Exchange and Correlation

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Rhône-Alpes Associated Node

DFT and Beyond
Trieste, Italy
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50 min.

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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

I. Chemistry vs Physics

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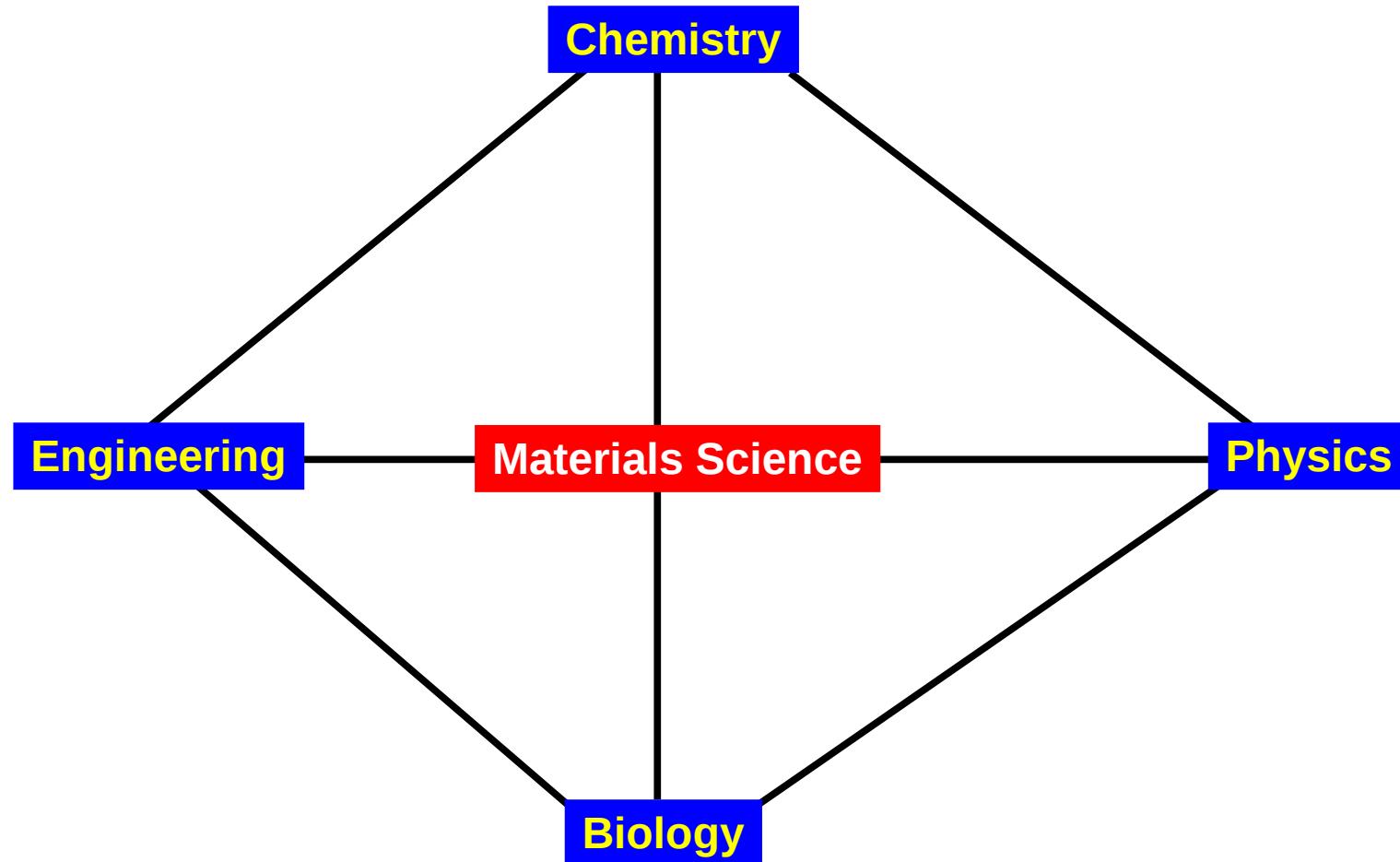
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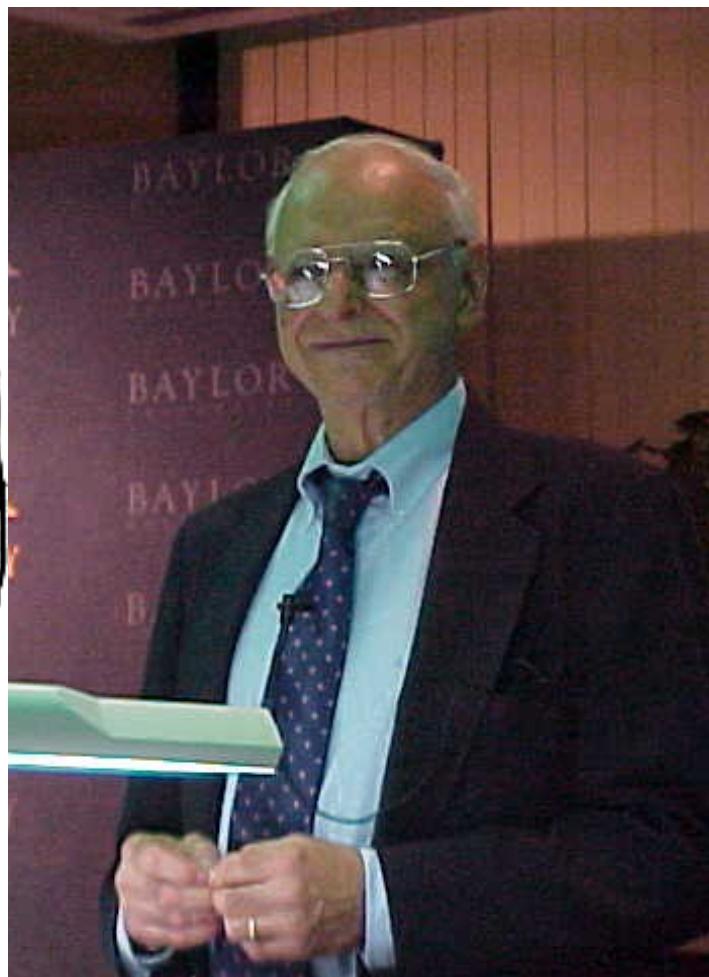
"I'm on the verge of a major breakthrough, but I'm also at that point where chemistry leaves off and physics begins, so I'll have to drop the whole thing."

Of course not!

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*"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
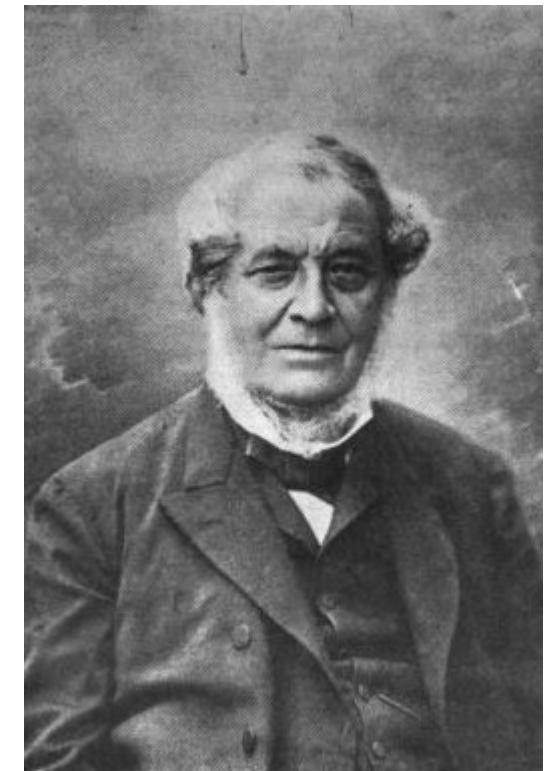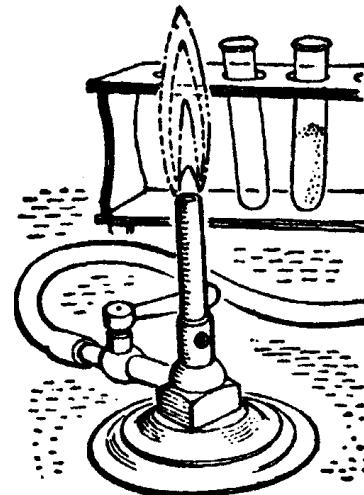
* "A chemist who is not at the same time a physicist is nothing at all."

CHEMISTRY VERSUS PHYSICS

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, ...

Increasing reliability and computational cost.

COMIC BOOK INTERPRETATION

Les deux solitudes/The two solitudes

Captain Canada
(English speaker)

Fleur de Lys
(French 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 ← We don't always speak the same language, but more and more we work together. → Quantum Chemistry

VARIATIONAL PRINCIPLE*

Seek solutions to

$$\hat{H}\,\Psi_I = E_I\,\Psi_I\,;\, E_0 \le E_1 \le E_2 \le \cdots \qquad (1)$$

Then

$$E_0 \le W[\Psi_{trial}] = \frac{\langle \Psi_{trial}|\hat{H}|\Psi_{trial}\rangle}{\langle \Psi_{trial}|\Psi_{trial}\rangle} \qquad (2)$$

For any trial wavefunction Ψ_{trial}, satisfying the same boundary conditions as the Ψ_I.

$W[\Psi]$ is a *functional* --- that is, a function of a function.

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* Quantum Chemistry 101?

Multivariable calculus

$$\vec{f} = \begin{pmatrix} f_1 \\ f_2 \\ \vdots \end{pmatrix} \quad \text{(1a)}$$

$$d F(\vec{f}) = \sum_i \frac{\partial F}{\partial f_i} df_i \quad \text{(2a)}$$
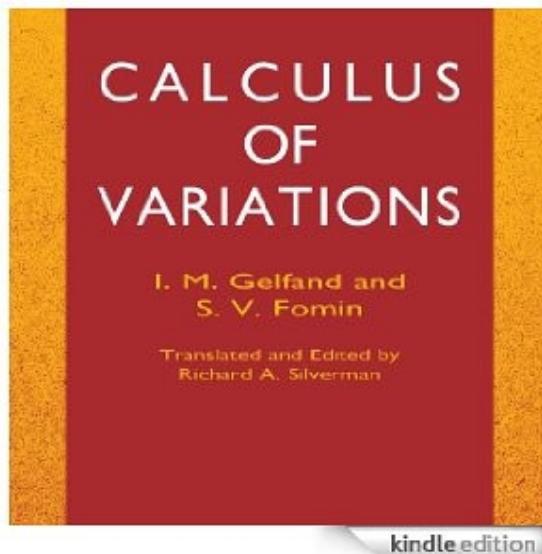
Variational calculus

$$f = f(x) \quad \text{(1b)}$$

$$\delta F[f] = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx \quad \text{2b)}$$

CALCULUS OF VARIATIONS

I. M. Gelfand and S. V. Fomin

Translated and Edited by Richard A. Silverman

kindle edition

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

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

Minimize

$$W[\Psi,\Psi^*]=\int \Psi^*(\tau)\hat{H}\Psi(\tau)d\tau \qquad (1)$$

subject to the contraint

$$\int \Psi^*(\tau)\Psi(\tau)d\tau=1 \qquad (2)$$

Use the method of Lagrange multipliers !

$$L[\Psi,\Psi^*]=\int \Psi^*(\tau)\hat{H}\Psi(\tau)d\tau-E\int \Psi^*(\tau)\Psi(\tau)d\tau \qquad (3a)$$

$$=\int \Psi^*(\tau)\left[\hat{H}\Psi(\tau)-E\Psi(\tau)\right]d\tau \qquad (3b)$$

$$0=\delta L[\Psi,\Psi^*]=L[\Psi,\Psi^*+\delta\Psi^*]-L[\Psi,\Psi^*] \qquad (4a)$$

$$=\int \delta\Psi^*(\tau)\left[\hat{H}\Psi(\tau)-E\Psi(\tau)\right]d\tau \qquad (4b)$$

True $\quad \forall \Psi^* \Rightarrow \quad \hat{H}\Psi(\tau)-E\Psi(\tau)=0 \qquad (5)$

i.e.,

$$\hat{H}\Psi(\tau)=E\Psi(\tau) \qquad (6)$$

$$L[\Psi,\Psi^*]=\int \Psi^*(\tau)\hat{H}\Psi(\tau)d\tau-E\int \Psi^*(\tau)\Psi(\tau)d\tau \qquad \text{(1a)}$$

$$=\int \left[\left(\hat{H}\Psi(\tau)\right)^*-E\Psi^*(\tau)\right]\Psi(\tau)d\tau \qquad \text{(1b)}$$

$$0=\delta L[\Psi,\Psi^*]=L[\Psi+\delta\Psi,\Psi^*]-L[\Psi,\Psi^*] \qquad \text{(2a)}$$

$$=\int \left[\left(\hat{H}\Psi^*(\tau)\right)-E\Psi^*(\tau)\right]\delta\Psi(\tau)d\tau \qquad \text{(2b)}$$

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

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

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

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

So the Lagrange multiplier is real (which is good since it is the energy!)

