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Exchange and Correlation
I. Chemistry vs Physics
II. Variational Calculus
III. Hohenberg-Kohn Theory
IV. Kohn-Sham Formulation
V. From a Four-Letter to a House-Hold Word (GGAs)
VI. Death of DFT (Hybrid Functionals)
VII. Perdew's Reinterpretation of Jacob's Ladder
VIII. Selected Topics
IX. Conclusion
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A HIGHLY INTERDISCIPLINARY AREA

Chemistry

Materials Science

Engineering

Biology

Physics
"I'm on the verge of a major breakthrough, but I'm also at that point where chemistry leaves off and physics begins, so I'll have to drop the whole thing."

Of course not!
“Ein Chemiker, der nicht gleichzeitig Physiker ist, ist gar nichts.”*
Robert Eberhard Wilhelm Bunsen (1811-1899)

- Spectroscopy for chemical characterization
- Photochemistry
- A nifty little burner -->
- and quite a few other things

* “A chemist who is not at the same time a physicist is nothing at all.”
There is no “versus.”

“Chemistry” = chemical physics/physical chemistry
“Physics” = solid-state physics

… and of course, we are talking about theory here!
“When cultures clash a country can be torn apart.”

Sometimes the chemistry and physics also feel like two cultures in conflict:

- Make different approximations
- Calculate different properties
- Use different language

But of course chemistry and physics have to meet in areas such as materials science.
**Ab Initio** means first-principles theories based upon Hartree-Fock plus correlation.  
**Parameters:**  $e, m_e, \hbar, c \approx 137, ...$  
**Alphabet soup:** HF, SCF, CASSCF, MP2, CC2(T), ...

DFT is not *ab initio* but may be *ab-initio* based. It tries to extrapolate *ab-initio* accuracy to larger systems.  
**Parameters:** half-dozen to dozen for the entire periodic table and all properties  
**Alphabet soup:** LDA, BLYP, PBE, B3LYP, LRH,, ...

**Semi-empirical** methods are designed to interpolate specific properties for specific classes of compounds.  
**Parameters:** half-dozen per element  
**Alphabet soup:** Extended Hückel (tight-binding), ZINDO, ...
**Les deux solitudes/The two solitudes**

**Captain Canada** (English speaker)

They don't speak the same language.

They don't have the same politics.

But they are united in their efforts to fight crime!

Condensed Matter Physics

**Condensed Matter Physics** ➙ We don't always speak the same language, but more and more we work together. ➙ **Quantum Chemistry**

Fleur de Lys (French speaker)

https://sites.google.com/site/markcasida/dft
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VARIATIONAL PRINCIPLE

Seek solutions to

\[ \hat{H} \Psi_i = E_i \Psi_i; \quad E_0 \leq E_1 \leq E_2 \leq \cdots \] (1)

Then

\[ E_0 \leq W[\Psi_{\text{trial}}] = \frac{\langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle} \] (2)

For any trial wavefunction \( \Psi_{\text{trial}} \), satisfying the same boundary conditions as the \( \Psi_i \).

\( W[\Psi] \) is a functional --- that is, a function of a function.

* Quantum Chemistry 101?
VARIATIONAL CALCULUS

Multivariable calculus

\[ \vec{f} = \begin{bmatrix} f_1 \\ f_2 \\ \vdots \end{bmatrix} \]  
\[ dF(\vec{f}) = \sum_i \frac{\partial F}{\partial f_i} df_i \]  

Variational calculus

\[ f = f(x) \]  
\[ \delta F[f] = \int \frac{\delta F}{\delta f(x)} \delta f(x) \, dx \]  

Prentice-Hall 1963
McGraw Hill 1968
Dover 1974
... now in e-book format

https://sites.google.com/site/markcasida/dft
EASY EXAMPLE (1)

Minimize \[ W[\Psi, \Psi^*] = \int \Psi^*(\tau) \hat{H} \Psi(\tau) d\tau \] subject to the constraint \[ \int \Psi^*(\tau) \Psi(\tau) d\tau = 1 \]

Use the method of Lagrange multipliers!

\[ L[\Psi, \Psi^*] = \int \Psi^*(\tau) \hat{H} \Psi(\tau) d\tau - E \int \Psi^*(\tau) \Psi(\tau) d\tau \]

\[ = \int \Psi^*(\tau) (\hat{H} \Psi(\tau) - E \Psi(\tau)) d\tau \]

\[ 0 = \delta L[\Psi, \Psi^*] = L[\Psi, \Psi^* + \delta \Psi^*] - L[\Psi, \Psi^*] \]

\[ = \int \delta \Psi^*(\tau) (\hat{H} \Psi(\tau) - E \Psi(\tau)) d\tau \]

True \[ \forall \Psi^* \Rightarrow \hat{H} \Psi(\tau) - E \Psi(\tau) = 0 \]

i.e., \[ \hat{H} \Psi(\tau) = E \Psi(\tau) \]
EASY EXAMPLE (2)

\[ L[\Psi, \Psi^*] = \int \Psi^*(\tau) \hat{H} \Psi(\tau) d\tau - E \int \Psi^*(\tau) \Psi(\tau) d\tau \]  
\[ = \int \left[ (\hat{H} \Psi(\tau))^* - E \Psi^*(\tau) \right] \Psi(\tau) d\tau \]  

\[ 0 = \delta L[\Psi, \Psi^*] = L[\Psi + \delta \Psi, \Psi^*] - L[\Psi, \Psi^*] \]  
\[ = \int \left[ (\hat{H} \Psi^*(\tau)) - E \Psi^*(\tau) \right] \delta \Psi(\tau) d\tau \]  

True \quad \forall \Psi^* \Rightarrow \quad \hat{H} \Psi^*(\tau) - E \Psi^*(\tau) = 0 \quad (3) 

i.e., \quad \hat{H} \Psi^*(\tau) = E \Psi^*(\tau) \quad (4) 

or \quad \hat{H} \Psi(\tau) = E^* \Psi(\tau) \quad (5) 

Compare with \quad \hat{H} \Psi(\tau) = E \Psi(\tau) \quad (6) 

So the Lagrange multiplier is real (which is good since it is the energy!)
HARTREE-FOCK TOTAL (ELECTRONIC) ENERGY

Minimizing

$$E_0 \leq W[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

with

$$\Phi = |\psi_1, \psi_2, \cdots, \psi_N| = \frac{1}{\sqrt{N!}} \text{det} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix}$$

subject to the constraint

$$\langle \psi_i | \psi_j \rangle = \delta_{i,j}$$

gives

$$E = E_{\text{core}} + E_H + E_x$$

$$E_{\text{core}} = \sum_i n_i \langle \psi_i | \hat{t} + \nu_{\text{ext}} | \psi_i \rangle = \sum_i n_i \langle \psi_i | \hat{h}_{\text{core}} | \psi_i \rangle$$
HARTREE-FOCK TOTAL (ELECTRONIC) ENERGY

\[ E = E_{\text{core}} + E_H + E_x \]  \hspace{1cm} (1)

