

# Exchange and Correlation

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**DFT and Beyond  
Trieste, Italy  
7 August 2013  
50 min.**

Rhône-Alpes Associated Node

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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**

II. Variational Calculus

III. Hohenberg-Kohn Theory

IV. Kohn-Sham Formulation

V. From a Four-Letter to a House-Hold Word (GGAs)

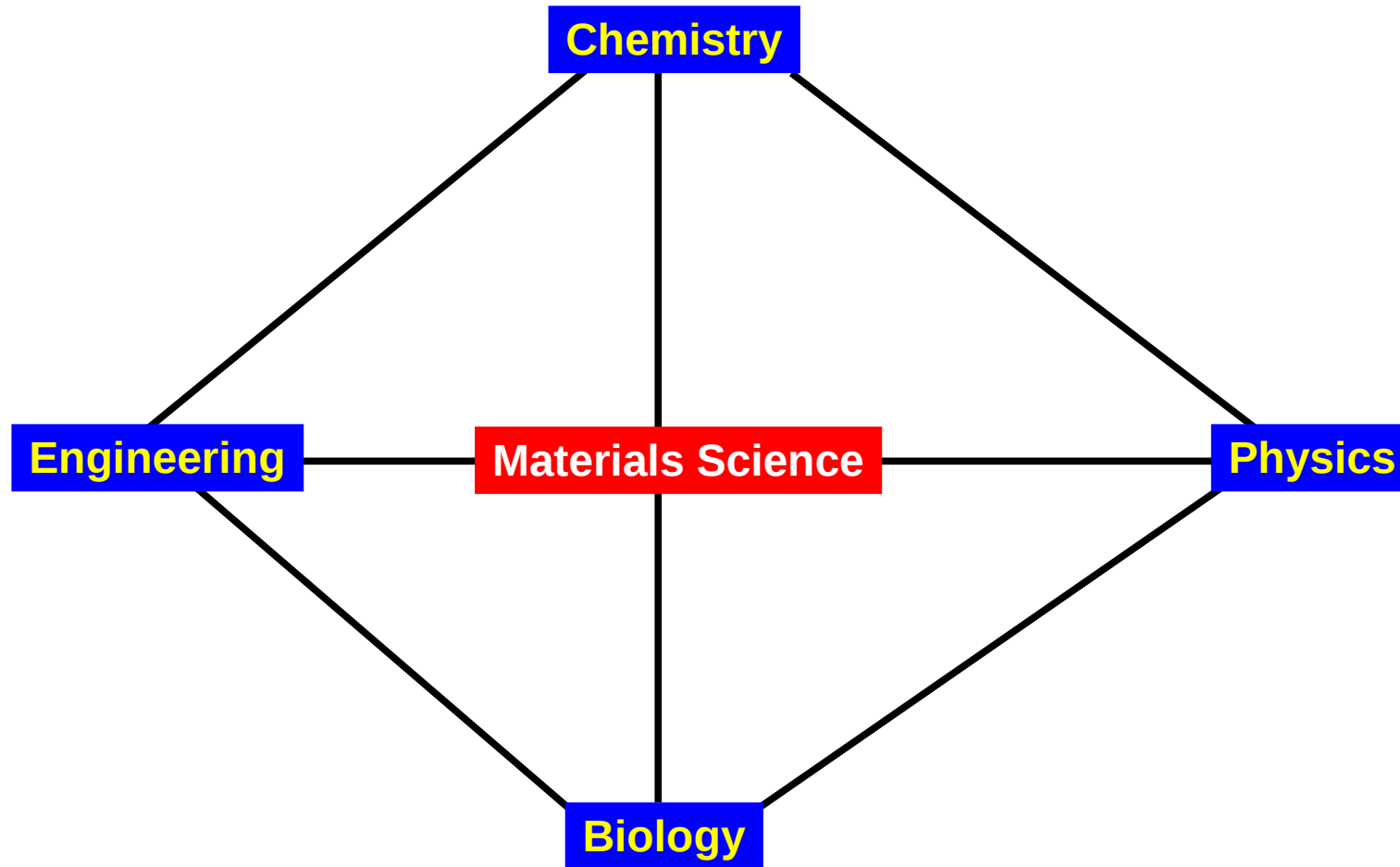
VI. Death of DFT (Hybrid Functionals)

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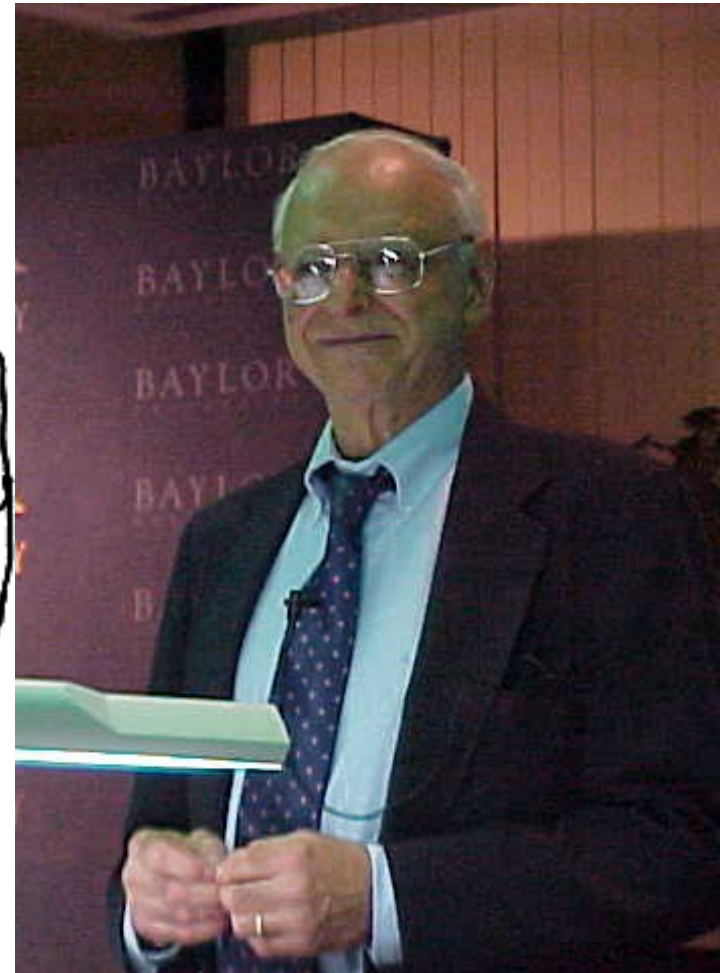
# A HIGHLY INTERDISCIPLINARY AREA



With permission from  
Sidney Harris  
[www.sciencecartoonsplus.com](http://www.sciencecartoonsplus.com)



*"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!**

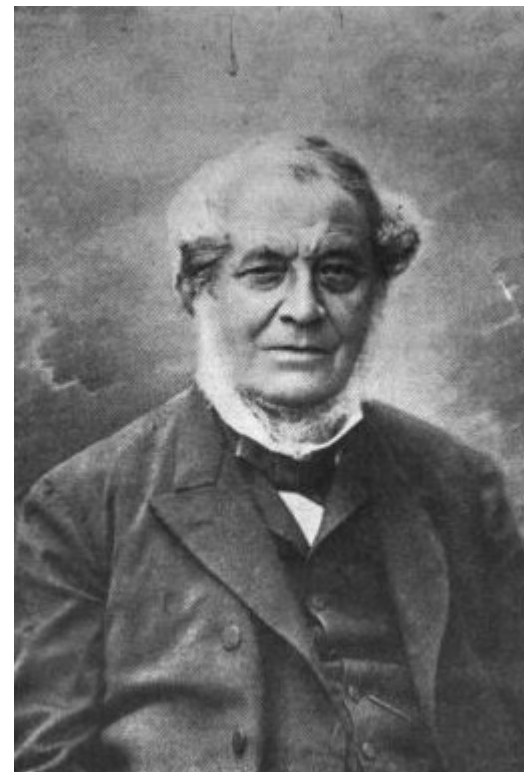
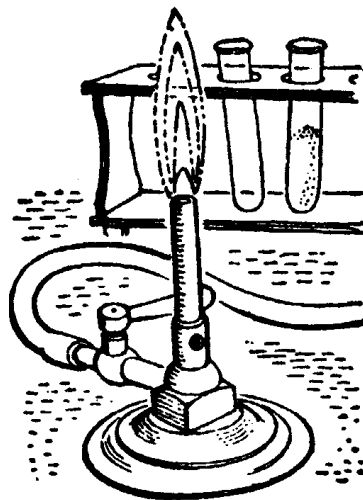


## BUT ULTIMATELY CHEMISTRY IS ALSO PHYSICS

*“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 !

# Language and Culture Problems



“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:  $e, m_e, \hbar, c \approx 137, \dots$

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, ...

# 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

- I. Chemistry vs Physics
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Seek solutions to

$$\hat{H}\Psi_I = E_I\Psi_I; E_0 \leq E_1 \leq E_2 \leq \dots \quad (1)$$

Then

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

For any trial wavefunction  $\Psi_{trial}$ , satisfying the same boundary conditions as the  $\Psi_I$ ,

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

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\* Quantum Chemistry 101?

# VARIATIONAL CALCULUS

## Multivariable calculus

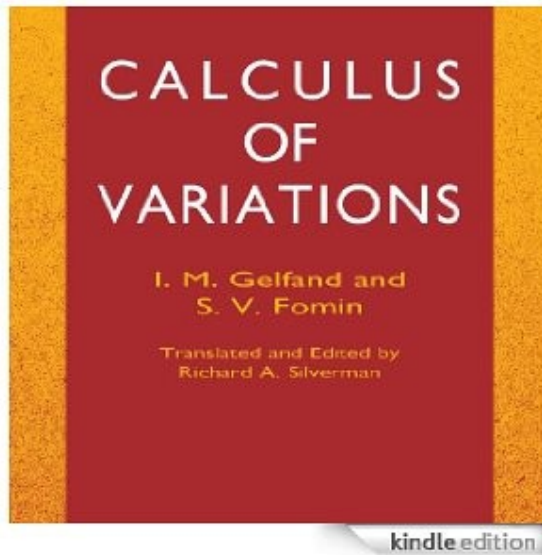
$$\vec{f} = \begin{pmatrix} f_1 \\ f_2 \\ \vdots \end{pmatrix} \quad (1a)$$

$$dF(\vec{f}) = \sum_i \frac{\partial F}{\partial f_i} df_i \quad (2a)$$

## Variational calculus

$$f = f(x) \quad (1b)$$

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



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

## EASY EXAMPLE (1)

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

subject to the constraint  $\int \Psi^*(\tau) \Psi(\tau) d\tau = 1$  (2)

Use the method of Lagrange multipliers !