HARTREE-FOCK TOTAL (ELECTRONIC) ENERGY

Minimizing

$$E_0 \leq W[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$ (1)

$$i = (\vec{r}_i, \sigma_i)$$ (3)

with

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

subject to the constraint

$$\langle \psi_i | \psi_j \rangle = \delta_{i,j}$$ (4)

gives

$$E = E_{core} + E_H + E_x$$ (5)

$$E_{core} = \sum_i n_i \langle \psi_i | \hat{t} + v_{ext} | \psi_i \rangle = \sum_i n_i \langle \psi_i | \hat{h}_{core} | \psi_i \rangle$$ (6)

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

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$$E = E_{core} + E_H + E_x \tag{1}$$

Hartree (Coulomb) energy

occupation numbers

$$E_H = \frac{1}{2} \int \int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{1}{2} \sum_{i,j} n_i n_j (ii|f_H|jj) \tag{2}$$

Charge density

$$\rho(1) = \sum_i n_i |\psi_i(1)|^2 \tag{3}$$

Mulliken charge cloud notation

$$(pq|f|rs) = \int \int \psi_p^*(1)\psi_q(1)f(1,2)\psi_r^*(2)\psi_s(2)\,d1\,d2 \tag{4}$$

Exchange energy

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

One-electron reduced density matrix

$$\gamma(1,2) = \sum_i \psi_i(1) n_i \psi_i^*(2) \tag{6}$$

$$L = E_{core} + E_H + E_x - \sum_i n_i \epsilon_i \left(\langle \psi_i | \psi_i \rangle - 1 \right) \quad (1) \qquad 0 = \frac{\delta L}{\delta \psi_i^*(1)} \quad (2)$$

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

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

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

$$\frac{\delta E_H[\rho]}{\delta \psi_i^*(1)} = \int \frac{\delta E_H}{\delta \rho(2)} \frac{\delta \rho(2)}{\delta \psi_i^*(1)} d2 = n_i \underbrace{\int \frac{\rho(2)}{r_{12}} d2}_{v_H[\rho](\vec{r}_1) \quad (6b)} \psi_i(1) \quad (6a) \qquad \cancel{v_H[\rho(\vec{r}_1)]}$$
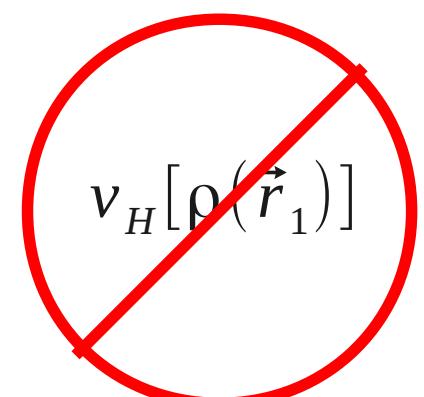
$$E_x[\gamma]=-\int\int\frac{\gamma(2,3)\gamma(3,2)}{r_{23}}d2\,d3 \quad \text{(1a)} \Rightarrow \quad \frac{\delta E_x[\gamma]}{\delta\gamma(2,3)}=-\frac{\gamma(3,2)}{r_{23}} \quad \text{(1b)}$$

$$\gamma(2,3)=\int\left(\sum_i\psi_i(2)n_i\psi_i^*(1)\right)\delta(1-3)d1 \quad \text{(2a)} \Rightarrow \frac{\delta\gamma(2,3)}{\delta\psi_i^*(1)}=n_i\psi_i(2)\delta(1-3) \quad \text{(2b)}$$

$$\frac{\delta E_x[\gamma]}{\delta\psi_i^*(1)}=\int\int\frac{\delta E_x}{\delta\gamma(2,3)}\frac{\delta\gamma(2,3)}{\delta\psi_i^*(1)}d2\,d3=-n_i\int\underbrace{\frac{\gamma(1,2)}{r_{12}}\psi_i(2)d2}_{-\hat{\Sigma}_x^\sigma[\gamma](\vec{r}_1,\vec{r}_2)\text{(3b)}} \quad \text{(3a)}$$

$$\frac{\delta\left(\sum_j n_j\langle\psi_j|\psi_j\rangle\right)}{\delta\psi_i^*(1)}=n_i\psi_i(1) \quad \text{(4)}$$

Putting it all together,

$$0 = \frac{\delta L}{\delta \psi_i^*(1)} = n_i \left(\hat{f} \psi_i(1) - \epsilon_i \psi_i(1) \right) \qquad (1)$$

or

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

where the Fock operator,

$$\hat{f}[\gamma] = h_{core} + v_H[\rho](\vec{r}) + \hat{\Sigma}_x[\gamma] \qquad (3)$$

… and the Kohn-Sham equations of DFT are very similar !

THE HOHENBERG-KOHN THEOREMS GIVE A RIGOROUS BASIS TO THOMAS-FERMI THEORY

L.H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927). E. Fermi, Rend. Accad. Naz. Linzei **6**, 602 (1927). E. Fermi, Z. Phys. **48**, 73 (1928).

Llewellyn Hilleth THOMAS

Electronic energy
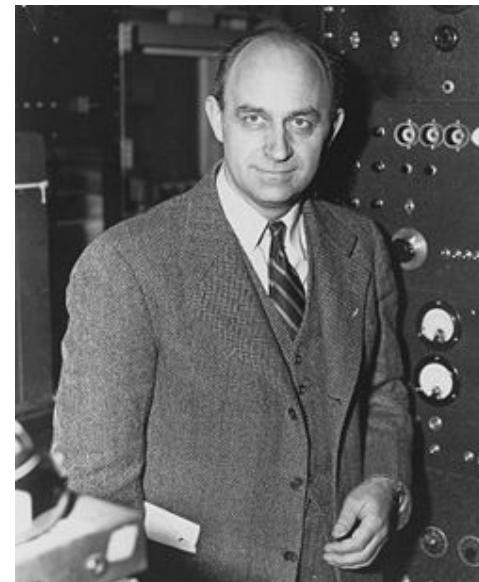
Enrico FERMI

$$E \approx T[\rho] + \int v_{ext}(1)\rho(1)d1 + E_x[\rho]$$

The system is the electrons. All else is external.

Can it be made exact ?

P. HOHENBERG AND W. KOHN, PHYS. REV. 136, B864 (1964). "INHOMOGENOUS ELECTRON GAS"

Walter KOHN

Pierre C. HOHENBERG

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.)

$$\rho(\vec{r}) \quad \xrightarrow{\text{1-1}} \quad v_{ext}(\vec{r}) + const. \qquad (1)$$

Comments

1) so the charge density determines just about everything
2) but how accurately ? (e.g. it can only determine the v_{ext} where ρ 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
$$V_{ext}^{(1)} \to \rho \leftarrow V_{ext}^{(2)} \quad (1)$$
with
$$V_{ext}^{(1)} - V_{ext}^{(2)} \neq const. \quad (2)$$

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

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

The variational principle then tells us that

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

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

Adding leads to the contradiction
$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)} \quad (7) \quad \blacksquare$$

EDGER BRIGHT WILSON ARGUMENT
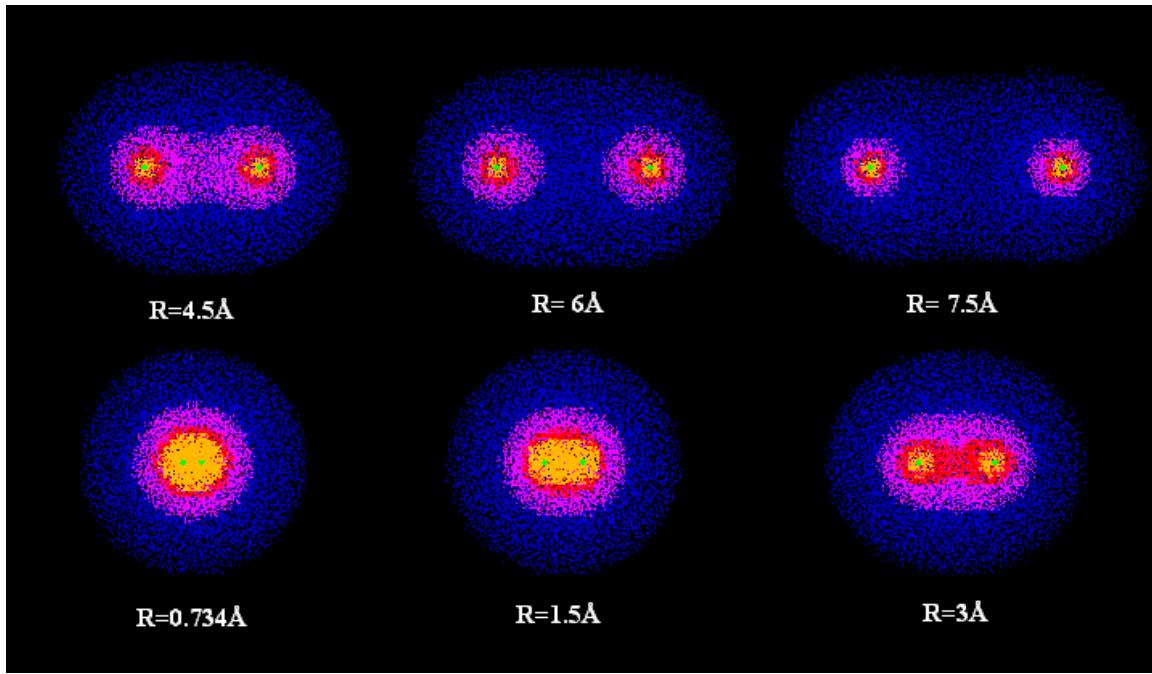
H$_2$ charge density*

- Integrating ρ gives N .
- Cusp positions locate the nuclei.
- Nuclear charge is given by the slope at the cusp.**

$$Z_A = -\frac{\lim_{r \to r_A} \frac{\partial}{\partial r} \int \rho(\vec{r}) d\Omega}{2 \lim_{r \to r_A} \int \rho(\vec{r}) d\Omega}$$

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

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

** E.R. Davidson, *Reduced Density Matrices* (Academic Press: New York, 1976), pp. 43-44.

This gives us a
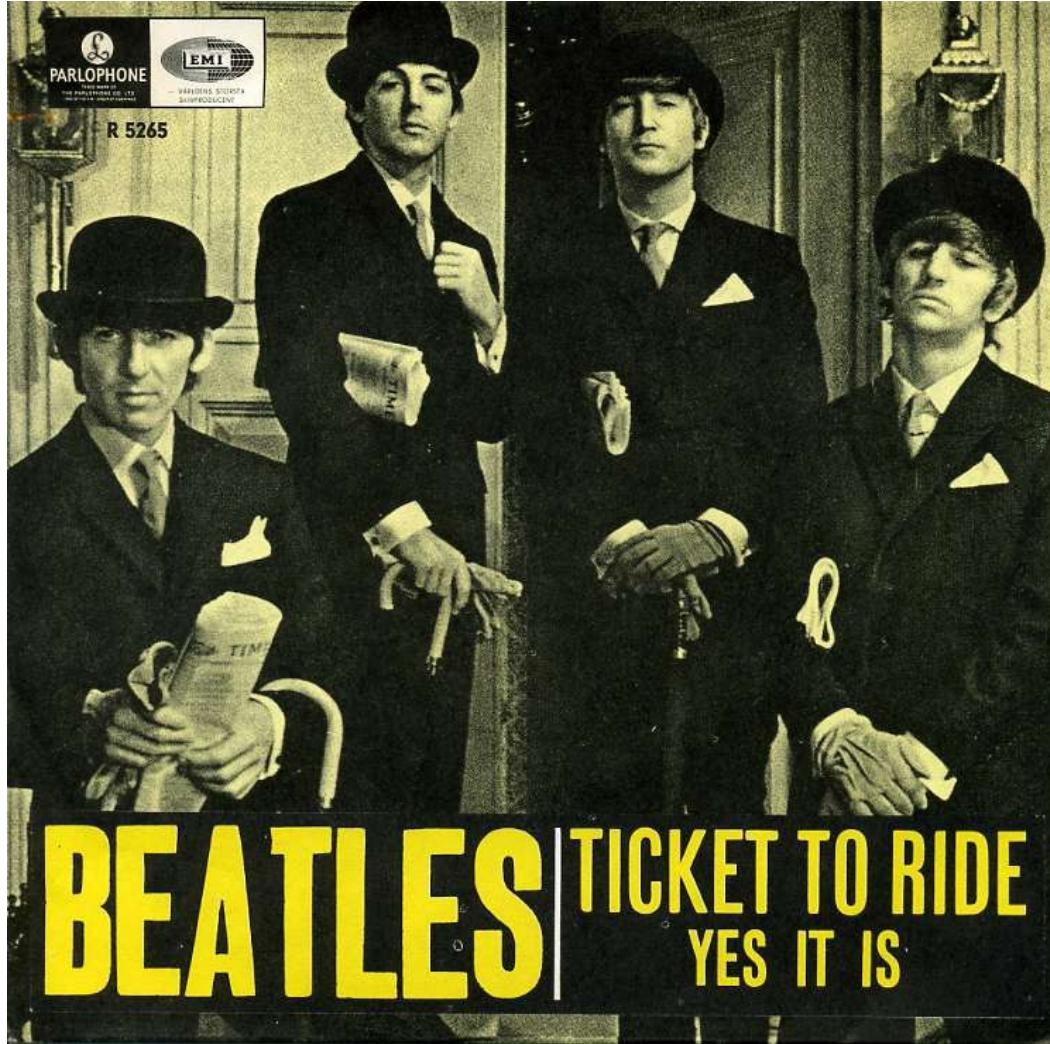
but we still need a way to find the charge density!