Hartree (Coulomb) energy

\[ E_H = \frac{1}{2} \int \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} \, dr_1 \, dr_2 = \frac{1}{2} \sum_{i,j} n_i n_j (ii|f_H|jj) \]  \hspace{1cm} (2)

Charge density

\[ \rho(1) = \sum_i n_i |\psi_i(1)|^2 \]  \hspace{1cm} (3)

Mulliken charge cloud notation

\[ (pq|f|rs) = \int \int \psi_p^*(1) \psi_q(1) f(1,2) \psi_r^*(2) \psi_s(2) \, d1 \, d2 \]  \hspace{1cm} (4)

Exchange energy

\[ E_x = -\frac{1}{2} \int \int \frac{|\gamma(1,2)|^2}{r_{12}} \, d1 \, d2 = -\frac{1}{2} \sum_{i,j} n_i n_j (ij|f_H|ji) \]  \hspace{1cm} (5)

One-electron reduced density matrix

\[ \gamma(1,2) = \sum_i \psi_i(1) n_i \psi_i^*(2) \]  \hspace{1cm} (6)
HARTREE-FOCK ORBITAL EQUATION (1)

\( L = E_{\text{core}} + E_H + E_x - \sum_i n_i \varepsilon_i \langle \psi_i | \psi_i \rangle - 1 \) \hspace{1cm} (1)

\( E_{\text{core}} = \sum_i n_i \int \psi_i(1) \hat{h}_{\text{core}} \psi_i(1) d1 \) \hspace{1cm} (3a) \quad \Rightarrow \quad \frac{\delta E_{\text{core}}}{\delta \psi_i^*(1)} = n_i \hat{h}_{\text{core}} \psi_i(1) \hspace{1cm} (3b)

\( E_H[\rho] = \frac{1}{2} \int \int \frac{\rho(1) \rho(2)}{r_{12}} d1 d2 \) \hspace{1cm} (4a) \quad \Rightarrow \quad \frac{\delta E_H[\rho]}{\delta \rho(1)} = \int \frac{\rho(2)}{r_{12}} d2 \hspace{1cm} (4b)

\( \rho(1) = \int \left| \sum_i n_i |\psi_i(2)|^2 \right| \delta (1-2) d2 \) \hspace{1cm} (5a) \quad \Rightarrow \quad \frac{\delta \rho(1)}{\delta \psi_i^*(2)} = n_i \psi_i(1) \delta (1-2) \hspace{1cm} (5b)

\( \frac{\delta E_H[\rho]}{\delta \psi_i^*(1)} = \int \frac{\delta E_H}{\delta \rho(2)} \frac{\delta \rho(2)}{\delta \psi_i^*(1)} d2 = n_i \int \frac{\rho(2)}{r_{12}} d2 \psi_i(1) \) \hspace{1cm} (6a)

\( \nu_H[\rho](\vec{r}_1) \) \hspace{1cm} (6b)

https://sites.google.com/site/markcasida/dft
HARTREE-FOCK ORBITAL EQUATION (2)

\[ E_x[\gamma] = -\int \int \frac{\gamma(2,3) \gamma(3,2)}{r_{23}} \, d2 \, d3 \quad (1a) \Rightarrow \frac{\delta E_x[\gamma]}{\delta \gamma(2,3)} = -\frac{\gamma(3,2)}{r_{23}} \quad (1b) \]

\[ \gamma(2,3) = \int |\sum_i \psi_i(2) n_i \psi_i^*(1)| \delta(1-3) \, d1 \quad (2a) \Rightarrow \frac{\delta \gamma(2,3)}{\delta \psi_i^*(1)} = n_i \psi_i(2) \delta(1-3) \quad (2b) \]

\[ \frac{\delta E_x[\gamma]}{\delta \psi_i^*(1)} = \int \int \frac{\delta E_x}{\delta \gamma(2,3)} \frac{\delta \gamma(2,3)}{\delta \psi_i^*(1)} \, d2 \, d3 = -n_i \int \frac{\gamma(1,2)}{r_{12}} \psi_i(2) \, d2 \quad (3a) \]

\[ -\hat{\Sigma}_x[\gamma](\vec{r}_1, \vec{r}_2) \quad (3b) \]

\[ \frac{\delta \left( \sum_j n_j \langle \psi_j | \psi_j \rangle \right)}{\delta \psi_i^*(1)} = n_i \psi_i(1) \quad (4) \]
Putting it all together,
\[
0 = \frac{\delta L}{\delta \psi_i^*(1)} = n_i \left( \hat{f} \psi_i(1) - \epsilon_i \psi_i(1) \right)
\]  
(1)

or
\[
\hat{f} [\gamma] \psi_i(1) = \psi_i(1)
\]  
(2)

where the Fock operator,
\[
\hat{f} [\gamma] = h_{\text{core}} + v_H [\rho](\vec{r}) + \Sigma_x [\gamma]
\]  
(3)

... and the Kohn-Sham equations of DFT are very similar !
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THE HOHENBERG-KOHN THEOREMS GIVE
A RIGOROUS BASIS TO THOMAS-FERMI THEORY


Electronic energy

\[ E \approx T[\rho] + \int \mathbf{v}_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_x[\rho] \]

\textbf{The system is the electrons. All else is external.}

\textbf{Can it be made exact?}

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Theorem (HK1)
For a nondegenerate ground state, the external potential is determined by the charge density up to an arbitrary additive constant (i.e., an energy zero.)

\[ \rho(\vec{r}) \overset{1-1}{\longleftrightarrow} v_{\text{ext}}(\vec{r}) + \text{const.} \] (1)

Comments
1) so the charge density determines just about everything
2) but how accurately? (e.g. it can only determine the \( v_{\text{ext}} \) where \( \rho \) is nonzero)
3) proof is trivially based upon the variational principle
4) the theorem is physically obvious for a molecule or solid in the absence of applied fields
Theorem (HK1)  
For a nondegenerate ground state, the external potential is determined by the charge density up to an arbitrary additive constant (i.e., an energy zero.)

Proof  
By contradiction.

