_i} \delta_{\sigma' \sigma'_j} \]

Notice! The same electron cannot be in two different places.

We have
\[ \Gamma_0^{(3)} (\mathbf{F}, \mathbf{F'}) = \langle 41 | \hat{n}_{\sigma \sigma'} (\mathbf{F}, \mathbf{F'}) | 14 \rangle \]
THE SUM RULE

\[ \int \delta_{oo'}(\mathbf{r}, \mathbf{r}') d^3r' = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta_{oo'} \delta_i j \]

\[ = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta_{oo'} \sum_j \delta_{o'j} - \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta_{oo'} \delta_i j \]

\[ = \eta_o(\mathbf{r}) [\hat{N}_o - \delta_{oo'}] \]

\( \hat{N}_o \) is the operator giving the total number of spin \( \sigma \) electrons. For any finite system without spin interactions, \( \hat{N}_o \) is a constant of motion

\[ \hat{N}_o |\psi\rangle = N_o |\psi\rangle = \int \eta_o(\mathbf{r}) d^3r |\psi\rangle \]

Taking expectation values above yields

\[ \int \Gamma_o(\mathbf{r}, \mathbf{r}') d^3r' = \eta_o(\mathbf{r}) [N_o - \delta_{oo'}] \]

\( \eta_o(\mathbf{r}) \) is obviously a factor in \( \Gamma^{(o)} \) and, by symmetry, so is \( \eta_o(\mathbf{r}') \). Thus, define
\[ \Gamma_{\sigma \sigma'}^{(2)}(r, r') \equiv n_\sigma(r) n_{\sigma'}(r') \cdot g_{\sigma \sigma'}(r, r') \]

the pair-correlation function

The sum rule becomes

\[ \int n_{\sigma'}(r') \left\{ g_{\sigma \sigma'}(r, r') - 1 \right\} = -\delta_{\sigma \sigma'} \]

and the interaction energy

\[ U = \frac{1}{2} \sum_{\sigma \sigma'} \int d^3r d^3r' n_\sigma(r) n_{\sigma'}(r') g_{\sigma \sigma'}(r, r') U(r, r') \]

It is customary to split off the classical Coulomb result

\[ U_0 = \frac{1}{2} \int d^3r d^3r' n(r) n(r') U(r, r') \]

and write

\[ U = U_0 + U_{xc} \]

where

\[ U_{xc} = \frac{1}{2} \sum_{\sigma \sigma'} \int d^3r d^3r' n_\sigma(r) n_{\sigma'}(r') \left[ g_{\sigma \sigma'}(r, r') - 1 \right] U(r, r') \]

In atomic and molecular systems \( U_0 \gg U_{xc} \).
The kinetic energy is a large part of the total energy and accurate enough approx. to $\Gamma^{(0)}$ are hard to come by. The Hellman-Feynman trick of textbook Quantum Mechanics

\[ H \to H_\lambda = \hat{T} + \hat{\omega}_\lambda + \lambda \hat{U} \]

\[ E_\lambda = \langle \psi_\lambda | H_\lambda | \psi_\lambda \rangle \]

\[ \frac{\partial E_\lambda}{\partial \lambda} = \langle \psi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \psi_\lambda \rangle \quad \text{Hellm-Fey. trick} \]

\[ \frac{\partial E_\lambda}{\partial \lambda} = \langle \psi_\lambda | \frac{\partial \hat{\omega}_\lambda}{\partial \lambda} + \hat{U} | \psi_\lambda \rangle \]

Change the external $\omega \to \omega_\lambda$ such that the density remains constant when the strength of the Coulomb interaction is scaled down!

The $\omega$-representability problem!
Thus,
\[ \eta_\lambda (\tilde{F}) = \langle \psi_\lambda | \hat{n}(\tilde{F}) | \psi_\lambda \rangle = n(\tilde{F}) \]

Then
\[ \frac{\partial E_\lambda}{\partial \lambda} = \int \frac{\partial \omega_\lambda (\tilde{F})}{\partial \lambda} n(\tilde{F}) d^3 r + \]
\[ + \frac{1}{2} \int d^3 r d^3 r' n(\tilde{F}) n(\tilde{F}') g_\lambda(\tilde{F}, \tilde{F}') \varphi(\tilde{F}-\tilde{F}') \]

where we, for simplicity, have defined a spin averaged pair-correlation function as
\[ \sum_{\sigma_0} \eta_\sigma(\tilde{F}) \eta_{\sigma'}(\tilde{F}') g_{\sigma_0, \sigma_0}(\tilde{F}, \tilde{F}') = g(\tilde{F}, \tilde{F}') n(\tilde{F}) n(\tilde{F}') \]

Let us now integrate the Hellman-Feynman result with respect to \( \lambda \) - from 0 to 1.
\[ E - E_0 = \int [\omega(\tilde{F}) - \omega_0(\tilde{F})] n(\tilde{F}) d^3 r + \]
\[ + \frac{1}{2} \int d^3 r d^3 r' n(\tilde{F}) n(\tilde{F}') \tilde{g}(\tilde{F}, \tilde{F}') \varphi(\tilde{F}-\tilde{F}') \]

where
\[ \tilde{g}(\tilde{F}, \tilde{F}') = \int g_\lambda(\tilde{F}, \tilde{F}') d\lambda \]
$E$ is our full energy

$E_0$ is the total energy of $N$ non-interacting electrons moving in the external potential $w_0(F)$ and having the same density $n(F)$ as the interacting system.

We know how to get $E_0$ and $n(F)$ if we know $w_0(F)$:

$$\left\{ -\frac{1}{2} \nabla^2 + w_0(F) \right\} \Phi_k(F) = \varepsilon_k \Phi_k(F)$$

$$n(F) = \sum_{k} \left| \Phi_k(F) \right|^2$$

$$E_0 = \sum_{k} \varepsilon_k$$

$$E_0 = \sum_{k} \left< \Phi_k \left| -\frac{1}{2} \nabla^2 \right| \Phi_k \right> + \int w_0(F) n(F) d^3r$$

Summing up our results we have

$$E = \sum_{k} \left< \Phi_k \left| -\frac{1}{2} \nabla^2 \right| \Phi_k \right> + \int w n + \frac{1}{2} \int n v n + \text{Exc}$$
where
\[ E_{xc} = \frac{1}{2} \int n \, n' \, [\tilde{g} - 1] \, v \]

suppressing integration variables

\( E_{xc} \) is a relatively small part of the total energy and \( \tilde{g} \) can be approximated, e.g., with the help of the sum rule

\[ \int n(\mathbf{r}') \, [\tilde{g}(\mathbf{r}, \mathbf{r}') - 1] \, d\mathbf{r}' = -1 \]