N-representability : Can we always find a Ψ that will give us any given (reasonable) ρ ?

The answer turns out to be yes.
J.E. Harriman, _Phys. Rev. A_ **24**, 680 (1981).
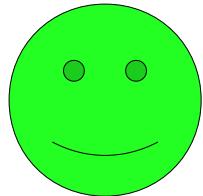
(equidensity orbitals)

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

Some external potentials are ensemble v-representable but not pure-state v-representable.
M. Levy, _Phys. Rev. A_ **26**, 1200 (1982)
E. Lieb, _Int. J. Quant. Chem._ **24**, 243 (1983).

Even for N=1 and 1D some densities fail to be v-representable in the strict sense.
H. Englisch and R. Englisch, _Physica_ **121A**, 253 (1983).
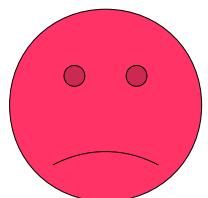
$$\rho(x) = \left(a + b|x|^{\alpha+1/2}\right)^2 \quad ; \quad a,b > 0 \quad ; \quad 0 \le \alpha \le 1/2$$

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

Walter KOHN

Pierre C. HOHENBERG

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

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

The functional F[ρ] is universal in the sense of being independent of v_{ext}.

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

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

The functional F[ρ] is universal in the sense of being independent of v_{ext} .

Proof (Levy-Lieb*)

$$F[\rho] = min_\Psi^{\Psi \to \rho} \langle \Psi | \hat{T} + V_{ee} | \Psi \rangle \qquad (2) \qquad \blacksquare$$

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

* M. Levy, *Proc. Nat. Acad. Sci. USA* **76**, 6062 (1979).
 M. Levy, *Phys. Rev. A* **26**, 1200 (1982).
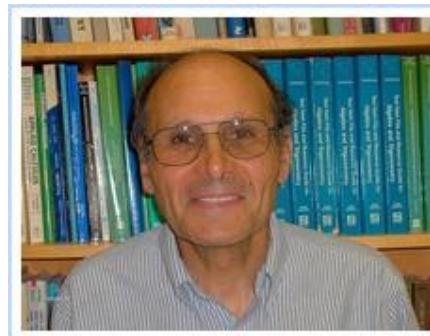
Mel LEVY
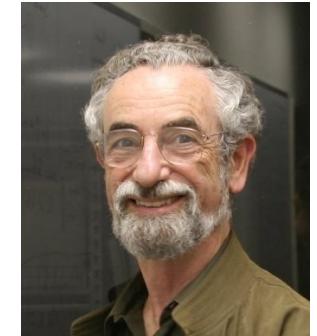
Elliott LIEB

COMPUTATIONALLY CONVENIENT EFFECTIVE APPROXIMATIONS, TYPICALLY OF THE FORM

$$F[\rho] = \int f[\rho](\vec{r})\rho(\vec{r})\,d\vec{r}$$

DFAs 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

Red bubble t-shirts http://www.redbubble.com/

My page web (not quite up to date) to help you become familiar with DFAs :

https://sites.google.com/site/markcasida/dft
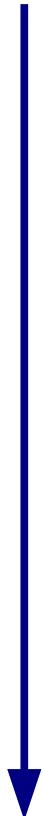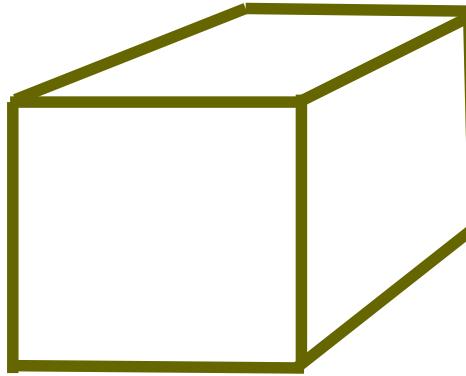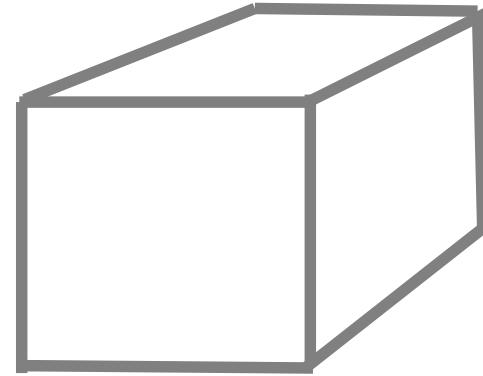
+   =   " jellium "

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

A positive background
with a uniform charge
$\square = +e\,n\,/\,V$

Now take the infinite volume limit while keeping the density constant.

Wigner-Seitz radius

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

Orbitals

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \qquad \text{(2)}$$

Quantization   Density of states

$$k_x = \frac{2\pi}{l} n_x \qquad \text{(3)} \qquad\qquad d\vec{n} = \frac{V}{8\pi^3} d\vec{k} \qquad \text{(4)}$$

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

So

$$k_F = \left(3\pi^2 \rho\right)^{1/3} \qquad (2)$$

Also

$$k_F r_s = \left(\frac{9\pi}{4}\right)^{1/3} \qquad (3)$$

$$t_{HEG} = \frac{T_{HEG}}{V} = \frac{2}{V} \int \int \psi_{\vec{k}}^*(\vec{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_{\vec{k}}(\vec{r}) \, d\vec{n} \, d\vec{r} \quad (1)$$

$$\nabla^2 \psi_{\vec{k}}(\vec{r}) = -k^2 \psi_{\vec{k}}(\vec{r}) \quad (3) \qquad\qquad \psi_{\vec{k}}^*(\vec{r}) \psi_{\vec{k}}(\vec{r}) = \frac{1}{V} \quad (4)$$

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

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

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

$$t_{HEG} = \frac{3}{10} \left(3\pi^2 \right)^{2/3} \rho^{5/3} \quad (8)$$

$$E_x[\gamma] = -\int \int \frac{\gamma(2,3)\,\gamma(3,2)}{r_{23}}\,d2\,d3 \qquad (1)$$

Dirac result*

$$e_x^{HEG} = \frac{E_x^{HEG}}{V} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3} \qquad (2)$$

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* See Appendix A of J.C. Slater, *Quantum Theory of Atomic Structure, Vol. II* (McGraw-Hill: New York, 1960).

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

$$f_{HEG}(\rho(\vec{r}_1))$$

$$f_{HEG}(\rho(\vec{r}_2))$$

$$f_{HEG}(\rho(\vec{r}_3))$$

O

H   H
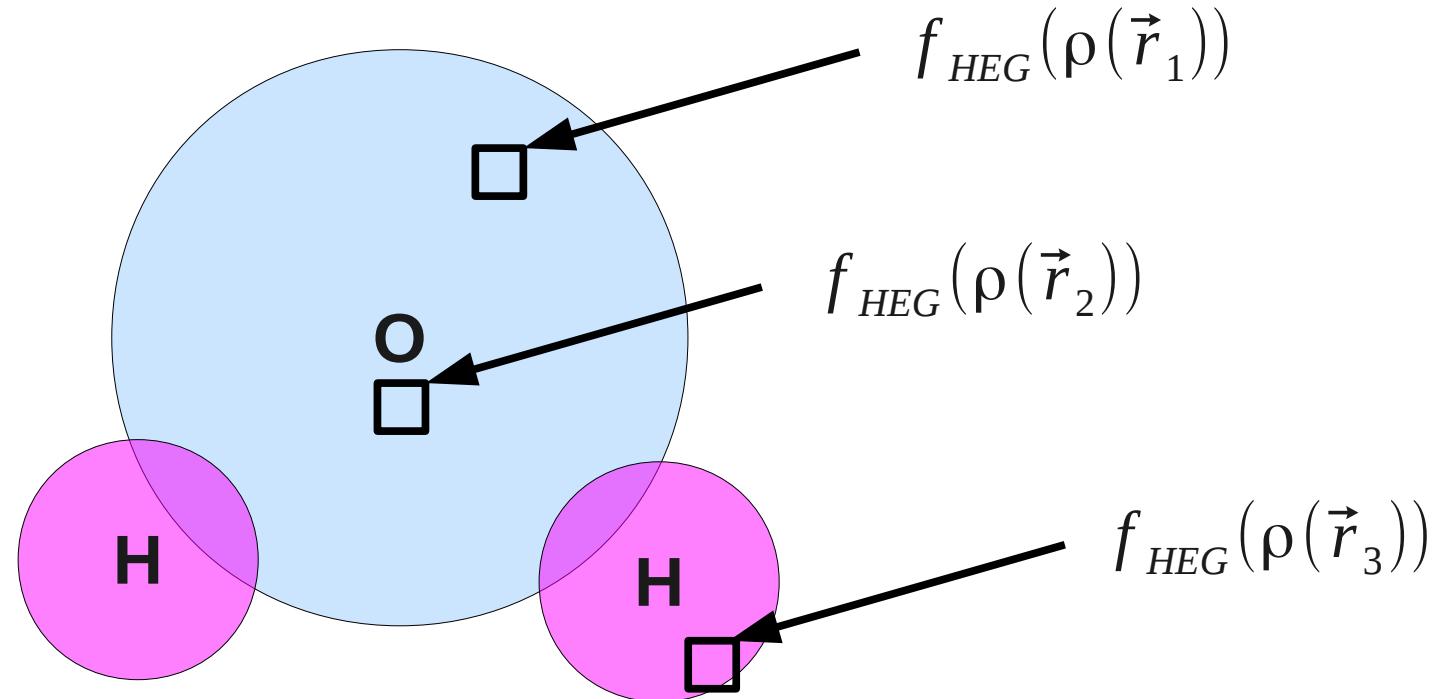
$$F[\rho]\approx F^{LDA}=\int \underbrace{f_{HEG}(\rho(\vec{r}))\rho(\vec{r})}_{\Delta F/\Delta V}d\vec{r}\approx\sum_i \underbrace{f_{HEG}(\rho(\vec{r}_i))}_{\Delta F/\Delta N}\underbrace{\rho(\vec{r}_i)\Delta v(\vec{r}_i)}_{\Delta N} \qquad (2)$$

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

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

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

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.