Suppose $V_{ext}^{(1)} \rightarrow \rho \leftarrow V_{ext}^{(2)}$ (1) with $V_{ext}^{(1)} - V_{ext}^{(2)} \neq \text{const.}$ (2)

Now $(\hat{T} + V_{ee} + V_{ext}) \Psi = E \Psi$ (3) so $V_{ext} = \frac{\hat{T} \Psi}{\Psi} + V_{ee} - E$ (4)

Which means that $\Psi^{(1)} \neq \Psi^{(2)} e^{i\theta}$ (5)

The variational principle then tells us that

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} + \int \left( v_{ext}^{(1)}(\vec{r}) - v_{ext}^{(2)}(\vec{r}) \right) \rho(\vec{r}) d\vec{r}$$ (6a)

and $$E^{(2)} = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle < \langle \Psi^{(1)} | \hat{H}^{(2)} | \Psi^{(1)} \rangle = E^{(1)} + \int \left( v_{ext}^{(2)}(\vec{r}) - v_{ext}^{(1)}(\vec{r}) \right) \rho(\vec{r}) d\vec{r}$$ (6b)

Adding leads to the contradiction $E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$ (7)
Integrating $\rho$ gives $N$. Cusp positions locate the nuclei. Nuclear charge is given by the slope at the cusp.**

So the ground-state density contains everything you need to set up and solve the time-independent Schrödinger equation.

$$Z_A = -\lim_{r \to r_A} \frac{\partial}{\partial r} \int \rho(\vec{r}) \, d\Omega$$

$$= \frac{1}{2} \lim_{r \to r_A} \frac{1}{r} \int \rho(\vec{r}) \, d\Omega$$

* http://phelafel.technion.ac.il/~orcohen/h2.html

This gives us a

but we still need a way to find the charge density!
BUT WHAT ABOUT ... ?

N-representability: Can we always find a $\Psi$ that will give us any given (reasonable) $\rho$?


(v-representability): Can we always find an external potential which will give us any given (reasonable) $\rho$?


$$\rho(x) = \left(a + b |x|^{\alpha + 1/2}\right)^2 \quad ; \quad a, b > 0 \quad ; \quad 0 \leq \alpha \leq 1/2$$

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Fortunately DFT really rests on HK2 which requires only N-representability, not \( v \)-representability.

Theorem (HK2)
The ground state energy and density are determined the variational principle,

\[
E = \min_{\rho} \left[ F[\rho] + \int v_{\text{ext}}(\vec{r}) \rho(\vec{r}) \, d\vec{r} \right] \quad (1)
\]

The functional \( F[\rho] \) is universal in the sense of being independent of \( v_{\text{ext}} \).
Theorem (HK2)
The ground state energy and density are determined the variational principle,

\[ E = \min_{\rho} \left( F[\rho] + \int v_{\text{ext}}(\vec{r}) \rho(\vec{r}) \, d\vec{r} \right) \]  

The functional \( F[\rho] \) is universal in the sense of being independent of \( v_{\text{ext}} \).

Proof (Levy-Lieb*)

\[ F[\rho] = \min_{\Psi} \langle \Psi | \hat{T} + V_{ee} | \Psi \rangle \]  

So the exact “unknown” functional is known, but just impossibly difficult to calculate!

COMPUTATIONALLY CONVENIENT EFFECTIVE APPROXIMATIONS, TYPICALLY OF THE FORM

\[ F[\rho] = \int f[\rho](\vec{r}) \rho(\vec{r}) d\vec{r} \]
DFA VERSUS DFT

**Density-Functional Theory**
- Formally exact
- Computationally useless
- What DFAs try to approximate

**Density-Functional Approximations**
- Never exact
- But computationally useful
- Try to approximate the behavior of DFT

https://sites.google.com/site/markcasida/dft
My page web (not quite up to date) to help you become familiar with DFAs:

https://sites.google.com/site/markcasida/dft
HOMOGENEOUS ELECTRON GAS (HEG, JELLIUM)

$n$ electrons in a box of volume $V = l^3$

A positive background with a uniform charge

$$\boxplus = +e \, n / V$$

Now take the infinite volume limit while keeping the density constant.
ALL PROPERTIES OF THE HEG DEPEND ON
THE SINGLE PARAMETER $\rho$

Wigner-Seitz radius

$$\frac{4}{3} \pi r_s^3 = \frac{1}{\rho} \quad (1a) \quad \Rightarrow \quad r_s = \left( \frac{3}{4 \pi \rho} \right)^{1/3} \quad (1b)$$

Orbitals

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{r}} \quad (2)$$

Quantization

$$k_x = \frac{2 \pi}{l} n_x \quad (3)$$

Density of states

$$d \tilde{n} = \frac{V}{8 \pi^3} d \tilde{k} \quad (4)$$
FERMI MOMENTUM (WAVE NUMBER)

\[ N = 2 \int d\vec{n} = \frac{V}{4\pi^3} \int d\vec{k} = \frac{V}{\pi^2} \int_0^{k_F} k^2 \, dk = \frac{V}{3\pi^2} k_F^3 \]  \hspace{1cm} (1)

So

\[ k_F = \left( 3\pi^2 \rho \right)^{1/3} \]  \hspace{1cm} (2)

Also

\[ k_F r_s = \left( \frac{9\pi}{4} \right)^{1/3} \]  \hspace{1cm} (3)
HEG KINETIC ENERGY

\[ t_{\text{HEG}} = \frac{T_{\text{HEG}}}{V} = \frac{2}{V} \int \int \psi^*_k(\vec{r}) \left( -\frac{1}{2} \nabla^2 \right) \psi_k(\vec{r}) \, d\vec{n} \, d\vec{r} \quad (1) \]

\[ \nabla^2 \psi_k(\vec{r}) = -k^2 \psi_k(\vec{r}) \quad (3) \]

\[ \psi^*_k(\vec{r}) \psi_k(\vec{r}) = \frac{1}{V} \quad (4) \]

\[ t_{\text{HEG}} = \frac{1}{V^2} \int \int k^2 \, d\vec{n} \, d\vec{r} = \frac{1}{V} \int k^2 \, d\vec{n} \quad (5) \]

\[ d\vec{n} = \frac{V}{8 \pi^3} \, d\vec{k} \quad (6) \]

\[ t_{\text{HEG}} = \frac{1}{8 \pi^3} \int k^2 \, d\vec{k} = \frac{1}{2 \pi^2} \int_0^{k_F} k^4 \, dk = \frac{k_F^5}{10 \pi^2} \quad (7) \]

\[ t_{\text{HEG}} = \frac{3}{10} \left( \frac{3}{2} \pi^2 \right)^{2/3} \rho^{5/3} \quad (8) \]
HEG EXCHANGE ENERGY

\[ E_x[\gamma] = -\int \int \frac{\gamma(2,3)\gamma(3,2)}{r_{23}} \, d2 \, d3 \]  

(1)

Dirac result*

\[ e_x^{HEG} = \frac{E_x^{HEG}}{V} = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{4/3} \]  

(2)

CONCEPT OF A LOCAL DENSITY APPROXIMATION (LDA)

\[ F[\rho] = \int f[\rho](\vec{r}) \rho(\vec{r}) d\vec{r} \quad (1) \]

\[ f_{HEG}(\rho(\vec{r}_1)) \]

\[ f_{HEG}(\rho(\vec{r}_2)) \]

\[ f_{HEG}(\rho(\vec{r}_3)) \]

\[ F[\rho] \approx F^{LDA} = \int f_{HEG}(\rho(\vec{r})) \rho(\vec{r}) d\vec{r} \approx \sum_i f_{HEG}(\rho(\vec{r}_i)) \rho(\vec{r}_i) \Delta v(\vec{r}_i) \quad (2) \]

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THOMAS-FERMI-DIRAC (TFD) DFA TO THE HOHENBERG-KOHN FUNCTIONAL

$$F_{TFD}[\rho] = \frac{3}{10} \left(3\pi^2\right)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r} + \int \frac{\rho(\vec{r}_2)}{|\vec{r} - \vec{r}_2|} d\vec{r}_2 - \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\vec{r}) d\vec{r} \quad (1)$$

$$E_{TFD}[\rho] = F_{TFD}[\rho] + \int v_{ext}(\vec{r}) \rho(\vec{r}) d\vec{r} \quad (2)$$

Unfortunately atoms do not bind together to form molecules in this approximation!*

The problem is the LDA for the kinetic energy so let us look in more detail at the exchange and correlation energy for the HEG.