**But we do not know \( W_0(\mathbf{F}) \) and for this we need DFT**

But why not follow Thomas and Fermi and minimize our energy expression with respect to \( W_0 \)? Look for the first-order change \( \delta E \) produced by a small change \( \delta W_0 \) in \( W_0 \). Of course, \( n - n + \delta n \)
First-order pert. theory:

$$S \left[ \sum_k \epsilon_k \right] = \sum_k \langle \phi_k | s \psi_0 | \phi_k \rangle = \int \nabla \cdot \mathbf{n} s \psi_0$$

$$S \left[ \sum_k \langle \phi_k | -\frac{1}{2} \nabla^2 | \phi_k \rangle \right] = S \left[ \sum_k \epsilon_k - \int n \psi_0 \right] =$$

$$\int n s \psi_0 - \int \nabla n s \psi_0 - \int n s \nabla \psi_0 = -\int \psi_0 \nabla n$$

$$S \left[ \int \psi_0 \right] = \int \psi \cdot \nabla n$$

$$S \left[ \frac{1}{2} \int \nabla \psi \cdot \nabla \psi \right] = \int \nabla \psi \cdot \nabla \psi s n = \int V_H \cdot \nabla n$$

$$S E_{xc} = \int \frac{S E_{xc}}{s \psi_0} s \psi_0 = \int \frac{S E_{xc} \cdot s \psi_0}{s n} s n = \int \frac{S E_{xc}}{s n}$$

All together

$$S E = \int \left[ -\psi_0^2 + \psi + V_H + \frac{S E_{xc}}{s n} \right] s n$$

Choose the potential $$\psi_0$$ which makes the total energy stationary

$$\psi_0 = \psi + V_H + \frac{S E_{xc}}{s n}$$

**Kohn-Sham**

**Without DFT**
DFT
DFT á la Mel Levy (pedagogical)
We start with the kinetic energy
\[ T = -\frac{1}{2} \sum_{i}^{N} \nabla_i^2 \]
Positive definite and bounded from below
Define an N-electron density
\[ n(\mathbf{r}) \geq 0 \]
\[ \int d^3r \ n(\mathbf{r}) = N \]
Define a set \( M \) of many-electron antisymmetrized wave functions according to
\[ M = \{ | \psi \rangle | \langle \psi | \hat{n}(\mathbf{r}) | \psi \rangle = n(\mathbf{r}) \} \]
Is doable - N-representability
The numbers \( \langle \psi | \hat{\mathbf{r}} | \psi \rangle \) with \( | \psi \rangle \in M \) are bounded from below. Define
\[ T_0[n] = \inf \langle \psi \hat{1} \psi \rangle \]

We thus want to minimize \( \langle \psi \hat{1} \psi \rangle \)
among all wave functions which produce \( n(\vec{r}) \). USE LAGRANGIAN MULTIPLIERS,
one for each constraint, i.e., one for each point \( \vec{r} \) in space \( \Rightarrow \) FREE MINIMIZATION OF

\[ \langle \psi \hat{1} \psi \rangle + \sum \nabla V \cdot n(\vec{r}_c) = \]
\[ = \langle \psi \hat{1} \psi \rangle + \sum \nabla V(\vec{r}_c) \cdot n(\vec{r}_c) = \]
\[ = \langle \psi \hat{1} \psi \rangle + \int V(\vec{r}) \langle \psi \hat{1} \psi \rangle d^3r \]
\[ = \langle \psi \hat{1} + \hat{V} \psi \rangle \]

where
\[ \hat{V} = \sum \nabla V(\vec{r}_c) \]

A NON-INTERACTING HAMILTONIAN PROBLEM!
\[-\frac{1}{2} \nabla^2 + V(\vec{r}) \] \( \Phi_k(\vec{r}) = \varepsilon_k \cdot \Phi_k(\vec{r}) \)

\[ \langle \psi \hat{\mathbf{1}} + \hat{\mathbf{v}} \psi \rangle = \sum_k \varepsilon_k \]

And then we must adjust the Lagrangian multipliers \( V(\vec{r}_c) \) such that

\[ \sum_c |\Phi_c(\vec{r})|^2 = n(\vec{r}) \]

**Can we? Non-interacting \( \omega \)-representation stability!**

..., and then

\[ T_0 [n] = \langle \psi \hat{\mathbf{1}} \psi \rangle = \langle \psi \hat{\mathbf{v}} \psi \rangle - \int V(\vec{r}) n(\vec{r}) d^3r = \]

\[ = \sum_k \varepsilon_k - \int V(\vec{r}) \cdot n(\vec{r}) d^3r = \sum_k \langle \Phi_k \mid -\frac{1}{2} \nabla^2 \mid \Phi_k \rangle \]
How does $T_0[n]$ change with $n(F)$?
Change in $n$ requires change in Lagr. mult $V \rightarrow V + \delta V$. First order pert. theory:

$$
\delta T_0 = \delta \langle \psi | \hat{H} | \psi \rangle = \\
\delta \left[ \sum_k \varepsilon_k - \int v \cdot n \right] = \\
\sum_k \delta \varepsilon_k - \int \delta v \cdot n - \int v \cdot \delta n = \\
\int n \cdot \delta v - \int n \cdot \delta v - \int v \cdot \delta n = \\
= -\int v \delta n
$$

$$
\frac{\delta T_0}{\delta n(F)} = -V(F) + \mu_0 \\
\text{FINITE N!}
$$

This was first-order change! What about second order?
Well, vary the density and thus the Lagrangian multipliers $V$ in the eqn. above

$$
\int \frac{\delta^2 T_0}{\delta n(F') \delta n(F)} \delta n(F') d^3r' = -SV(F) + \delta \mu_0
$$
First order perturbation theory applied to non-interacting electrons gives a change $SN$ in the density proportional to the change $SV$ in the potential:

$$Sn(F) = \int X_o(F,F') SV(F') \, d^3r'$$

Here, $X_o$ is called the static non-interacting linear density response function, or irreducible polarizability, or the Lindhardt function. For any finite system

$$\int X_o(F,F') \, d^3r' = 0$$

Apply to previous eqn.:

$$\int X_o(F,F'') \frac{\delta^2 T_o}{Sn(F''),Sn(F')} \, Sn(F') \, d^3r'' d^3r' = -SN(F)$$

$$\frac{\delta^2 T_o}{Sn Sn'} = -X_o^{-1}$$
Let us now repeat the procedure we applied to the kinetic energy $\hat{T}$ but now to the operator $\hat{T} + \hat{U}$, $\hat{U}$ being the interaction energy.

Thus,

$$F[n] = \inf_{\Psi \in \mathcal{M}} \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle$$

Notice that $\hat{T} + \hat{U}$ is also a positive definite operator. Using again $V(F)$ as Lagrangian multipliers for the constraint of keeping the density equal to the chosen density at every point in space - we do a free minimization over all wave functions $|\Psi\rangle$ of $\langle \Psi | \hat{T} + \hat{U} + \hat{V} | \Psi \rangle$.