---

* E. Teller, "On the stability of molecules in the Thomas-Fermi theory," *Rev. Mod. Phys.* **34**, 627 (1962).

$$e_x = \frac{E_x}{V} = \rho\, \epsilon_x \quad \text{(1a)}$$

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

$$e_x = \rho_\alpha\, \epsilon_x^\alpha + \rho_\beta\, \epsilon_x^\beta \quad \text{(2a)}$$

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

Alternatively,

$$\epsilon_x = \epsilon_x^P + f(\xi)\left(\epsilon_x^F - \epsilon_x^P\right) \quad \text{(3)}$$

Paramagnetic part

Ferromagnetic part

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

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

Spin polarization

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

$$f(\xi) = \frac{(1+\xi)^{4/3} + (1-\xi)^{4/3} - 2}{2\left(2^{1/3} - 1\right)} \quad \text{(5b)}$$

ρ

$\xi = 0$

Paramagnetic solution

Ferromagnetic solution $\xi = 1$

Wigner crystal (bcc)

r_s
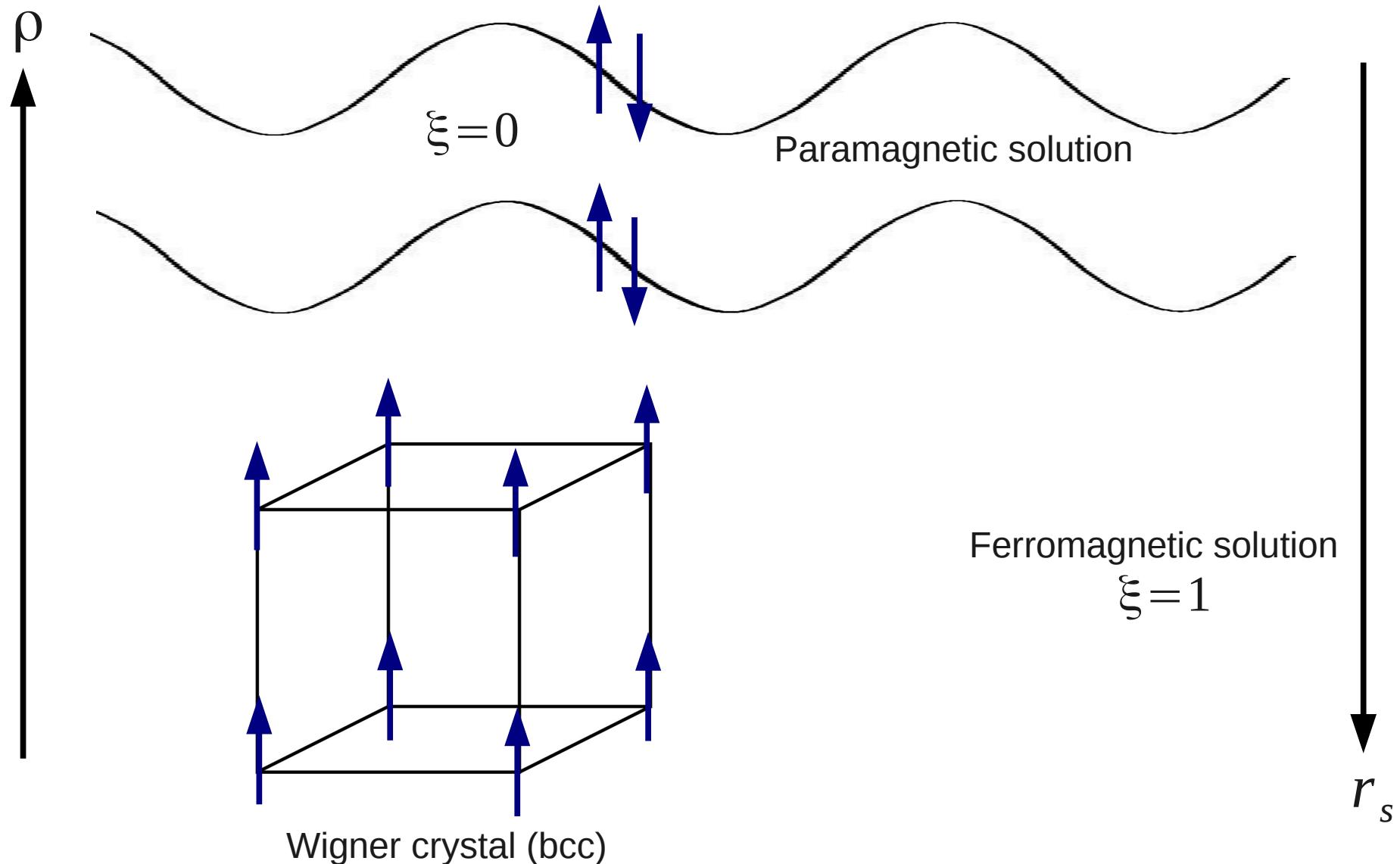
Per Olaf LÖWDIN definition $E_c = E - E_{HF} < 0$ (1)

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

$$\epsilon_c \approx -\frac{0.44}{7.8 + r_s}$$ (2)   (Wigner)

E.P. Wigner, *Phys. Rev.* **46**, 1002 (1934).
E.P. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938).
D. Pines, *Solid State Physics* **1**, 367 (1955).
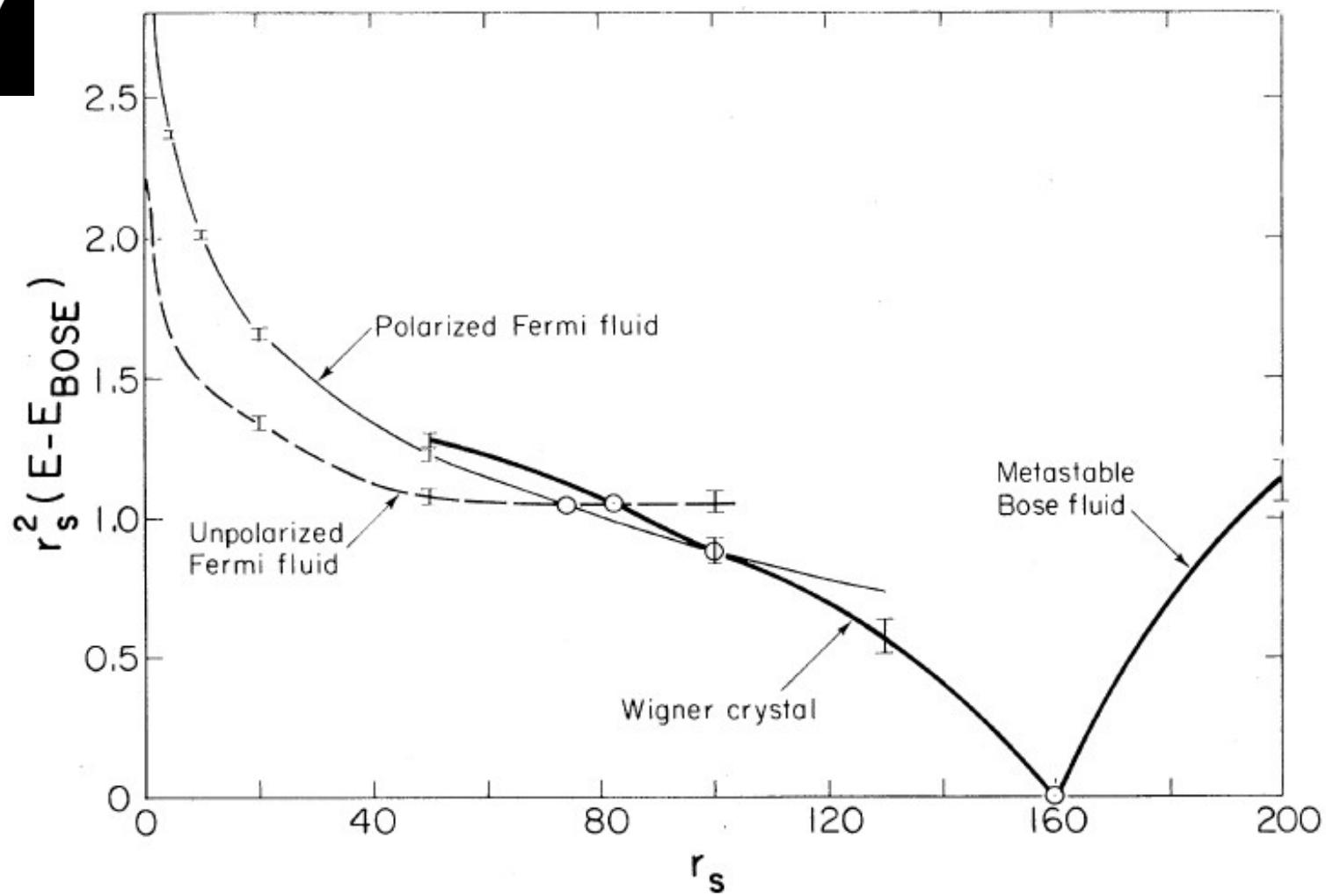
D. Ceperley, *Phys. Rev. B* **18**, 3126 (1978).
D.M. Ceperley and B.J. *Alder, Phys. Rev. Lett.* **45**, 566 (1980). <--- above image
D. Ceperley and B. Alder, *Science* **231**, 555 (1986).

S.H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
The VWN parameterization in most quantum chemistry programs, but VWN5 in **Gaussian**.

J.P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
PZ parameterization often preferred in solid-state physics programs.

J.P. Perdew and Y. Yang, *Phys. Rev. B* **45**, 13244 (1992).

All give pretty similar results!

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

$$E_{HF} = E_{core} + E_H + \frac{1}{2} \sum_i n_i \langle \psi_i | \hat{\Sigma}_x | \psi_i \rangle \qquad \text{(1a)}$$

$$= E_{core} + E_H + \frac{1}{2} \sum_i n_i \langle \psi_i | v_x^S | \psi_i \rangle \qquad \text{(1b)}$$

John SLATER

J. Slater, *Phys. Rev.* **81**, 385 (1951).

where the Slater potential,

$$v_x^S(1) = \frac{\sum_i n_i \psi_i^*(1) \hat{\Sigma}_x \psi_i(1)}{\sum_j n_j \psi_j^*(1) \psi_j(1)} \qquad \text{(2)}$$

Comparison with Dirac's local exchange gives

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

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

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

where

$$\rho(\vec{r}) = \sum_{i\sigma} n_{i\sigma} |\psi_{i\sigma}(\vec{r})|^2 \quad (2)$$

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

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

where the exchange-correlation potential is

$$v_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})} \quad (4)$$

Fictitous system of noninteracting electrons ("s" for single particle)

$$\sigma_u$$

$$\sigma_g$$

(1)
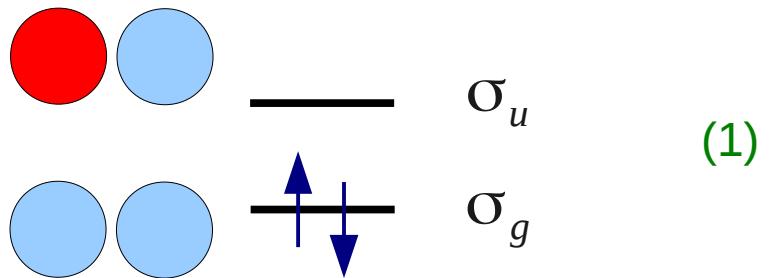
- *Aufbau* filling

Kohn-Sham determinant

$$\Phi_s = |\sigma_g , \bar{\sigma}_g| \qquad (2)$$

Density

$$\rho(\vec{r}) = 2|\sigma_g(\vec{r})|^2 \qquad (3)$$
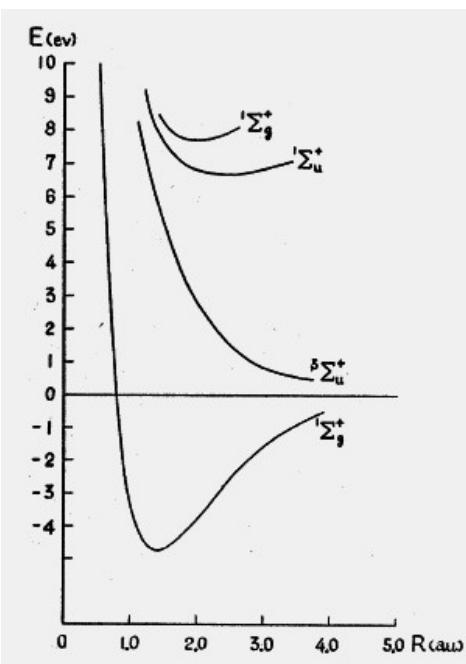
Real system of interacting electrons

(4)

Interacting wavefunction

$$\Psi = C_0|\sigma_g , \bar{\sigma}_g| + C_5|\sigma_u , \bar{\sigma}_u| \qquad (5)$$

Density

$$\rho(\vec{r}) = 2\left(|C_0|^2|\sigma_g(\vec{r})|^2 + |C_5|^2|\sigma_u(\vec{r})|^2 \right) \qquad (6)$$

The density is the same on the LHS and on the RHS !

For a 2-electron system,

$$\psi(\vec{r}) = \sqrt{\rho(\vec{r})} \qquad (1)$$

$$E = T_s + \int v_{ext}\,\rho + E_H + E_{xc} \qquad (2)$$

$$E_{xc} = \left(E_{ee} - E_H\right) + \underbrace{\left(T - T_s\right)}_{\Delta T} \qquad (3)$$

Atom	ΔT (eV)
H⁻	0.8
He	1.0
Li⁺	1.1
Be²⁺	1.1
Li	1.7
Be	2.0

*

* C.-O. Almbladh and A.C. Pedroza, *Phys. Rev. A* **29**, 2322 (1984).

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

<u>Answer</u> (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.**

---

* M. Levy, *Phys. Rev*. A **26**, 2100 (1982).
** See M.E. Casida and M. Huix-Rotllant, *Annu. Rev. Phys. Chem.* **63**, 287 (2012).