SPIN AND EXCHANGE

\[ e_x = \frac{E_x}{V} = \rho \epsilon_x \quad (1a) \]

\[ \epsilon_x = \frac{E_x}{N} = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{1/3} \quad (1b) \]

\[ e_x = \rho_\alpha \epsilon_x^\alpha + \rho_\beta \epsilon_x^\beta \quad (2a) \]

\[ \epsilon_x^\sigma = \frac{E_x}{N} = -\frac{3}{4} \left( \frac{6}{\pi} \right)^{1/3} \rho_\sigma^{1/3} \quad (2b) \]

Alternatively,

\[ \epsilon_x = \epsilon_x^P + f(\xi) \left( \epsilon_x^F - \epsilon_x^P \right) \quad (3) \]

Paramagnetic part

\[ \epsilon_x^P = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{1/3} \quad (4a) \]

Ferromagnetic part

\[ \epsilon_x^P = -\frac{3}{4} \left( \frac{6}{\pi} \right)^{1/3} \rho^{1/3} \quad (4b) \]

Spin polarization

\[ \xi = \frac{\rho_\alpha - \rho_\beta}{\rho} \quad (5a) \]

\[ f(\xi) = \frac{\left( 1 + \xi \right)^{4/3} + \left( 1 - \xi \right)^{4/3} - 2}{2 \left( 2^{1/3} - 1 \right)} \quad (5b) \]
ELECTRON CORRELATION IN THE HEG (I)

\[ \rho \]

\[ \xi = 0 \quad \text{Paramagnetic solution} \]

\[ \xi = 1 \quad \text{Ferromagnetic solution} \]

Wigner crystal (bcc)

https://sites.google.com/site/markcasida/dft
Per Olaf Löwdin definition \[ E_c = E - E_{HF} < 0 \quad (1) \]

The last simple formula for electron correlation? (Too bad it is not more accurate.)

\[ \epsilon_c \approx -\frac{0.44}{7.8 + r_s} \quad (2) \quad \text{(Wigner)} \]


https://sites.google.com/site/markcasida/dft


*All give pretty similar results!*
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THE KOHN-SHAM REFORMULATION OF DFT GIVES
A RIGOUROUS BASIS TO SLATER’S Xα MODEL

Sought to simplify Hartree-Fock calculations by eliminating the nonlocal integral exchange operator.

\[
E_{HF} = E_{core} + E_H + \frac{1}{2} \sum_i n_i \langle \psi_i | \hat{\Sigma}_x | \psi_i \rangle \quad (1a)
\]
\[
= E_{core} + E_H + \frac{1}{2} \sum_i n_i \langle \psi_i | v_x^S | \psi_i \rangle \quad (1b)
\]

where the Slater potential,

\[
v_x^S(r) = \frac{\sum_i n_i \psi_i^*(1) \hat{\Sigma}_x \psi_i(1)}{\sum_j n_j \psi_j^*(1) \psi_j(1)} \quad (2)
\]

Comparison with Dirac's local exchange gives

\[
v_x(r) = -\alpha \frac{3}{2} \left( \frac{3}{\pi} \right)^{1/3} \rho^{1/3}(\vec{r}) \quad ; \quad \alpha = 1
\]

John SLATER

Introducing N orthonormal Kohn-Sham orbitals allows the most important contributions to the total energy to be written exactly.

\[
E = \sum_{i\sigma} n_{i\sigma} \langle \psi_{i\sigma} | -\frac{1}{2} \nabla^2 + v_{\text{ext}} | \psi_{i\sigma} \rangle + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + E_{\text{xc}}[\rho] \tag{1}
\]

where

\[
\rho(\vec{r}) = \sum_{i\sigma} n_{i\sigma} |\psi_{i\sigma}(\vec{r})|^2 \tag{2}
\]

Minimizing subject to the orbital orthnormality constraint gives the Kohn-Sham equation.

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{\text{xc}}(\vec{r}) \right] \psi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma} \psi_{i\sigma}(\vec{r}) \tag{3}
\]

where the exchange-correlation potential is

\[
v_{\text{xc}}[\rho](\vec{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\vec{r})} \tag{4}
\]
Fictitious system of noninteracting electrons ("s" for single particle)

\[ \Phi_s = |\sigma_g, \bar{\sigma}_g| \]  

(2)

\[ \rho(\vec{r}) = 2|\sigma_g(\vec{r})|^2 \]  

(3)

Aufbau filling

Kohn-Sham determinant

Real system of interacting electrons

\[ \Psi = C_0 |\sigma_g, \bar{\sigma}_g| + C_5 |\sigma_u, \bar{\sigma}_u| \]  

(5)

Density

\[ \rho(\vec{r}) = 2\left(|C_0|^2 |\sigma_g(\vec{r})|^2 + |C_5|^2 |\sigma_u(\vec{r})|^2\right) \]  

(6)

The density is the same on the LHS and on the RHS!
For a 2-electron system, \[ \psi(\vec{r}) = \sqrt{\rho(\vec{r})} \quad (1) \]

\[ E = T_s + \int \nu_{\text{ext}} \rho + E_H + E_{\text{xc}} \quad (2) \]

\[ E_{\text{xc}} = (E_{ee} - E_H) + \left( T - T_s \right) \frac{\Delta T}{\Delta T} \quad (3) \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \Delta T ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^-)</td>
<td>0.8</td>
</tr>
<tr>
<td>He</td>
<td>1.0</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>1.1</td>
</tr>
<tr>
<td>Be(^{2+})</td>
<td>1.1</td>
</tr>
<tr>
<td>Li</td>
<td>1.7</td>
</tr>
<tr>
<td>Be</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Question**: Is there always a noninteracting system whose ground state *with integer occupation numbers* has the same density as the interacting system?

**Answer (Levy*)**: There is always a noninteracting system with the same density as the interacting system but it is not necessarily the ground state! In fact, NIVR is known to fail in the presence of strong correlation due to quasidegeneracies. This is typical at points on the potential energy surface when bonds are being made or broken.

