Density functional theory for emergents

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Emergent Phenomena in Correlated Matter, 23 September 2013:

"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

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

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, ... 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?**

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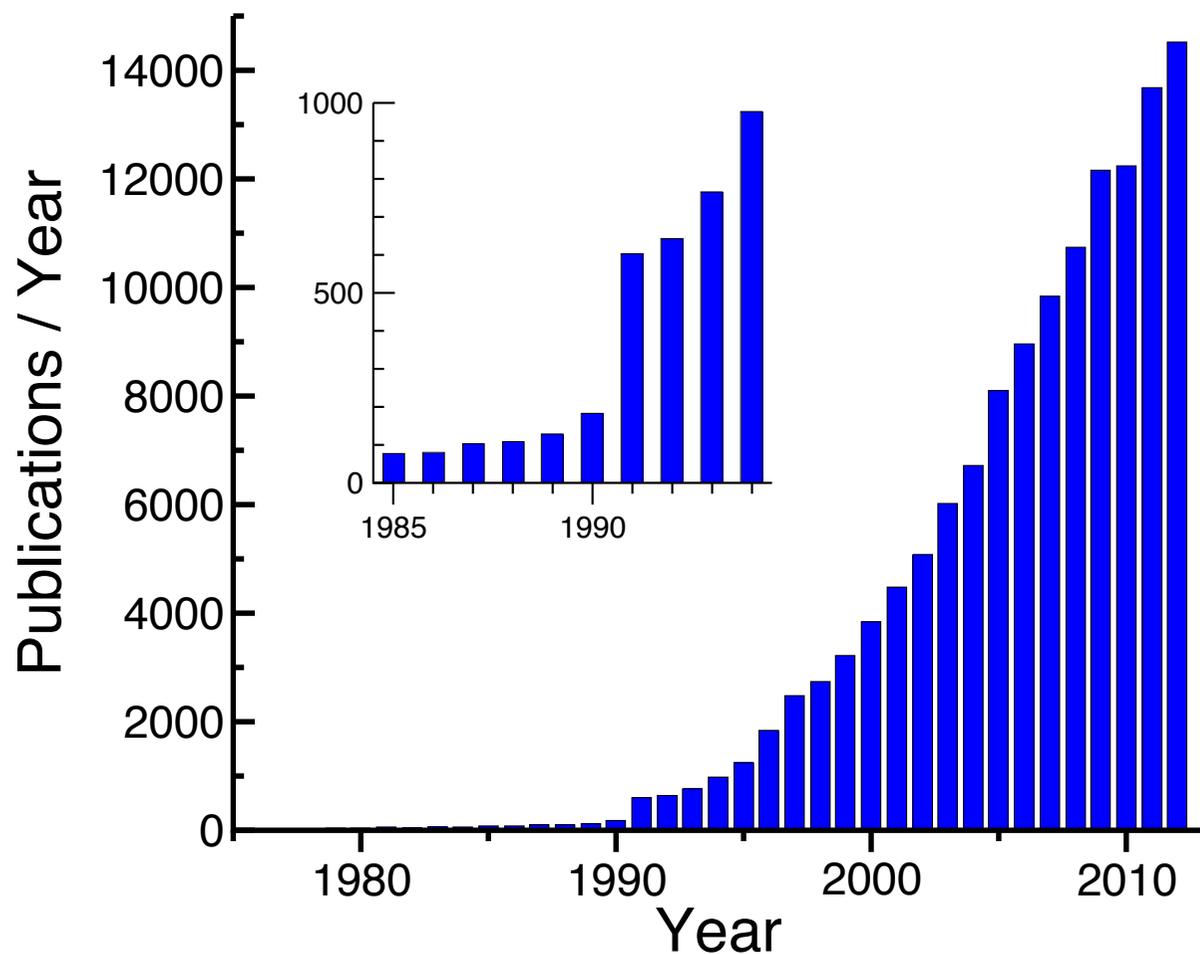
Figure 1: Number of publications per year (1975-2012) on topics **"density functional"** and **"DFT"**, according to ISI Web of Knowledge (May 2012). Inset shows data near 1990 on an expanded scale [**Ph. Mavropoulos, Φ. *Μαυρόπουλος*** (private communication)]