Walter KOHN

Lu Jeu SHAM

John SLATER

$$E_x^{LDA} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(\vec{r})\,d\vec{r} \qquad (1)$$

$$v_x^{LDA}(\vec{r}) = -\alpha\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3}(\vec{r}) \qquad (2)$$

with $\qquad \alpha = \dfrac{2}{3} \qquad (3)$

Originally Slater had $\quad \alpha = 1 \qquad (4)$

In the Xα method, α is a semi-empirical parameter fit to atomic Hartree-Fock energies. Typically, $\quad 0.70 \leq \alpha \leq 1$

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

LSD*

No, not *lysergic acid diethylamide*
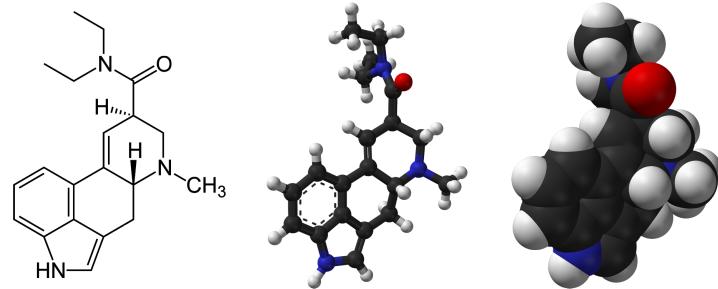
but rather the local spin density (LSD) approximation,

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

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

---

* U. van Barth and L. Hedin, *J. Phys. C.* **5**, 1629 (1972)

"**We do not expect an accurate description of chemical bonding**."

W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (1965)

Walter KOHN

Lu Jeu SHAM

1 eV = 23.06 kcal/mol   "Chemical accuracy" is 1 kcal/mol

TABLE I. LDA spectroscopic constants.

	r_e (bohrs)		D_e (eV)		ω_e (cm^{-1})	
	Expt.	LDA	Expt.	LDA	Expt.	LDA
H_2	1.40	1.45	4.8	4.9	4400	4190
Li_2	5.05	5.12	1.1	1.0	350	330
B_2	3.00	3.03	3.0	3.9	1050	1030
C_2	2.35	2.35	6.3	7.3	1860	1880
N_2	2.07	2.07	9.9	11.6	2360	2380
O_2	2.28	2.27	5.2	7.6	1580	1620
F_2	2.68	2.61	1.7	3.4	890	1060
Na_2	5.82	5.67	0.8	0.9	160	160
Al_2	4.66	4.64	1.8	2.0	350	350
Si_2	4.24	4.29	3.1	4.0	510	490
P_2	3.58	3.57	5.1	6.2	780	780
S_2	3.57	3.57	4.4	5.9	730	720
Cl_2	3.76	3.74	2.5	3.6	560	570

* A. Becke, "Completely numerical calculations on diatomic molecules in the local density Approximation," *Phys. Rev. A* **33**, 2786 (1986).
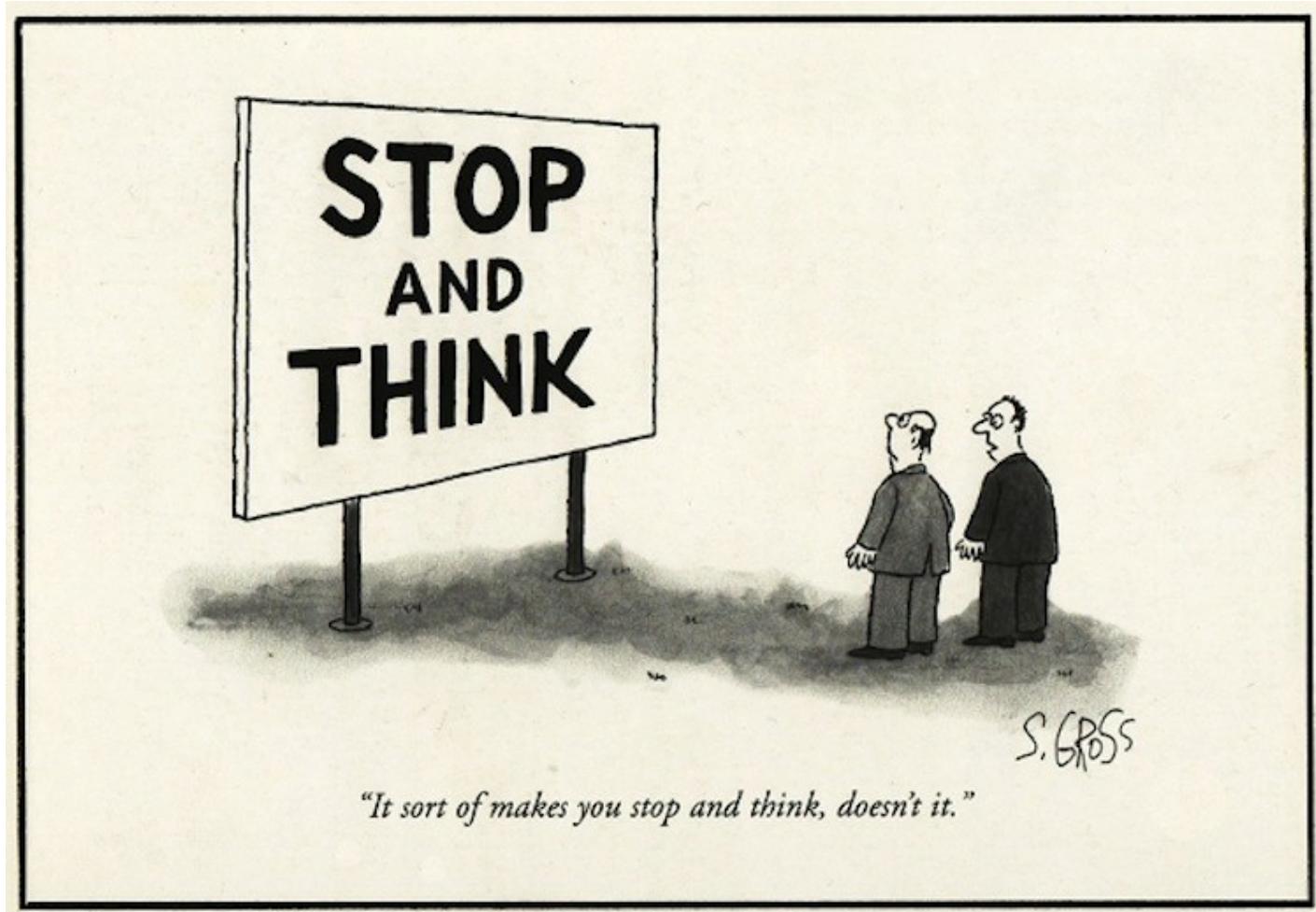
What is in common between electrons in a molecule and in the HEG !?
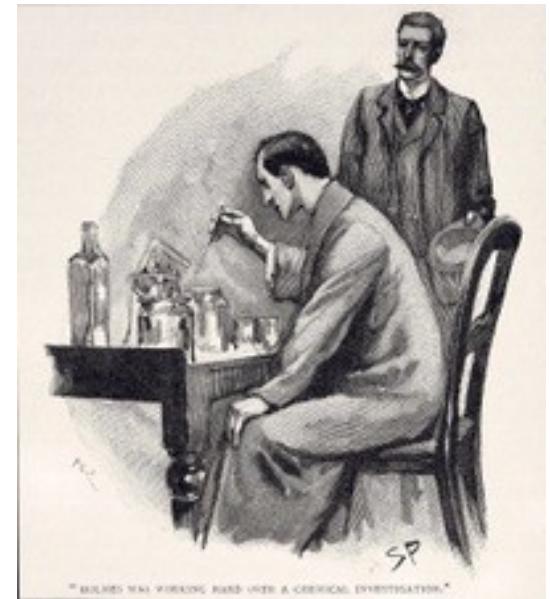
$$\hat{H} = \hat{H}_s + \lambda V_{ee} + W_\lambda[\rho]$$

Kohn-Sham
hamiltonian

Electron
repulsion

Local restoring
Potential to fix ρ

Exists as long as ρ
is v-representable
for all λ .

$\lambda = 0$ Fictitious system of noninteracting electrons

λ varies but ρ does not

$\lambda = 1$ Real system of interacting electrons

* J. Harris and R.O. Jones, *J. Phys. F* **4**, 1170 (1974).

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

The exchange-correlation hole,

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

$$\tilde{\rho}(1) = \hat{\rho}(1) - \rho(1) \qquad (3)$$

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

Neglecting the λ-dependence of Ψ,

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

* J. Harris and R.O. Jones, *J. Phys. F* **4**, 1170 (1974).

Only the spherical average is important,

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

$$\epsilon_{xc}(\vec{r})=\sqrt{\pi}\int_0^\infty \rho_{0,0}^{xc}(\vec{r},y)\,y\,dy \qquad (2)$$

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

$$\int \rho(\vec{r},\vec{r};)\,d\vec{r}\,'=\sqrt{4\pi}\int_0^\infty \rho_{0,0}^{xc}(\vec{r},y)\,y^2\,dy=-1 \qquad (3)$$

$$\frac{y\,\rho_{0,0}^{xc}(\vec{r}, y)}{\sqrt{4\pi}} \quad *$$
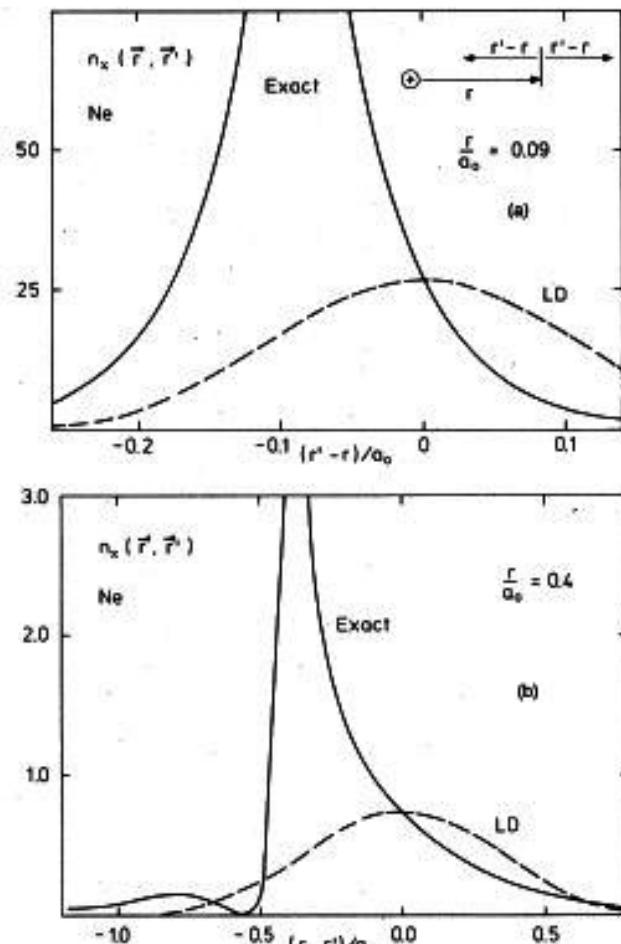
FIG. 5. Exchange hole $n_x(\vec{r}, \vec{r}')$ for a neon atom. The full curves show exact results and the dashed curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of r.
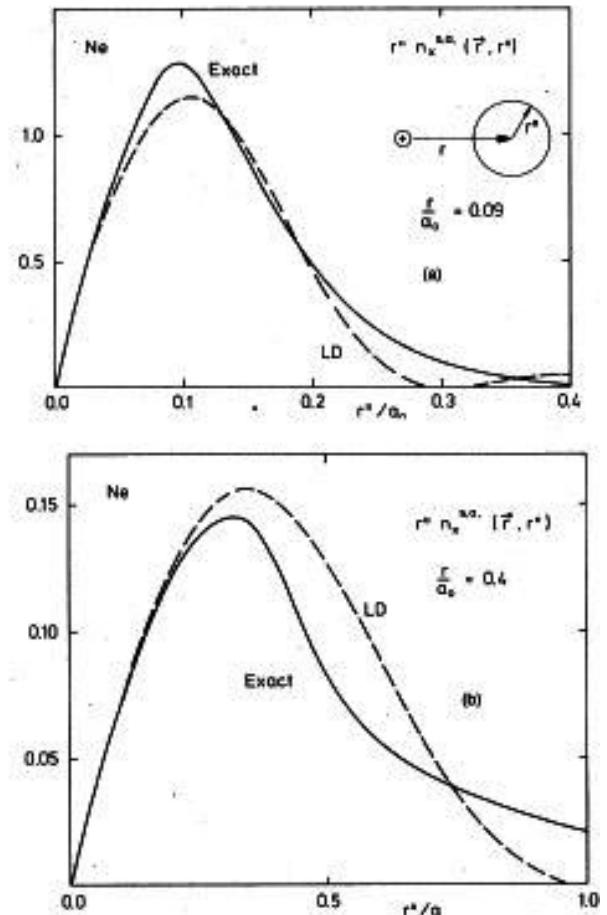
FIG. 7. Spherical average of the neon exchange hole [Eq. (17)] times r'' for (a) $r = 0.09$ a. u. and (b) $r = 0.4$ a.u. The full curves give the exact results and the dashed curves are obtained in the LD approximation.