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

$$= \int \Psi^*(\tau) (\hat{H} \Psi(\tau) - E \Psi(\tau)) d\tau \quad (3b)$$

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

$$= \int \delta \Psi^*(\tau) (\hat{H} \Psi(\tau) - E \Psi(\tau)) d\tau \quad (4b)$$

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

i.e.,  $\hat{H} \Psi(\tau) = E \Psi(\tau)$  (6)

## EASY EXAMPLE (2)

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

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

$$0 = \delta L[\Psi, \Psi^*] = L[\Psi + \delta \Psi, \Psi^*] - L[\Psi, \Psi^*] \quad (2a)$$

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

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

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

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

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

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

# HARTREE-FOCK TOTAL (ELECTRONIC) ENERGY

Minimizing

$$E_0 \leq W[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \quad i = (\vec{r}_i, \sigma_i) \quad (3) \quad (1)$$

with

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

subject to the constraint

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

gives

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

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



# HARTREE-FOCK TOTAL (ELECTRONIC) ENERGY

$$E = E_{core} + E_H + E_x \quad (1)$$

Hartree (Coulomb) energy

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

← occupation numbers

Charge density

$$\rho(1) = \sum_i n_i |\psi_i(1)|^2 \quad (3)$$

Mulliken charge cloud notation

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

Exchange energy

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

One-electron reduced density matrix

$$\gamma(1,2) = \sum_i \psi_i(1)n_i\psi_i^*(2) \quad (6)$$

# HARTREE-FOCK ORBITAL EQUATION (1)

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

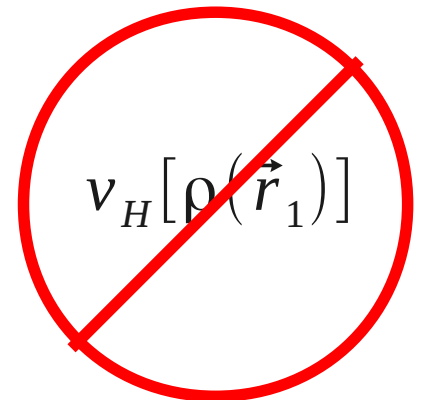
$$E_{core} = \sum_i n_i \int \psi_i(1) \hat{h}_{core} \psi_i(1) d1 \quad (3a) \quad \Rightarrow \quad \frac{\delta E_{core}}{\delta \psi_i^*(1)} = n_i \hat{h}_{core} \psi_i(1) \quad (3b)$$

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

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

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

$$\underbrace{\int \frac{\rho(2)}{r_{12}} d2}_{v_H[\rho](\vec{r}_1)} \quad (6b)$$



## HARTREE-FOCK ORBITAL EQUATION (2)

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

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

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

$$= \underbrace{-\hat{\Sigma}_x^\sigma[\gamma]}_{-\hat{\Sigma}_x^\sigma[\gamma]}(\vec{r}_1, \vec{r}_2) \quad (3b)$$

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

## HARTREE-FOCK ORBITAL EQUATION (3)

Putting it all together,

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

or

$$\hat{f}[\gamma] \psi_i(\mathbf{1}) = \epsilon_i \psi_i(\mathbf{1}) \quad (2)$$

where the Fock operator,

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

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

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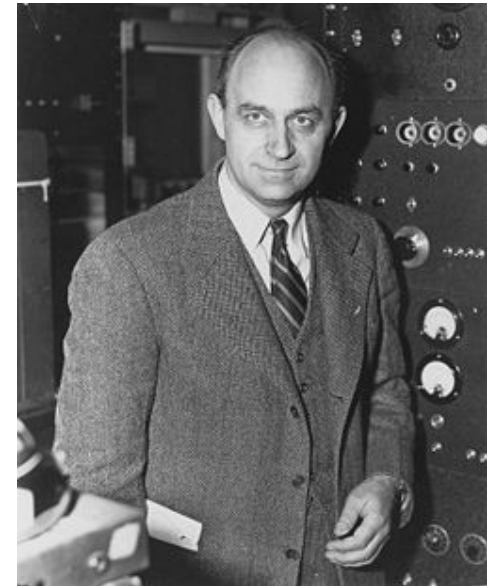
# THE HOHENBERG-KOHN THEOREMS GIVE A RIGOROUS BASIS TO THOMAS-FERMI THEORY

L.H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927). E. Fermi, Rend. Accad. Naz. Lincei **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.)

$$\rho(\vec{r}) \overset{1-1}{\longleftrightarrow} v_{ext}(\vec{r}) + const. \quad (1)$$

Comments

- 1) so the charge density determines just about everything
- 2) but how accurately? (e.g. it can only determine the  $v_{ext}$  where  $\rho$  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

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

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  $V_{ext}^{(1)} - V_{ext}^{(2)} \neq const.$  (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

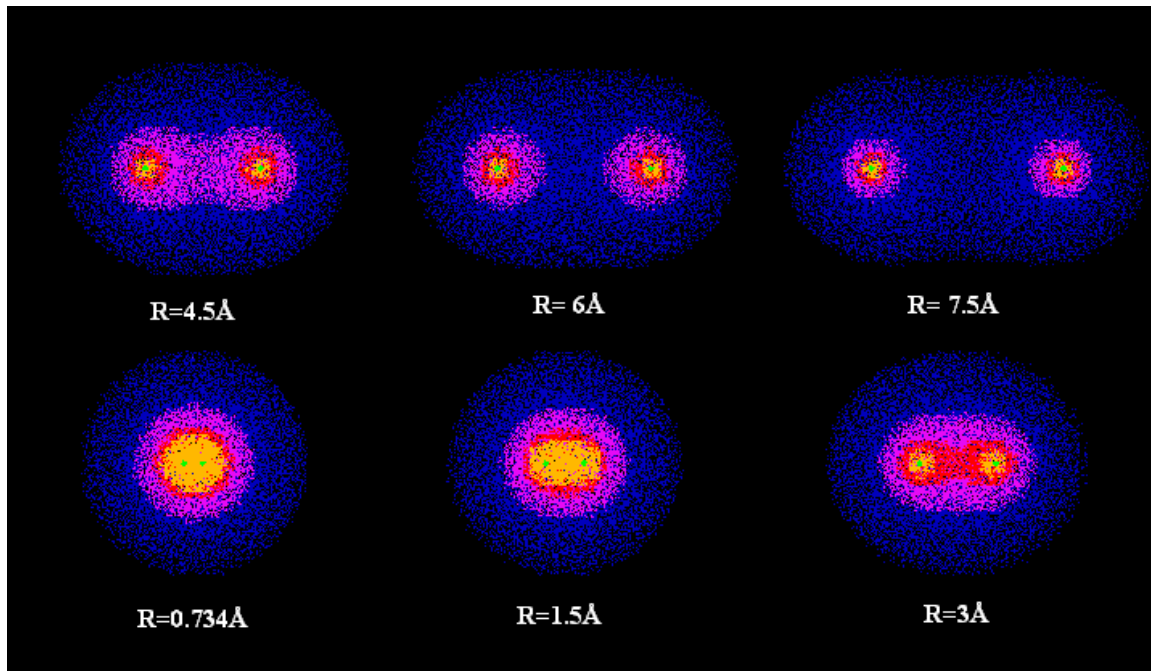
$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} + \int (v_{ext}^{(1)}(\vec{r}) - v_{ext}^{(2)}(\vec{r})) \rho(\vec{r}) d\vec{r} \quad (6a)$$

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

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



## EDGER BRIGHT WILSON ARGUMENT



H<sub>2</sub> charge density\*

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

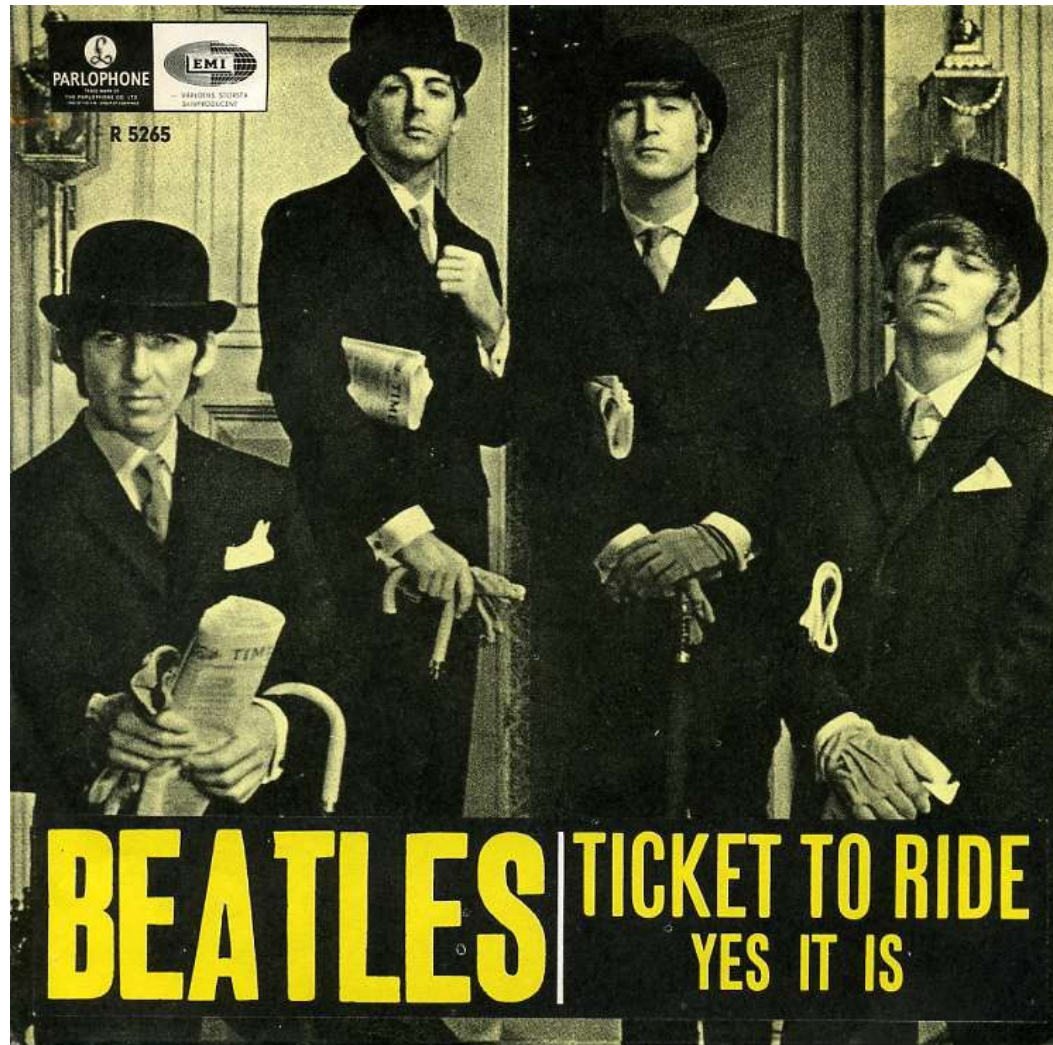
$$Z_A = - \frac{\lim_{r \rightarrow r_A} \frac{\partial}{\partial r} \int \rho(\vec{r}) d\Omega}{2 \lim_{r \rightarrow r_A} \int \rho(\vec{r}) d\Omega}$$

***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



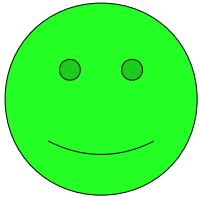
but we still need a way to find the charge density!