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.
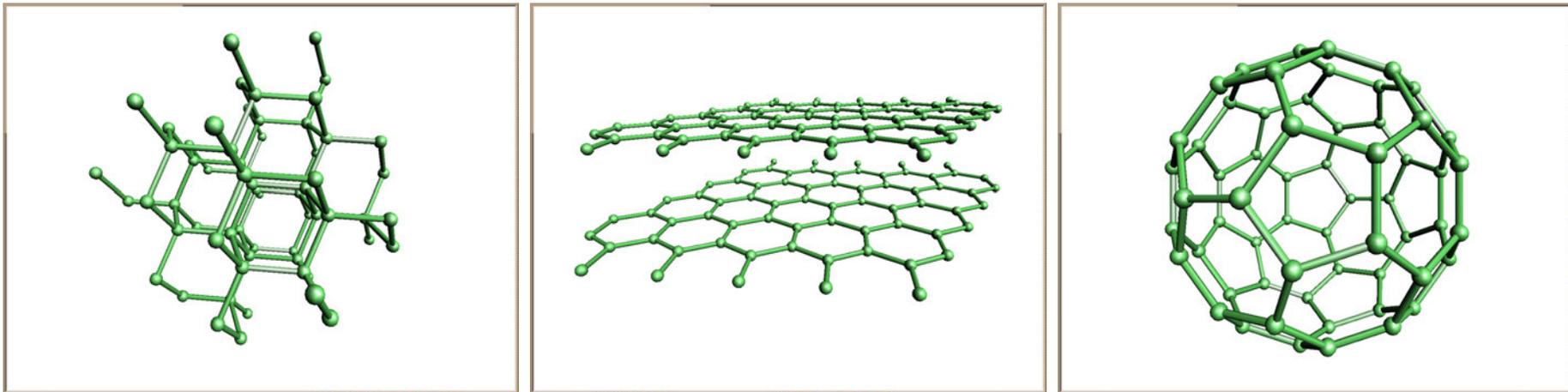
Forms of carbon with quite different properties

Geometric structure: Role of theory

Problem very simple to state:

(1) Calculate the total energy E for a single geometry
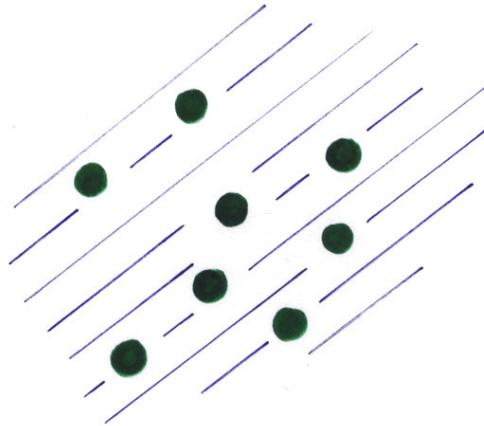
(2) Repeat this calculation for *all* possible structures $\longrightarrow$ energy surface;

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:
$E = \langle \Psi | \widehat{H} | \Psi \rangle$, where $\widehat{H}$ 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:
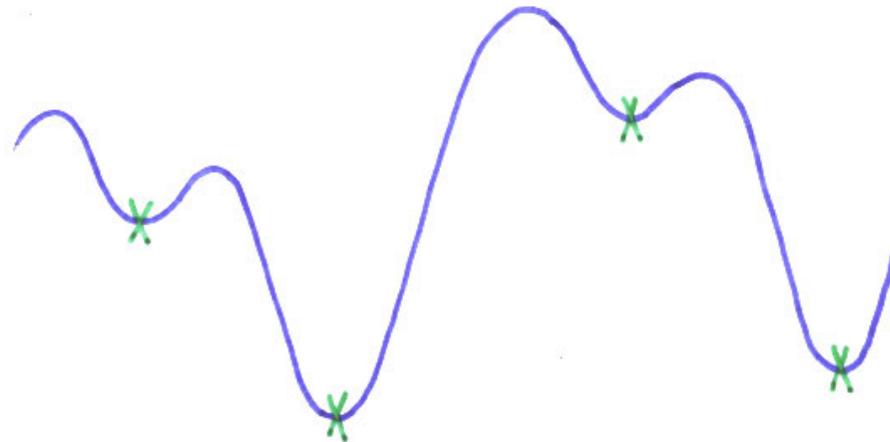
Energy calculations via **density functional (DF)** theory are effective for many systems

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 biequivalent 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

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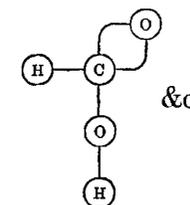
This method seems to me to present advantages over the methods used by Professors Kekulé and Erlenmeyer; and while it is no doubt liable, when not explained, to be mistaken for a representation of the physical position of the atoms, this misunderstanding can easily be prevented.

