

Density Functional Theory for the Correlated

R. O. Jones

*Peter-Grünberg-Institut PGI-1
Forschungszentrum Jülich
52425 Jülich, Germany*

E-mail: `r.jones@fz-juelich.de`

`https://pgi-jcns.fz-juelich.de/~jones/R.Jones.shtml`

Autumn School on Correlated Electrons, 21 September 2020:

Where does density functional theory fit in this discussion?

Preface

Density-functional theory (DFT) is considered the Standard Model of solid-state physics. The state-of-the-art approximations to DFT, the local-density approximation (LDA) or its simple extensions, fail, however, even qualitatively, for strongly-correlated systems. When correlations are strong, electrons become entangled and novel properties emerge. Mott-transitions, Kondo- and heavy-fermion behavior, non-conventional superconductivity and orbital-order are just some examples of this emergent behavior.

The realistic description of emergent properties is one of the grand-challenges of modern condensed-matter physics. To understand this physics beyond the Standard Model, non-perturbative many-body techniques are essential. Still, DFT-based methods are needed to devise materials-specific Hamiltonians for strong correlations. Mastering these novel techniques requires a vast background, ranging from DFT to model building and many-body physics.

:

Eva Pavarini, Erik Koch, Frithjof Anders, and Mark Jarrell

August 2012

Lecture Notes of the Autumn School Correlated Electrons: From Models to Materials,
3-7 September 2012

“Emergence vs. Reductionism”:

“The starting point, to which all explanations can be traced, is what I mean by a final theory”.

S. Weinberg: *Dreams of a Final Theory: The Scientist’s Search for the Ultimate Laws of Nature*

(PWA) “The only really *fundamental* science is the search for the ultimate constituents of matter.”

“What really is the problem is called ‘broken symmetry’: the underlying laws have a certain symmetry and simplicity that is not manifest in the consequences of these laws. To put it crudely, a simple atom of gold cannot be shiny and yellow and conduct electricity: Metallicity is a property with meaning only for a macroscopic sample ...”

P. W. Anderson, *More and Different: notes from a thoughtful curmudgeon*”, p. 134-139.

curmudgeon: (1577) churlish or miserly fellow

churl: 2. (M.E.) Ill-bred fellow, surly or niggardly person

surly: Uncivil, given to making rude answers, showing unfriendly temper, churlish

Concise Oxford English Dictionary

In density functional seminars one can hear strange expressions:

ab initio **first principles** TD-DFT *Hartree-Fock approximation*
exchange-correlation hole *strongly correlated systems* excited states
“ ... parameter-free calculations ... with the E_{XC} parameterization of ... ” **LSD, PBE,**
B3LYP, BLYP, PBE0, PBEsol, TPSS, HSE06, SCAN, **LMTO, NMTO, EMTO**
..... FLEUR KKR-GF CPMD TURBOMOLE fhi96 ABINIT Gaussian VASP
KKRnano JDFT ...

One almost *always* hears:

*The density functional formalism was derived by **Hohenberg and Kohn** in 1964 and extended by **Kohn and Sham** in 1965*

- **Look back from 1990 at the history of DF and related theories**
- **Developments since 1990, present status, future?**

Some references:

R. O. Jones and O. Gunnarsson:

The density functional formalism, its applications, and prospects,
Rev. Mod. Phys. **61**, 689 (1989)

R. O. Jones:

Density functional theory: Its origins, rise to prominence, and future,
Rev. Mod. Phys. **87**, 897 (2015)

R. O. Jones:

Bonding in phase change materials: concepts and misconceptions,
J. Phys.: Condens. Matter **30**, 153001 (2018)

Why 1990?

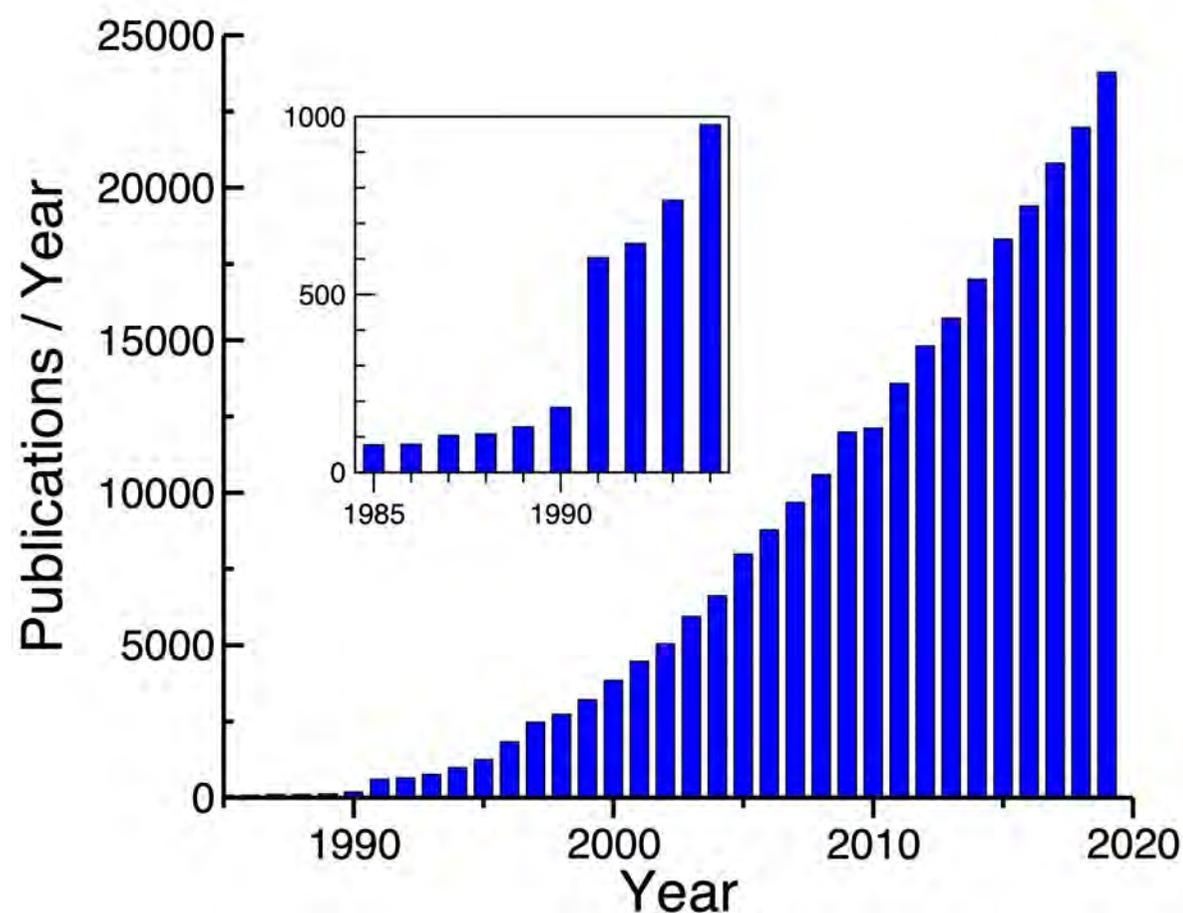


Figure 1: Number of publications per year (1975-2012) on topics “density functional” and “DFT”, according to ISI Web of Knowledge (May 2020). Inset shows data near 1990 on an expanded scale [Ph. Mavropoulos, Φ. Μαυρόπουλος (private communication)]

N.B.: **Chemical** applications outweigh **materials** applications up to 2012.
K. Burke, J. Chem. Phys. **136**, 150901 (2012).

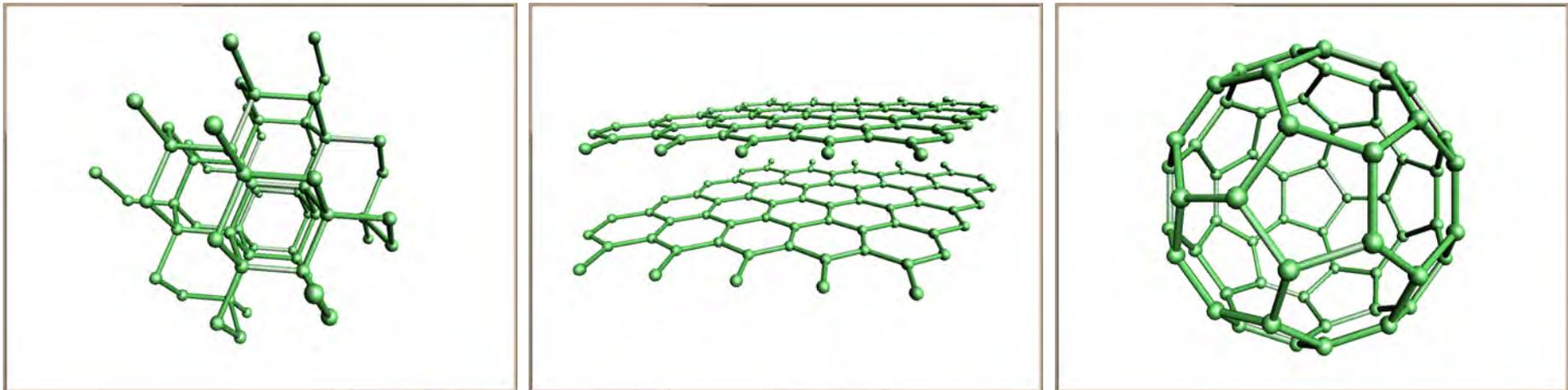
Geometric structure:

Central problem in condensed matter physics, chemistry, biology

Relationship between structure and function

“If you want to study **function**, study **structure**”

Francis Crick, *What mad pursuit*, (Penguin, 1988), p. 150.