## BUT WHAT ABOUT ... ?

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

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)  $\rho$  ?

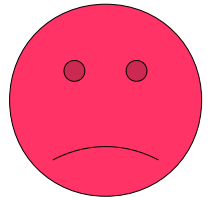
Some external potentials are ensemble v-representable but not pure-state v-representable.

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).



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

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

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



Walter KOHN



Pierre C. HOHENBERG

Theorem (HK2)

The ground state energy and density are determined the variational principle,

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

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

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

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  $v_{\text{ext}}$ .

Proof (Levy-Lieb\*)

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

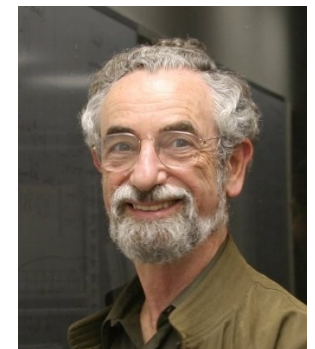
***So the exact “unknown” functional is known, but just impossibly difficult to calculate !***

---

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



Mel LEVY



Elliott LIEB

# WANTED

**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



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

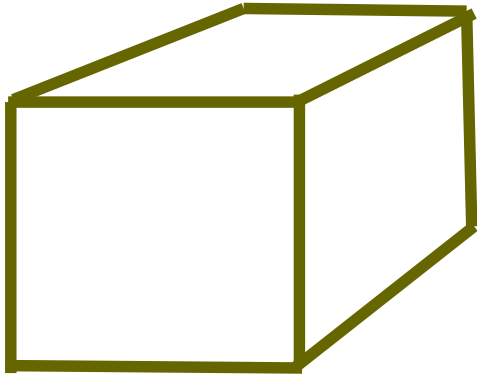
[\*\*https://sites.google.com/site/markcasida/dft\*\*](https://sites.google.com/site/markcasida/dft)



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

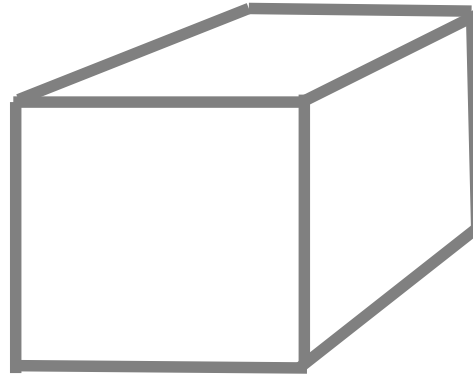


# HOMOGENEOUS ELECTRON GAS (HEG, JELLIUM)



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

+



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

=

“jellium”

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

$$\frac{4}{3} \pi r_s^3 = \frac{1}{\rho} \quad (1a)$$

$\Rightarrow$

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

Orbitals

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

Quantization

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

Density of states

$$d\vec{n} = \frac{V}{8\pi^3} d\vec{k} \quad (4)$$



## FERMI MOMENTUM (WAVE NUMBER)



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

So

$$k_F = (3\pi^2 \rho)^{1/3} \quad (2)$$

Also

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



## HEG KINETIC ENERGY



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

$$\nabla^2 \psi_{\vec{k}}(\vec{r}) = -k^2 \psi_{\vec{k}}(\vec{r}) \quad (3)$$

$$\psi_{\vec{k}}^*(\vec{r}) \psi_{\vec{k}}(\vec{r}) = \frac{1}{V} \quad (4)$$

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

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

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

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



# HEG EXCHANGE ENERGY



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

Dirac result\*

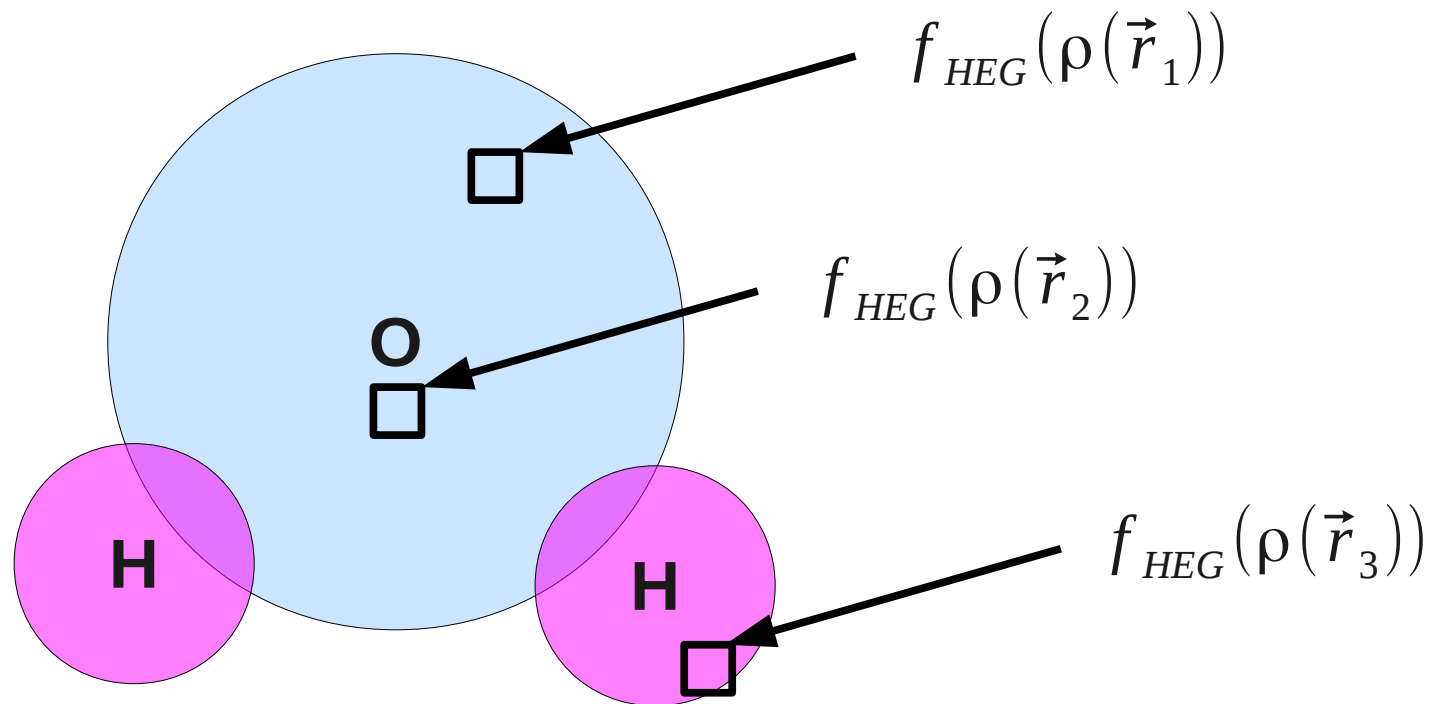
$$e_x^{HEG} = \frac{E_x^{HEG}}{V} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \rho^{4/3} \quad (2)$$

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

# CONCEPT OF A LOCAL DENSITY APPROXIMATION (LDA)



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



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



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



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

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

**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.

---

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



## 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

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

Spin polarization

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

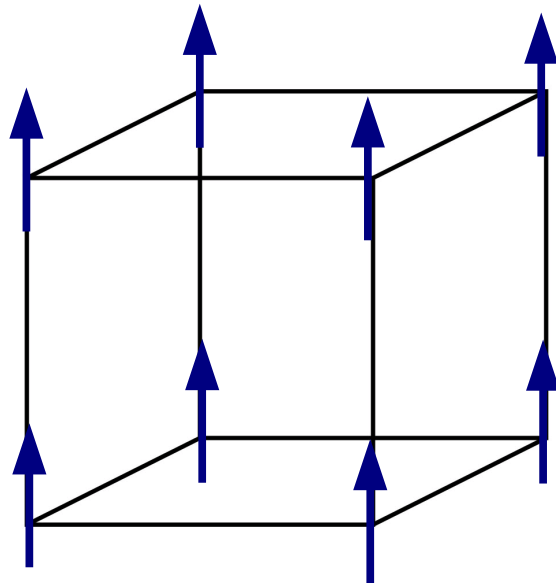
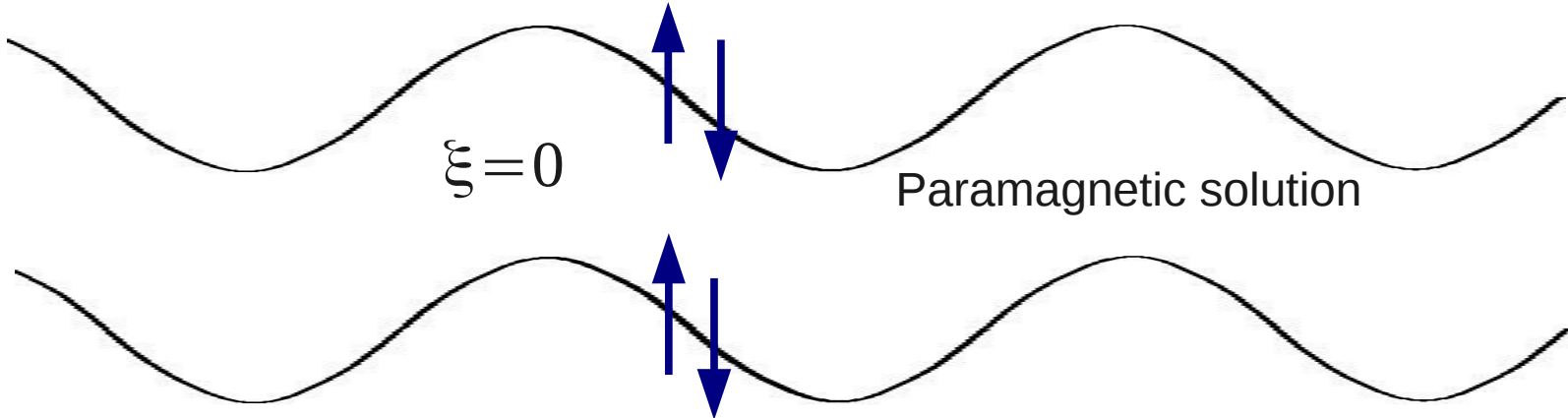
$$f(\xi) = \frac{(1+\xi)^{4/3} + (1-\xi)^{4/3} - 2}{2(2^{1/3} - 1)} \quad (5b)$$





# ELECTRON CORRELATION IN THE HEG (I)

$\rho$



Wigner crystal (bcc)

Ferromagnetic solution  
 $\xi = 1$

$r_s$



## ELECTRON CORRELATION IN THE HEG (II)



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.)