* O. Gunnarsson, M. Jonson, and B.I. Lundqvist, *Phys. Rev. B* **20**, 3136 (1979).

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

Require

$$\left(\hat{h}_H + v_x\right)\psi_i^{KS} = \epsilon_i \psi_i^{KS} \qquad (1)$$

and

$$\left(\hat{h}_H + \hat{\Sigma}_{xc}\right)\psi_i^{HF} = \epsilon_i \psi_i^{HF} \qquad (2)$$

to produce the same charge density,

$$0 = \rho^{HF}(1) - \rho^{KS}(1) = \sum_i n_i \left(\Delta\psi_i(1)\psi_i^{KS*}(1) + \psi_i^{HF}(1)\Delta\psi_i^*(1)\right) \qquad (3)$$

where

$$\Delta\psi_i(1) = \psi_i^{HF}(1) - \psi_i^{KS}(1) \qquad (4)$$

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.

Now

$$\Delta \psi_i(1) = \psi_i^{HF}(1) - \psi_i^{KS}(1) \tag{1a}$$

$$= \sum_j \left(\psi_j^{KS}(1) \langle \psi_j^{KS} | \psi_i^{HF} \rangle \right) - \psi_i^{KS}(1) \tag{1b}$$

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

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

Similarly

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

$$= \sum_j \psi_j^{HF}(1) \left(\delta_{i,j} - \frac{\langle \psi_j^{HF} | \hat{\Sigma}_x - v_x | \psi_i^{KS} \rangle}{\epsilon_j^{HF} - \epsilon_i^{KS}} \right) \tag{2d}$$

$$0 = \rho^{HF}(1) - \rho^{KS}(1) = \sum_i n_i \left(\Delta \psi_i(1) \psi_i^{KS*}(1) + \psi_i^{HF}(1) \Delta \psi_i^*(1) \right) \quad \text{(1a)}$$

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

$$= \int X(1,1;2,2') \left(\Sigma_x(2,2') - v_x(2) \delta(2-2') \right) d2\, d2' \quad \text{(1c)}$$

with

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

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

* L. J. Sham and M. Schlüter, "Density-functional theory of the band gap," *Phys. Rev. Lett.* **51**, 1888 (1983).

R.T. Sharp and G.K. Horton, "A Variational Approach to the Unipotential Many-Electron Problem," *Phys. Rev.* **90**, 317 (1953).

$$\psi_i^{KS} \leftarrow \psi_i^{HF} \qquad (1)$$

$$\epsilon_i^{KS} \leftarrow \epsilon_i^{HF} \qquad (2)$$

Solves the problem of finding the v_x whose orbitals minimize the Hartree-Fock energy expression.

This is *almost* the same thing as asking for v_x whose orbitals produce the Hartree-Fock charge density.

Outer-valence IPs for a number of small molecules.
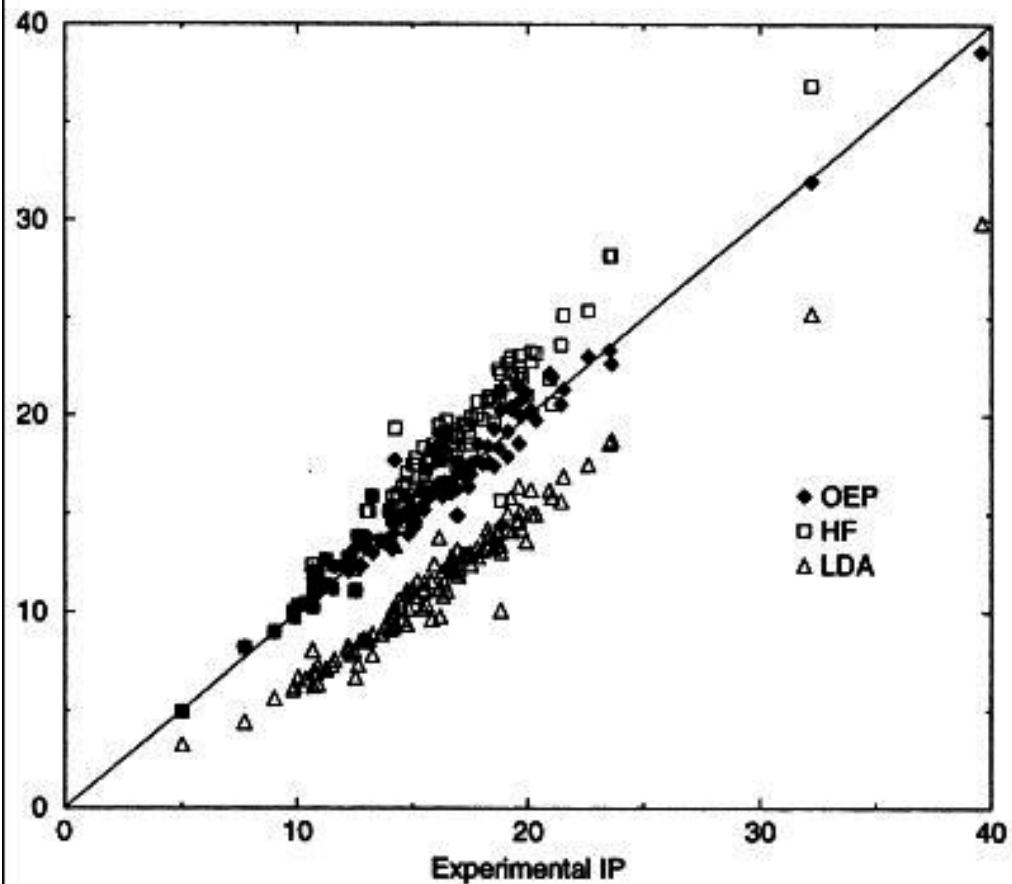
(a) All.
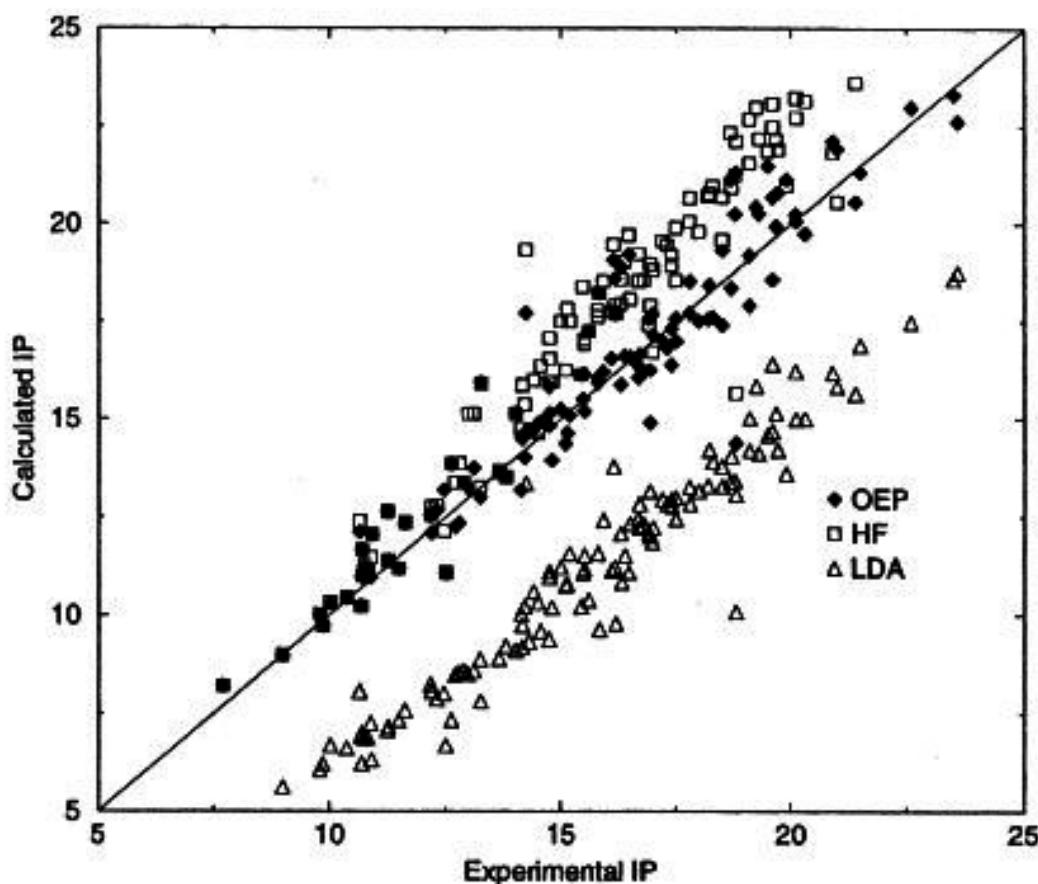
(b) Enlargement.

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

S. Hamel, P. Duffy, M.E. Casida, and D.R. Salahub, *J. Electr. Spectr. and Related Phenomena* **123**, 345 (2002).

Average denominator approximation

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

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

Leads to

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

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

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

Krieger-Li-Iafrate (LHF) approximation**

$$v_x(1) = v_x^S(1) - \frac{\sum_i n_i \psi_i^{KS}(1) \langle \psi_i^{KS} | \hat{\Sigma}_x - v_x | \psi_i^{KS} \rangle \psi_j^{KS*}(1)}{\rho(1)}$$

* F. Dela Salla and A. Görling, *J. Chem. Phys.* **115**, 5718 (2001). O. Gritsenko and E.J. Baerends, *Research on Chemical Intermediates* **30**, 87 (2004). (MEC, presented in a seminar in Toulouse in Jan. 2000, but never published.) V.N. Staroverov, G.E. Scuseria, and E.R. Davidson, *J. Chem. Phys.* **125**, 081104 (2006).

** J.B. Krieger, Y. Li, and G.J. Iafrate, *Phys. Rev. A* **45**, 101 (1992).

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

$$\left(\hat{h}_H + \hat{\Sigma}_x\right)\psi_i(1) = \epsilon_i^{HF}\psi_i(1) \qquad (1)$$

$$\left(\hat{h}_H + v_x(1)\right)\psi_i(1) = \epsilon_i^{KS}\psi_i(1) \qquad (2)$$