The obvious way around would seem to be to allow fractional occupation numbers corresponding to an ensemble theory, but it is not quite so simple.**

---

LOCAL DENSITY APPROXIMATION (I)

\[ E^{LDA}_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho^{4/3}(\mathbf{r}) \, d\mathbf{r} \quad (1) \]

\[ v^{LDA}_x(\mathbf{r}) = -\alpha \frac{3}{2} \left( \frac{3}{\pi} \right)^{1/3} \rho^{1/3}(\mathbf{r}) \quad (2) \]

with \[ \alpha = \frac{2}{3} \quad (3) \]

Originally Slater had \[ \alpha = 1 \quad (4) \]

In the X\(\alpha\) method, \(\alpha\) is a semi-empirical parameter fit to atomic Hartree-Fock energies. Typically, \[ 0.70 \leq \alpha \leq 1 \]
No, not lysergic acid diethylamide

but rather the local spin density (LSD) approximation,

$$E_{xc} = E_{xc}[\rho_\alpha, \rho_\beta] = E_{xc}[r_s, \xi]$$

These days, LDA means LSD, with very few acceptions.

---

“We do not expect an accurate description of chemical bonding.”

GEOMETRIES AND FREQUENCIES NOT BAD.  
BUT SERIOUS OVERBINDING!

1 eV = 23.06 kcal/mol    “Chemical accuracy” is 1 kcal/mol

**TABLE I. LDA spectroscopic constants.**

<table>
<thead>
<tr>
<th></th>
<th>$r_e$ (bohrs)</th>
<th>$D_e$ (eV)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
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<td>LDA</td>
<td>Expt.</td>
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<tr>
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<td>B$_2$</td>
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<td>5.2</td>
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<td>Cl$_2$</td>
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<td>3.74</td>
<td>2.5</td>
</tr>
</tbody>
</table>

“It sort of makes you stop and think, doesn’t it.”
What is in common between electrons in a molecule and in the HEG !?
ADIABATIC CONNECTION*

\[ \hat{H} = \hat{H}_s + \lambda V_{ee} + W_\lambda[\rho] \]

- Kohn-Sham Hamiltonian
- Electron repulsion
- Local restoring potential to fix \( \rho \)

\( \lambda = 0 \)
Fictitious system of noninteracting electrons

\( \lambda = 1 \)
Real system of interacting electrons

\( \lambda \) varies but \( \rho \) does not

Exists as long as \( \rho \) is \( v \)-representable for all \( \lambda \).

**ADIABATIC CONNECTION**

\[ E_{xc}[\rho] = \frac{1}{2} \int \int \frac{\rho(1) \rho_{xc}(1,2)}{r_{12}} \, d1 \, d2 \] (1)

The exchange-correlation hole,

\[ \rho_{xc}(1,2) = \frac{\int_{0}^{1} \langle \Psi_{\lambda}[\rho]|\tilde{\rho}(1)\tilde{\rho}(2)|\Psi_{\lambda}[\rho]\rangle \, d\lambda}{\rho(1)} - \delta(1-2) \] (2)

\[ \tilde{\rho}(1) = \hat{\rho}(1) - \rho(1) \] (3)

is closely related to the 2-electron reduced density matrix.

Neglecting the \( \lambda \)-dependence of \( \Psi \),

\[ \rho_{xc}(1,2) = \frac{\Gamma(1,2;1,2)}{\rho(1)} - \rho(2) \xrightarrow{\text{HF}} - \frac{\gamma(1,2)\gamma(2,1)}{\rho(1)} \] (4)

Only the spherical average is important,

\[ \rho_{0,0}^{xc}(\vec{r}, \Delta r) = \frac{1}{4\pi} \int \rho_{xc}(\vec{r}, \vec{r}') d\Omega \]  (1)

\[ \epsilon_{xc}(\vec{r}) = \sqrt{\pi} \int_{0}^{\infty} \rho_{0,0}^{xc}(\vec{r}, y) y dy \]  (2)

It “contains” (i.e., excludes) exactly one electron,

\[ \int \rho(\vec{r}, \vec{r}'; d\vec{r}' = \sqrt{4\pi} \int_{0}^{\infty} \rho_{0,0}^{xc}(\vec{r}, y) y^2 dy = -1 \]  (3)
\[
y \rho_{0,0}^{xc}(\vec{r}, y) \frac{y}{\sqrt{4\pi}}
\] *


https://sites.google.com/site/markcasida/dft
Can we interpret the xc-potential?

“It is nice to know that the computer understands the problem. But I would like to understand it too.”

Eugene WIGNER
OPTIMIZED EFFECTIVE POTENTIAL (OEP) MODEL (I)

Present derivation may be found in M.E. Casida, in Recent Developments and Applications of Modern Density Functional Theory, J.M. Seminario Ed. (Elsevier: Amsterdam, 1996) p. 391.

Require

\[
\left( \hat{h}_H + \nu_x \right) \psi_i^{KS} = \epsilon_i \psi_i^{KS}
\]  \hspace{1cm} (1)

and

\[
\left( \hat{h}_H + \hat{\Sigma}_{xc} \right) \psi_i^{HF} = \epsilon_i \psi_i^{HF}
\]  \hspace{1cm} (2)

to produce the same charge density,

\[
0 = \rho^{HF}(1) - \rho^{KS}(1) = \sum_i n_i \left( \Delta \psi_i(1) \psi_i^{KS*}(1) + \psi_i^{HF}(1) \Delta \psi_i^*(1) \right)
\]  \hspace{1cm} (3)

where

\[
\Delta \psi_i(1) = \psi_i^{HF}(1) - \psi_i^{KS}(1)
\]  \hspace{1cm} (4)
\[ \Delta \psi_i(1) = \psi_i^{HF}(1) - \psi_i^{KS}(1) \]

(1a)

\[ = \sum_j \left( \psi_j^{KS}(1) \langle \psi_j^{KS} | \psi_i^{HF} \rangle \right) - \psi_i^{KS}(1) \]

(1b)

\[ = \sum_j \psi_j^{KS}(1) \left( \langle \psi_j^{KS} | \psi_i^{HF} \rangle - \delta_{i,j} \right) \]

(1c)

\[ = \sum_j \psi_j^{KS}(1) \left( \frac{\langle \psi_j^{KS} | \hat{\Sigma}_x - v_x | \psi_i^{HF} \rangle}{\epsilon_i^{HF} - \epsilon_j^{KS}} \right) - \delta_{i,j} \]

(1d)

Similarly

\[ \Delta \psi_i(1) = \psi_i^{HF}(1) - \psi_i^{KS}(1) \]

\[ = \sum_j \psi_j^{HF}(1) \left( \delta_{i,j} - \frac{\langle \psi_j^{HF} | \hat{\Sigma}_x - v_x | \psi_i^{KS} \rangle}{\epsilon_j^{HF} - \epsilon_i^{KS}} \right) \]