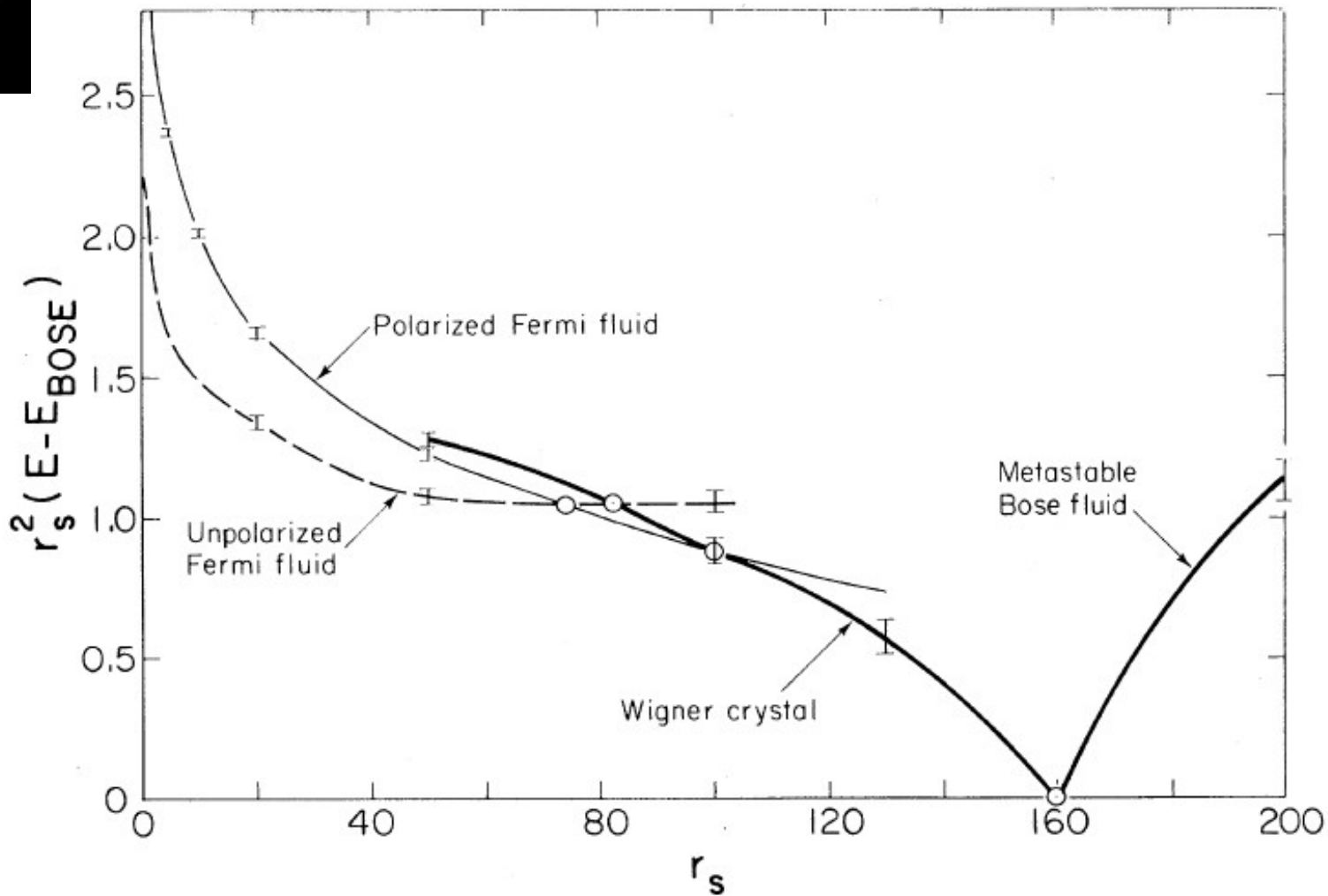
$$\epsilon_c \approx -\frac{0.44}{7.8 + r_s} \quad (2) \quad (\text{Wigner})$$

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).

# QUANTUM MONTE CARLO (QMC) RESULTS FOR THE HEG



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).



## LDA PARAMETERIZATIONS OF THE $x_c$ -ENERGY



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!***

- 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



# THE KOHN-SHAM REFORMULATION OF DFT GIVES A RIGOUROUS BASIS TO SLATER'S X<sub>a</sub> MODEL



John SLATER

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,

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

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

Comparison with Dirac's local exchange gives

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



W. KOHN AND L.J. SHAM, PHYS. REV. 140, A1133 (1965)  
 “SELF-CONSISTENT EQUATIONS INCLUDING  
 EXCHANGE AND CORRELATION EFFECTS”



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

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

where

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

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

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

where the exchange-correlation potential is

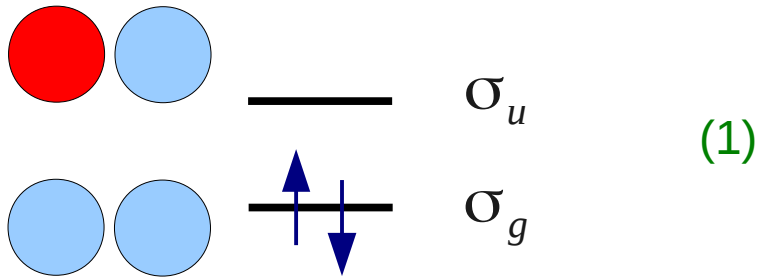
$$v_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \quad (4)$$



W. KOHN AND L.J. SHAM, PHYS. REV. 140, A1133 (1965)  
 “SELF-CONSISTENT EQUATIONS INCLUDING  
 EXCHANGE AND CORRELATION EFFECTS”



Fictitious system of noninteracting electrons (“s” for single particle)



• Aufbau filling

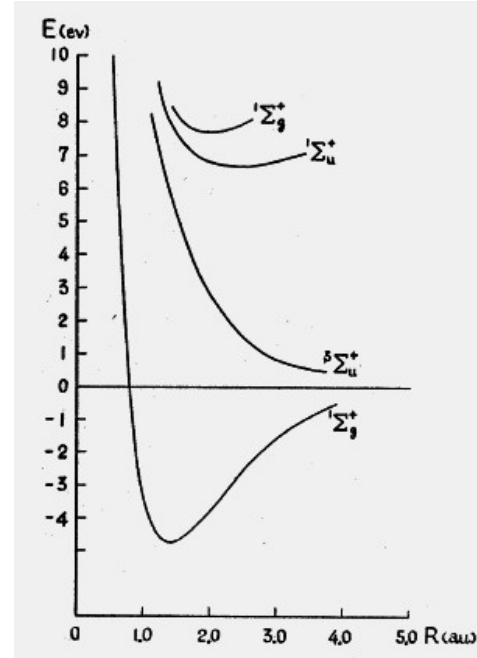
Kohn-Sham determinant

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

Density

$$\rho(\vec{r}) = 2|\sigma_g(\vec{r})|^2 \quad (3)$$

Real system of interacting electrons



(4)

Interacting wavefunction

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

Density

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

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





# $E_{xc}$ IS NOT *JUST* EXCHANGE AND CORRELATION



For a 2-electron system,  $\psi(\vec{r}) = \sqrt{\rho(\vec{r})}$  (1)

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

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

Atom	$\Delta T$ (eV)
H <sup>-</sup>	0.8
He	1.0
Li <sup>+</sup>	1.1
Be <sup>2+</sup>	1.1
Li	1.7
Be	2.0

\*

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



## NON-INTERACTING $v$ -REPRESENTABILITY (NIVR)



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.\*\*

---

\* M. Levy, *Phys. Rev. A* **26**, 2100 (1982).

\*\* See M.E. Casida and M. Huix-Rotllant, *Annu. Rev. Phys. Chem.* **63**, 287 (2012).