But this is the full many-body problem in the external potential $V$. "Having solved that" we "simply" adjust the potential $V$ until the fully interacting density becomes equal to the chosen one, $n(F)$.
If $E$ is the ground state energy of the interacting system in the external potential $V$ we get for $F(n)$

$$F(n) = E - \int V(f)n(f)df$$

As with $T_0$, we can study first- and second-order changes in $F(n)$ when $n$ is changed.
In order to change $n \rightarrow n + \delta n$, the Lagrangian multipliers $V$ have to be readjusted
$V \rightarrow V + \delta V$. First-order pert. theory gives

$$SE = \int n \cdot \delta V$$

Thus, to first order,

$$\delta F = SE - \int \delta V \cdot n - \int V \delta n = -\int V \cdot \delta n$$

and we conclude that (constant?)

$$\frac{\delta F}{\delta n(f)} = -V(f) + \mu$$

Varying this eqn. once more with respect to $n$

$$\int \frac{\delta^2 F}{\delta n \delta n'} \delta n' = -\delta V + \delta \mu$$
V produces $n$ in the interacting system
$V + SV$ produces $n + Sn$ in the same system

$$\delta n(\vec{r}) = \int X(\vec{r}, \vec{r'}) SV(\vec{r'}) d\vec{r'}$$

$X$ is the density response function (static) of the interacting system. We obtain

$$\frac{\delta^2 F}{\delta n \delta n'} = -X^{-1}$$

**CONNECTION TO "KOHN-SHAM WITHOUT DFT"**

$\omega$ produces $n(\vec{r})$ in the interacting system. For the total energy $E$ we have

$$E = F[n] + \int n \cdot \omega$$

$\omega_0(\vec{r})$ produces $n(\vec{r})$ in the non-interacting system.

$$T_0[n] = \sum_k \langle \phi_k | -\frac{1}{2} \nabla^2 | \phi_k \rangle$$

But we also have from previously

$$E = \sum_k \langle \phi_k | -\frac{1}{2} \nabla^2 | \phi_k \rangle + \sum n_n + \frac{1}{2} \sum n_n^2 + E_{xc}$$
Combine results

\[ F[n] = T_0[n] + \frac{1}{2} \int n \nu n + E_{xc}[n] \]

PROVES THAT \( E_{xc} \) IS A FUNCTIONAL OF \( n \)!

Take functional derivatives

\[ \frac{\delta F}{\delta n} = \frac{\delta T_0}{\delta n} + \int n \nu + \frac{\delta E_{xc}}{\delta n} \]

\[ \omega_n = \omega + V_n + v_{xc} \]

\[ \frac{\delta E_{xc}}{\delta n} = v_{xc} \]

Take one more functional derivative

\[ \frac{\delta^2 F}{\delta n \delta n'} = \frac{\delta^2 T_0}{\delta n \delta n'} + \omega + K_{xc} \]

\[ K_{xc}(F,F') = \frac{\delta^2 E_{xc}[n]}{\delta n(F) \delta n(F')} \]

\[ X_0^{-1} = X^{-1} + \omega + K_{xc} \]

or

\[ X = X_0 + X_0(\omega + K_{xc})X \]

DFT GIVES EXACT \( X \)!
The energy functional:
\[ E[n, \omega] = F[n] + \int n \cdot \omega \]

The minimum principle:
The interacting ground state corresponding to the external potential \( \omega \) is \( |\psi> \) and its density is \( n(\vec{r}) \). \( |\psi> \) corresponds to \( \omega \), giving the density \( n, (\vec{r}) \). \( n \neq n_1 \Rightarrow \omega \) and \( \omega_1 \) differ by more than a constant.

\[ E[n, \omega] = \langle \psi | \hat{\mathcal{H}} + \hat{\mu} | \psi \rangle + \int n \cdot \omega = \langle \psi | \hat{\mathcal{H}} + \hat{\mu} + \hat{\omega} | \psi \rangle < \langle \psi | \hat{\mathcal{H}} + \hat{\mu} + \hat{\omega} | \psi \rangle = F[n_1] + \int n_1 \cdot \omega = E[n_1, \omega] \]

Stationarity:
\[ \left( \frac{\delta E}{\delta n} \right)_\omega = \frac{\delta F}{\delta n} + \omega = -\omega + \mu + \omega = \mu ! \]

Really: \( E - \mu \cdot N \)
THE LDA

\[ E_{xc}[n] = \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) n(\mathbf{r}') \{ \mathcal{G}(\mathbf{r}, \mathbf{r}') - 1 \} \psi(\mathbf{r} - \mathbf{r}') \]

\( \mathcal{G} - 1 \) is localized \( \Rightarrow n(\mathbf{r}') \rightarrow n(\mathbf{r}) \)

\( \mathcal{G}_h(\mathbf{r}, \mathbf{r}'; \bar{n}) \)

\[ \bar{n} = \frac{1}{2} [ n(\mathbf{r}) + n(\mathbf{r}') ] \quad ? \quad \bar{n} = n(\frac{\mathbf{r} + \mathbf{r}'}{2}) \quad ? \quad \bar{n} = \sqrt{n(\mathbf{r}) n(\mathbf{r}') : ?} \]

Here: \( \bar{n} = n(\mathbf{r}) \)

\[ \frac{1}{2} \int d^3r' \{ \mathcal{G}(\mathbf{r}, \mathbf{r}'; n(\mathbf{r})) - 1 \} \psi(\mathbf{r} - \mathbf{r}') = \frac{E_{xc}(n(\mathbf{r}))}{n(\mathbf{r})} \]

non-symmetric!

\[ E_{xc}^{\text{LDA}}[n] = \int n(\mathbf{r}) E_{xc}(n(\mathbf{r})) d^3r \]

\[ v_{xc}^{\text{LDA}}([n]; \mathbf{r}) = \frac{SE_{xc}^{\text{LDA}}}{\delta n(\mathbf{r})} = \mu_{xc}(n(\mathbf{r})) \]
\[ E_{xc} = \frac{1}{2} \int n(f) n(f+\vec{r}) \{ \tilde{g}(f, f+\vec{r}) - 1 \} \frac{d\vec{r}}{R} d\vec{r} \]

\[ \int \frac{d\Omega}{4\pi} n(f+\vec{r}) \{ \tilde{g}(f, f+\vec{r}) - 1 \} = \tilde{\eta}_{xc}(f, \vec{r}) \]

\[ E_{xc} = \frac{1}{2} \int n(f) \tilde{\eta}_{xc}(f, \vec{r}) v(\vec{r}) d\vec{r} d\vec{r} \]

\( \tilde{\eta}_{xc}(f, \vec{r}) \) is called the xc-hole at \( f \).

Only the spherical average of xc-hole matters for the xc-energy \( E_{xc} \)!

It is much easier to model the spherical average of the hole than the hole itself.