(2d)
OPTIMIZED EFFECTIVE POTENTIAL (OEP) MODEL (III)

\[
0 = \rho^{HF}(1) - \rho^{KS}(1) = \sum_i n_i \left( \Delta \psi_i(1) \psi_i^{KS*}(1) + \psi_i^{HF}(1) \Delta \psi_i^*(1) \right)
\]

\[
= \sum_{i,j} \frac{n_i - n_j}{\epsilon_i^{KS} - \epsilon_j^{HF}} \psi_i^{HF}(1) \psi_j^{KS*}(1) \langle \psi_i^{HF} | \hat{\Sigma}_x - v_x | \psi_j^{KS} \rangle
\]

\[
= \int X(1,1'; 2,2') \left| \Sigma_x(2,2') - v_x(2) \delta(2 - 2') \right| d2 d2'
\]

with

\[
X(1,1'; 2,2') = \sum_{i,j} \frac{n_i - n_j}{\epsilon_i^{KS} - \epsilon_j^{HF}} \psi_j^{HF}(1) \psi_i^{KS*}(1') \psi_i^{HF*}(2) \psi_j^{KS}(2')
\]

This is the same as the exchange-only form of the Sham-Schlüter equation* but derived without any reference to Green's functions.


\[
\psi_{i}^{KS} \leftarrow \psi_{i}^{HF} \quad (1)
\]
\[
\epsilon_{i}^{KS} \leftarrow \epsilon_{i}^{HF} \quad (2)
\]

Solves the problem of finding the \( \nu_x \) whose orbitals minimize the Hartree-Fock energy expression.

This is almost the same thing as asking for \( \nu_x \) whose orbitals produce the Hartree-Fock charge density.
THE OEP IMPROVES KOOPMANS' THEOREM

Outer-valence IPs for a number of small molecules.

Fig. 4. Correlation graph of calculated IPs and experimental ones for all the molecules in the tables. Units are in eV.


https://sites.google.com/site/markcasida/dft
Average denominator approximation

\[ \chi(1,1';2,2') = \sum_{i,j} \frac{n_i - n_j}{\epsilon_i^{KS} - \epsilon_j^{KS}} \psi_i^{KS}(1) \psi_i^{KS*}(2) \psi_j^{KS}(1') \psi_j^{KS*}(2') \]

\[ \approx -\frac{2}{\Delta} \sum_i \psi_i^{KS}(1) \psi_i^{KS*}(1') \psi_i^{KS*}(2) \psi_i^{KS}(2') \sum_j^{unocc} \sum_j^{occ} \]

Leads to

\[ v_x(1) = v_x^S(1) - \sum_{i,j} n_i \psi_i^{KS}(1) \langle \psi_i^{KS} | \hat{\Sigma}_x - v_x | \psi_j^{KS} \rangle \psi_j^{KS*}(1) \psi_j^{KS*}(1') \psi_j^{KS}(2') \]

\[ \frac{\rho(1)}{\rho(1)} \]
RECOVERY OF SLATER'S PICTURE

Localized Hartree-Fock (LHF), Common Energy Denominator Approximation (CEDA), Effective Local Potential (ELP)*

\[ v_x (1) = v_x^S (1) - \sum_{i,j} n_i \psi_i^{KS} (1) \langle \psi_i^{KS} | \hat{\Sigma}_x - v_x | \psi_j^{KS} \rangle \psi_j^{KS*} (1) \]

Krieger-Li-Iafrate (LHF) approximation**

\[ v_x (1) = v_x^S (1) - \sum_{i} n_i \psi_i^{KS} (1) \langle \psi_i^{KS} | \hat{\Sigma}_x - v_x | \psi_i^{KS} \rangle \psi_i^{KS} (1) \]


RECOVERY OF SLATER'S PICTURE

Assume that HF and KS orbitals are on average about the same.

\[
\left( \hat{h}_H + \hat{\Sigma}_x \right) \psi_i(1) = \epsilon_i^{HF} \psi_i(1) \quad (1)
\]

\[
\left( \hat{h}_H + v_x(1) \right) \psi_i(1) = \epsilon_i^{KS} \psi_i(1) \quad (2)
\]

\[
\left( v_x(1) - \hat{\Sigma}_x \right) \psi_i(1) = \left( \epsilon_i^{KS} - \epsilon_i^{HF} \right) \psi_i(1) \quad (3)
\]

\[
\sum_i n_i \psi_i^*(1) \left( v_x(1) - \hat{\Sigma}_x \right) \psi_i(1) = \sum_i n_i \psi_i^*(1) \left( \epsilon_i^{KS} - \epsilon_i^{HF} \right) \psi_i(1) \quad (4)
\]

\[
v_x(1) \rho(1) - \sum_i n_i \psi_i^*(1) \hat{\Sigma}_x \psi_i(1) = \sum_i n_i \left( \epsilon_i^{KS} - \epsilon_i^{HF} \right) |\psi_i(1)|^2 \quad (5)
\]

\[
v_x(1) = \frac{\sum_i n_i \psi_i^*(1) \hat{\Sigma}_x \psi_i(1)}{\rho(1)} + \frac{\sum_i n_i \left( \epsilon_i^{KS} - \epsilon_i^{HF} \right) |\psi_i(1)|^2}{\rho(1)} \quad (6)
\]

\begin{align*}
\text{Slater} & \quad \text{derivative discontinuity}
\end{align*}

https://sites.google.com/site/markcasida/dft

https://sites.google.com/site/markcasida/dft
I. Chemistry vs Physics
II. Variational Calculus
III. Hohenberg-Kohn Theory
IV. Kohn-Sham Formulation
V. From a Four-Letter to a House-Hold Word (GGAs)
VI. Death of DFT (Hybrid Functionals)
VIII. Selected Topics
IX. Conclusion
CHEMISTRY NOBEL PRIZE 1998
"to Walter Kohn for his development of the density-functional theory
and to John Pople for his development of computational methods in quantum chemistry."

Some of us think someone else also
deserves a bit of credit here!

https://sites.google.com/site/markcasida/dft
The development of the xc-functional in gradients was already suggested in the seminal paper of Hohenberg and Kohn in 1964.