## LOCAL DENSITY APPROXIMATION (I)



Walter KOHN

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

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



Lu Jeu SHAM

$$\text{with } \alpha = \frac{2}{3} \quad (3)$$

$$\text{Originally Slater had } \alpha = 1 \quad (4)$$

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



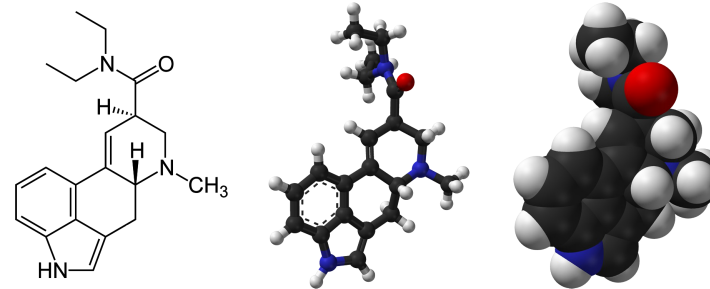
John SLATER



## 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 exceptions.***

---

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



## SO HOW DO YOU EXPECT THE LDA TO WORK?



“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



## GEOMETRIES AND FREQUENCIES NOT BAD. BUT SERIOUS OVERBINDING!

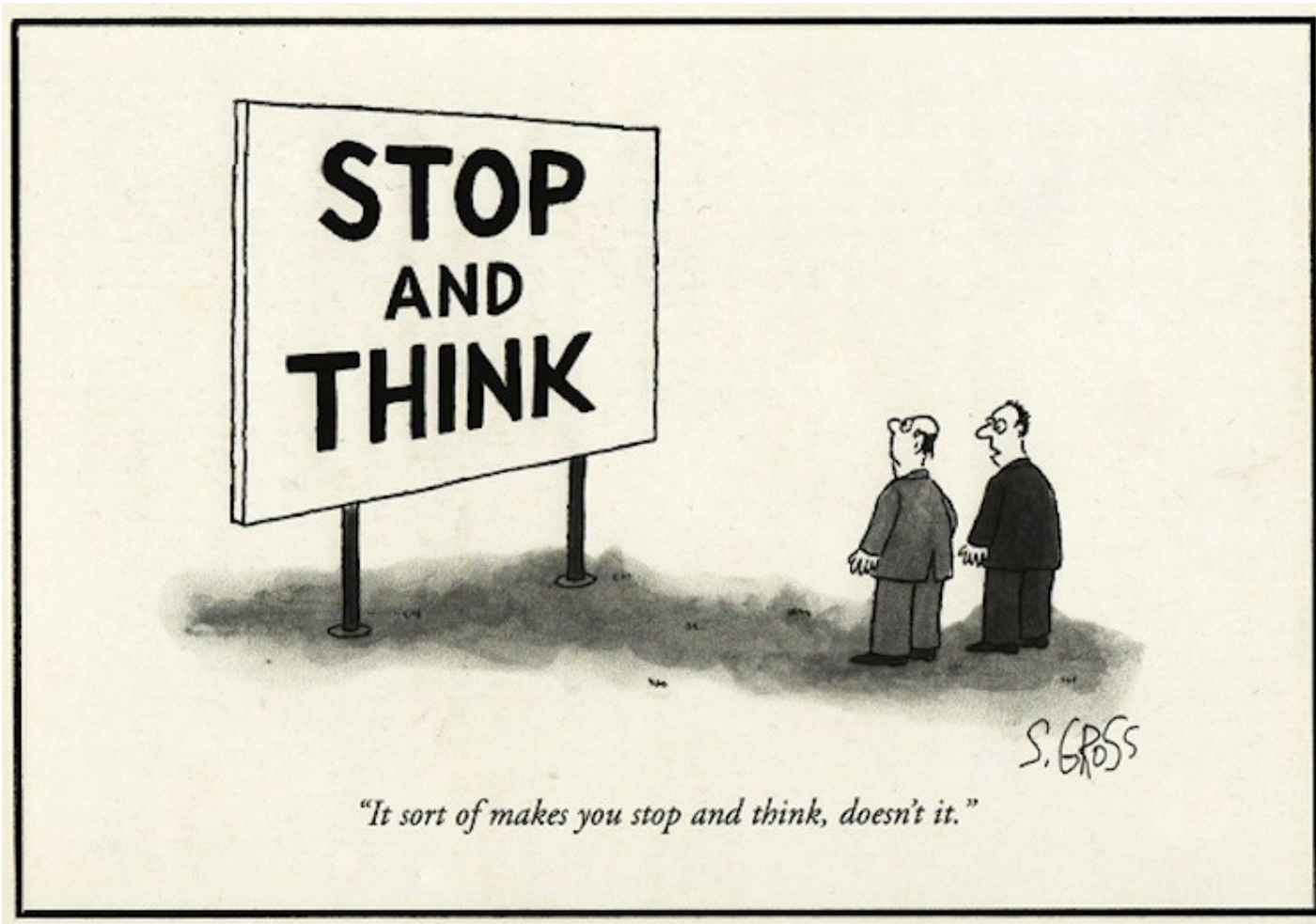


**1 eV = 23.06 kcal/mol** “Chemical accuracy” is 1 kcal/mol

TABLE I. LDA spectroscopic constants.

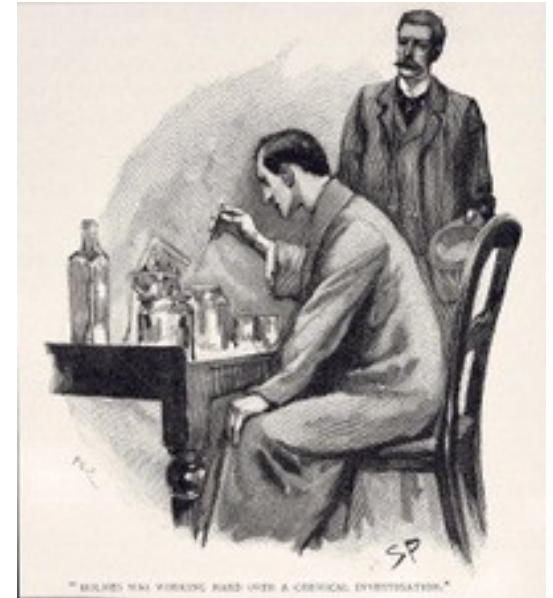
	$r_e$ (bohrs)		$D_e$ (eV)		$\omega_e$ (cm <sup>-1</sup> )	
	Expt.	LDA	Expt.	LDA	Expt.	LDA
H <sub>2</sub>	1.40	1.45	4.8	4.9	4400	4190
Li <sub>2</sub>	5.05	5.12	1.1	1.0	350	330
B <sub>2</sub>	3.00	3.03	3.0	3.9	1050	1030
C <sub>2</sub>	2.35	2.35	6.3	7.3	1860	1880
N <sub>2</sub>	2.07	2.07	9.9	11.6	2360	2380
O <sub>2</sub>	2.28	2.27	5.2	7.6	1580	1620
F <sub>2</sub>	2.68	2.61	1.7	3.4	890	1060
Na <sub>2</sub>	5.82	5.67	0.8	0.9	160	160
Al <sub>2</sub>	4.66	4.64	1.8	2.0	350	350
Si <sub>2</sub>	4.24	4.29	3.1	4.0	510	490
P <sub>2</sub>	3.58	3.57	5.1	6.2	780	780
S <sub>2</sub>	3.57	3.57	4.4	5.9	730	720
Cl <sub>2</sub>	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 !?**







# ADIABATIC CONNECTION\*

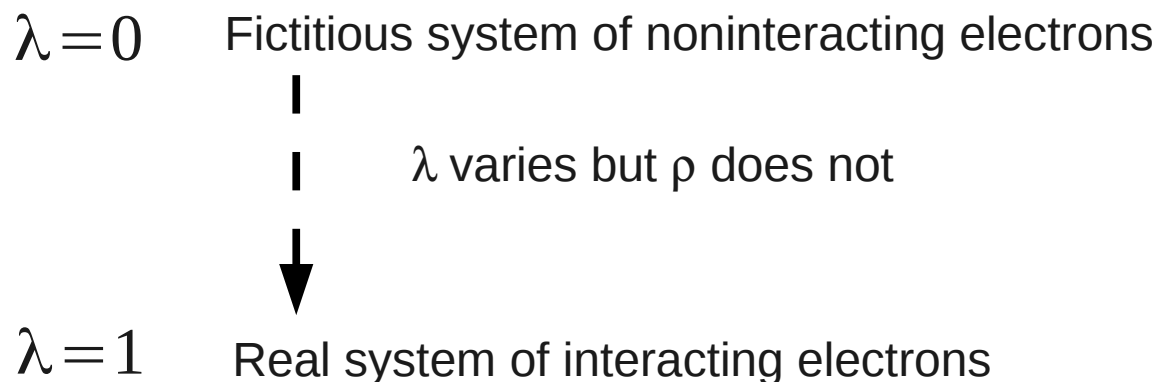
$$\hat{H} = \hat{H}_s + \lambda V_{ee} + W_\lambda[\rho]$$

Kohn-Sham  
hamiltonian

Electron  
repulsion

Local restoring  
Potential to fix  $\rho$

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



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

## ADIABATIC CONNECTION\*

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

The exchange-correlation hole,

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

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

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

Neglecting the  $\lambda$ -dependence of  $\Psi$ ,

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

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



## xc-HOLE



Only the spherical average is important,

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

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

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

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



$$\frac{y \rho_{0,0}^{xc}(\vec{r}, y)}{\sqrt{4\pi}} \quad *$$

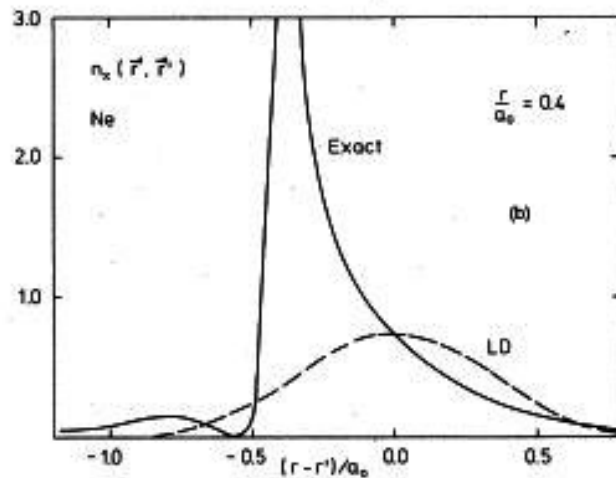
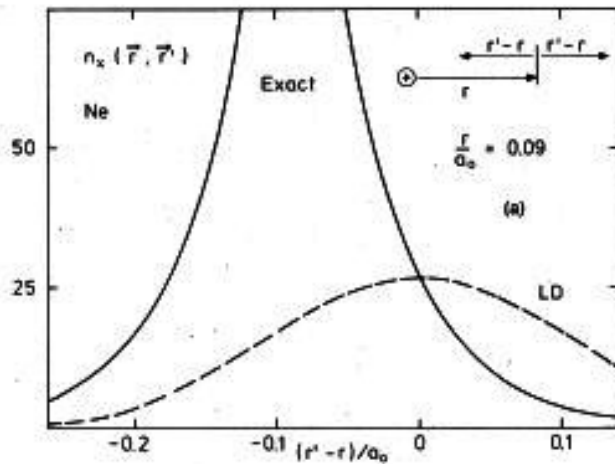


FIG. 5. Exchange hole  $n_x(\vec{r}, \vec{r}')$  for a neon atom. The full curves show exact results and the dashed curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of  $r$ .

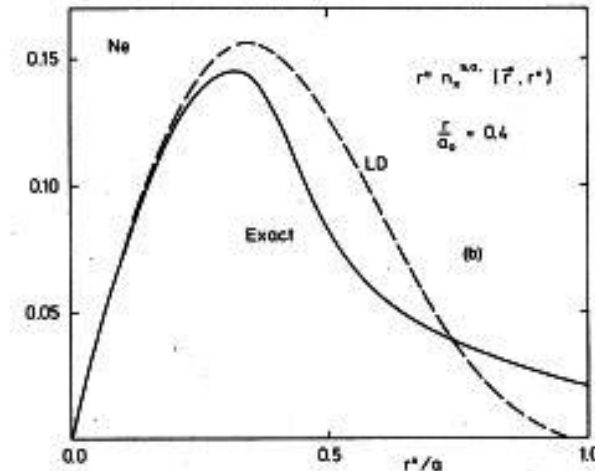
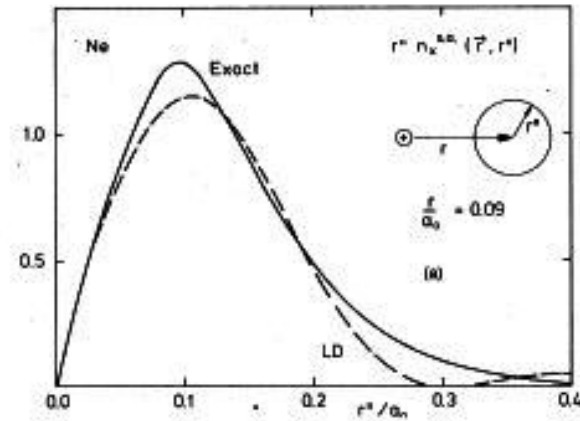


FIG. 7. Spherical average of the neon exchange hole [Eq. (17)] times  $r'^2$  for (a)  $r=0.09$  a. u. and (b)  $r=0.4$  a. u. The full curves give the exact results and the dashed curves are obtained in the LD approximation.

\* 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



## OPTIMIZED EFFECTIVE POTENTIAL (OEP) MODEL (I)



Require

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

and

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

to produce the same charge density,

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

where

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

---

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.

## OPTIMIZED EFFECTIVE POTENTIAL (OEP) MODEL (II)



Now

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

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

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

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

Similarly

$$\Delta \psi_i(1) = \psi_i^{HF}(1) - \psi_i^{KS}(1) \quad (2d)$$

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

## OPTIMIZED EFFECTIVE POTENTIAL (OEP) MODEL (III)



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

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

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

with

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

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).