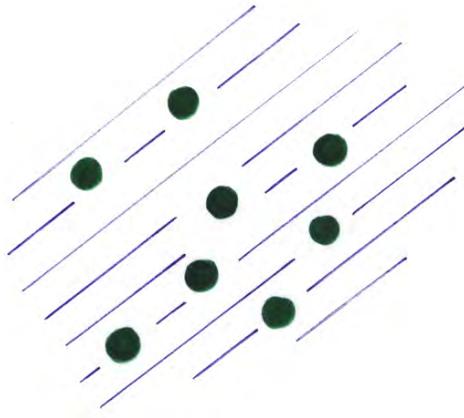


Forms of carbon with quite different properties

Geometric structure: Role of theory

Problem very simple to state:

(1) Calculate the total energy E for a single geometry



(2) Repeat this calculation for *all possible structures* \longrightarrow energy surface;

Minima \longrightarrow stable (and metastable) isomers,

Energy variation between minima \longrightarrow heats and paths of reactions

Two distinct problems:

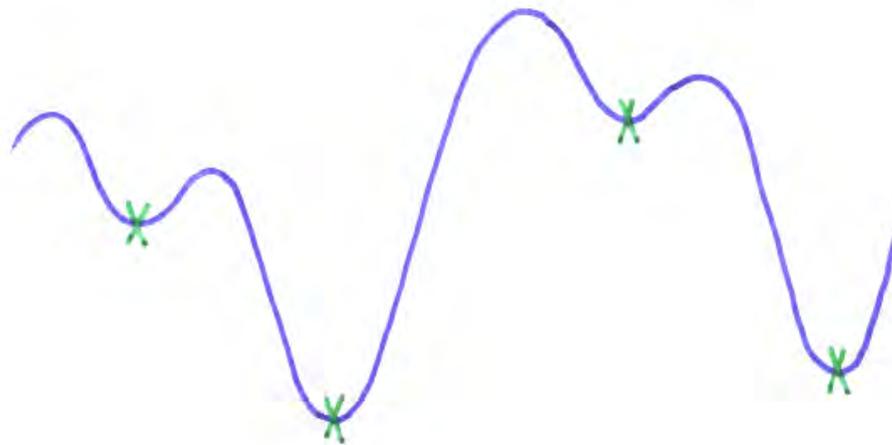
(1) **Energy calculation:** traditionally via wave function Ψ :

$E = \langle \Psi | \hat{H} | \Psi \rangle$, where \hat{H} contains all interactions in the system.

Numerical difficulty grows very rapidly with increasing number of electrons.

(2) **Number of possible structures** (isomers) grows *exponentially* with increasing number of atoms.

e.g., for a given molecule or cluster:



Energy calculations via **density functional (DF)** theory are effective for many systems

Number of isomers:

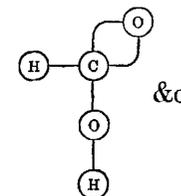
A. Crum Brown, *On the theory of isomeric compounds*, Trans. Roy. Soc. Edin. **23**, 707 (1864)

XXXVII.—*On the Theory of Isomeric Compounds.*

By Dr. A. CRUM BROWN.

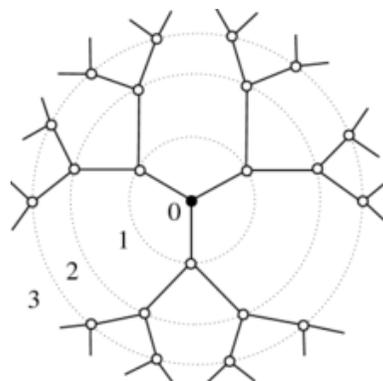
IN the following remarks I intend to confine myself to the consideration of those compounds which have not only the same composition per cent., and the same molecular weight, but also the same constitutional formula. Such compounds may be termed absolutely isomeric. As the constitutional formula of few substances is fully known, this class is of course a small one, or rather there are few substances of which we can certainly say that they belong to this class.

* I may here shortly explain the graphic notation which I employ to express constitutional formulæ, and by which, it is scarcely necessary to remark, I do not mean to indicate the physical, but merely the chemical position of the atoms. An atom is represented by its usual symbol, surrounded by a circle with as many lines proceeding from it as the atom contains equivalents, thus an uniequivalent atom is represented by $(A)-$, a bivalent atom by $-(B)-$ or $(B)-$, and so on of the others. When equivalents mutually saturate one another, the two lines representing the equivalents are made continuations of one another, thus water is $(H)-(O)-(H)$. Formic acid



This method seems to me to present advantages over the methods used by Professors Kekulé and Erlenmeyer; and while it is no doubt liable, when not explained, to be mistaken for a representation of the physical position of the atoms, this misunderstanding can easily be prevented.

A. Cayley, *A theorem on trees*, Quart. J. Pure Appl. Math, **23**, 376 (1889).



The number of trees with $(n + 1)$ knots is $(n + 1)^{n-1}$

Solutions of the Schrödinger equation (1926): Variational principle

Approximate many-electron wave function: $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$, where \vec{r}_i : particle coordinates and spins.

D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89, 111 (1928)

Separation of $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ into *core* and *valence* components, each determined from a “self-consistent field” of the others.

V. Fock, Z. Phys. **61**, 126 (1930)

J. C. Slater, Phys. Rev. **35**, 210 (1930)

“**Hartree equation**” can be derived from the trial function: $\Psi(\vec{r}_1, \vec{r}_2, \dots) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \dots\dots\dots$

Fermi statistics incorporated by replacing **product** of single-particle functions $\psi_i(\vec{r}_i)$ by a **determinant**

—→ **Hartree-Fock equations** (1930)

Linear combination of determinants

—→ **Configuration Interaction, CI**

Quantum Monte Carlo (QMC): accurate, perfectly parallelizable, computationally expensive

Thomas-Fermi (TF) Approximation :

L. H. Thomas, Proc. Camb. Phil. Soc. **23**, 542 (1927)

The calculation of atomic fields. By L. H. THOMAS, B.A.,
Trinity College.

[Received 6 November, read 22 November 1926.]

The theoretical calculation of observable atomic constants is often only possible if the effective electric field inside the atom is known. Some fields have been calculated to fit observed data* but for many elements no such fields are available. In the following paper a method is given by which approximate fields can easily be determined for heavy atoms from theoretical considerations alone.



E. Fermi, Z. Physik **48**, 73 (1928)

Eine statistische Methode zur Bestimmung einiger
Eigenschaften des Atoms und ihre Anwendung auf die
Theorie des periodischen Systems der Elemente.

Von E. Fermi in Rom.

Mit 1 Abbildung. (Eingegangen am 23. Februar 1928.)

Bei einem schweren Atom können die Elektronen als eine Art Atmosphäre um den Kern betrachtet werden, welche sich in einem Zustand vollständiger Entartung befindet. Man kann die Verteilung der Elektronen um den Kern angenähert durch eine statistische Methode berechnen; diese wird auf die Theorie der Bildung der Elektronengruppen im Atom angewendet. Die Übereinstimmung mit der Erfahrung ist befriedigend.



TF approximation : a density functional theory

Electrons independent fermions with Coulomb energy:

$$E_{es}[n] = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

Kinetic energy:

$$T[n] = \int d\mathbf{r} t[n(\mathbf{r})],$$

$t[n]$: K.E. density for system of *non-interacting* electrons with density n .

$$t[n] = 2 \frac{1}{(2\pi)^3} \int_{|k| \leq k_F} d\mathbf{k} \frac{\hbar^2 k^2}{2m}; \quad 2(4\pi/3)k_F^3 / (2\pi)^3 = n$$

$$T_0[n] = C_k \int d\mathbf{r} \{n(\mathbf{r})\}^{\frac{5}{3}}; \quad C_k = 3\hbar^2(3\pi^2)^{\frac{2}{3}}/10m.$$

Minimize $E[n]$ for constant electron number $N [= \int d\mathbf{r} n(\mathbf{r})]$

$$\longrightarrow E[n] + \lambda N = T[n] + E_{es}[n] + \int d\mathbf{r} n(\mathbf{r}) \{V_{\text{ext}}(\mathbf{r}) + \lambda\}$$

The corresponding Euler equation is the **Thomas-Fermi** equation,

$$\frac{5}{3}C_k n(\mathbf{r})^{\frac{2}{3}} + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}}(\mathbf{r}) + \lambda = 0.$$

Thomas-Fermi (TF) Approximation: Good news

- Well-defined mathematical model
(Rev. Mod. Phys. articles by **E. H. Lieb** and **L. Spruch**)
- reasonable total energies for atoms
- Exact in the limit $Z \longrightarrow \infty$

However:

- Atoms do not bind to give molecules or solids
- No shell structure (no periodic table):
e.g. $[core]s^2p^3$: N, P, As, Sb, Bi ($Z = 7, 15, 33, 51, 83$)
- Atoms *shrink* with increasing atomic number Z ($\sim Z^{-1/3}$)

“ ... approximate practical methods ...”:

P. A. M. Dirac, Proc. Roy. Soc. (London) A **123**, 714 (1929)

Quantum Mechanics of Many-Electron Systems.

By P. A. M. DIRAC, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Exchange energy in homogeneous electron gas:

P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930)

(added exchange to results for the “**Thomas** atom”)

Note on Exchange Phenomena in the Thomas Atom. By P. A. M. DIRAC, Ph.D., St John's College.

[Read 19 May 1930.]

“For dealing with atoms involving many electrons the accurate quantum theory, involving **the solution of the wave equation in many-dimensional space, is far too complicated to be practicable**. One must therefore resort to **approximate methods**. The best of these is **Hartree**'s method of the self-consistent field. Even this, however, is hardly practicable, ... so that one then requires a still simpler and rougher method. Such a method is provided by **Thomas**' atomic model, ...

Homogeneous electron gas of density n : $E_x = -6 \left(\frac{3}{8\pi} n \right)^{\frac{1}{3}}$

In the (semi-classical) Thomas-Fermi model, density $n(\mathbf{r})$.

Exchange correction \longrightarrow **Thomas-Fermi-Dirac** theory.

N.B. F. Bloch, Z. Physik **57**, 545 (1929) [also spin-polarized n_\uparrow, n_\downarrow]

P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930)

Exchange energy in homogeneous electron gas:

“..... This means that **the whole state of the atom is completely determined by this electric density; it is not necessary to specify the individual three-dimensional wave functions that make up the total electric density.** Thus one can deal with any number of electrons by working with just one matrix density function.”

P. A. M. Dirac, Proc. Camb. Phil. Soc. **27**, 240 (1931)

Dirac had defined here what we know today as the **one-particle reduced density matrix**

$$\gamma(\mathbf{r}, \mathbf{r}') = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (1)$$

where $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the wave function of the N -electron system.