Now lots of LDA results!
Fig. 3. The exchange hole around an electron at \( r \) in the neon atom is here shown as a function of distance from the electron along a line connecting the electron and the nucleus. The full curves show the exact hole (Eq. 43) and the dashed curves show the results obtained within the local-density approximation (Eq. 46) which is seen to give a rather poor description of the hole. The two sets of curves correspond to the electron being at two different distances from the nucleus. Distances are measured in Bohr radii. The figure is taken from Ref. 44.
Fig. 4. The spherical average (Eq. 48) of the exchange hole surrounding an electron at \( r \) in the neon atom is here shown as a function of the distance from the electron. The full curves show exact results and the dashed curves were obtained using the local-density approximation. The hole is shown multiplied by \( R \) so that the area under each curve is directly proportional to the exchange-energy density (Eq. 50). When the curves shown here are compared with the corresponding curves in Fig. 3, it is seen that the local-density approximation gives a much more accurate description of the spherical average of the exchange hole than it gives of the hole itself. It is important to note in this context that the exchange energy depends only on the spherical average. Distances are measured in Bohr radii (From Ref. 44).
Geometry data for molecules

as obtained from the LDA and from experiment.

The results are taken from the work by Müller, Jones, and Harris.\textsuperscript{21}

We assume that the numerical errors involved in obtaining the LDA results are negligible in comparison to the deviation between theory and experiment.

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th></th>
<th>$NH_3$</th>
<th></th>
<th>$CO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LDA</td>
<td>exp</td>
<td>LDA</td>
<td>exp</td>
<td>LDA</td>
</tr>
<tr>
<td>$d$</td>
<td>1.84</td>
<td>1.81</td>
<td>1.94</td>
<td>1.91</td>
<td>2.21</td>
</tr>
<tr>
<td>$\theta$</td>
<td>106</td>
<td>105</td>
<td>108</td>
<td>107</td>
<td>180</td>
</tr>
<tr>
<td>$\omega_s$</td>
<td>3680</td>
<td>3657</td>
<td>3335</td>
<td>3337</td>
<td>1420</td>
</tr>
<tr>
<td>$\omega_b$</td>
<td>1590</td>
<td>1595</td>
<td>820</td>
<td>950</td>
<td>730</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.732</td>
<td>0.730</td>
<td>0.564</td>
<td>0.583</td>
<td>0</td>
</tr>
</tbody>
</table>

d is the equilibrium distance in atomic units.

$\theta$ is the equilibrium bond angle in degrees.

$\omega_s$ is the stretching frequency in cm$^{-1}$.

$\omega_b$ is the bending frequency in cm$^{-1}$.

$\mu$ is the dipole moment in atomic units.
Table 4. Cohesive energies (in eV) of a few solids as obtained from the LDA and from experiment. The Si result is from Ref. 25. The other results are taken from the book by Moruzzi et al.\textsuperscript{26} and from Refs. 27-29.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Si</th>
<th>Ti</th>
<th>Zr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>1.1</td>
<td>1.5</td>
<td>4.6</td>
<td>4.9</td>
<td>6.3</td>
<td>4.4</td>
</tr>
<tr>
<td>LDA</td>
<td>1.1</td>
<td>1.6</td>
<td>5.1</td>
<td>6.1</td>
<td>6.8</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Table 5. Lattice parameters in atomic units for a few solids as obtained from the LDA and from experiment. With one exception, Si, the data are taken from the book by Moruzzi et al.\textsuperscript{26} The Si result is from Ref. 25.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Si</th>
<th>Ti</th>
<th>Zr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>8.0</td>
<td>8.5</td>
<td>10.3</td>
<td>7.8</td>
<td>8.2</td>
<td>6.7</td>
</tr>
<tr>
<td>LDA</td>
<td>7.7</td>
<td>8.4</td>
<td>10.2</td>
<td>7.6</td>
<td>8.2</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Table 6. The binding energies (in eV) of the first-row dimers as obtained from the LDA, from the LPM scheme, and from experiment. The results are taken from the work by Becke.\textsuperscript{30,31}

<table>
<thead>
<tr>
<th></th>
<th>$H_2$</th>
<th>$Li_2$</th>
<th>$B_2$</th>
<th>$C_2$</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>$F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>4.8</td>
<td>1.1</td>
<td>3.0</td>
<td>6.3</td>
<td>9.9</td>
<td>5.2</td>
<td>1.7</td>
</tr>
<tr>
<td>LDA</td>
<td>4.9</td>
<td>1.0</td>
<td>3.9</td>
<td>7.3</td>
<td>11.6</td>
<td>7.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Table 7. Equilibrium distances in Bohr of the first-row dimers. The LDA results are from the work by Becke.  

<table>
<thead>
<tr>
<th></th>
<th>$H_2$</th>
<th>$Li_2$</th>
<th>$B_2$</th>
<th>$C_2$</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>$F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>1.40</td>
<td>5.05</td>
<td>3.00</td>
<td>2.35</td>
<td>2.07</td>
<td>2.28</td>
<td>2.68</td>
</tr>
<tr>
<td>LDA</td>
<td>1.45</td>
<td>5.12</td>
<td>3.03</td>
<td>2.35</td>
<td>2.07</td>
<td>2.27</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Table 8. Vibrational frequencies in cm$^{-1}$ of the first- and second-row dimers as obtained from the LDA and from experiment. The results are taken from the work by Becke.  

<table>
<thead>
<tr>
<th></th>
<th>$H_2$</th>
<th>$Li_2$</th>
<th>$B_2$</th>
<th>$C_2$</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>$F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>4400</td>
<td>350</td>
<td>1050</td>
<td>1860</td>
<td>2360</td>
<td>1580</td>
<td>890</td>
</tr>
<tr>
<td>LDA</td>
<td>4190</td>
<td>330</td>
<td>1030</td>
<td>1880</td>
<td>2380</td>
<td>1620</td>
<td>1060</td>
</tr>
</tbody>
</table>

Table 9. Heat of formation (in eV) of a few compounds as obtained from the LDA and from experiment. The data are taken from the work by Williams, Kübler, and Gelatt.  

<table>
<thead>
<tr>
<th></th>
<th>MgAg</th>
<th>AlZr</th>
<th>SiZr</th>
<th>NiAl</th>
<th>CuZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>0.19</td>
<td>0.44</td>
<td>0.81</td>
<td>0.61</td>
<td>0.12</td>
</tr>
<tr>
<td>LDA</td>
<td>0.24</td>
<td>0.44</td>
<td>0.73</td>
<td>0.74</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Table 10. 10a) The saturated magnetic moment (Bohr magnetons), 10b) the hyperfine field (kiloGauss), and 10c) the spin-susceptibility enhancement factor for a few metals. The data are taken from the work by Janak et al. 28,34-36

<table>
<thead>
<tr>
<th>Magnetic moment</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>2.22</td>
<td>1.56</td>
<td>0.61</td>
</tr>
<tr>
<td>LDA</td>
<td>2.15</td>
<td>1.56</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Table 10b.