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

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

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

$$v_x(1) = \underbrace{\frac{\sum_i n_i \psi_i^*(1)\hat{\Sigma}_x\psi_i(1)}{\rho(1)}}_{Slater} + \underbrace{\frac{\sum_i n_i\left(\epsilon_i^{KS} - \epsilon_i^{HF}\right)\left|\psi_i(1)\right|^2}{\rho(1)}}_{derivative\,discontinuity} \qquad (6)$$
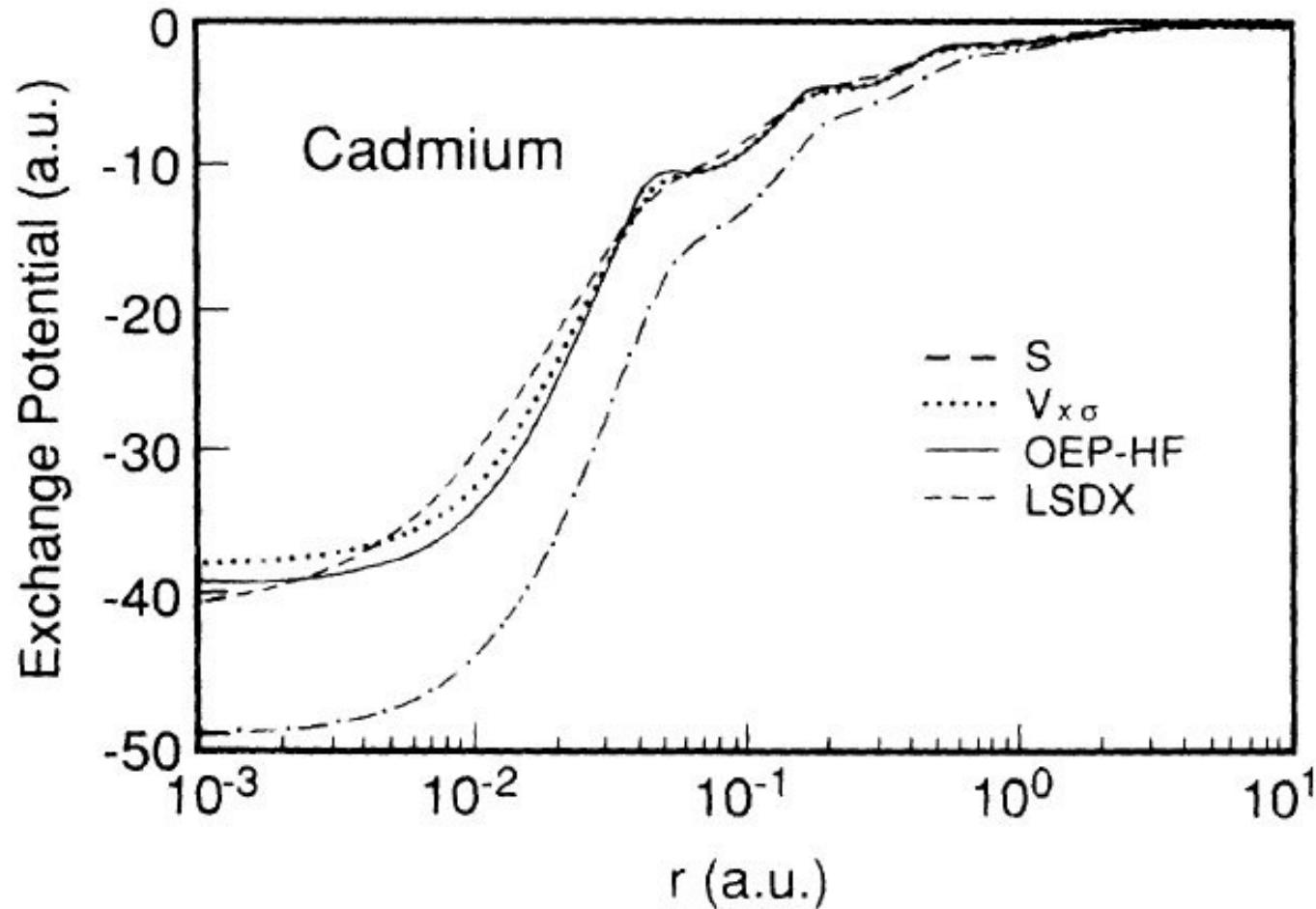
J.B. Krieger, Y. Li, and G.J. Iafrate, *Phys. Rev. A* **45**, 101 (1992).

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."

Walter KOHN
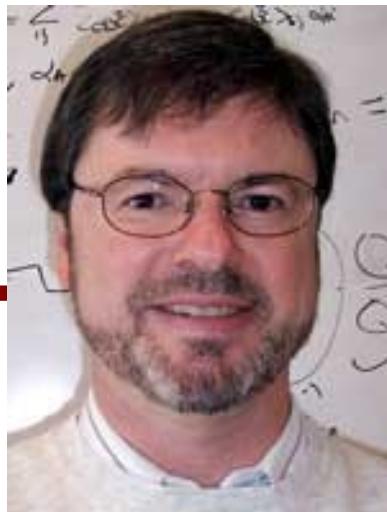
Axel BECKE
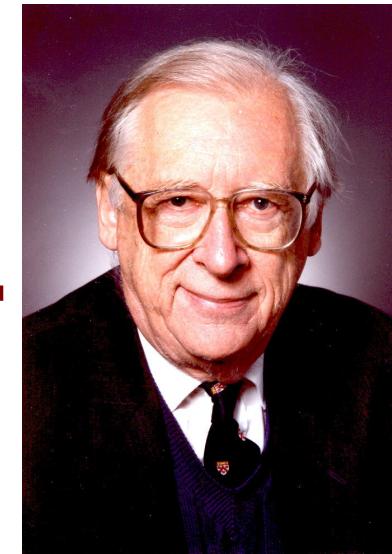
John Pople

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

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.

$$f[\rho](x) = f(\rho(x), \rho'(x), \rho''(x), \cdots) \qquad (1)$$

$$f[\rho+\delta\rho](x) = f[\rho] + \int \frac{\partial f}{\partial\rho(y)} \delta\rho(y)\,dy + \int \frac{\partial f}{\partial\rho'(y)} \delta\rho'(y)\,dy \qquad (2a)$$

$$+ \int \frac{\partial f}{\partial\rho''(y)} \delta\rho''(y)\,dy + \cdots \qquad (2b)$$

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

$$+ \int \left(\frac{\partial^2}{\partial y^2} \frac{\partial f}{\partial\rho''(y)} \right) \delta\rho(y)\,dy + \cdots \qquad (3b)$$

So
$$\frac{\delta f(x)}{\delta\rho(y)} = \frac{\partial f(x)}{\partial\rho(y)} - \frac{\partial}{\partial y} \frac{\partial f}{\partial\rho'(y)} + \frac{\partial^2}{\partial y^2} \frac{\partial f}{\partial\rho''(y)} + \cdots \qquad (4)$$

After much manipulation, Kohn and Sham arrive at

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

$$+\left(\epsilon^{(4a)}(\rho(\vec{r}))\nabla^2\rho(\vec{r})\nabla^2\rho(\vec{r}) + \epsilon_{xc}^{(4b)}(\rho(\vec{r}))\nabla^2\rho(\vec{r})|\vec{\nabla}\rho(\vec{r})|^2 + \epsilon_{xc}^{(4c)}(\rho(\vec{r}))|\vec{\nabla}\rho(\vec{r})|^4\right)$$

+ HOT*

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

* Higher-Order Terms

DIMENSIONAL ANALYSIS

$$\int \rho(\vec{r})\,d\vec{r} = N \qquad \Rightarrow \qquad \begin{aligned} \rho &\sim \frac{1}{L^3} \\[1em] \vec{\nabla}\rho &\sim \frac{1}{L^4} \\[1em] \nabla^2\rho &\sim \frac{1}{L^5} \end{aligned}$$

For proper convergence, we need

$$\frac{|\vec{\nabla}\rho|}{\rho} \quad , \quad \frac{\nabla^2\rho}{|\vec{\nabla}\rho|} \qquad << \qquad k_F = \left(3\pi^2\rho\right)^{1/3}$$

all of which scale as 1/L .

Neon Convergence Ratios

$$\frac{|\nabla \rho|}{2 k_F \rho}$$

$$\frac{|\nabla^2 \rho|}{2 k_F |\nabla \rho|}$$
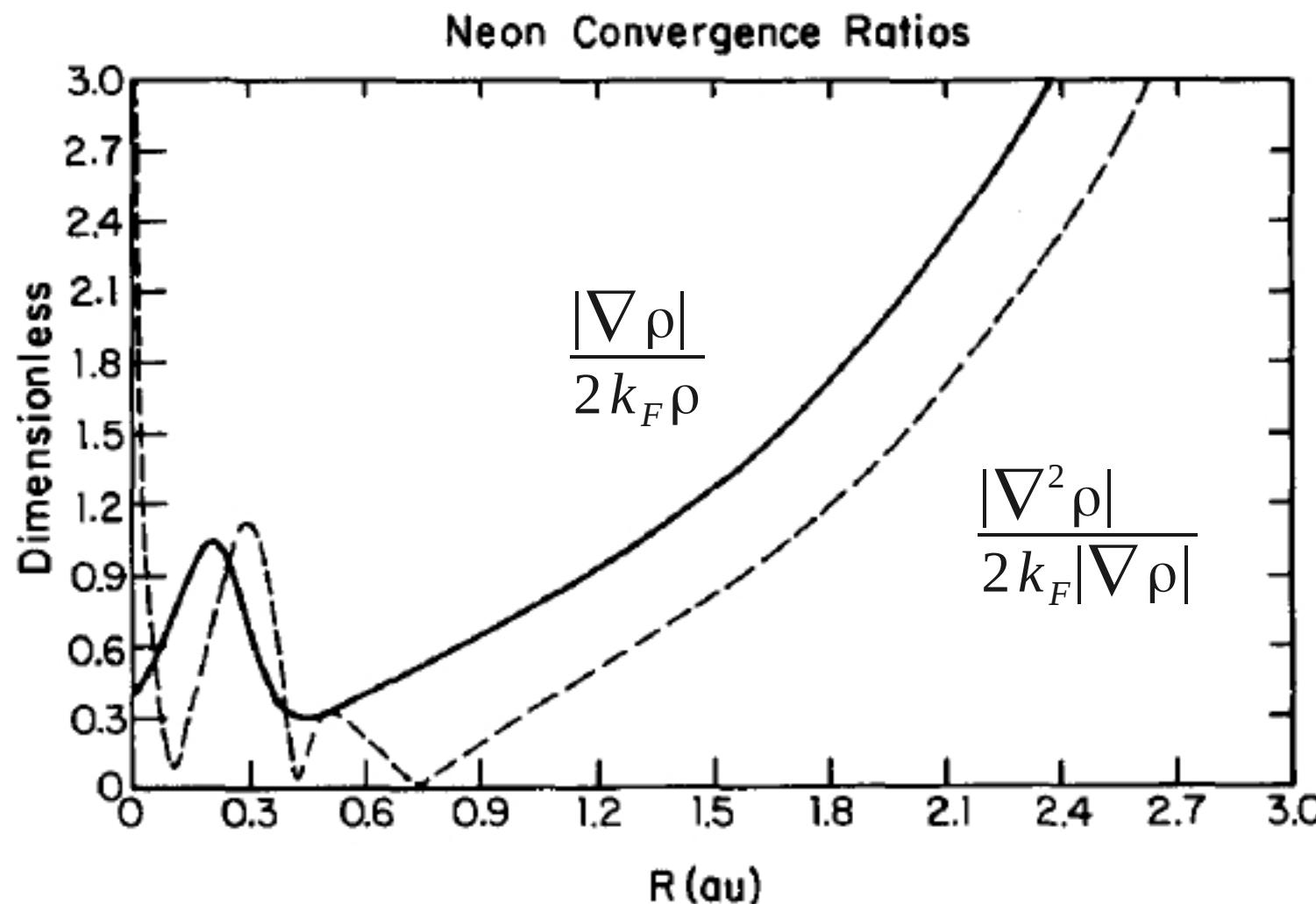
E.W. Pearson and R.G. Gordon, *J. Chem. Phys.* **82**, 881 (1985)

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

$$\alpha = \frac{2}{3}$$ *ab initio*

$$\beta = 0.0055$$ Fit to Xe

* C.C. Shih, D.R. Murphy, and W.-P. Wang, *J. Chem. Phys.* **73**, 1340 (1980).

GENERALIZED GRADIENT APPROXIMATION (GGA)

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

Use linear response theory to derive the gradient correction.

$$E_{xc} = \frac{1}{(2\pi)^3} \int E_{xc}(\vec{k}) \, d\vec{k} = \frac{1}{2\pi^2} \int E_{xc}(k) k^2 \, dk \qquad (1)$$

$$E_{xc}^{(2)}(\vec{k}) = \frac{1}{(2\pi)^3} \int \delta\rho(\vec{q}) K_{xc}(\vec{k},\vec{q}) \delta\rho(-\vec{q}) \, d\vec{q} \qquad (2)$$

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

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(Received 6 November 1979)

p. 5469
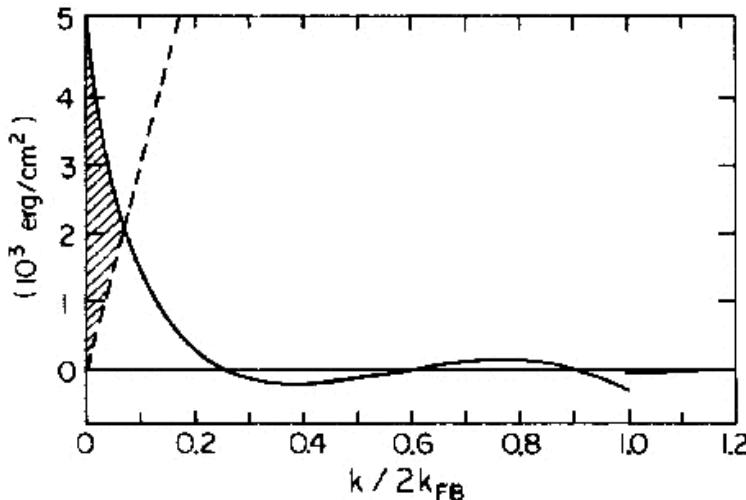
FIG. 7. Wave-vector decomposition of the gradient component of the surface energy $\delta_{gr}\gamma$ for the "Fermi-function" density profile. The bulk density corresponds to $r_s = 2.07$. The broken line is the exact asymptote.

$$E_{xc}^{(2)}(\vec{k}) = \int \left[z_x(\vec{k}, k_F(r)) + z_c(\vec{k}, k_F(\vec{r})) \theta(k - k_c) \right] |\vec{\nabla} k_F(\vec{r})|^2 d\vec{r} \qquad (1)$$

cutoff

$$k_c = \frac{|\vec{\nabla}\rho|}{6\rho} \qquad (2)$$

Back transforming gives finally

$$E_{xc}^{GGA} = \int \rho^{4/3}(\vec{r}) \left[2 e^{-\beta x(\vec{r})\rho^{1/6}(\vec{r})} - \frac{7}{9} \right] x^2(\vec{r}) d\vec{r} \qquad (3)$$

$$x = \frac{|\vec{\nabla}\rho|}{\rho^{4/3}} \qquad (4)$$

$$E_x = \int \epsilon_x[\rho](\vec{r})\rho(\vec{r})d\vec{r} \qquad (1)$$

$$\epsilon_x(\vec{r}) = \frac{1}{2}\int \frac{\rho_x(\vec{r},\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,' \qquad (2a) \qquad \xrightarrow{r\to\infty} \qquad -\frac{1}{2r} \qquad (2b)$$

What happens in Xαβ ? $\qquad \rho(\vec{r}) \sim c\,e^{-\zeta r} \qquad (3)$

LDA part $\qquad \rho^{4/3}(\vec{r}) \sim c^{4/3}e^{-(4/3)\zeta r}$ (4a) $\xrightarrow[\text{Fast!}]{\text{Too}}$ $0 \qquad (4b)$

Gradient correction $\qquad x = \dfrac{|\vec{\nabla}\rho|}{\rho^{4/3}}\ \zeta\rho^{-1/3} \qquad (5)$

$$\rho^{4/3}x^2 \sim \zeta\rho^{2/3} \sim \zeta c^{2/3}e^{-(2/3)\zeta r} \qquad (6a) \qquad \xrightarrow[\text{Fast!}]{\text{Too}} \qquad 0 \qquad (6b)$$

* A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).