$\gamma(\mathbf{r}, \mathbf{r}')$ is related to the density by

$$n(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'}$$

E. Wigner, F. Seitz, Phys. Rev. **43**, 804 (1933)

MAY 15, 1933

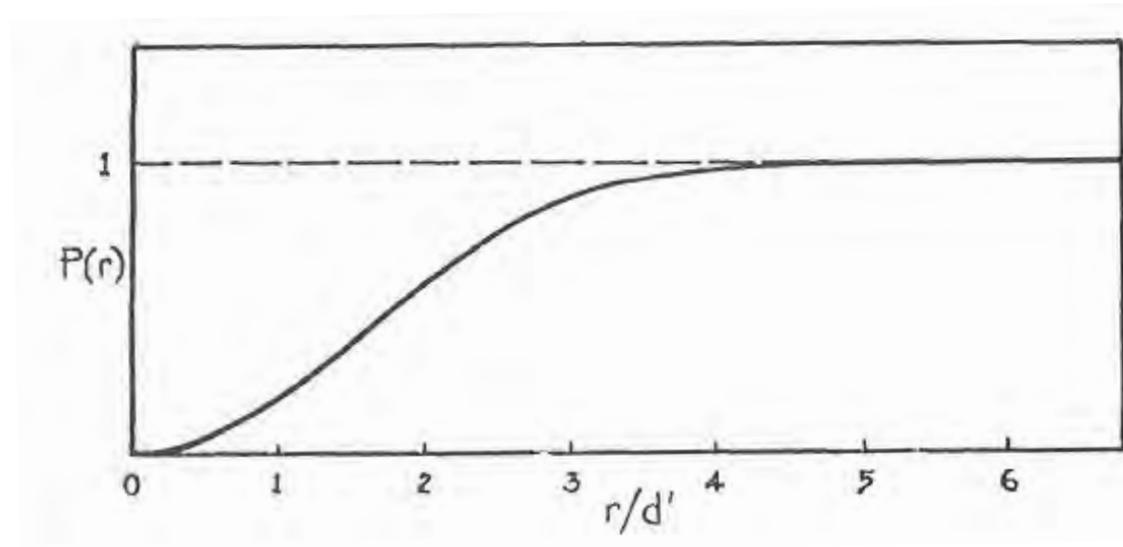
PHYSICAL REVIEW

VOLUME 43

On the Constitution of Metallic Sodium

E. WIGNER AND F. SEITZ, *Department of Physics, Princeton University*

(Received March 18, 1933)



$P(r)$: Probability of electrons with parallel spin being distance r apart
[$d' = (v_0/3\pi^2)^{1/3}$, v_0 atomic volume]

“Fermi” hole

L. Brillouin, J. Phys. Rad. **5**, 413 (1934)

Local exchange potential, J. C. Slater, Phys. Rev. **81**, 385 (1951)

PHYSICAL REVIEW

VOLUME 81, NUMBER 3

FEBRUARY 1, 1951

A Simplification of the Hartree-Fock Method

J. C. SLATER

Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received September 28, 1950)

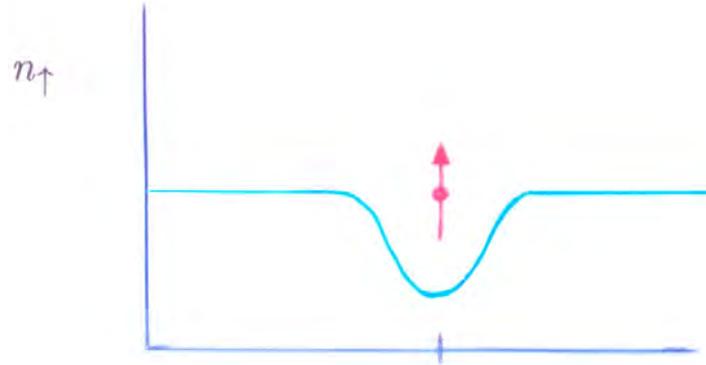
It is shown that the Hartree-Fock equations can be regarded as ordinary Schrödinger equations for the motion of electrons, each electron moving in a slightly different potential field, which is computed by electrostatics from all the charges of the system, positive and negative, corrected by the removal of an exchange charge, equal in magnitude to one electron, surrounding the electron whose motion is being investigated. By forming a weighted mean of the exchange charges, weighted and averaged over the various electronic wave functions at a given point of space, we set up an average potential field in which we can consider all of the electrons to move, thus leading to a great simplification of the Hartree-Fock method, and bringing it into agreement with the usual band picture of solids, in which all electrons are assumed to move in the same field. We can further replace the average exchange charge by the corresponding value which we should have in a free-electron gas whose local density is equal to the density of actual charge at the position in question; this results in a very simple expression for the average potential field, which still behaves qualitatively like that of the Hartree-Fock method. This simplified field is being applied to problems in atomic structure, with satisfactory results, and is adapted as well to problems of molecules and solids.

For free electrons density n , the Slater potential is

$$V_X^{\text{Sl}} = -\frac{3}{2\pi} (3\pi^2 n)^{\frac{1}{3}}$$

“Fermi” or “exchange” hole

“Fermi” [E. Wigner, F. Seitz (1933)] or “exchange” hole [(J. C. Slater, Phys. Rev. **81**, 385 (1951))]



Estimate of size: sphere of radius r_0 contains unit charge:

$$\frac{4\pi}{3}r_0^3n_\uparrow = 1 \rightarrow r_0 = \left(\frac{3}{4\pi n_\uparrow}\right)^{\frac{1}{3}}$$

Electrostatic potential at centre of uniformly charged sphere of radius r_0 is $\sim (1/r_0)$: $\rightarrow V_x \sim (n_\uparrow)^{\frac{1}{3}}$
cf. Exchange energy of homogeneous electron gas [Bloch (1929), Dirac (1930)]

$$E_x = -6 \left(\frac{3}{8\pi}n\right)^{\frac{1}{3}} = \frac{0.458}{r_0} \text{ a.u.}$$

Exchange hole argument leads to energy of same form, but is *not* based on a homogeneous system

Use of Dirac exchange in atoms

R. Gáspár, Acta Phys. Hung. **3**, 263 (1954)

ÜBER EINE APPROXIMATION DES HARTREE- FOCKSCHEN POTENTIALS DURCH EINE UNIVERSELLE POTENTIALFUNKTION

Von

R. GÁSPÁR

ZENTRALFORSCHUNGSINSTITUT FÜR PHYSIK, BUDAPEST*
ABTEILUNG FÜR THEORETISCHE PHYSIK

(Vorgelegt von P. Gombás. — Eingegangen: 12. XI. 1953.)

“Dirac potential”, $\frac{2}{3}$ of the “Slater potential”

Cu atom: → Good agreement with H-F eigenvalues and eigenfunctions

1960's-1970's: vast numbers of electron band structures calculated using V_X^{Sl} or αV_X^{Sl} ($\alpha \sim \frac{2}{3}$, “**X α method**”). Molecular calculations often called “**Hartree-Fock-Slater**”.

N. W. Ashcroft, N. D. Mermin:

Solid State Physics, (Holt Reinhardt Winston, 1976) pp. 336–337

3. The *average* change in the energy of an electron from $\hbar^2 k^2/2m$ due to exchange is just the second term in E/N ; i.e.,

$$\langle \mathcal{E}^{\text{exch}} \rangle = -\frac{3}{4} \frac{e^2 k_F}{\pi} = -\frac{0.916}{(r_s/a_0)} \text{ Ry.} \quad (17.25)$$

This form led Slater¹⁵ to suggest that in nonuniform systems and, in particular, in the presence of the periodic potential of the lattice, one could simplify the Hartree-Fock equations by replacing the exchange term in (17.15) by a local energy given by twice (17.25) with k_F evaluated at the local density; i.e., he proposed an equation in which the effect of exchange was taken into account by merely adding to the Hartree term $U^{\text{el}}(\mathbf{r})$ an additional potential $U^{\text{exch}}(\mathbf{r})$, given by

$$U^{\text{exch}}(\mathbf{r}) = -2.95(a_0^3 n(\mathbf{r}))^{1/3} \text{ Ry.} \quad (17.26)$$

This procedure, **gross and *ad hoc*** though it is, is actually followed in many band structure calculations. There have been some controversies¹⁶ over whether it is better to average the free electron exchange over all k or to evaluate it at $k = k_F$, but the **crude nature of the approximation makes the dispute one of limited content.** It is hard to say more for this simplification than that it approximates the effects of exchange by introducing a potential that favors regions of high density, in a way that roughly mimics the density dependence of the exchange term in the free electron energy density.

Density functional formalism: P. Hohenberg, W. Kohn, Phys. Rev. 136, B864 (1964)

(1) **Ground state properties** of a system of electrons and ions, in an external field, V_{ext} , are determined by the electron density $n(\mathbf{r})$ alone, i.e. they are “functionals” of the density.

Example: Total energy, $E[n(\mathbf{r})]$.

(2) There is a **variational principle** for $E[n]$:

$$\begin{aligned} E[n] &\geq E_{GS} \\ E[n_{GS}] &= E_{GS} \end{aligned}$$

Proof:

$$H = T + V_{\text{ee}} + \sum_{i=1}^N V_{\text{ext}}(\vec{r}_i),$$

where T and V_{ee} are the kinetic and electron-electron interaction operators, respectively. For all “ N -representable” densities, $n(\vec{r})$, i.e. those obtainable from some antisymmetric wave function, $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$, **M. Levy** (1979) defined the functional

$$F[n] = \min_{\psi \rightarrow n} \langle \psi | T + V_{\text{ee}} | \psi \rangle$$

(the minimum taken over all ψ that give density n).

Simple “proof” of DF theory for Coulomb systems

E. B. Wilson, Harvard University (1965)?

Shorter, less general, proof of the definitive role of the electron density, based on “**cusp condition**” (**T. Kato**, 1957) satisfied by the density at the nucleus

$$Z_\alpha = \frac{-1}{2\langle n(0) \rangle} \left[\frac{\partial \langle n(r_\alpha) \rangle}{\partial r_\alpha} \right]_{r_\alpha=0},$$

where $\langle \dots \rangle$ denote a spherical average.

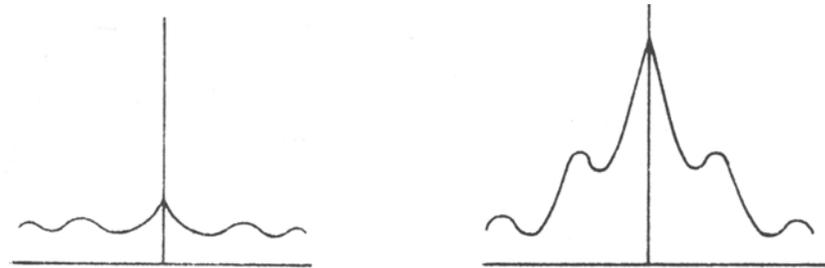
Density $n(r)$ determines uniquely:

- The nuclear positions
- The charges on the nuclei Z_α
- Integration of $n(r)$ gives the total charge

and hence the Hamiltonian.

What does the density $n(r)$ look like in an atom, solid, or molecule?

It is *NOT* uniform, and it does *NOT* look like this?