# LINEAR RESPONSE APPROXIMATION



LETTERS TO THE EDITOR

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## A Variational Approach to the Unipotential Many-Electron Problem

R. T. SHARP AND G. K. HORTON  
University of Alberta, Edmonton, Canada  
(Received January 28, 1953)

SLATER has pointed out the advantage of an approximate solution of the many-electron problem in which all the electrons move in the same potential field. He gave us one technique for constructing such a potential by averaging the Hartree-Fock potentials<sup>1</sup> of the various electrons in a certain way. For the exchange part of the potential, he gave

$$\frac{\sum_{i,j} \psi_i^*(r_j) \psi_j(r_i) \int d\tau_1 \psi_i^*(\tau_1) \psi_j(\tau_1) / r_{1i}}{[\sum_i \psi_i^*(r) \psi_i(r)]}$$

Slater's work suggests the following variational problem. Find that potential, the same for all the electrons, such that when it, and consequently the wave functions, are given a small variation, the energy of the system remains stationary. A Slater determinant constructed from the one-electron wave functions is used as the wave function of the system.

The potential which fulfills this prescription turns out to be

$$V(r) = V_c(r) + \sum_i \int d\tau_1 \frac{\psi_i^*(\tau_1) \psi_i(\tau_1)}{r_{1i}} - \beta V(r), \quad (1)$$

where the exchange potential  $\beta V(r)$  is the solution of the integral equation

$$\int d\tau_1 \beta V(\tau_1) \sum_i \frac{\psi_i^*(\tau_1) \psi_i(r) \psi_i(r) \psi_i^*(\tau_1)}{E_i - E_0} - \sum_{i,j} \sum_{k,l} \int d\tau_1 \frac{\psi_i^*(\tau_1) \psi_j(\tau_1) \psi_k(r) \psi_l^*(r)}{E_i - E_0} \int d\tau_2 \frac{\psi_k^*(\tau_2) \psi_l(\tau_2) \psi_j(\tau_2) \psi_i^*(\tau_2)}{r_{2k}}$$

Here  $V_c(r)$  represents the external field acting on the electrons. The  $\psi_i$ 's are the solutions of the Schrödinger equation:

$$-\nabla^2 \psi_i(r) + V(r) \psi_i(r) = E_i \psi_i(r). \quad (2)$$

Greek subscripts refer to all bound solutions of Eq. (2). Roman subscripts refer to occupied levels only. Hartree units<sup>2</sup> are used throughout.

The integral equation (2) can be solved approximately if  $E_i$  is replaced by a suitable average value  $\bar{E}_i$ . The approximate solution<sup>3</sup> is

$$\beta V(r) = \frac{\sum_i \frac{\psi_i^*(r) \psi_i(r)}{E_i - \bar{E}_i} \int d\tau_1 \frac{\psi_i^*(\tau_1) \psi_i(\tau_1)}{r_{1i}}}{\left( \sum_i \frac{\psi_i^*(r) \psi_i(r)}{E_i - \bar{E}_i} \right)}$$

Slater's result is obtained from Eq. (4) by making the further approximation that all the  $E_i - \bar{E}_i$  are equal.

Equation (4) is being applied to the quadrivalent state of the carbon atom.

<sup>1</sup>J. C. Slater, *Phys. Rev.*, **35**, 207 (1935).  
<sup>2</sup>Actually the potentials averaged differ from the Hartree-Fock potentials in that their spin-orbitals include Slater's spin functions.  
<sup>3</sup>Horton, *Proc. Roy. Soc. (London)*, **44B**, 444 (1949).  
<sup>4</sup>After including  $E_0$  by  $\bar{E}_i$ , the summation over  $i$  are allowed to include  $i=0$ . This implies adding to both sides of the equation terms which would be equal if the Pauli exchange potential did not differ from Eq. (2).

## The Electronic Structure of Diamond

G. C. HAZZ  
Department of Theoretical Chemistry, University of Cambridge,  
Cambridge, England  
(Received January 28, 1953)

IN a letter under the above title Herring<sup>1</sup> has made several references to a paper of mine<sup>2</sup> in a way likely to cause misunderstanding. He claimed the method used as a "tight-binding

approximation" and suggested that it was inappropriate for valence bands. I should like to make clear that the method of this paper is an equivalent orbital one, first applied to the electronic structure of a solid in that paper, and has no connection, other than an unfortunate superficial resemblance, with any tight-binding method.

The equivalent orbital method assumes that the wave function for the crystal is a determinant of orbitals. These orbitals are taken as the best possible ones. The energy contours are thus derived using only the transformation properties of such a wave function and the symmetry of the diamond lattice. The second assumption, that only first neighbor equivalent orbitals interact, is not essential to the argument. It can be justified theoretically and empirically but could be relaxed if necessary. The generality of the argument means that the results apply equally to diamond, silicon, or germanium. The difference between these lies in the values of the parameters  $a$  and  $b$  and in the presence of extra inner shells.

This equivalent orbital method applies only to the valence bands of diamond, because it is concerned only with the orbitals occupied in the ground state. It says nothing about the conduction bands and, indeed, without some further assumption, those bands cannot even be defined.

In practice all other methods of treating the electronic structure of solids make assumptions like those above and several others in addition. Other methods are analytical, but this is algebraic and so involves no approximate expansions of the orbitals, whether as atomic orbitals or plane waves, as approximate core or exchange potentials, and no difficulties with overlap integrals or boundary conditions.

<sup>1</sup>J. Herring, *Phys. Rev.*, **88**, 1278 (1943).  
<sup>2</sup>G. C. Hazz, *Phil. Mag.*, **47**, 441 (1953).

## Lattice Sums: The Validity of Evjen's Method

I. D. C. GOSWAMI<sup>1</sup>  
Royal Society Mond Laboratory, Cambridge, England  
(Received October 6, 1952)

A PARADOX appears in Evjen's method of evaluating the Madelung constant for the cesium chloride lattice.<sup>2</sup> Kristman and Roy<sup>3</sup> discuss it, according to the choice of unit cell, and giving a general condition for the cell to satisfy. The implication is that the method otherwise fails. Evjen's own argument is no doubt wrong, but it is easily corrected, and the method is actually valid without restriction.

When only finite arrays of charges are considered at each stage, all quantities evaluated are defined by finite sums over the charges, in which we are free to rearrange the terms. In principle, a definite bounding surface exists before such rearrangement, but the principle need not always be explicit. Planes, unit cells, and subcells have all been used to group the charges during summation (Sherman<sup>4</sup> and Frank<sup>5</sup> give detailed references). However, any convenient grouping will in general leave a remainder, of incomplete groups, at the surface. This residual layer may change if the grouping alters, but will prove negligible in determining the energy of a complete group, provided the groups have no dipole moments, and we do not choose one near the surface. The lattice potential is, however, sensitive to surface structure, so that the separate contributions of such ions may be changed, although their sum will not. This resolves the paradox in Evjen's paper.<sup>6</sup>

He groups the charges by unit cells (one pair of unlike charges in each), choosing a cube with one charge at the center and the other shared by the eight corners. The error is also a cube, consisting of  $8^3$  complete cells, and having a charge of given sign at the center, where Evjen distributes the potential. As  $n$  is odd or even, this charge lies at the center or the corner of a cell; the consequent charges alternate correspondingly in sign, and the potential is bound to oscillate between two asymptotically convergent

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

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

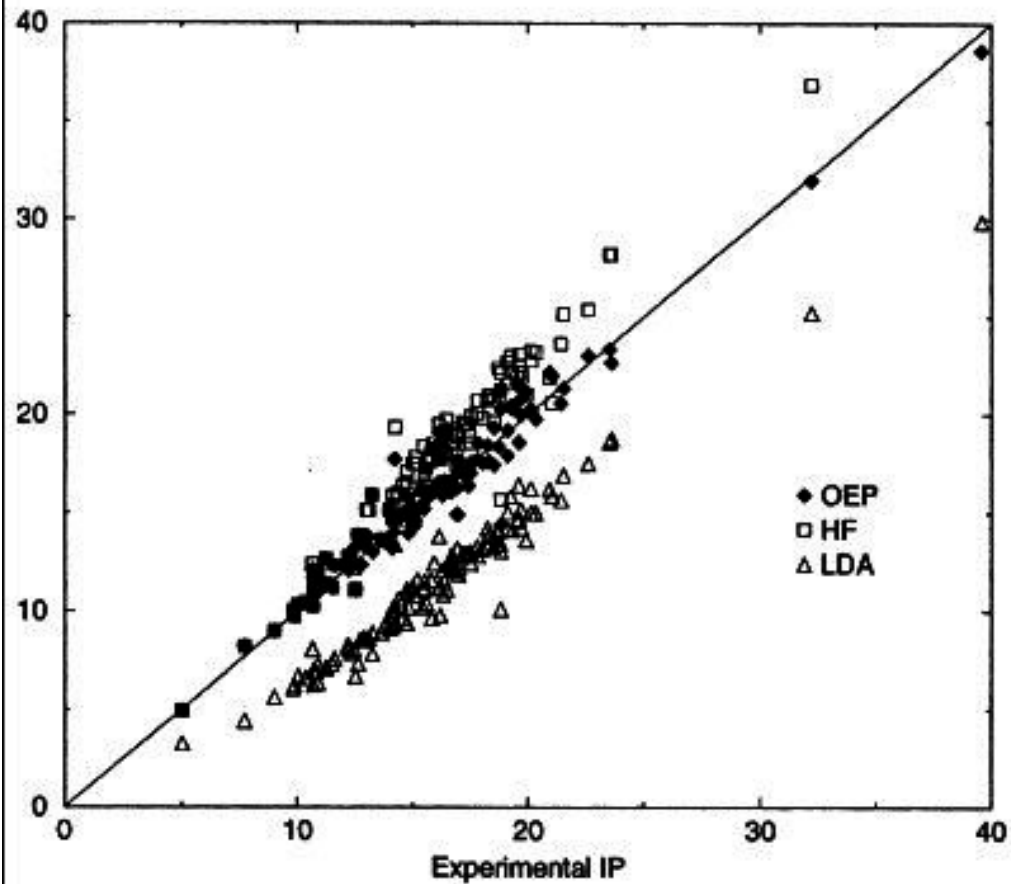
$$\epsilon_i^{KS} \leftarrow \epsilon_i^{HF} \quad (2)$$