<table>
<thead>
<tr>
<th>Hyperfine field</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>339</td>
<td>217</td>
<td>75</td>
</tr>
<tr>
<td>LDA</td>
<td>260</td>
<td>220</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 10c.

<table>
<thead>
<tr>
<th>Susceptibility enhancement</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>2.50</td>
<td>1.65</td>
<td>1.70</td>
</tr>
<tr>
<td>LDA</td>
<td>2.25</td>
<td>1.71</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Successes of the LDA.

a. Binding energies are often better than 1 eV but in some systems (s-d bonded) the error can be twice or even three times as large. The error is systematic. Overbinding!

b. Equilibrium distances are generally accurate to within 0.1 Å. The error is systematic.

c. Vibrational frequencies are accurate to within 10-20%. There are occasional cases with larger errors.

d. Electron densities are better than 2%.

e. LDA results are nearly always better than those of the HFA.

f. Most importantly, physical trends are generally correct!
Deficiencies of the LDA.

a. The transition-metal oxides FeO and CoO are erroneously predicted to be metals. (MnO and NiO come out as antiferromagnetic insulators in accordance with experiment.)

b. Solid Fe is predicted to be an fcc paramagnet, but is a bcc ferromagnet at low temperature.

c. In semiconductors, the LDA gives the metal-insulator transition at much too large volumes.

d. The LDA predicts the wrong dissociation limits for a large number of molecules.

e. The LDA predicts incorrect ground states for many atoms.
f. The LDA predicts many stable atomic negative ions to be unstable.

g. There is a three-fold overbinding of CO molecules on Cu and Pd surfaces.

h. There is no dissociation barrier for $\text{H}_2$ on Cu (100) et cetera.
S-p transfer energies

In molecular binding electrons are transferred from lower to higher angular momentum states

Simulate in HF for F atom

$$2s^2 2s^2 2p^2 2p^2 \rightarrow 2s^2 2p^2 2p^2$$

Results:

<table>
<thead>
<tr>
<th></th>
<th>$2s^2 2s^2 2p^2 2p^2$</th>
<th>$2s^2 2p^2 2p^2$</th>
<th>$\Delta E_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>272.5</td>
<td>264.4</td>
<td>8.1</td>
</tr>
<tr>
<td>LDA</td>
<td>246.4</td>
<td>244.1</td>
<td>2.2</td>
</tr>
<tr>
<td>LPM</td>
<td>267.4</td>
<td>264.6</td>
<td>2.8</td>
</tr>
<tr>
<td>LPM-NS</td>
<td>267.6</td>
<td>264.6</td>
<td>3.0</td>
</tr>
</tbody>
</table>
NEAR-DEGENERACY PROBLEM

Example: \( H_2^+ \)

\[
H = -\frac{1}{2} \nabla^2 - \frac{1}{r} - \frac{1}{|F-R|} + \frac{1}{R}
\]

\[
\psi(F) \approx \frac{1}{\sqrt{2}} \left\{ \varphi(F) + \varphi(F-R) \right\}
\]

\[
\varphi(F) = e^{-r_1/r} \sqrt{r}
\]

\[
\langle \psi | H | \psi \rangle \rightarrow -\frac{1}{2} \quad \text{when} \quad R \rightarrow \infty
\]

Extra terms in DFT

\[
\frac{1}{2} \int n u n + E_{xc}[n]
\]

These must cancel in the one-electron case.

For the one-proton case we obtain

\[
n = \varphi^2
\]

Thus, \[
\frac{1}{2} \int \varphi^2 \nu \varphi^2 + E_{xc}[\varphi^2] = 0
\]
For the two-proton case

\[ n = \frac{1}{2} [\phi_a^2 + \phi_b^2 + 2\phi_a\phi_b] \approx \frac{1}{2} \phi_a^2 + \frac{1}{2} \phi_b^2 \]

\[ \frac{1}{2} \int n(n) = \frac{1}{8} \int (\phi_a^2 + \phi_b^2) \nu(\phi_a^2 - \phi_b^2) = \]

\[ = \frac{1}{4} \int \phi_a^2 \nu \phi_b^3 + \frac{1}{4R} = -\frac{1}{2} E_{xc}[\phi^2] + \frac{1}{4R} \]

For any local approximation to \( E_{xc} \) we have (LDA, GGA) etc.

\[ E_{xc}[n] \approx E_{xc}[\frac{1}{2} \phi_a^2 + \frac{1}{2} \phi_b^2] = 2 E_{xc}[\frac{1}{2} \phi^2] \]

Error in local theory \( \Delta E \)

\[ \Delta E = \frac{1}{2} \int n(n) + E_{xc}[n] = \]

\[ = \frac{1}{4R} + 2E_{xc}[\frac{1}{2} \phi^2] - \frac{1}{2} E_{xc}[\phi^2] \approx \]

\[ \approx \frac{1}{4R} + 2.2^{-4/3} E_{xc}[\phi^2] - \frac{1}{2} E_{xc}[\phi^2] \]

\[ = \frac{1}{4R} + 0.7 E_{xc} \approx \frac{1}{4R} - 2.5 \text{ in eV} \]

Basically wrong!

DO ONE ELECTRON ON ONE PROTON
GRADIENTS

Natural extension beyond LDE
Gradients for slowly varying densities
NOT necessarily small perturbations
BUT valid also for small perturbations

\[ E_{xc} = E_{xc}[n_0] + \int u_{xc} \delta n + \frac{1}{2} \int k_{xc} \delta n \delta n' + \]
\[ + \frac{1}{6} \int l_{xc} \delta n \delta n' \delta n'' + \ldots \]

\[ u_{xc} = \frac{\delta E_{xc}}{\delta n(F)} = \text{const} \]

\[ k_{xc} = \frac{\delta^3 E_{xc}}{\delta n(F) \delta n(F') \delta n(F'')} \]

\[ l_{xc}(F, F', F'') = \frac{\delta^4 E_{xc}}{\delta n(F) \delta n(F') \delta n(F'') \delta n(F''')} \]

For illustration we skip the \( l_{xc} \) for a moment. We do the same expansion for the LDA - only corrections to LDA
$$E_{xc}^{LDA}[n] = E_{xc}[n_0] + \int \frac{\partial (n n_{xc})}{\partial n_0} \delta n + $$
$$ + \frac{1}{2} \int \frac{\partial^2 (n n_{xc})}{\partial n_0^2} (\delta n)^2 + \frac{1}{6} \int \frac{\partial^3 (n n_{xc})}{\partial n_0^3} (\delta n)^3 + \ldots$$

Subtract:

$$E_{xc}[n] = E_{xc}^{LDA}[n] + \frac{1}{2} \int n [K_{xc} - \mu_{xc}^1 \delta (F - F')] n'$$

Go to Fourier space

$$E_{xc}[n] = E_{xc}^{LDA}[n] + \frac{1}{2} \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \left[ K_{xc}(\mathbf{q}) - K_{xc}(0) \right] |\mathbf{q}| \delta n_{\mathbf{q}}^1$$

Compressibility sum rule

$$K_{xc}(0) = \mu_{xc}^1$$

Assume $n_{\mathbf{q}}$ to have little amplitude on high Fourier components - slowly varying!

$$K_{xc}(\mathbf{q}) = K_{xc}(0) + 2 B_{xc} (2\pi)^2 q^2 + \ldots$$

$$E_{xc}[n] = E_{xc}^{LDA}[n] + \int \frac{d^3 \mathbf{q}}{(2\pi)^3} B_{xc} q^2 |\mathbf{q}| \delta n_{\mathbf{q}}^1 + \ldots$$
Go back to real space:

\[ E_{xc}[n] = E_{xc}^{LDA}[n] + \int dr \, B_{xc}(\bar{n}) |\nabla n|^2 + \ldots \]

What should be put in for \( \bar{n} \)?