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

$$\longrightarrow \begin{cases} X\alpha\beta; x_\sigma \ll 1 & (2a) \\ -\dfrac{1}{2r}; x_\sigma \gg 1 & (2b) \end{cases}$$

$$\beta = 0.0042 \quad (3) \qquad \text{determined by fitting}$$

* A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).

TABLE II. Atomic exchange energies (a.u.).

	Exact	LDA[a]	PW[b]
H	−0.313	−0.268	−0.310
He	−1.026	−0.884	−1.025
Li	−1.781	−1.538	−1.775
Be	−2.667	−2.312	−2.658
B	−3.744	−3.272	−3.728
C	−5.045	−4.459	−5.032
N	−6.596	−5.893	−6.589
O	−8.174	−7.342	−8.169
F	−10.00	−9.052	−10.02
Ne	−12.11	−11.03	−12.14
Na	−14.02	−12.79	−14.03
Mg	−15.99	−14.61	−16.00
Al	−18.07	−16.53	−18.06
Si	−20.28	−18.59	−20.27
P	−22.64	−20.79	−22.62
S	−25.00	−23.00	−24.98
Cl	−27.51	−25.35	−27.49
Ar	−30.19	−27.86	−30.15

[a]LDA: Eq. (1).
[b]Present work: Eq. (8) with $\beta = 0.0042$ a.u.

A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).

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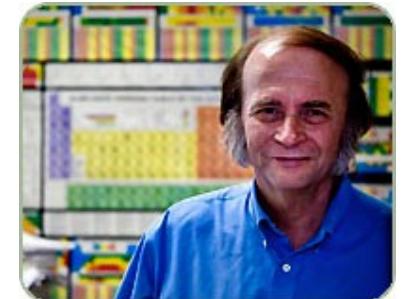
John PERDEW

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!

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

The exchange-correlation hole,

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

$$\tilde{\rho}(1) = \hat{\rho}(1) - \rho(1) \qquad (3)$$

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

Neglecting the λ-dependence of Ψ,

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

---

* J. Harris and R.O. Jones, *J. Phys. F* **4**, 1170 (1974).

This suggests

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

(Though Becke was actually thinking ...

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

There is a theoretical rationalization that $\quad f \approx 0.25 \quad * \qquad (3)$

B3PW91 functional**

$$E_{xc} = E_{xc}^{LSDA} + a_0\left(E_x^{exact} - E_x^{LSDA} \right) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{PW91} \qquad (4)$$

---

* J.P. Perdew, M. Ernzerhof, and K. Burke, *J. Chem. Phys.* **105**, 9982 (1996).

** A.D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

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

A.D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

Nearly *ab initio* accuracy !

TABLE VI. Maximum absolute deviations.

	G2[a]	Eq. (2)	GC[b]
Atomization energies (kcal/mol)	5.1	7.6	18.4
Ionization potentials (eV)	0.19	0.41	0.44
Proton affinities (kcal/mol)	2.0	4.7	4.2
Total energies (mhartree)		10.0	29.0

[a]G2: Gaussian-2 theory (Refs. 13 and 14).
[b]GC: Gradient-corrected DFT of Ref. 5.

Birth
(stage 1)

Born as Thomas-Fermi theory
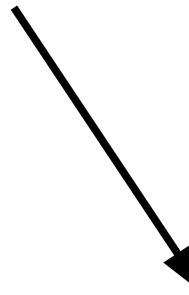
Peter M. W. Gill, "Obituary: Density-Functional Theory (1927-1993)",
Aust. J. Chem. **54**, 661-662 (2001).
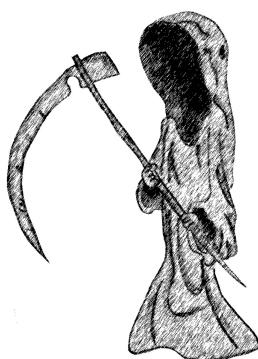
Died when Axel Becke introduced
hybrid functionals

https://sites.google.com/site/markcasida/dft
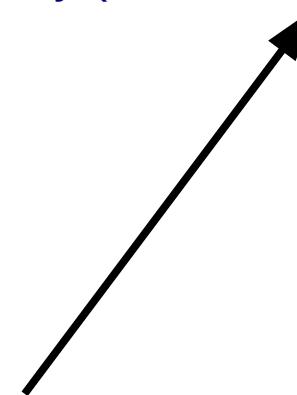
Hartree-Fock
Occupied orbitals see N-1 electrons. Unoccupied orbitals see N electrons.
Orbital energies may be interpreted as minus ionization potentials and electron affinities
(or as band energies if you like) --- i.e., Koopmans' theorem.

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!

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

"Jacob's ladder"
William Blake
water color
1799-1800

Jacob's ladder

THEORETICAL CHEMISTRY HEAVEN

MBPT   *ab initio* DFT

$\hat{K}_x^{HF}$ hybrid/OEP

$\tau(\vec{r}) = \sum_i n_i |\nabla \psi_i|^2$ mGGA*

$x(\vec{r}) = \dfrac{|\nabla \rho(\vec{r})|}{\rho(\vec{r})^{4/3}}$ GGA

Pure DFT

$\rho(\vec{r})$ LDA

HARTREE WORLD

No computer land

Molecular size $\rightarrow$

* or include $\nabla^2 \rho$
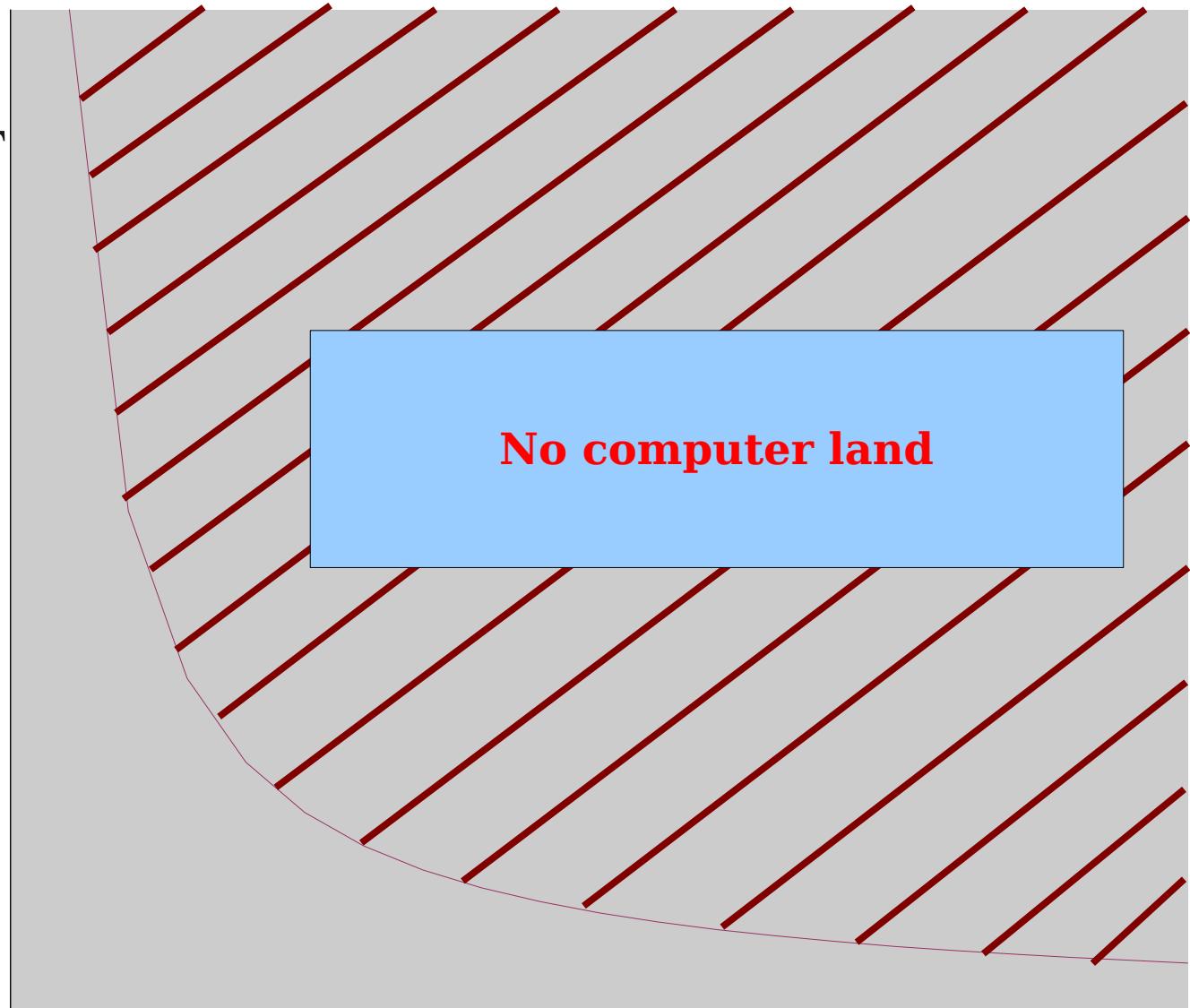
Modern GKS is
- less and less B3LYP
- more and more RSH

$$\frac{1}{r_{12}} = \underbrace{\frac{erfc\,(\gamma\,r_{12})}{r_{12}}}_{SHORT\ RANGE} + \underbrace{\frac{erf\,(\gamma\,r_{12})}{r_{12}}}_{LONG\ RANGE}$$

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:
- Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, *J. Chem. Phys.* **120**, 8425 (2004).
- S. Tokura, T. Tsuneda, and K. Hirao, *J. Theoretical and Computational Chem.* **5**, 925 (2006).
- O.A. Vydrov and G.E. Scuseria, *J. Chem. Phys.* **125**, 234109 (2006).
- M.J.G. Peach, E.I. Tellgrent, P. Salek, T. Helgaker, and D.J. Tozer, *J. Phys. Chem. A* **111**, 11930 (2007).
- E. Livshits and R. Baer, *Phys. Chem. Chem. Phys.* **9**, 2932 (2007).

* Because Nature is often, *but not always*, nearsighted.

Fluctuation-Dissipation Theorem

Quantity closely related to xc-hole of DFT

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

$$\tilde{\rho}(\mathbf{1}) = \hat{\rho}(\mathbf{1}) - \langle \Psi_0 | \hat{\rho}(\mathbf{1}) | \Psi_0 \rangle \qquad \mathbf{i} = (i, t_i) = (x_i, y_i, z_i, t_i)$$

Electron repulsion energy

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

Correlation energy

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

5th rung functionals from TDDFT

A.L. Fetter and J.D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill Book Company, New York, 1971), p. 152.

Sorry, no time!

IX. Conclusion

- 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/
  - ✱ In 2012, PBE came in first
  - ✱ In 2011, PBE0 came in first
  - ✱ In 2010, PBE0 came in first

Does this really mean anything !?

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