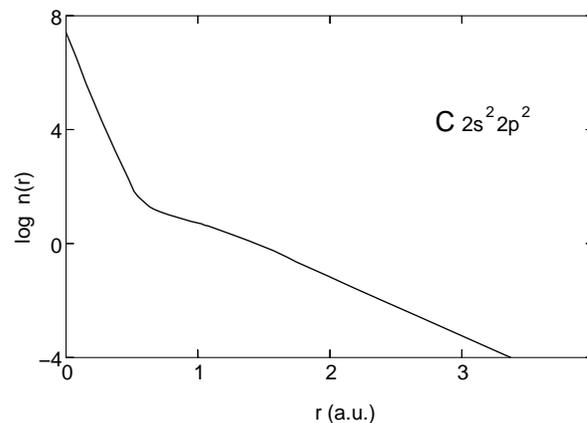


1 a. Electron density in the presence of a small point charge Q .

1 b. Electron density in the presence of a heavy atomic nucleus.

Fig. 1. Transition between Friedel screening charge oscillations and radial density fluctuations in an atom. (Schematic)

In ground state of C atom ($1s^2 2s^2 2p^2$), the spherically averaged density is:



Density $n(r)$ is rather featureless, in molecules and solids close to a superposition of atomic densities.

Calculation of total energy E : W. Kohn, L. J. Sham, Phys. Rev. **140**, A1133 (1965)

$$E[n] = T_0[n] + \int d\mathbf{r} n(\mathbf{r})(V_{\text{ext}}(\mathbf{r}) + \frac{1}{2}\Phi(\mathbf{r})) + E_{\text{xc}}[n]$$

T_0 : K.E. of system with density n without e-e interactions

$\Phi(\mathbf{r})$: Coulomb potential

E_{xc} : exchange-correlation energy.

Variational principle (μ : Lagrange multiplier) \longrightarrow

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) + \Phi(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} = \mu$$

Self-consistent solution of

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$V(\mathbf{r}) = V_{\text{ext}} + \Phi(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

yields

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

Determine energy for the physical, **interacting** system by solving equations for system of **non-interacting** electrons

Local spin density (LSD) approximation:

$$E_{\text{XC}}^{\text{LSD}} = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{XC}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})]$$

$\varepsilon_{\text{XC}}[n_{\uparrow}, n_{\downarrow}]$: Exchange and correlation energy per particle of a homogeneous, spin-polarized electron gas.

W. Kohn, L. J. Sham (1965): LD approximation for exchange $\varepsilon_{\text{X}}(n(\mathbf{r}))$

[same form as **Bloch** (1929), **Dirac** (1930), **Gáspár** (1954), $\frac{2}{3}$ of **Slater** exchange potential]

Exact in two limiting cases:

- Slowly varying density
- High density (kinetic energy dominates)

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

1975 – ... : Many calculations of small molecules showed surprisingly good geometries, vibration frequencies, and (sometimes) energy differences

Problems with original density functional theory

- Functional of **Hohenberg** and **Kohn** (1964) is not even *defined* for all n , since not all densities can be derived from the ground state of some single-particle potential (“ V -representable”) [**M. Levy** (1982), **E. Lieb** (1983)].
- **Kohn, Sham** $E(n)$ is not really a “functional” of n , since T_0 is defined by an effective potential $V(\mathbf{r}) \longrightarrow n$.
- Approximations to E_{xc} are unavoidable and must be tested.
The LDA approximation (and electron gas) very unfamiliar to chemists.
- There is no *systematic* (i.e., mechanical) way to improve the results.

Beryllium dimer Be₂: 4 valence electrons ($2\sigma_g^2, 2\sigma_u^2$), same occupancy of bonding, antibonding orbitals

R. O. Jones: in A. Avella and F. Mancini (eds.), *Strongly Correlated Systems*, Springer Series in Solid-State Sciences 171 ©Springer-Verlag Berlin Heidelberg 2012

“Two normal beryllium atoms repel each other”.

J. H. Bartlett, Jr, W. H. Furry, Phys. Rev. **38**, 1615 (1931) [Heitler-London]

“There is no evidence from this calculation that the ground state of Be-Be is bound ... The CI results are just as repulsive as the SCF results”

C. F. Bender, E. R. Davidson, J. Chem. Phys. **47**, 4792 (1967) [MO SCF CI]

“.. the van der Waals bound molecule Be₂, which should have a dissociation energy less than 1.2 kcal/mol, the experimental D_0 for Mg₂ .. To obtain a realistic result, say 0.7 kcal/mol, for the dissociation energy”

E. Dykstra, H. F. Schaefer III, W. Meyer, J. Chem. Phys. **65**, 5141 (1976) [SCEP/CEPA]

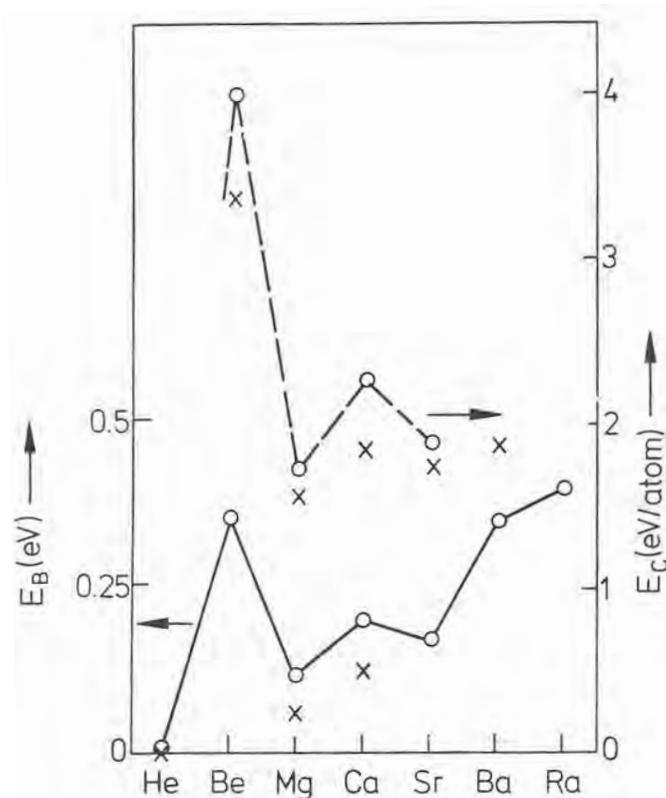
“Because the ground state of Be₂ has not been detected experimentally, it appears that the van der Waals minimum is very shallow (\lesssim 1kcal/mol), it may even be too shallow to support vibrational levels.”

K. D. Jordan and J. Simons, J. Chem. Phys. **67**, 4027 (1977) [GTO].

“Since a system of two Be atoms, each with closed shell ($1s^2s^2$) electronic configurations, does not show appreciable bonding, substantial changes must occur in the nature of bonding if beryllium metal is to be formed. ... At the highest level of theory used, RMP4(SDQ)/6-31G*, the bond length is 3.999 Å, and the binding is 0.3 kcal/mol.”

R. A. Whiteside, R. Krishnan, J. A. Pople, M. B. Krogh-Jespersen, P. von R. Schleyer, G. Wenke, J. Comput. Chem. **1**, 307 (1980).

Beryllium dimer Be_2 : R. O. Jones, J. Chem. Phys. **71**, 1300 (1979)



“It is perfectly obvious to any solid state physicist that Be_2 must be more strongly bound than Mg_2 ”.

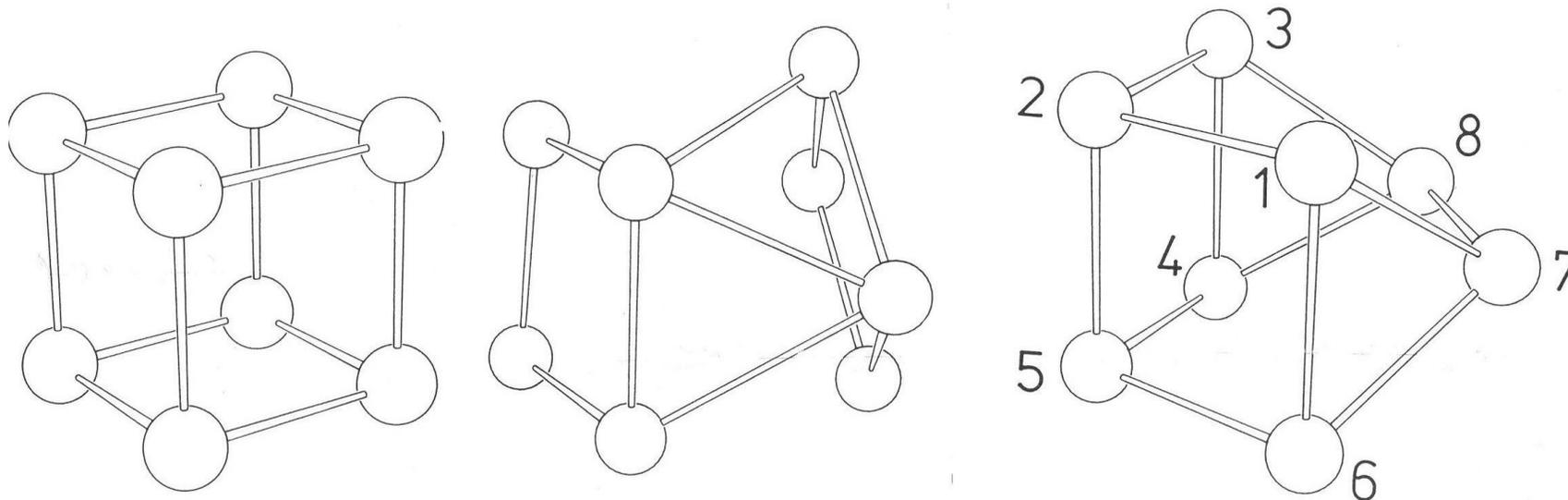
V. Heine (private communication)

“Jones was the first theoretician to suggest that Be_2 had a potential minimum near 2.45 \AA , ... All other *ab initio* calculations to that date (1979) had predicted a minimum near 4.5 \AA , principally because of deficient basis sets. Jones result was one of the first successes of DFT to the study of small molecules”.

C. W. Murray, N. C. Handy, R. D. Amos, J. Chem. Phys. **98**, 7145 (1993)

P₈: Simulated annealing (DF/MD) of cube (O_h) to wedge (C_{2v})

(ca. 40 kcal/mol more stable)



R. O. Jones, D. Hohl, J. Chem. Phys. **92, 6710 (1990)**

Local spin density approximation – solid state view (late 1980's)

“The present results indicate the *reliability* of LSD theory for very inhomogeneous systems ... Our calculated values are in *excellent* agreement with experiment, and thus represent a *triumph* for LSD theory”.

B. Delley, A. J. Freeman, D. Ellis, Phys. Rev. Lett. **50**, 488 (1983).

“It is by now *well accepted* that the DF theory provides an *accurate* description of the electronic structure of both *small* and *extended* systems.