Correct answer: \( n(\mathbf{F}) \)

Follows from properties of \( L_{xc}, M_{xc} \), etc!

The full expansion to fourth order:

\[ E_{xc}[n] = E_{xc}^{LDA}[n] + \int dr^2 \, B_{xc}^{(2)} \frac{|\nabla n|^2}{n^{4/3}} + \]

\[ + \int dr^2 \, B_{xc}^{(4)} \frac{|\nabla^2 n|^2}{n^2} + \int dr \, C_{xc} \frac{|\nabla n|^2 \cdot \nabla^2 n}{n^2} + \]

\[ + \int dr \, D_{xc} \frac{|\nabla n|^4}{n^4} + \ldots \]

Dimensionally correct powers of \( n \) have been moved out of coefficients so that remaining density dependence is weak.

Gradients to infinite order
Compressibility sum rule
\[ \int [k_{xc}(F-F'; \bar{n}) - \mu_{xc} \delta(F-F')] d\bar{r}' = 0 \]

Rearrange the second-order correction to LDA
\[ E_{xc}[n] = E_{xc}^{LDA}[n] - \frac{1}{4} \int k_{xc}(F-F'; \bar{n}) [n(F) - n(F')]^2 d\bar{r} d\bar{r}' + \ldots \]

What to choose for \( \bar{n} \)?

Olle G has shown that, for finite systems, some choices (reasonable) give infinite results!
Results from the new code written by Ulf in June, 1999.

Negative of Exchange Energies in Ry.
V111 = V200, all other Fourier components vanish.

<table>
<thead>
<tr>
<th>Potential (in EF)</th>
<th>LDX</th>
<th>GEA1</th>
<th>GEA2</th>
<th>Becke88</th>
<th>PBE</th>
<th>Meta-GGA tau</th>
<th>Meta-GGA del2n</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>.077709</td>
<td>.3388</td>
<td>.3424</td>
<td>.3425</td>
<td>.3445</td>
<td>.3437</td>
<td>.3426</td>
<td>.3427</td>
<td>.3425</td>
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<tr>
<td>.116563</td>
<td>.3509</td>
<td>.3586</td>
<td>.3583</td>
<td>.3624</td>
<td>.3611</td>
<td>.3590</td>
<td>.3592</td>
<td>.3580</td>
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<td>.155417</td>
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<td>.3798</td>
<td>.3782</td>
<td>.3848</td>
<td>.3831</td>
<td>.3801</td>
<td>.3805</td>
<td>.3778</td>
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<tr>
<td>.165131</td>
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<td>.3856</td>
<td>.3834</td>
<td>.3908</td>
<td>.3891</td>
<td>.3859</td>
<td>.3863</td>
<td>.3831</td>
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<tr>
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<td>.3951</td>
<td>.3917</td>
<td>.3923</td>
<td>.3884</td>
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<td>.3942</td>
<td>.4030</td>
<td>.4012</td>
<td>.3976</td>
<td>.3982</td>
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<tr>
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<td>.3993</td>
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<tr>
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<td>.3897</td>
<td>.4099</td>
<td>.4050</td>
<td>.4154</td>
<td>.4135</td>
<td>.4096</td>
<td>.4104</td>
<td>.4047</td>
</tr>
</tbody>
</table>

Notice! Here the Meta-GGA has been evaluated with the full kinetic-energy density and with D= .113! All values are calculated using a new plane-wave code which explains the differences of one unit in the last digit as compared to results from 1995 (SSvB). (There is a slight increase in the exchange energies when the number of plane waves are increased.)

GEA very accurate (1 mRy), an order of magnitude better than GGA.
TABLE IV. Exchange energies for Si and Si-related models. The symbol $\Delta$ indicates that the corresponding quantity is given as a difference to the exact result.

<table>
<thead>
<tr>
<th>Model</th>
<th>Exact</th>
<th>$\Delta \varepsilon_x^{LX}$</th>
<th>$\Delta (\varepsilon_x^{LX} + \varepsilon_x^{GE1})$</th>
<th>$\Delta (\varepsilon_x^{LX} + \varepsilon_x^{GE1} + \varepsilon_x^{GE2})$</th>
<th>$\Delta \varepsilon_x^{GGA} (B)$</th>
<th>$\Delta \varepsilon_x^{GGA} (P)$</th>
<th>$\Delta E_x^{MGLA} (\tau)$</th>
<th>$\Delta E_x^{MGLA} (\nabla^2 \rho)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-0.5321</td>
<td>0.0280</td>
<td>0.0072</td>
<td>0.0148</td>
<td>0.0058</td>
<td>0.0060</td>
<td>0.0118</td>
<td>0.0112</td>
</tr>
<tr>
<td>SiX</td>
<td>-0.5539</td>
<td>0.0353</td>
<td>-0.0006</td>
<td>0.0219</td>
<td>0.0071</td>
<td>0.0074</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>-0.5340</td>
<td>0.0233</td>
<td>0.0090</td>
<td>0.0125</td>
<td>0.0049</td>
<td>0.0050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>-0.5550</td>
<td>0.0283</td>
<td>0.0079</td>
<td>0.0157</td>
<td>0.0055</td>
<td>0.0057</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIG. 1. Total energy difference \( \Delta E = E - E_0 - E_1 - E_2 - E_3 \) for the noninteracting solid versus strength of the effective potential. Here \( E \) is the total energy and \( E_n \) the \( n \)th-order contribution from perturbation theory (arb. units).
Kinetic energies with gradients.

Crazy? Maybe not!

\[ T_0[n] = \int n t_0(n) F(p, q, \ldots) \, d^3r \]

\[ F = 1 + \frac{5}{27} p + \frac{8}{81} q^2 - \frac{1}{9} p q + \frac{8}{243} p^2 + \ldots \]

TF \quad \text{Lin. resp} \quad \frac{1}{9} v \text{W}e

Try it on largest potential!