The calculus of variations is a bit subtle in this case.

\[
f[\rho](x) = f(\rho(x), \rho'(x), \rho''(x), \ldots) \quad (1)
\]

\[
f[\rho + \delta \rho](x) = f[\rho] + \int \frac{\partial f}{\partial \rho(y)} \delta \rho(y) dy + \int \frac{\partial f}{\partial \rho'(y)} \delta \rho'(y) dy \]

\[
+ \int \frac{\partial f}{\partial \rho''(y)} \delta \rho''(y) dy + \ldots \quad (2a)
\]

\[
= f[\rho] + \int \frac{\partial f}{\partial \rho(y)} \delta \rho(y) dy - \int \left( \frac{\partial}{\partial y} \frac{\partial f}{\partial \rho(y)} \right) \delta \rho(y) dy \quad (3a)
\]

\[
+ \int \left( \frac{\partial^2}{\partial y^2} \frac{\partial f}{\partial \rho''(y)} \right) \delta \rho(y) dy + \ldots \quad (3b)
\]

So

\[
\frac{\delta f(x)}{\delta \rho(y)} = \frac{\partial f(x)}{\partial \rho(y)} - \frac{\partial}{\partial y} \frac{\partial f}{\partial \rho'(y)} + \frac{\partial^2}{\partial y^2} \frac{\partial f}{\partial \rho''(y)} + \ldots \quad (4)
\]
After much manipulation, Kohn and Sham arrive at

\[
\epsilon_{xc}[\rho] = \epsilon_{xc}^{(0)}(\rho(\vec{r})) + \epsilon_{xc}^{(2)}(\rho(\vec{r}))|\vec{\nabla}\rho(\vec{r})|^2 + \epsilon_{xc}^{(4)}(\rho(\vec{r}))\nabla^2\rho(\vec{r})\nabla^2\rho(\vec{r}) + \epsilon_{xc}^{(4b)}(\rho(\vec{r}))\nabla^2\rho(\vec{r})|\vec{\nabla}\rho(\vec{r})|^2 + \epsilon_{xc}^{(4c)}(\rho(\vec{r}))|\vec{\nabla}\rho(\vec{r})|^4
\]

+ HOT*

Many erratum have been published for the xc-potential of gradient expansions because the algebra is really not so trivial ...

* Higher-Order Terms
\[ \int \rho(\vec{r}) \, d\vec{r} = N \Rightarrow \]
\[ \rho \sim \frac{1}{L^3} \]
\[ \vec{\nabla} \rho \sim \frac{1}{L^4} \]
\[ \nabla^2 \rho \sim \frac{1}{L^5} \]

For proper convergence, we need
\[ \left| \frac{\vec{\nabla} \rho}{\rho} \right| , \frac{\nabla^2 \rho}{|\vec{\nabla} \rho|} << \left( \frac{3 \pi \rho}{k_F} \right)^{1/3} \]

all of which scale as $1/L$. 
**Xαβ Functional***

\[
\epsilon_x = -\frac{9}{8} \alpha \left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(\vec{r}) - \beta \left(\frac{|\nabla \rho(\vec{r})|}{\rho^{4/3}(\vec{r})}\right)^2 \rho^{1/3}(\vec{r})
\]

\[
\alpha = \frac{2}{3} \quad \text{ab initio}
\]

\[
\beta = 0.0055 \quad \text{Fit to Xe}
\]

Sketch of the wave vector analysis of Langreth and Perdew for the jellium edge.

Use linear response theory to derive the gradient correction.

\[ E_{xc} = \frac{1}{(2\pi)^3} \int E_{xc}(\vec{k}) d\vec{k} = \frac{1}{2\pi^2} \int E_{xc}(k) k^2 dk \]  

\[ E^{(2)}_{xc}(\vec{k}) = \frac{1}{(2\pi)^3} \int \delta \rho(\vec{q}) K_{xc}(\vec{k},\vec{q}) \delta \rho(-\vec{q}) d\vec{q} \]

The small k limit is known for the jellium edge.
Theory of nonuniform electronic systems. I. Analysis of the gradient approximation and a generalization that works

David C. Langreth
Rutgers University, New Brunswick, New Jersey 08903

John P. Perdew
Tulane University, New Orleans, Louisiana 70118
(Received 6 November 1979)

FIG. 7. Wave-vector decomposition of the gradient component of the surface energy $\delta_{\sigma} \gamma$ for the "Fermi-function" density profile. The bulk density corresponds to $r_s = 2.07$. The broken line is the exact asymptote.
\begin{equation}
E_{xc}^{(2)}(\vec{k}) = \int \left( z_x(\vec{k}, k_F(r)) + z_c(\vec{k}, k_F(\vec{r})) \theta(k - k_c) \right) |\nabla k_F(\vec{r})|^2 d\vec{r} \tag{1}
\end{equation}

cutoff

\begin{equation}
k_c = \frac{\nabla \rho}{6 \rho} \tag{2}
\end{equation}

Back transforming gives finally

\begin{equation}
E_{xc}^{GGA} = \int \rho^{4/3}(\vec{r}) \left( 2 e^{-\beta x(\vec{r}) \rho^{1/6}(\vec{r})} - \frac{7}{9} \right) x^2(\vec{r}) d\vec{r} \tag{3}
\end{equation}

\begin{equation}
x = \frac{\nabla \rho}{\rho^{4/3}} \tag{4}
\end{equation}
BECKE'S INTERPOLATION*

\[ E_x = \int \epsilon_x[\rho](\vec{r}) \rho(\vec{r}) d\vec{r} \]  

(1)

\[ \epsilon_x(\vec{r}) = \frac{1}{2} \int \frac{\rho_x(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \]

(2a)

\[ r \to \infty \quad - \frac{1}{2r} \]  

(2b)

What happens in \( X_\alpha \beta \)?

\[ \rho(\vec{r}) \sim c e^{-\zeta r} \]  

(3)

LDA part

\[ \rho^{4/3}(\vec{r}) \sim c^{4/3} e^{-(4/3)\zeta r} \]  

(4a)

Too Fast!

\[ \to 0 \]  

(4b)

Gradient correction

\[ \chi = \frac{1}{\rho^{4/3}} \left( \frac{\vec{\nabla} \rho}{\rho^{4/3}} \right) \zeta \rho^{-1/3} \]  

(5)

\[ \rho^{4/3} \chi^2 \sim \zeta \rho^{2/3} \sim \zeta c^{2/3} e^{-(2/3)\zeta r} \]

(6a)

Too Fast!

\[ \to 0 \]  

(6b)


https://sites.google.com/site/markcasida/dft
**BECKE'S 1988 EXCHANGE FUNCTIONAL**

\[ E_x = \sum_{\sigma} \int \rho_{\sigma}^{4/3}(\vec{r}) \left[ -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{3/2} - \beta \frac{x_{\sigma}^2}{1 + 6 \beta x_{\sigma} \sinh^{-1}(x_{\sigma})} \right] \]  

(1)

\[ \begin{align*}
X & \propto \beta ; x_{\sigma} \ll 1 \\
& - \frac{1}{2r} ; x_{\sigma} \gg 1
\end{align*} \]  

(2a, 2b)

\[ \beta = 0.0042 \]  

(3) determined by fitting

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<th>Exact</th>
<th>LDA(^a)</th>
<th>PW(^b)</th>
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\(^a\) LDA: Eq. (1).

\(^b\) Present work: Eq. (8) with $\beta = 0.0042$ a.u.


https://sites.google.com/site/markcasida/dft
DIFFERENT APPROACHES TO MAKING DFAs

*ab initio*
Try to determine all the parameters from first principles arguments. John Perdew is champion at this!

*ab initio derived*
Start with parameters derived from first principles arguments and further adjust them to fit experiment. Gustavo Scuseria has done some of this.