J. W. D. Connolly, A. R. Williams, Phys. Rev. B **27**, 5169 (1983).

“The theory proceeded from success to success almost without effort. ... By 1970, (it) had gained almost *universal acceptance* and today stands virtually alone as the theory of the quantum structure of solids. Alchemy, the original black art of materials science, is now well on its way to becoming one of the *better developed parts of human knowledge*.

M. L. Cohen, V. Heine, J. C. Phillips, Sci. Amer. **246**, #6, 82 (1982).

“The error in the density gradient of the exchange energy has been explained and substantially expunged. The prospect of density functional calculations with *chemical accuracy* no longer seems remote”.

J. P. Perdew, Phys. Rev. Lett. **55**, 1665 (1985).

Ψ_k Newsletter:

(April 2002)

European Collaboration in Ab-Initio Computer Simulation

Volker Heine

Cavendish Laboratory, Madingley Road,
Cambridge CB3 0HE, England

Email: vh200@phy.cam.ac.uk

“Of course at the beginning of the 1960s the big event was the Kohn Hohenberg Sham reformulation of quantum mechanics in terms of density functional theory (DFT). Well, we recognize it now as a big event, but it did not seem so at the time. That was the second big mistake of my life, not to see its importance, but then **neither did the authors** judging from the talks they gave, nor anyone else. **Did you ever wonder why they never did any calculations with it?”**

Quotes from P. W. Anderson

“There is a school which essentially accepts the idea that nothing further is to be learned in terms of genuine fundamentals and all that is left for us to do is calculate. ... One is left, in order to explain any phenomenon occurring in ordinary matter, only with the problem of doing sufficiently accurate calculations. This is then the idea that I call it “*The Great Solid State Physics Dream Machine*” ... This attitude is closely associated with work in a second field called *quantum chemistry*.”

:

The density functional method is a “simplified rather mechanical kind of apparatus” that “shows disturbing signs of become a victim of the “*Dream Machine*” syndrome.

:

... a great deal of the physics is concealed inside the machinery of the technique, and that very often once one has the answers that these techniques provide, one is not exactly clear what the source of these answers is. In other words the better the machinery, the more likely it is to conceal the workings of nature, in the sense that it simply gives you the experimental answer without telling you why the experimental answer is true.”

P. W. Anderson, *La Recherche* **11**, 98 (1980) [in French].

“... the oxymoron ‘*computational physics*’ ”

P. W. Anderson, *Physics Today*, September 1999, p. 11.

“... ‘*theoretical chemistry*’ has become a service skill”

P. W. Anderson, *More and Different. Notes from a thoughtful curmudgeon*, World Scientific, Singapore (2011), pp. 113-114.

Local spin density approximation – view from chemistry

1990 – 2020: >250,000 publications (WoS)

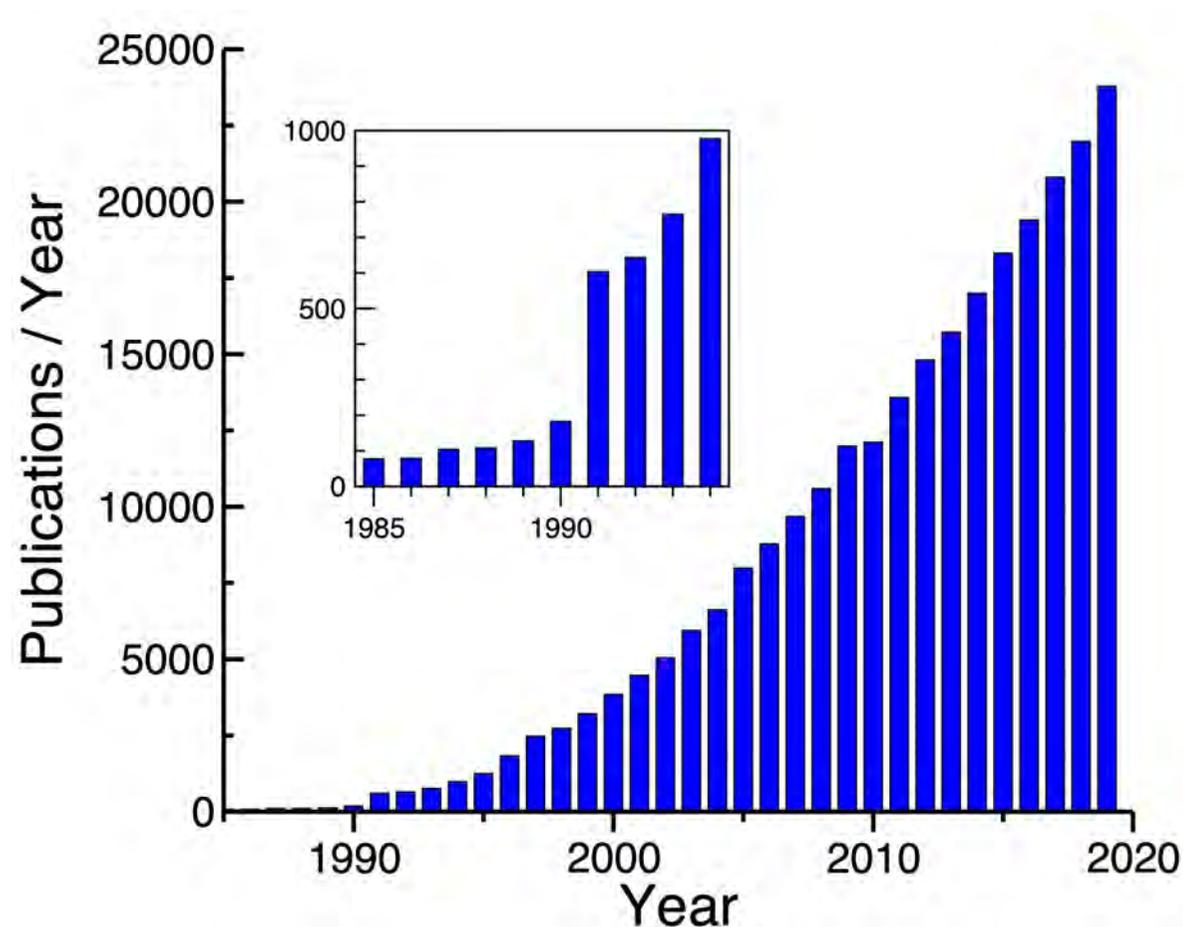


Figure 2: Number of publications per year (1975-2019) on topics “**density functional**” and “**DFT**”, according to ISI Web of Knowledge (September 2020). Inset shows data near 1990 on an expanded scale [Ph. Mavropoulos, Φ. Μαυρόπουλος (private communication)]

N.B.: **Chemical** applications outweigh **materials** applications up to 2012.
K. Burke, J. Chem. Phys. **136**, 150901 (2012).

1990

R. O. Jones, O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989)

- LD (LSD) approximation \longrightarrow reasonable structures (bond lengths, angles), vibration frequencies, energy differences are of variable quality.
- Major source of error in LSD binding energies: poor description of *exchange energy differences*:
F atom: ${}^2P [1s^2 2s^2 2p^5] \longrightarrow {}^2S [1s^2 2s 2p^6]$; $2s_{\downarrow} \longrightarrow 2p_{\downarrow}$
- Generalizations to finite T , spin systems, current- and spin-density functional theory, time dependent DF theory, combination of DF calculations with molecular dynamics **R. Car, M. Parrinello**, (1985)
- Better theoretical basis **M. Levy, E. Lieb**

Two questions:

- Why should approximations based on results for a *homogeneous* electron gas give sensible results for systems with *extremely inhomogeneous* densities?
- Development of approximate functionals for E_{xc}

Surface energy of a bounded electron gas

N. D. Lang, W. Kohn, Phys. Rev. B **1**, 4555 (1970)

R. A. Craig, Phys. Rev. B **6**, 1134 (1972)

J. Schmit, A. A. Lucas, Solid State Commun. **11**, 415 (1972)

Shift of zero-point energy of the collective modes (bulk, surface plasmons) when surface created

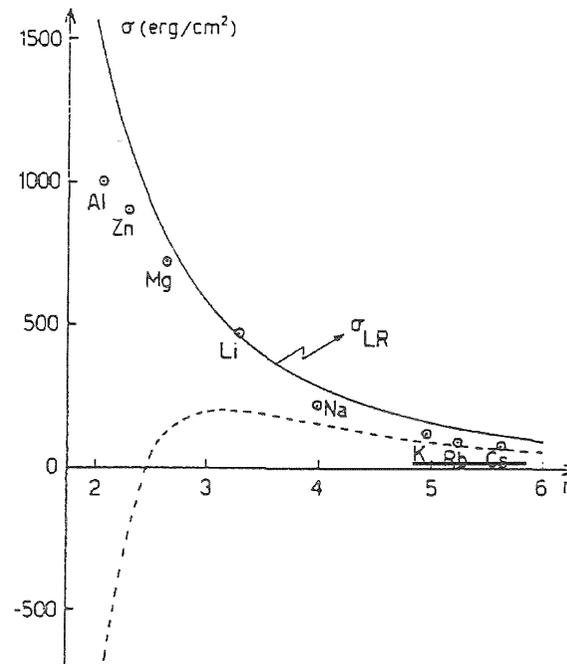


FIG. 2. Surface energies of simple metals. The circles give the same experimental values as those studied in reference 9, except for Zn which was chosen from reference 11. The broken line gives the theoretical values calculated by Lang and Kohn⁹ for the jellium model. The continuous line represents the theoretical result obtained in the present paper.

Adiabatic connection and DF theory:

Relationship between interacting ($\lambda = 1$) and non-interacting ($\lambda = 0$) systems

J. Harris, R. O. Jones, “*The surface energy of a bounded electron gas*”, J. Phys. F **4**, 1170 (1974)

Determine E using the relationship (λ a parameter) [**P. Güttinger**. Z. Phys. **73**, 169 (1931)]:

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle$$

Writing ($\lambda = e^2$)

$$H_\lambda = T + V_0 + \lambda(V - V_0)$$

and integrating over the coupling constant λ

$$E = \left\langle \psi_0 \left| T + V_0 \right| \psi_0 \right\rangle + \int_0^1 d\lambda \left\langle \psi_\lambda \left| V - V_0 \right| \psi_\lambda \right\rangle$$

—→ expression for E_x E_c in terms including fluctuations in the system, $\chi^\lambda(\mathbf{r}, \mathbf{r}', i\omega)$ and $n^\lambda(\mathbf{r})$.

Surface energy of a bounded electron gas (for different r_s):

E_x, E_c very different for “exact” and “LDA”, but the *sum* very similar.