A. Cayley, *A theorem on trees*, Quart. J. Pure Appl. Math, **23**, 376 (1889).
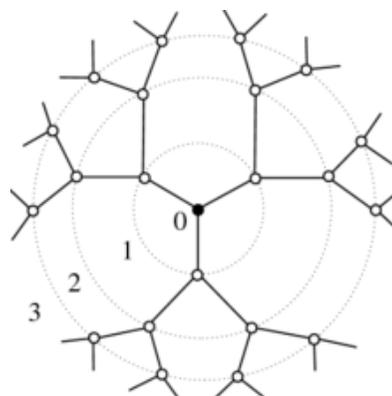
The number of trees with $(n+1)$ knots is $(n+1)^{n-1}$

Solutions of the Schrödinger equation (1926): Variational principle

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

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

Dr Hartree, The wave mechanics of an atom, etc.   89

The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. By D. R. HARTREE, Ph.D., St John's College.

[Received 19 November, read 21 November, 1927.]

Separation of $\Psi(\vec{r}_1, \vec{r}_2, ... \vec{r}_N)$ into *core* and *valence* components, each determined from a "self-consistent field" of the others.
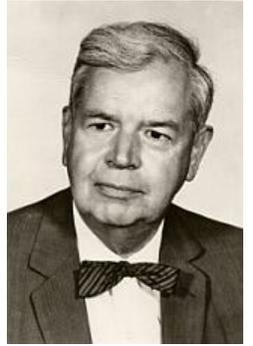
Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems *).

Von **V. Fock** in Leningrad.

(Eingegangen am 21. Februar 1930.)

Das Variationsprinzip $\int \delta \overline{\Psi} (L - E) \Psi d\tau = 0$ (L = Energieoperator) liefert bekanntlich die Wellengleichung im Konfigurationsraum. Es wird gezeigt, daß der Ansatz $\Psi = \psi_1(x_1)\, \psi_2(x_2) \ldots \psi_N(x_N)$ (N = Anzahl der Elektronen) zu den Gleichungen der Hartreeschen Theorie des „selfconsistent field" führt. Dieser Ansatz hat aber nicht die richtige Symmetrie. In dem wichtigen Spezialfall der „völligen Entartung des Termsystems" kann aber Ψ durch ein Produkt zweier Determinanten [Formel (50) des Textes] approximiert werden. Die entsprechende Rechnung wird durchgeführt. Die Gleichungen, die sich für $\psi_i(x)$ ergeben, enthalten „Austauschglieder" und können als Eulersche Gleichungen eines dreidimensionalen Variationsproblems mit der Energie als Wirkungsintegral [Formel (93)] aufgefaßt werden. Die Gleichungen sind nicht wesentlich komplizierter als die von Hartree, dürften aber viel genauere Resultate ergeben. Zum Schluß wird eine Formel für die Intensitäten angegeben, die Glieder enthält, welche einer „Umgruppierung" der inneren Elektronen bei einem Quantensprung entsprechen.

Note on Hartree's Method

Hartee's method of self-consistent fields, for determining atomic models, has seemed to many persons to stand rather apart from the main current of quantum theory; in spite of the papers of Gaunt and the writer, showing its connection with Schrödinger's equation, it has seemed to contain arbitrary and empirical elements. It appears, however, that it has a very close relation to the variation method. That principle states that, if one has an approximate wave function containing arbitrary parameters or arbitrary functions, one will have the best approximation to a solution of Schrödinger's equation if one chooses the parameters or functions so that the energy is stationary with respect to slight variations of them. Suppose one sets up an approximate wave function for the general problem of the motion of electrons among stationary nuclei, by assuming a product of functions of the various electrons $u = u_1(x_1) \cdots u_n(x_n)$; suppose further that

submitted 21 February 1930   submitted 19 December 1929

"Hartree equation" can be derived from the trial function:

$$\Psi(\vec{r}_1, \vec{r}_2, ...) = \psi_1(\vec{r}_1)......\psi_N(\vec{r}_N)$$

Each $\psi_i(\vec{r}_i)$ satisfies a one-electron Schrödinger equation with potential arising from average field of the other electrons ("self-consistent field")

Single-particle functions $\psi_i(\vec{r_i})$ to the "Hartree-Fock" equations

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}} + \Phi_i\right)\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}),$$

where the Coulomb potential Φ_i is given by Poisson's equation,

$$\nabla^2\Phi_i = 4\pi e^2 \sum_{\substack{j=1 \\ i\neq j}}^{N} |\psi_j|^2,$$

and V_{ext} is the potential due to the nuclei.

Fermi statistics incorporated by replacing product by a determinant (Fock, Slater)
$\longrightarrow$ **Hartree-Fock equations** (1930)

Linear combination of determinants
$\longrightarrow$ **Configuration Interaction, CI**

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

" ... 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, ...

The method of the self-consistent field has recently been established on a very much better theoretical basis in a paper by **Fock**, which shows how one can take into account the exchange phenomena between equivalent electrons. Fock shows that if one takes the best approximation to the many-dimensional wave function that is of the form of a product of a number of three-dimensional wave functions, one for each electron, then the three-dimensional wave functions will satisfy just Hartree's equations. ... .