TF: \quad 0.436 \quad \text{Ry/}e\text{l}

p: \quad 0.023

q^2: \quad 0.006

pq: \quad -0.002 \quad \text{Sum: 0.464}

p^2: \quad 0.002 \quad \text{Exact: 0.466}
Silicon (KE):

TF : 0.692 Ry/el
P : 0.022
q^2 : 0.011
pq : -0.004
Pq : 0.001
Sum : 0.723 +mRy
Exact: 0.716
How do we get the density?

Minimize!

\[ n(\tau) = \sum_c n_c e^{i\Theta_c} \]

Sc: \[ T_0 = 0.717 \quad (0.716) \]

Al*: \[ T_0 = 0.486 \quad (0.466) \]
GGA

\[ E_{xc}[n] = \int n \cdot \varepsilon_x(n) \cdot F_{xc}(n, p, q) \, d^3r \]

\[ P = \frac{1 \cdot n(F)}{4 k_f^2 n^2(F)} \quad q = \frac{\nabla^2 n(F)}{4 k_f^2(F) n(F)} \]

\[ \varepsilon_x(n) = -\frac{3}{4} \frac{k_f}{n} \]

\[ 3 \pi^2 n = k_f^3 \]

Example:

\[ F_{xc}(p, q) = 1 + \frac{10}{81} P + \frac{146}{2025} q^2 - \frac{33}{405} P q + \]

\[ + \text{D} \cdot p^2 + \ldots \]

GGA started by Langreth - Perdew

- but Frank Herman - van Dyke - Orthenburger

LPM

\[ \Delta E_{xc}^{GGA} = a \int \frac{19 n l^2}{n^{4/3}} \left\{ e^{-F} - \frac{3}{18} \right\} \, d^3r \]
GEA:

\[ F_{xc} = 1 + ap + bq + cp^2 + \ldots \]

GGA:

\[ F_{xc} = \frac{1 + ap + bq + cp^2}{1 + dq^2 + ep^4} \]
where \( F = b \lambda n \ln n^{-\frac{2}{3}} \)  \( b = \) fudge fact

**BECKE 88**

\[
\Delta E_x^{\text{CIA}} = \rho \int n^{4/3} \frac{x^2 d^3}{1 + 6 y x \text{arcsin}(x)}
\]

\[
x = 2^{4/3} \frac{\Delta n}{n^{4/3}}
\]

\[
\Delta \Delta E_x^{\text{CIA}} \propto - \int \frac{n(\rho)}{2r} d^3 r \quad x \gg 1
\]

\( r > R \)

**PBE**

\[
PBE \quad F_x (\rho) = 1 + x - \frac{x}{1 + \frac{\rho}{4x}}
\]

**SUM RULE OBEYED**

**LIEB-OXFORD BOUND**

**SCALING RELATIONS OF LEVY**

**BUT - NO LONGER CORRECT IN SLOWLY VAR.**
Table 14. The errors (in eV) in the binding energies of the first-row dimers as obtained from different density functionals defined below. Δ is the average absolute error for each functional.

<table>
<thead>
<tr>
<th></th>
<th>Li₂</th>
<th>Be₂</th>
<th>B₂</th>
<th>C₂</th>
<th>N₂</th>
<th>O₂</th>
<th>F₂</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>-0.1</td>
<td>0.5</td>
<td>0.8</td>
<td>1.0</td>
<td>1.7</td>
<td>2.4</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>LPM</td>
<td>-0.5</td>
<td>0.3</td>
<td>0.2</td>
<td>-0.2</td>
<td>0.3</td>
<td>1.2</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>PW86</td>
<td>-</td>
<td>0.2</td>
<td>-0.1</td>
<td>-</td>
<td>0.7</td>
<td>0.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>PW91</td>
<td>-0.1</td>
<td>0.3</td>
<td>-0.1</td>
<td>0.7</td>
<td>1.0</td>
<td>0.7</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>B86</td>
<td>-0.1</td>
<td>0.1</td>
<td>-0.5</td>
<td>-0.8</td>
<td>0.2</td>
<td>0.2</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>B I</td>
<td>-0.1</td>
<td>0.1</td>
<td>-0.3</td>
<td>-0.7</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>B II</td>
<td>-0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>0.8</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>B III</td>
<td>-0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.1</td>
<td>0.2</td>
<td>-0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

LDA the local-density approximation. Data from Ref. 62.
LPM the functional by Langreth, Perdew, Mehl, and Hu [8,9,55]. Data from Ref. 63
PW86 the older functional by Perdew and Wang [76,77]. Data from Ref. 99.
PW91 the latest functional by Perdew et al. [93]. Data from Ref. 79.
B86 an older exchange approximation by Becke [63] plus correlation from Stoll et al. [103]. Data from Ref. 63.
B I the functional of "Becke: Thermo-chemistry I" [102]. Data from Ref. 79.
B II the functional of "Becke: Thermo-chemistry II" [105]. Data from Ref. [105].
B III the functional of "Becke: Thermo-chemistry III" [107]. Data from Ref. [107].

Table 15. The errors (in eV) in the correlation-energy contributions to the binding energies of the first-row dimers as obtained from different correlation functionals defined below. Δ is the average absolute error for each functional.

<table>
<thead>
<tr>
<th></th>
<th>Li₂</th>
<th>Be₂</th>
<th>B₂</th>
<th>C₂</th>
<th>N₂</th>
<th>O₂</th>
<th>F₂</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDC</td>
<td>-0.1</td>
<td>-0.3</td>
<td>-1.9</td>
<td>-4.1</td>
<td>-2.4</td>
<td>-2.9</td>
<td>-2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>LPMC</td>
<td>0.1</td>
<td>0.1</td>
<td>-0.8</td>
<td>-2.7</td>
<td>-1.0</td>
<td>-1.2</td>
<td>-1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>PW91C</td>
<td>-0.3</td>
<td>-0.2</td>
<td>-1.5</td>
<td>-3.9</td>
<td>-2.4</td>
<td>-2.1</td>
<td>-2.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Philipsen & Baerends

![Graph showing cohesive energy (eV) for various elements: Sc, Ti, V, Cr, Mn, Fe, Ni, Zn. The graph compares LDA, PW, BP, and EXP results.](image-url)
FIG. 4. Enhancement factor $F(s)$ [see Eq. (1)] of the exchange energy for the gradient-corrected functionals under study.
Meta-GGA (Perdew, Kurth, Zupan, Blaha)

PRL 82, 2544 (99).

\[ X = \frac{10}{81} P + \frac{146}{2025} q^2 - \frac{73}{405} P q + \left[ D + \frac{1}{\chi} \left( \frac{10}{81} \right)^2 \right] P^2 \]

\[ E_{\chi}^{\text{MGGA}} (P, q) = 1 + \chi - \frac{\chi^2}{1 + \frac{X}{\chi}} \]