Exchange-correlation energy, xc-hole:

D. C. Langreth, J. P. Perdew, Solid State Commun. **17**, 1425 (1975)

O. Gunnarsson, B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976)

$$H_\lambda = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_\lambda + \lambda V_{\text{ee}},$$

where V_λ is chosen so that the ground state of H_λ has **density** $n(\mathbf{r})$ for all λ .

$$E_{\text{xc}} = \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$$

$$n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) \equiv n(\mathbf{r}') \int_0^1 d\lambda (g(\mathbf{r}, \mathbf{r}', \lambda) - 1).$$

$$\mathbf{R} \equiv \mathbf{r}' - \mathbf{r} \longrightarrow E_{\text{xc}} = \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int_0^\infty dR R^2 \frac{1}{R} \int d\Omega n_{\text{xc}}(\mathbf{r}, \mathbf{R}).$$

- E_{xc} depends only on spherical average of $n_{\text{xc}}(\mathbf{r}, \mathbf{R})$. Many details of the xc -hole do not affect E_{xc}

Exchange hole spin-up electron in N atom

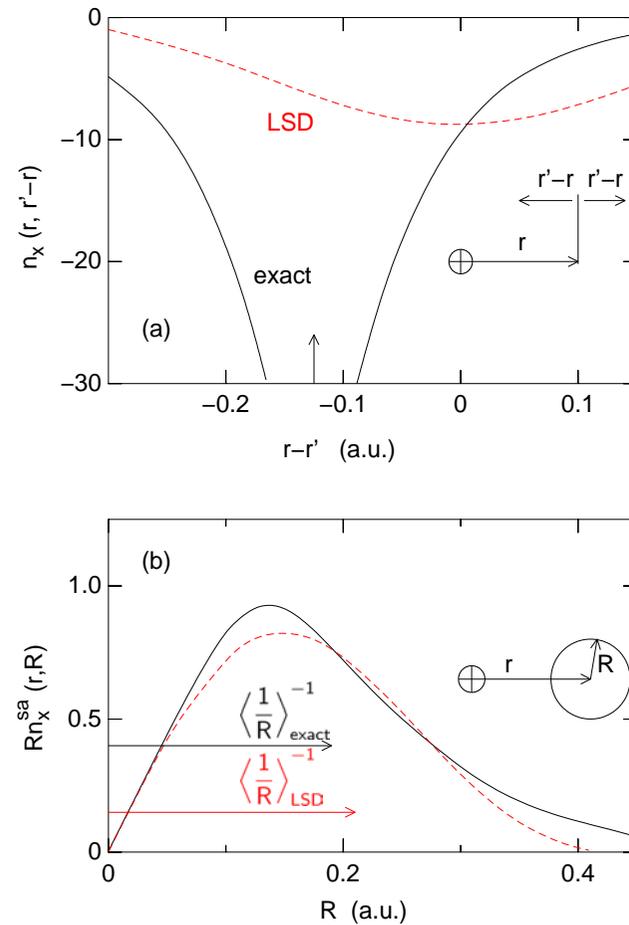


Figure 3: Magnitude of exact (solid) and LSD (red, dashed) exchange holes $n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$ for spin up electron in N atom for $r = 0.13$ a.u. (a) Hole along line through nucleus (arrow) and electron ($\mathbf{r} - \mathbf{r}' = 0$). (b) spherical averages of holes, and $\langle 1/R \rangle$.

Adiabatic connection between non-interacting and interacting systems

$$E = \langle \psi_0 | T + V_0 | \psi_0 \rangle + \int_0^1 d\lambda \langle \psi_\lambda | V - V_0 | \psi_\lambda \rangle$$

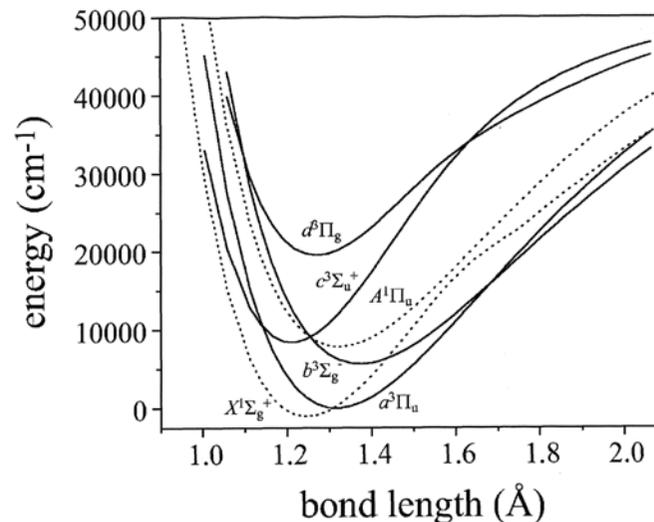
→ expression for E_x E_c in terms including fluctuations in the system, $\chi^\lambda(\mathbf{r}, \mathbf{r}', i\omega)$ and $n^\lambda(\mathbf{r})$.

Implies that the λ variation results in a “smooth” transition from non-interacting to interacting systems

Discontinuities, unexpected λ -dependence → “strong correlations”?

Carbon dimer: $^1\Sigma_g^+ : \pi_u^4(2p)$; $^3\Pi_u : \sigma_g^1(2p)\pi_u^3(2p)$

The $2s$ and $2p$ orbitals have similar extent, and $\pi_u(2p)$ to $\sigma_g(2p)$ transfer costs little energy.



Solved for C₂ by “constrained search” (fix the occupation numbers).

Free electron theory in chemistry:

F. Bloch, Z. Phys. **52**, 555 (1929) (“Bloch functions”, LCAO)

E. Hückel, Z. Phys. **70**, 204 (1931) (delocalized π -electrons in benzene, HMO)

O. Schmidt, Z. Elektrochem. **43**, 238 (1937).

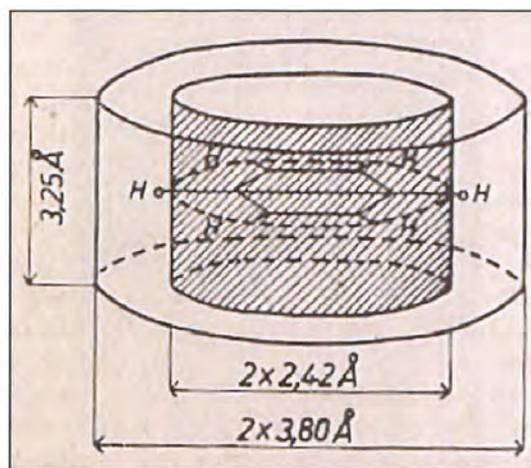


Figure 4. Schmidt's cylindrical box model for the π -electrons of benzene.

N. S. Bayliss, J. Chem. Phys. **16**, 287 (1948) (absorption spectra of organic dye molecules).

H. Kuhn, J. Chem. Phys. **16**, 840 (1948).

W. T. Simpson, J. Chem. Phys. **16**, 1124 (1948).

“ ... it is not easy to give theoretical reasons for the relative success of the FE model. Indeed, one wonders how any simple theoretical approach can achieve quantitative success when applied to a system as complex as an organic molecule.” (**Bayliss**, 1952)

J. R. Platt, Handbuch der Physik **37/2**, 173 (1961)

K. Ruedenberg and C. W. Scherr, J. Chem. Phys. **21**, 1565 (1953) (HMO, FE math. equivalent).

LSD results; general trends

Structural, elastic, vibrational properties

- lattice constants within 1-2%, usually underestimated
- bulk moduli too large (up to 10%)
- phonon frequencies too high

Binding energies:

- cohesive energies of solids too high (overbound)
- atomization energies of molecules too high (average in 148 G2 molecules ~ 3 eV)
- activation energies variable

Generalized gradient expansions (GGA)

$$E_{\text{XC}}^{\text{GGA}}(n) = \int d\vec{r} \varepsilon_{\text{XC}}(n, |\nabla n|, \nabla^2 n).$$

Exchange energy $\varepsilon_{\mathbf{X}}$:

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

$$\varepsilon_{\mathbf{X}} = \varepsilon_{\mathbf{X}}^{\text{LD}} \left[1 - \frac{\beta}{2^{1/3} A_{\mathbf{X}}} \frac{x^2}{1 + 6\beta x \operatorname{arcsinh}(x)} \right],$$

where $x = 2(6\pi^2)^{1/3} s = 2^{1/3} |\nabla n| / n^{4/3}$, $A_{\mathbf{X}} = \frac{3}{4}(3/\pi)^{1/3}$.

β (0.0042) optimized to give exchange energies of noble gas atoms using HF orbitals.

Correlation energy $\varepsilon_{\mathbf{C}}$:

C. T. Lee, W. T. Yang, R. G. Parr, Phys. Rev. B **37**, 785 (1988).

$$\varepsilon_{\mathbf{C}} = -a \frac{1}{1 + dn^{1/3}} \left\{ n + bn^{-2/3} \left[C_F n^{5/3} - 2t_W + \frac{1}{9} \left(t_W + \frac{1}{2} \nabla^2 n \right) \right] \exp(-cn^{-1/3}) \right\},$$

where

$$t_W = \frac{1}{8} \left(\frac{|n|^2}{n} - \nabla^2 n \right), C_F = 3/10(3\pi^2)^{2/3}, a = 0.04918, b = 0.132, c = 0.2533, d = 0.349$$

→ “BLYP”.

7th INTERNATIONAL CONGRESS OF QUANTUM CHEMISTRY

Under the auspices of the International Academy of Quantum Molecular Sciences
2-5 JULY 1991, MENTON, FRANCE



Preliminary results on the performance of a family of density functional methods

B. G. Johnson, P. M. W. Gill, J. A. Pople, J. Chem. Phys. **97**, 7846 (1992)

“In summary, these initial results indicate that DFT is a promising means of obtaining quantum mechanical atomization energies: here, DFT methods B-VWN and B-LYP outperformed correlated *ab initio* methods, which are computationally more expensive. Good agreement with experiment was obtained with a small basis set.”

The performance of a family of density functional methods

B. G. Johnson, P. M. W. Gill, J. A. Pople, J. Chem. Phys. **98**, 5612 (1993)

“The density functional vibrational frequencies compare favorably with the *ab initio* results, while for atomization energies, two of the DFT methods give excellent agreement with experiment and are clearly superior to all other methods considered.”