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

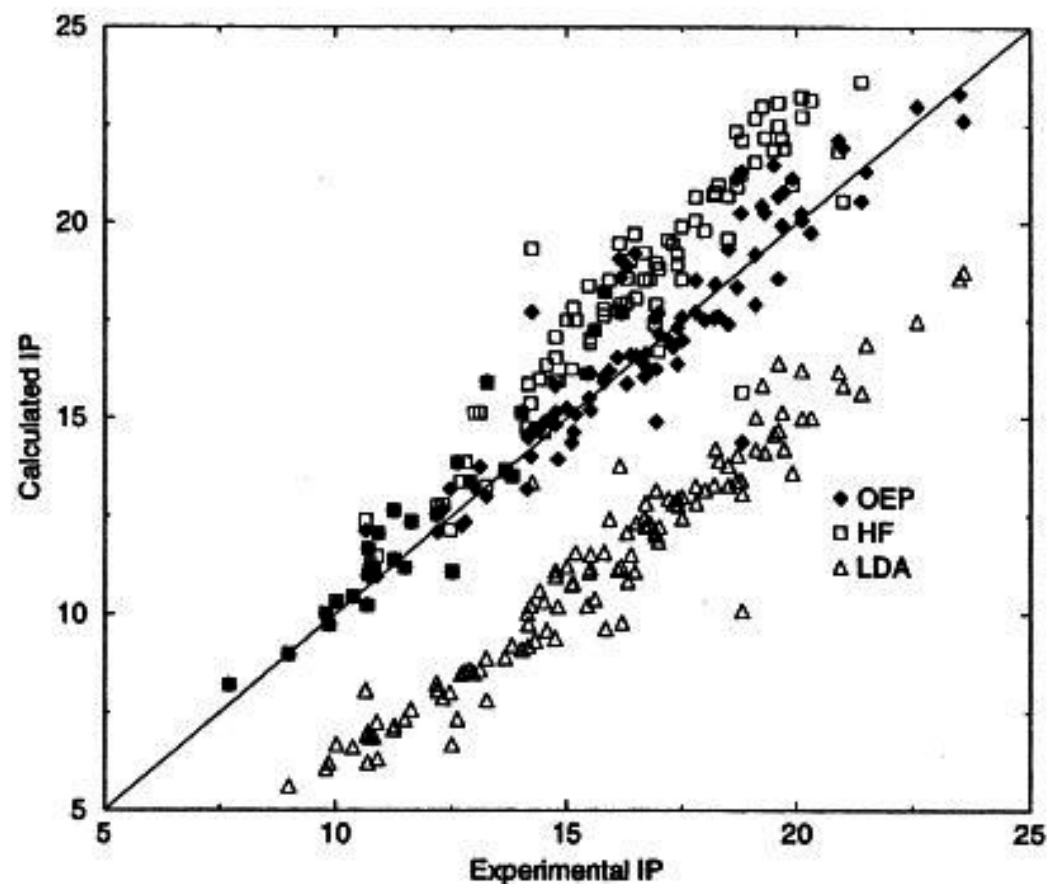
This is *almost* the same thing as asking for  $v_x$  whose orbitals produce the Hartree-Fock charge density.

# THE OEP IMPROVES KOOPMANS' THEOREM

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).

## RECOVERY OF SLATER'S PICTURE



Average denominator approximation

$$\begin{aligned}\chi(1,1';2,2') &= \sum_{i,j} \frac{n_i - n_j}{\epsilon_i^{KS} - \epsilon_j^{KS}} \psi_j^{KS}(1) \psi_i^{KS*}(1') \psi_i^{KS*}(2) \psi_j^{KS}(2') \\ &\approx -\frac{2}{\Delta} \sum_i^{unocc} \sum_j^{occ} \psi_j^{KS}(1) \psi_i^{KS*}(1') \psi_i^{KS*}(2) \psi_j^{KS}(2')\end{aligned}$$

Leads to

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

## RECOVERY OF SLATER'S PICTURE



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

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

Krieger-Li-Iafrate (LHF) approximation\*\*

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

\* 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).

## RECOVERY OF SLATER'S PICTURE



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

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

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

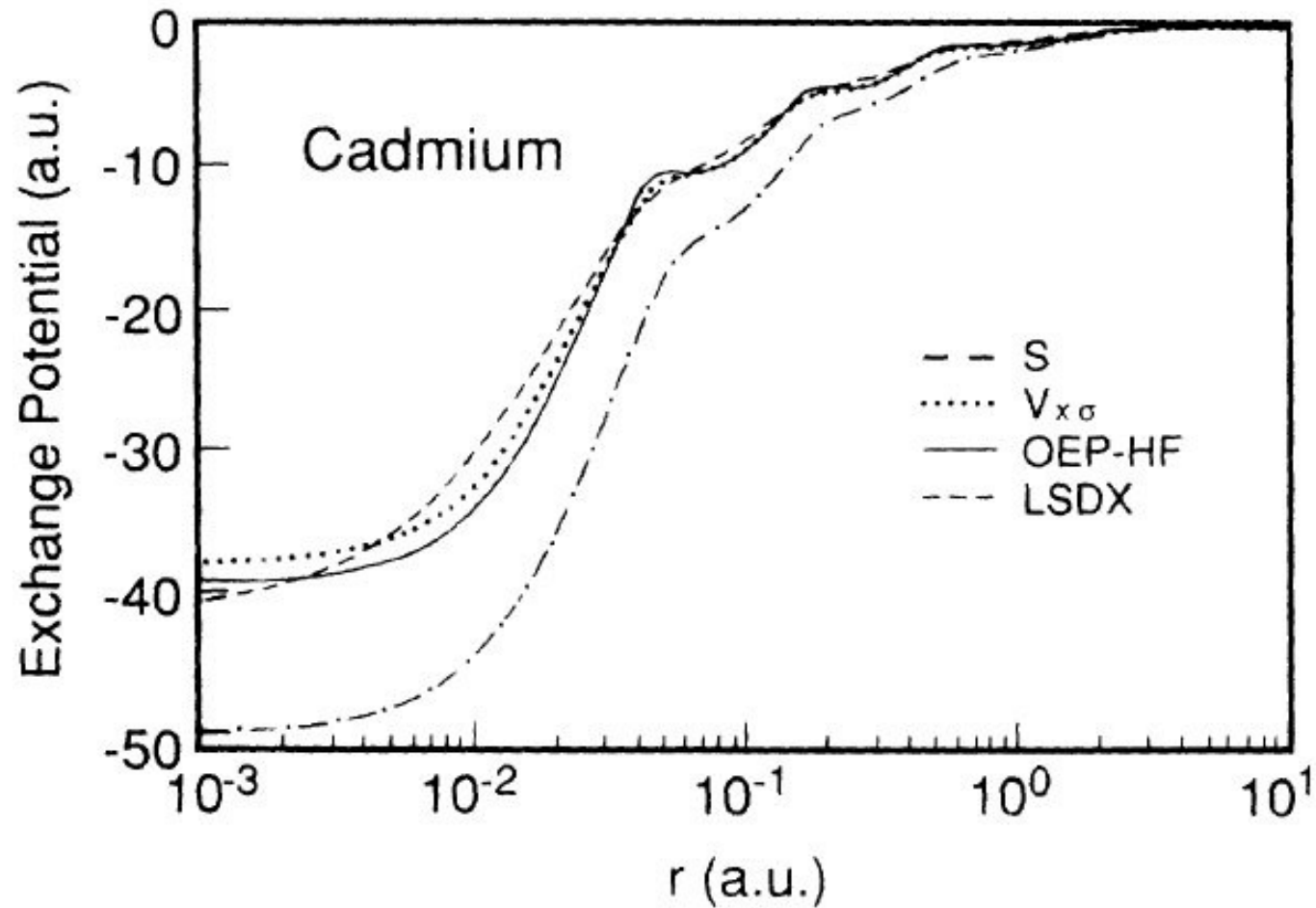
$$\left(v_x(1) - \hat{\Sigma}_x\right) \psi_i(1) = \left(\epsilon_i^{KS} - \epsilon_i^{HF}\right) \psi_i(1) \quad (3)$$

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

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

$$v_x(1) = \underbrace{\frac{\sum_i n_i \psi_i^*(1) \hat{\Sigma}_x \psi_i(1)}{\rho(1)}}_{\text{Slater}} + \underbrace{\frac{\sum_i n_i \left(\epsilon_i^{KS} - \epsilon_i^{HF}\right) |\psi_i(1)|^2}{\rho(1)}}_{\text{derivative discontinuity}} \quad (6)$$

## RECOVERY OF SLATER'S PICTURE



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

- I. Chemistry vs Physics
- II. Variational Calculus
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## 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.

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

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

$$+ \int \frac{\partial f}{\partial \rho''(y)} \delta\rho''(y) dy + \dots \quad (2b)$$

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

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

So

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

After much manipulation, Kohn and Sham arrive at

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

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

+ 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

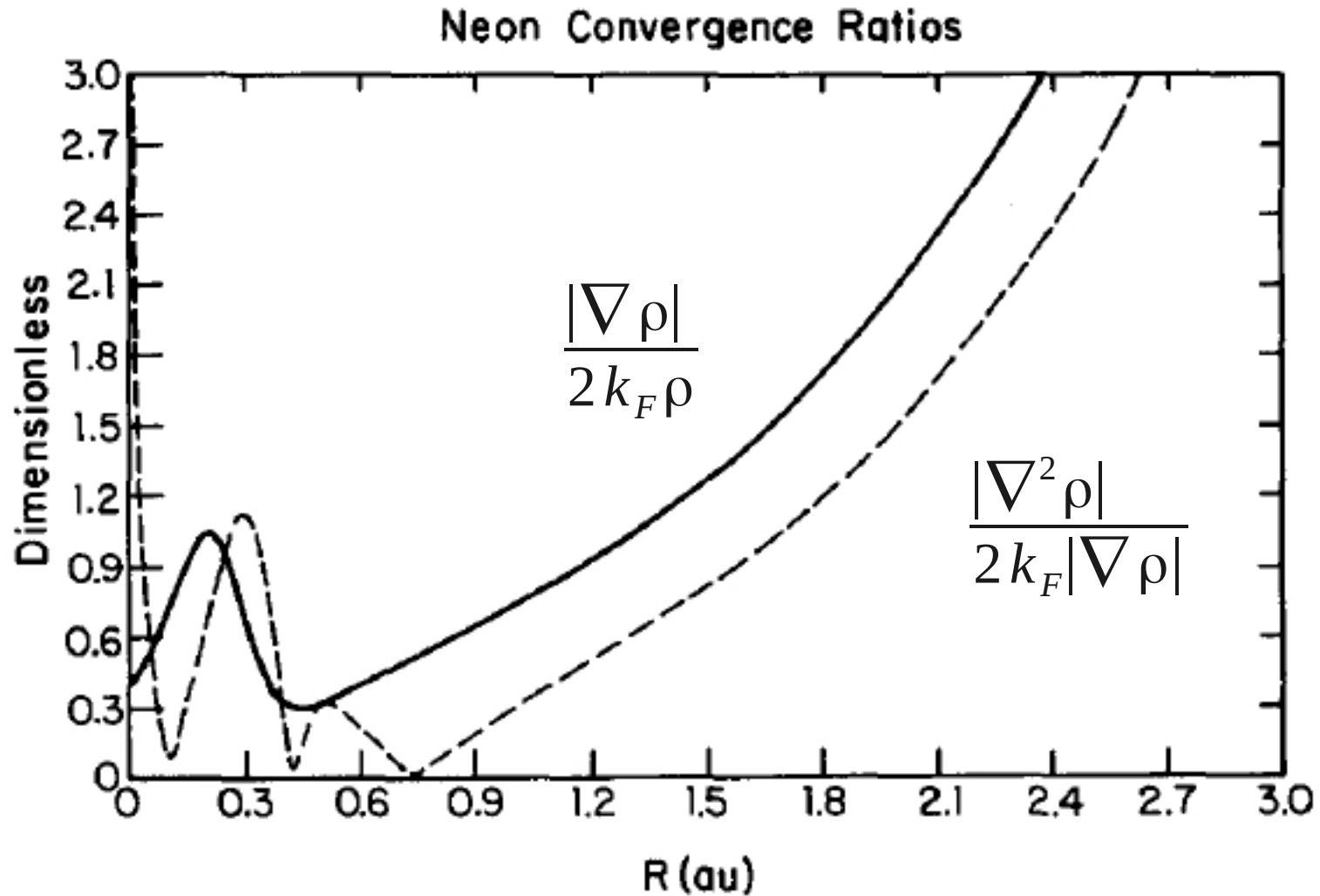
$$\int \rho(\vec{r}) d\vec{r} = N \quad \Rightarrow \quad \begin{aligned} \rho &\sim \frac{1}{L^3} \\ \vec{\nabla} \rho &\sim \frac{1}{L^4} \\ \nabla^2 \rho &\sim \frac{1}{L^5} \end{aligned}$$

For proper convergence, we need

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

all of which scale as  $1/L$ .