Physically motivated
Make reasonable arguments about the form of the functional based upon the xc-hole and then obtain any needed parameters by fitting. Many people (e.g., Axel Becke) have done this in their functionals.

Frankly semi-empirical
Write down the most general GGA possible and fit, fit, fit … Nicholas Handy did some perfectly splendid work along these lines!
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ADIABATIC CONNECTION*

\[ E_{xc}[\rho] = \frac{1}{2} \int \int \frac{\rho(1) \rho_{xc}(1,2)}{r_{12}} \, d1 \, d2 \]  \hspace{1cm} (1)

The exchange-correlation hole,

\[ \rho_{xc}(1,2) = \frac{\int_0^1 \langle \Psi_{\lambda}[\rho]|\tilde{\rho}(1)\tilde{\rho}(2)|\Psi_{\lambda}[\rho]\rangle \, d\lambda}{\rho(1)} - \delta(1-2) \]  \hspace{1cm} (2)

\[ \tilde{\rho}(1) = \hat{\rho}(1) - \rho(1) \]  \hspace{1cm} (3)

is closely related to the 2-electron reduced density matrix.

Neglecting the \(\lambda\)-dependence of \(\Psi\),

\[ \rho_{xc}(1,2) = \frac{\Gamma(1,2;1,2)}{\rho(1)} - \rho(2) \xrightarrow{\text{HF}} - \frac{\gamma(1,2)\gamma(2,1)}{\rho(1)} \]  \hspace{1cm} (4)

BECKE'S HYBRID FUNCTIONAL

This suggests

$$E_{xc} = f E_x^{HF} + (1-f) E_x^{GGA} \quad ; \quad 0 \leq f \leq 1$$ \tag{1}

(Though Becke was actually thinking ...)

$$E_{xc} = f E_x^{OEP} + (1-f) E_x^{GGA} \quad \text{(2)}$$

There is a theoretical rationalization that \( f \approx 0.25 \) \quad * \tag{3}

B3PW91 functional**

$$E_{xc} = E_{xc}^{LSDA} + a_0 \left( E_x^{exact} - E_x^{LSDA} \right) + a_x \Delta E_x^{BP86} + a_c \Delta E_c^{PW91} \quad \text{(4)}$$


\[ E_{xc} = E_{xc}^{\text{LSDA}} + a_0 \left( E_x^{\text{exact}} - E_x^{\text{LSDA}} \right) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{PW91} \]


Nearly \textit{ab initio} accuracy!

<table>
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<th>TABLE VI. Maximum absolute deviations.</th>
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<tr>
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<table>
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<tr>
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<th>G2\textsuperscript{a}</th>
<th>Eq. (2)</th>
<th>GC\textsuperscript{b}</th>
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<tr>
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<td>Proton affinities (kcal/mol)</td>
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<td>Total energies (mhartree)</td>
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</tbody>
</table>

\textsuperscript{a}G2: Gaussian-2 theory (Refs. 13 and 14).  
\textsuperscript{b}GC: Gradient-corrected DFT of Ref. 5.
KS RIP ... LONG LIVE GENERALIZED KS (GKS)


Born as Thomas-Fermi theory

Died when Axel Becke introduced hybrid functionals
Hartree-Fock
Occupied orbitals see N-1 electrons. Unoccupied orbitals see N electrons. Orbital energies may be interpreted as minus ionization potentials and electron affinities (or as band energies if you like) --- i.e., Koopmans' theorem.

Generalized Kohn-Sham
Orbital energies are somewhere between HF and KS unless an OEP procedure is applied.

Kohn-Sham
Occupied and unoccupied orbitals see the same potential --- so the same number of electrons. In exact KS theory HOMO gives IP and other occupied orbital energies give approximate other ionization potentials. Unoccupied orbital energies approximate local excitation energies, not electron affinities. Hence there is a band gap problem!
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“Jacob's ladder”
William Blake
water color
1799-1800
Jacob's ladder

\[ \tau(\mathbf{r}) = \sum_i n_i |\nabla \psi_i|^2 \text{ mGGA*} \]

\[ x(\mathbf{r}) = \frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})^{4/3}} \text{ GGA} \]

\( \rho(\mathbf{r}) \text{ LDA} \)

* or include \( \nabla^2 \rho \)

MBPT \( \text{ab initio DFT} \)

\( \hat{K}_x^{HF} \) \( \text{hybrid/OEP} \)

HARTREE WORLD

Molecular size →

THEORETICAL CHEMISTRY HEAVEN

No computer land

https://sites.google.com/site/markcasida/dft
Range-Separated Hybrids (RSH)*

Modern GKS is
- less and less B3LYP
- more and more RSH

\[
\frac{1}{r_{12}} = \frac{erfc(\gamma r_{12})}{r_{12}} + \frac{erf(\gamma r_{12})}{r_{12}}
\]

\text{SHORT RANGE} \quad \text{LONG RANGE}

Molecules:
- SR <-> DFT
- LR <-> WF (e.g. HF)

Solids:
- SR <-> WF
- LR <-> DFT

Idea originally due to Andreas Savin (Université Pierre et Marie Curie, Paris, France.)

Applications in TDDFT:

* Because Nature is often, \textit{but not always}, nearsighted.

https://sites.google.com/site/markcasida/dft
Fluctuation-Dissipation Theorem

Quantity closely related to xc-hole of DFT

\[ i \chi(1,2) = \langle \Psi_0 | [\hat{\rho}(1), \hat{\rho}(2)] | \Psi_0 \rangle = i \Pi(1,1^+;2,2^+) \]

\[ \hat{\rho}(1) = \hat{\rho}(1) - \langle \Psi_0 | \hat{\rho}(1) | \Psi_0 \rangle \]

Electron repulsion energy

\[ \langle \Psi_0 | v_{e,e} | \Psi_0 \rangle = \langle \Phi | v_{e,e} | \Phi \rangle + \frac{1}{2} \int \frac{1}{r_{12}} \left( i \chi(1,2) - i \chi_0(1,2) \right) \]

Correlation energy

\[ \Delta E_{corr} = \frac{1}{2} \int_0^1 d \lambda \int \frac{1}{r_{12}} \left( i \chi_{\lambda}(1,2) - i \chi_0(1,2) \right) \]

5th rung functionals from TDDFT

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Sorry, no time!
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CONCLUSIONS

- DFT and DFAs are different
- Both formally exact theory and approximations are important
- There is no universal DFA (even if DFT is formally exact)
- You have to prove that the DFA you chose works for your type of application.

- I have a page (a bit old though) to help you with functionals
- Marcel SWART, F.M. Bickelhaupt, and M. Duran maintain a DFA popularity pole: [http://www.marcelswart.eu/](http://www.marcelswart.eu/)
  - In 2012, PBE came in first
  - In 2011, PBE0 came in first
  - In 2010, PBE0 came in first

*Does this really mean anything!?!*