BUT

Obituary: Density Functional Theory (1927-1993)

P. M. W. Gill, Aust. J. Chem. **54**, 661 (2001)

Molecular Quantum Mechanics: Methods and Applications
An International Conference in Memory of Samuel Francis Boys and in Honor of Isaiah Shavitt

Nicholas C. Handy and Henry F. Schaefer III, Co-Chairmen
Ross H. Nobes, Administrator

University of Cambridge, Cambridge, England

September 3–7, 1995

Impressions of DF Theory (H. F. Schaefer III)

This conference has displayed a remarkable synthesis of density functional methods with *ab initio* quantum mechanical methods. In light of this successful synthesis, one might fairly ask the question, **why did it take some of us so long to accept DFT?**

As one of those who resisted DFT until a few years ago, I would suggest two reasons: (i) **The overselling of the $X\alpha$ method during the 1970's.** (ii) **Grave reservations concerning the numerical precision of early density functional computations.** I distinctly remember a discussion with Professor Handy five or six years ago in which we juggled the question, has any density functional calculation ever given a correct molecular energy to ± 0.01 hartree, other than fortuitously?

M. J. Frisch (first author, Gaussian program package):

“Ab initio calculations of vibrational circular dichroism and infrared spectra using SCF, MP2, and density functional theories for a series of molecules”

ACS National Meeting, San Francisco (April 13, 1997)

Unidentified questioner:

“What about Hartree-Fock?”

M. J. Frisch:

“It does not matter what you want to calculate, and it does not matter what functional you use. Density functional results are always better than Hartree-Fock.”

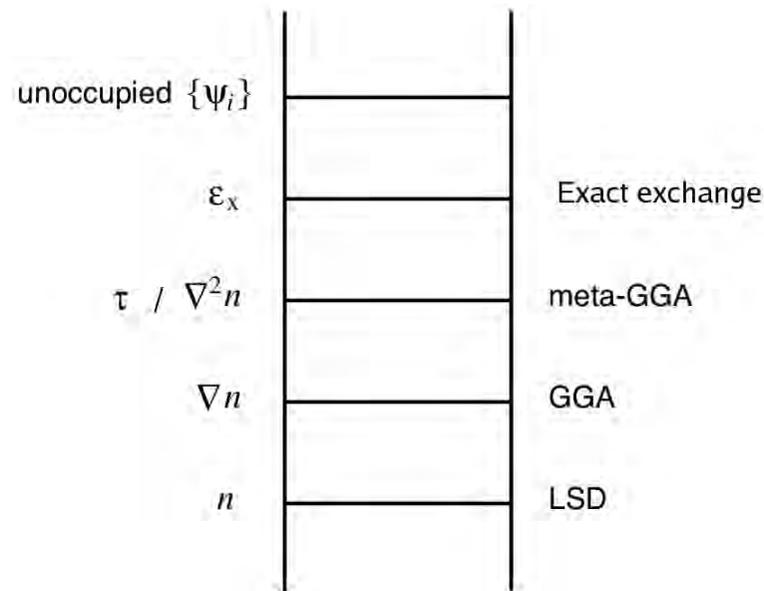
Progress since 1990

> 250000 publications since 1990.

TD-DFT, “van der Waals” (dispersion) forces,
DF perturbation theory, “strongly correlated” systems,
density matrix functional theory, DMRG, ...

Approximations for E_{xc} : “Jacob’s ladder” of approximations, according to J. P. Perdew

Improve LSD by incorporating **exact constraints** successively



“And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven: and behold the angels of God ascending and descending on it.” Genesis 28:12 (King James Version).

GGA (PBE) J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996):

$$E_X^{\text{PBE}} = \int d\vec{r} n(\vec{r}) \varepsilon_X^{\text{LD}}(n(\vec{r})) F_X(n, \zeta, s),$$

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu^2/\kappa}, \mu = \beta(\pi^2/3) = 0.21951, \beta = 0.066725$$

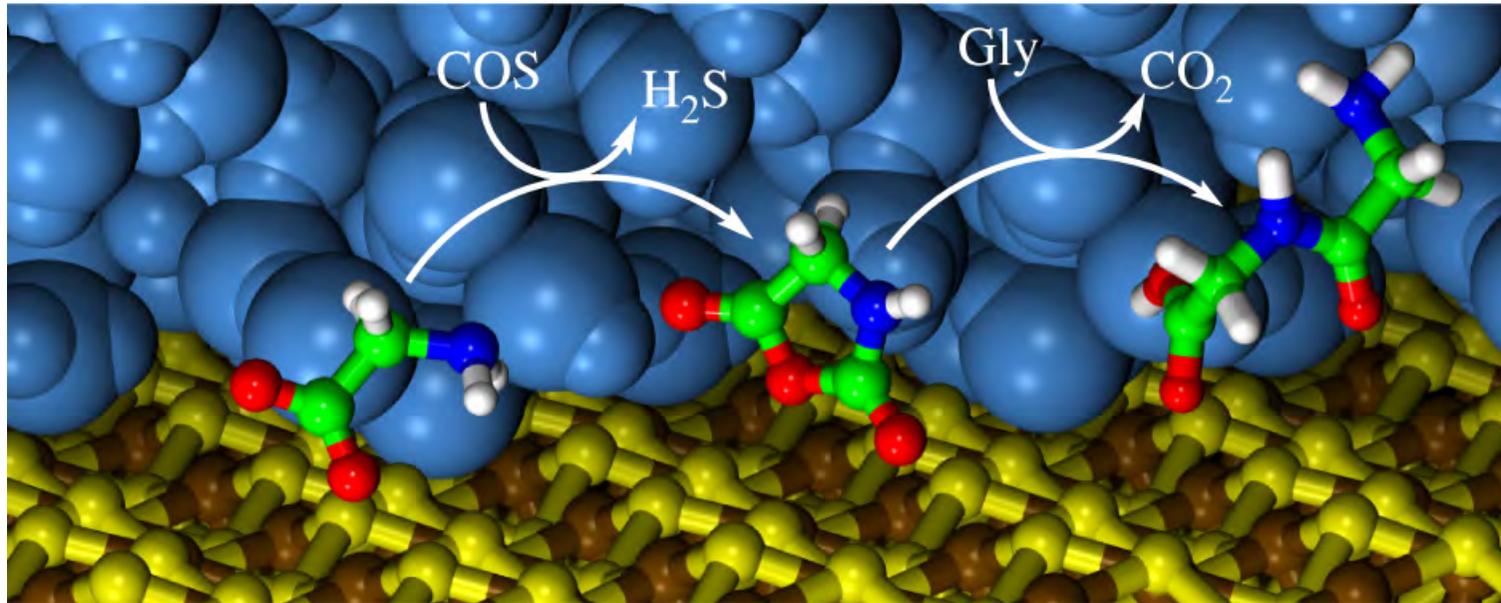
$$E_C^{\text{PBE}} = \int d\vec{r} n(\vec{r}) \left[\varepsilon_C^{\text{LSD}}(n, \zeta) + \left(\frac{e^2}{a_0} \right) \gamma \phi^3 \ln \left\{ 1 + \frac{\beta \gamma^2}{t} \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right\} \right]$$

$$\phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}] / 2, \gamma = (1 - \ln 2) / \pi^2 = 0.031091, A = \frac{\beta}{\gamma} \left[\exp \left(-\varepsilon_C^{\text{LD}}[n] / (\gamma \phi^3 e^2 / a_0) \right) - 1 \right]^{-1}$$

- In the slowly varying limit ($t \rightarrow 0$), H is given by the second-order GA
- In the rapidly varying limit ($t \rightarrow \infty$), $H \rightarrow -\varepsilon_C^{\text{LD}}$, and correlation vanishes
- It cancels logarithmic singularity of $\varepsilon_C^{\text{LD}}$ in the high density limit.

Improved atomic and molecular E_{tot} , cohesive energies, atomization energies, hydrogen bond strengths, **but** self-interaction problem remains, $V_{\text{XC}}^{\text{GGA}}$ vanishes exponentially far outside an atom, $V_{\text{XC}}^{\text{GGA}}(\vec{r} \rightarrow 0) \rightarrow -\infty$.

Formation of protein molecules under prebiotic conditions: “iron-sulphur world” of Wächtershäuser.



Reactions of N-carboxy anhydrides (a form of activated amino acids) in H₂O under high P , T in the presence of FeS₂ surface (72 atoms)

—→ changes free energetics of the reaction steps, stabilizes the peptide product against hydrolysis.

E. Schreiner, N. N. Nair, D. Marx, J. Am. Chem. Soc. **130**, 2768 (2008).

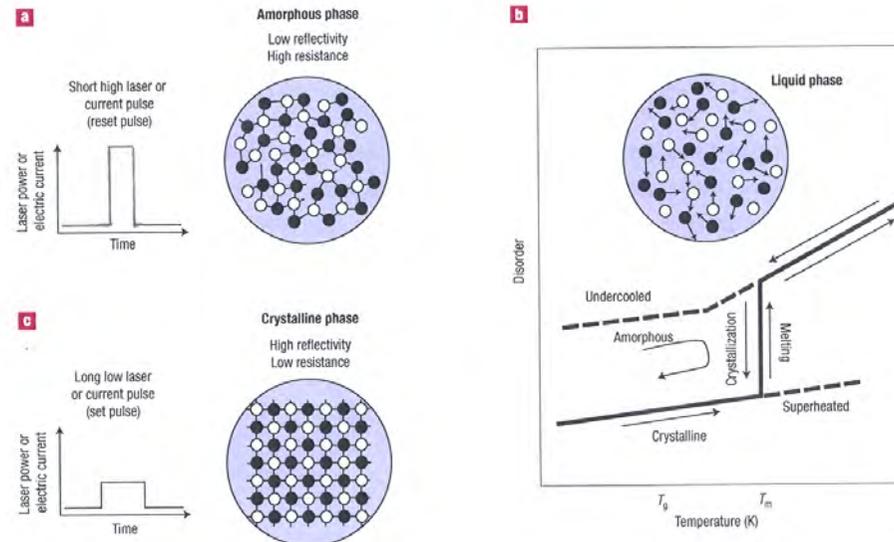
E. Schreiner, N. N. Nair, C. Wittekindt, D. Marx, J. Am. Chem. Soc. **133**, 8216 (2011).

Phase change memories

S. R. Ovshinsky, “Reversible electrical switching phenomena in disordered structures”, Phys. Rev. Lett. **21**, 1450 (1968)

Rapid and **reversible** transition between resistive and conducting state in semiconductor films (caused by electric field).