# FAILURE AT THE SURFACE OF ATOMS (AND JELLIUM EDGES)



E.W. Pearson and R.G. Gordon, *J. Chem. Phys.* **82**, 881 (1985)

## X $\alpha$ $\beta$ Functional\*

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

$$\alpha = \frac{2}{3} \quad \textit{ab initio}$$

$$\beta = 0.0055 \quad \text{Fit to Xe}$$

---

\* 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.

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

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

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

David C. Langreth

*Rutgers University, New Brunswick, New Jersey 08903*

John P. Perdew

*Tulane University, New Orleans, Louisiana 70118*

(Received 6 November 1979)

p. 5469

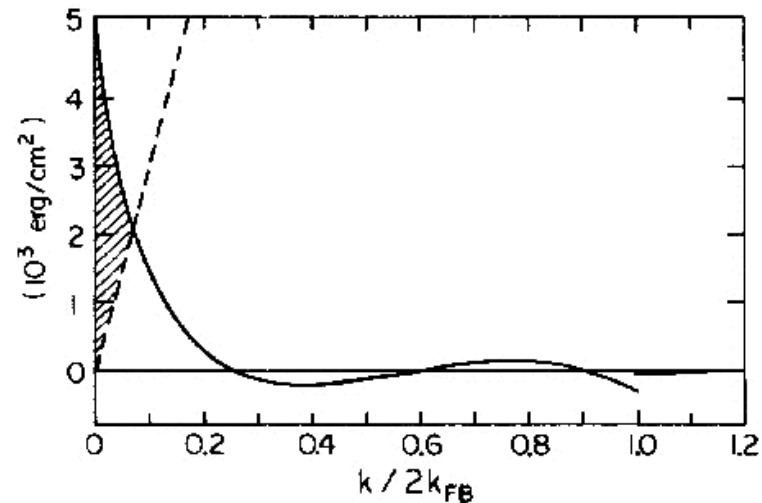


FIG. 7. Wave-vector decomposition of the gradient component of the surface energy  $\delta_{\text{gr}}\gamma$  for the "Fermi-function" density profile. The bulk density corresponds to  $r_s = 2.07$ . The broken line is the exact asymptote.

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

cutoff

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

Back transforming gives finally

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

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



# BECKE'S INTERPOLATION\*

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

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

What happens in  $X\alpha\beta$ ?  $\rho(\vec{r}) \sim c e^{-\zeta r} \quad (3)$

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

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

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

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

## BECKE'S 1988 EXCHANGE FUNCTIONAL

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

$$\longrightarrow \left\{ \begin{array}{l} X \propto \beta; x_{\sigma} \ll 1 \quad (2a) \\ -\frac{1}{2r}; x_{\sigma} \gg 1 \quad (2b) \end{array} \right.$$

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

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

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

	Exact	LDA <sup>a</sup>	PW <sup>b</sup>
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

<sup>a</sup>LDA: Eq. (1).

<sup>b</sup>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!

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## ADIABATIC CONNECTION\*

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

The exchange-correlation hole,

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

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

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

Neglecting the  $\lambda$ -dependence of  $\Psi$ ,

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

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

## BECKE'S HYBRID FUNCTIONAL

This suggests

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

(Though Becke was actually thinking ...

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

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

B3PW91 functional\*\*

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

---

\* 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 <sup>a</sup>	Eq. (2)	GC <sup>b</sup>
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

<sup>a</sup>G2: Gaussian-2 theory (Refs. 13 and 14).

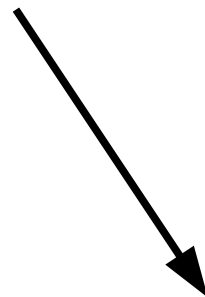
<sup>b</sup>GC: Gradient-corrected DFT of Ref. 5.



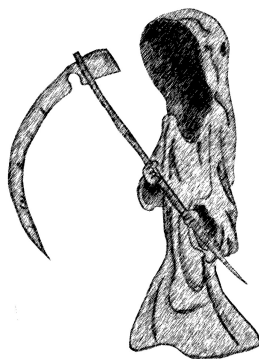
# KS RIP ... LONG LIVE GENERALIZED KS (GKS)



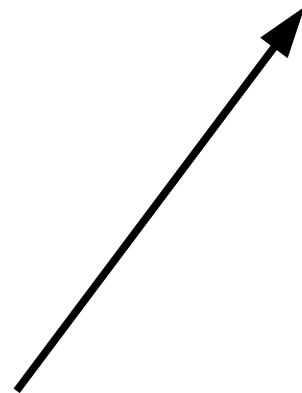
Born as Thomas-Fermi theory



Peter M. W. Gill, "Obituary: Density-Functional Theory (1927-1993)",  
*Aust. J. Chem.* **54**, 661-662 (2001).



Died when Axel Becke introduced  
hybrid functionals



## 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

**THEORETICAL  
CHEMISTRY  
HEAVEN**

# Jacob's Ladder

MBPT *ab initio* DFT

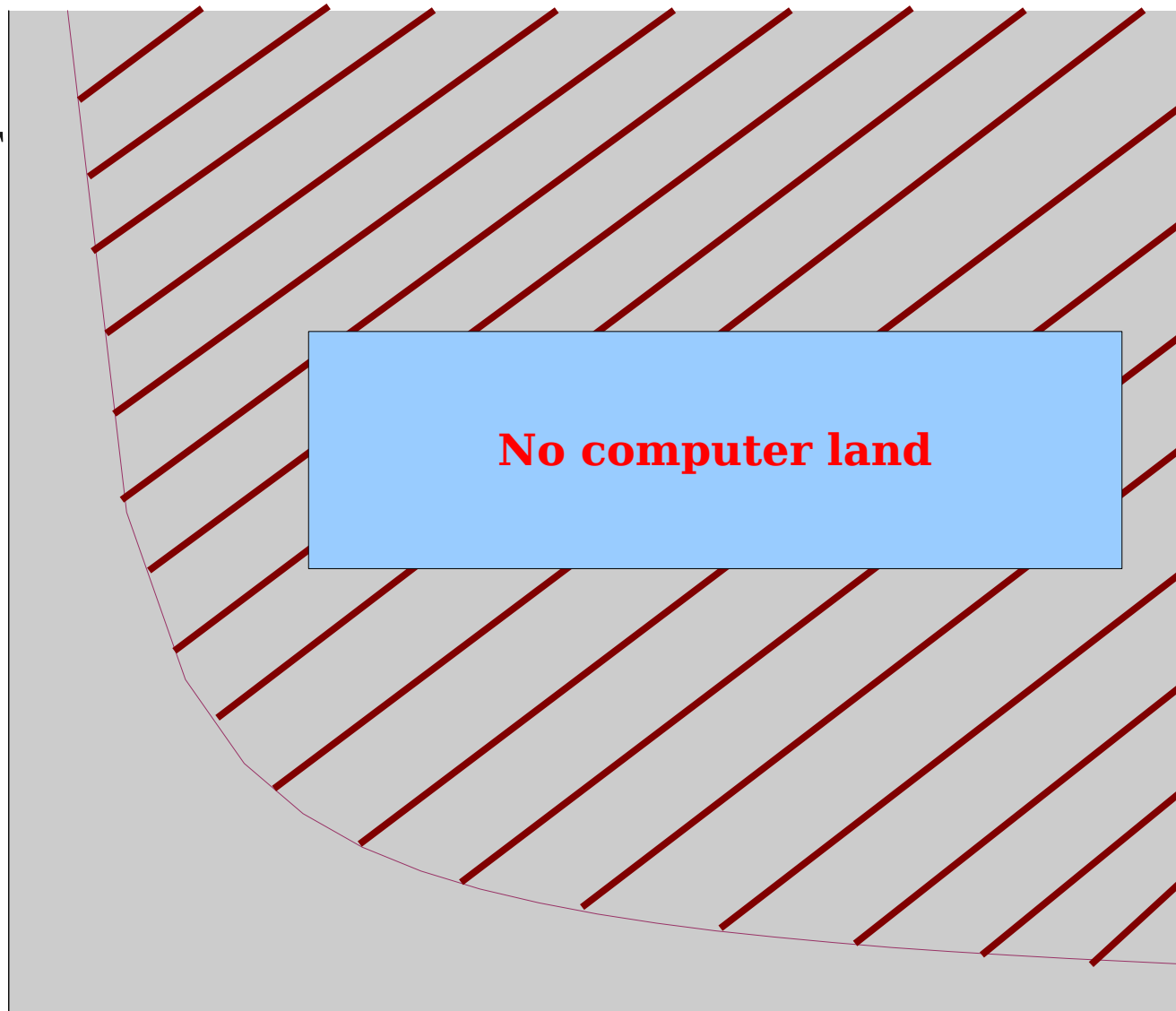
$\hat{K}_x^{HF}$  hybrid/OEP

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

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

**Pure DFT**

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



**HARTREE WORLD**

Molecular size →

\* or include  $\nabla^2 \rho$

Modern GKS is

- less and less B3LYP
- more and more RSH

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

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:

- ◆ 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. Tellgren, 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

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

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

Electron repulsion energy

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

Correlation energy

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

### 5<sup>th</sup> 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.

- 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



**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/>
  - ★ In 2012, PBE came in first
  - ★ In 2011, PBE0 came in first
  - ★ In 2010, PBE0 came in first

*Does this really mean anything !?*