D = unknown, adjustable

Also

\[ \tau(\vec{r}) = \sum_{k} \left| \nabla \phi_k(\vec{r}) \right|^2 \]

\[ \tau(\vec{r}) = \frac{3}{10} n k_F^2 \left( 1 + \frac{5}{27} P + \frac{20}{9} q \right) \]

Replace \( q \) in \( X \) by \( \tau ! \)

Correlation: Yes, but not here! SI free!
<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta E_{\text{LSD}}$</th>
<th>$\Delta E_{\text{GGA}}$</th>
<th>$\Delta E_{\text{MGGA}}$</th>
<th>$\Delta E_{\text{expt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>113.3</td>
<td>104.6</td>
<td>114.5</td>
<td>109.5</td>
</tr>
<tr>
<td>LiH</td>
<td>61.1</td>
<td>53.5</td>
<td>58.4</td>
<td>57.8</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>462.6</td>
<td>419.8</td>
<td>421.1</td>
<td>419.3</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>337.3</td>
<td>301.7</td>
<td>298.8</td>
<td>297.4</td>
</tr>
<tr>
<td>OH</td>
<td>124.2</td>
<td>109.8</td>
<td>107.8</td>
<td>106.4</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>266.6</td>
<td>234.2</td>
<td>230.1</td>
<td>232.2</td>
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<tr>
<td>HF</td>
<td>162.3</td>
<td>142.0</td>
<td>138.7</td>
<td>140.8</td>
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<tr>
<td>Li$_2$</td>
<td>23.8</td>
<td>19.9</td>
<td>22.5</td>
<td>24.4</td>
</tr>
<tr>
<td>LiF</td>
<td>156.1</td>
<td>138.6</td>
<td>128.0</td>
<td>138.9</td>
</tr>
<tr>
<td>Be$_2$</td>
<td>12.8</td>
<td>9.8</td>
<td>4.5</td>
<td>3.0</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>460.3</td>
<td>414.9</td>
<td>401.2</td>
<td>405.4</td>
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<tr>
<td>C$_2$H$_4$</td>
<td>632.7</td>
<td>571.5</td>
<td>561.5</td>
<td>562.6</td>
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<td>HCN</td>
<td>360.8</td>
<td>326.1</td>
<td>311.8</td>
<td>311.9</td>
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<tr>
<td>CO</td>
<td>298.9</td>
<td>268.8</td>
<td>256.0</td>
<td>259.3</td>
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<tr>
<td>N$_2$</td>
<td>266.9</td>
<td>243.2</td>
<td>229.2</td>
<td>228.5</td>
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<tr>
<td>NO</td>
<td>198.4</td>
<td>171.9</td>
<td>158.5</td>
<td>152.9</td>
</tr>
<tr>
<td>O$_2$</td>
<td>174.9</td>
<td>143.7</td>
<td>131.4</td>
<td>120.5</td>
</tr>
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<td>F$_2$</td>
<td>78.2</td>
<td>53.4</td>
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<td>38.5</td>
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<tr>
<td>P$_2$</td>
<td>143.0</td>
<td>121.1</td>
<td>117.8</td>
<td>117.3</td>
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<tr>
<td>Cl$_2$</td>
<td>82.9</td>
<td>65.1</td>
<td>59.4</td>
<td>58.0</td>
</tr>
<tr>
<td>Mean abs. error</td>
<td>31.69</td>
<td>7.85</td>
<td>3.06</td>
<td>...</td>
</tr>
</tbody>
</table>

2545
Conclusions from M-GGA. (Perdew?)

1. Slightly better than Becke for molec.
2. Very good for correlation energies - esp. for slowly varying systems. (Perdew)
3. Still occasional large errors for molecules
4. Not correct for slowly varying systems.
5. No improvement of bond lengths
6. Indication of bad description of Hydrogen bonds
7. Improvements?

\[ D(p) = D_0 + \frac{D_0 \alpha P}{1 + \alpha P^n} \]
SCREENED EXCHANGE MODEL

MOTIVATION

a. Exchange dominates
   \( E_x = 10 E_e \) (atom) \( E_x = 4 E_e \) (Na)

b. Old Slater rule.
   \( F_k \rightarrow 0.75 F_k \) ; \( G_k \rightarrow 0.75 G_k \)

c. Correlation reduces the range of the \( xc \)-hole.
   El. gas and molecules \( (r^{-4} \rightarrow r^{-5}) \)

---

**x-hole**

---

**c-hole**
d. S-p transfer energies.

The nodal structure of the wave function.

e. Becke's half-half method

Real exchange?
f. Potentials and response functions.

Van der Waals?

THE MODEL (WD, AD)

\[ E_{xc}[n] = -\frac{1}{4} \int \ln(r, r') r^2 F(r - r') u(r - r') \, dr \, dr' \]

\[ n(r, r') = 2 \sum_{k} \Phi_{k}(r) \Phi_{k}^{*}(r') \]

\[ u(r) = \frac{1}{r} \]

\[ F = 1 \quad \text{in Hartree-Fock} \]

Look at He!

\[ F(r, r') = 2 - 4 \frac{|\psi(r, r')|^2}{n(r)n(r')} \]

\[ F(r, r') \approx A(r) A(r') B(r - r') \]
Better model

\[ E_{xc}[n] = -\frac{1}{4} \int \ln(\bar{v}, \bar{v}') \bar{v}^2 A(\bar{v}) A(\bar{v}') B(\bar{v}-\bar{v}') \nu(\bar{v}-\bar{v}') d\bar{v}' \]

Sum rule!

\[ A(\bar{v}) \int \ln(\bar{v}, \bar{v}') \bar{v}^2 A(\bar{v}') B(\bar{v}-\bar{v}') d\bar{v}' = 2n(\bar{v}) \]

Integral eq. for \( A(\bar{v}) \! : \! \!

A slowly varying approx. between 1 & 2

\[ B(r) = \left[ 1 + a(n) \cdot r + b(n) r^2 \right] e^{-c(n)r} \]

For the gas:

a. \( E_{xc}(n) \)
b. \( \tilde{g}(0) \)
c. Sum rule

d. Cusp condition
Choice of $n$

\[
n = \tilde{n} = \sqrt{n(\bar{f}) n(\bar{f}')}\]

\[
\tilde{n} = \frac{1}{2} \left[ n(\bar{f}) + n(\bar{f}') \right]
\]

**Symmetry** $\bar{f} \leftrightarrow \bar{f}'$ **Important**

**Gives**

\[
u_{xc}(\bar{f}) \rightarrow -\frac{1}{r}
\]

**Results.**

Correct correlation energies for

1. El gas
2. He
3. H$_2$
DIFFICIENCIES WITH LOCAL OR SEMILOCAL APPROXIMATIONS

1. THE CORE PROBLEM
2. THE SURFACE PROBLEM
3. THE BANDGAP PROBLEM
4. THE SYMMETRY PROBLEM
5. THE NEAR DEGENERACY PROBLEM
6. THE LONG RANGE PROBLEM

THANK YOU

FOR YOUR ATTENTION!