Current view: Transition between crystalline (conducting) and amorphous (resistive) states. Can use laser pulses to cause reversible transitions in nanosized “bits” in a film



M. Wuttig and N. Yamada, Nature Mater. **6**, 824 (2007)

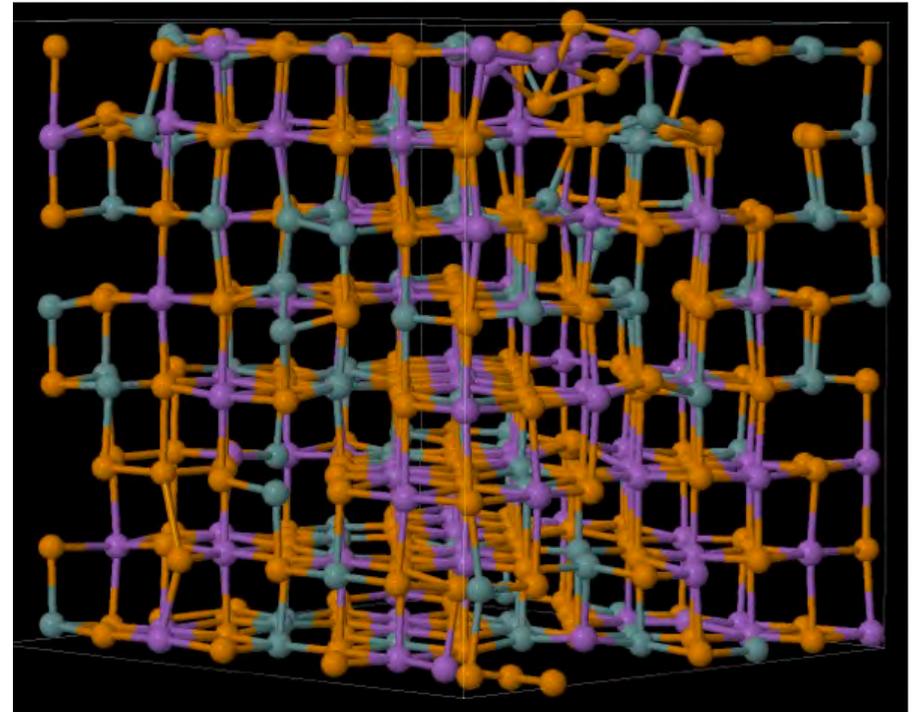
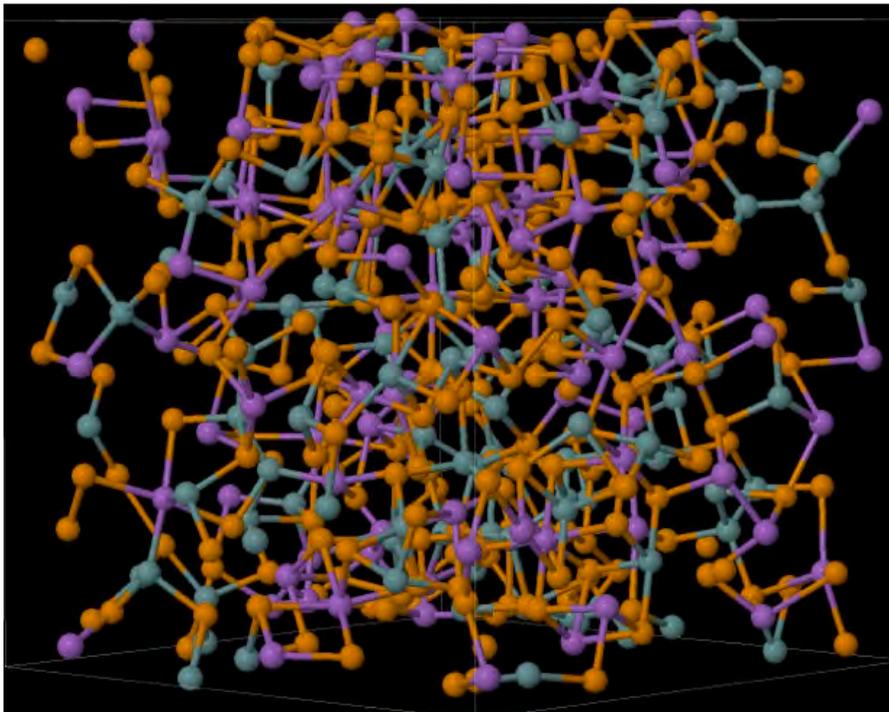
“Melt-quench” stage (~ 1 ns), “crystallization” stage ($\sim 5 - 100$ ns)

Almost all commercial optical PC memory materials are Sb/Te alloys.
Most common: Ge/Sb/Te alloys

Crystallization of $\text{Ge}_2\text{Sb}_2\text{Te}_5$: 460 atoms, 600 K

J. Kalikka, J. Akola, R. O. Jones, Phys. Rev. B **94**, 134105 (2016), and references therein.

- Four simulations, up to 8 ns (> 2 million time steps)



R. O. Jones,

Phase change memory materials: Rationalizing the dominance of Ge/Sb/Te alloys,
Phys. Rev. B **101**, 024103 (2020)

Meta-GGA (TPSS): Include kinetic energy density $\tau_{\sigma}(\vec{r}) = \sum_i^{\text{occ}} \frac{1}{2} |\nabla \psi_{i\sigma}(\vec{r})|^2$

TPSS:

J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003))

SCAN: strongly constrained and appropriately normed

J. Sun, A. Ruzsinsky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036401 (2015))

J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinsky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein, and J. P. Perdew, Nat. Chemistry **8**, 832 (2016)

T. Aschebrock and S. Kümmel, J. Chem. Phys. **151**, 154108 (2019).

Other schemes:

- Hybrid Schemes: Combination of HF and DF Scheme

$$E_{\text{xc}}^{\text{hybrid}} = E_{\text{xc}}^{\text{GGA}} + \alpha \left(E_{\text{x}}^{\text{HF}} - E_{\text{x}}^{\text{GGA}} \right) ,$$

where α can be chosen to satisfy particular criteria. e.g. B3LYP functional is widely used in chemistry. Three adjustable parameters are used to fit calculated values to a molecular data base.

- Adiabatic connection schemes (density response function)
- Orbital-dependent functionals
- ...

Alternative approaches:

- Abandon search for a functional. It is simply too difficult.
- Develop a reasonable form and **fit its adjustable parameters** to experiment (e.g. BLYP, B3LYP). DF theory becomes “of semi-empirical nature”

(**A. D. Boese, N. C. Handy**, J. Chem. Phys. **114**, 5497 (2001) [data from 407 atomic and molecular systems for a functional with 15 adjustable parameters.

D. G. Truhlar and coworkers

N.B. **Medvedev et al.** (2017): fitted functionals \longrightarrow better energies, worse densities.

- **Machine learning**

73.

UNDERSTANDING ELECTRON CORRELATION. *Nicholas Handy, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, England, Fax: 44-1223-336362, nch1@cam.ac.uk*

Density Functional Theory enables one to understand the nature of electron correlation in a better way. We define all the correlation in atoms as 'dynamic', or short range, meaning that the electrons want to avoid one another. Exact atoms are smaller than Hartree-Fock atoms! For atoms therefore, the exchange functional (e.g. B88X or OPTX) must reproduce the Hartree-Fock energy, and the correlation functional (e.g. LYP) must reproduce the correlation energy.

We argue in favour of a functional such as BLYP (B88X+LYP) or OLYP (OPTX+LYP) for molecules. It is an unbiased functional, with no semi-empirical parameters which have been determined from selected molecular data. The binding energy calculated with B88X or OPTX is (much) greater than the Hartree-Fock binding energy; it includes 'left-right correlation'. This is long range correlation, and is represented because these exchange functionals are solely GGA functionals. LYP predicts the dynamic correlation contribution to binding, and is approximately 20 kcal/mol for each pair bond created. The sum of the left-right and dynamic contributions is well known to be nearly always an accurate prediction for the correlation contribution to binding. Furthermore such an analysis holds (in principle) for all molecular geometries.

Functionals which include an orbital dependence (e.g. hybrid) do not allow this clear interpretation. Neither does quantum chemistry, for which it is impossible to separate forms of electron correlation.

The discussion will be amplified with many examples. We are returning to the view that the simplest parameter-free GGA functionals are the best functionals to use with DFT, because they offer the simplest interpretation and have greater global predictive power.

Machine learning techniques: A new paradigm?

- Assume that the system in question can be described by DF calculations with a reasonable functional approximation.
- Generate a database of structures appropriate for the system considered (clusters, results of MD and/or Monte Carlo simulations, etc.).
- Use neural network or machine learning algorithms to generate potential energy surface for system. Input to MD or MC simulations.

J. Behler and M. Parrinello, Phys. Rev. Lett. **98**, 146401 (2007)

GeTe: G. C. Sosso *et al.*, Phys. Rev. B **85**, 174103 (2012)

Machine learning “on the fly” (active learning)

Z. Li, J. R. Kermode, and A. De Vita, Phys. Rev. Lett. **114**, 096405 (2015)

R. Jinnouchi *et al.* J. Phys. Chem. Lett. **11**, 6946 (2020)

Density functional formalism:

reduces the many-electron problem to the solution of “single particle” equations.

It is an “**approximate practical method**” [Dirac (1929)] and is the work of many dating back to the 1920s.

(Fermi, Dirac, Bloch, Slater, Wigner, Schwinger, Kohn, Pople, ... and MANY others)

Relationship between geometrical arrangement of atoms (**Structure**) and **Properties**.

Goal: Understanding known properties and predict unknown ones.

1998: Nobel Prize for Chemistry awarded to W. Kohn and J. A. Pople

“the labours and controversies ... in understanding the chemical binding in materials had finally come to a resolution in favour of ‘LDA’ and the modern computer”

P. W. Anderson, *More and Different: notes from a thoughtful curmudgeon*”, p. 109.

“**Nevill Mott, John Slater, and the ‘Magnetic State’**: Winning the prize and losing the PR battle”

(“Dream Machine \uparrow Mott \downarrow ”)

P. W. Anderson, *More and Different: notes from a thoughtful curmudgeon*”, p. 120.

Quo vadis?

K. Burke, J. Chem. Phys. **136**, 150901 (2012)

“It is clearly the best of times and the worst of times for DFT. More calculations, both good and bad, are being performed than ever.”

“Time for a paradigm shift?”

Density matrix functional theory? **No** equations of **Kohn-Sham** type.

A. D. Becke, J. Chem. Phys. **140**, 18A301 (2014).

“Gill’s pronouncement of the death of DFT was perhaps premature, but not unfounded. The dispersion problem has, in large part, plunged DFT into an identity crisis. Have we forgotten why Kohn-Sham theory is so popular in the first place? If employment of the virtual orbitals increases, I am afraid that the beauty and simplicity of the K-S vision will be lost.”

“This is my position, today, on how to proceed in the future. We have come ‘full circle’ back to exact exchange or, if you prefer, Hartree-Fock.”

R. O. Jones, Rev. Mod. Phys. **87**, 897 (2015)

“Going around in circles is not usually a sign of progress. Have we overlooked something?”



THANK YOU !!