The exclusion principle of **Pauli**, however, requires that the wave function representing a number of electrons shall always be antisymmetrical. One would therefore expect to get a better approximation if one first made the the product of a number of three-dimensional wave functions antisymmetrical, by applying perturbations and taking a linear combination, and then made it approach as closely as possible to the accurate many-dimensional wave function. The three-dimensional wave functions will then, as found by Fock, satisfy equations somewhat different from Hartree's, containing extra terms which may be considered as representing the **exchange phenomena.**"

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.
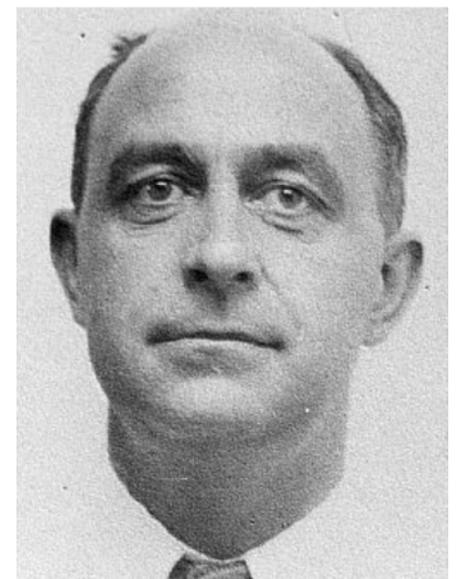
TF approximation : a density functional theory

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.

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

.

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

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 ($\sim Z^{-1/3}$)

Role of the density:

"Each three-dimensional wave function will give rise to a certain electric density. This electric density is really a matrix, like all dynamical variables in the quantum theory. By adding the electric densities from all the wave functions we can obtain the total electric density for the atom. If we adopt the equations of the self-consistent field as amended for exchange, then this total electric density (the matrix) has one important property, namely, *if the value of the total electric density at any time is given, then its value at any later time is determined by the equations of motion.* 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."

Exchange energy in homogeneous electron gas of density n:

$$E_x = -6 \left(\frac{3}{8\pi} n \right)^{\frac{1}{3}}$$

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

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

On the Constitution of Metallic Sodium

E. WIGNER AND F. SEITZ, *Department of Physics, Princeton University*
(Received March 18, 1933)
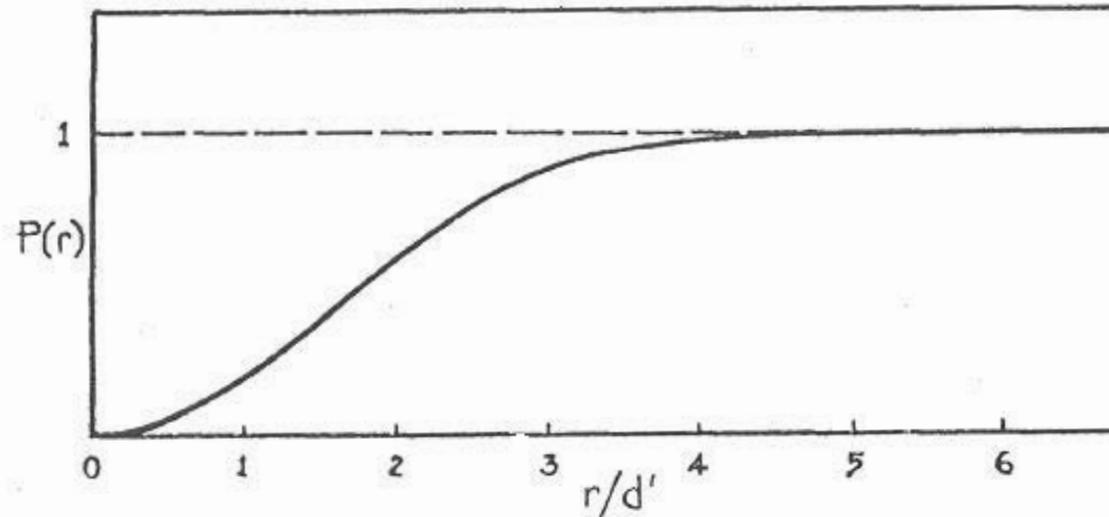
$P(r)$:Probability of electrons with parallel spin being distance r apart [$d' = (v_0/3\pi^2)^{1/3}$, v_0 atomic volume]

"Fermi" hole

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

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

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

$$V_{\mathrm{x}}^{\mathrm{Sl}} = -\frac{3}{2\pi}\left(3\pi^2 n\right)^{\frac{1}{3}}$$

"Fermi" or "exchange" hole

"Fermi" (**E. Wigner, F. Seitz** (1933)) or "exchange" hole (**J. C. Slater**, Phys. Rev. **81**, 385 (1951))
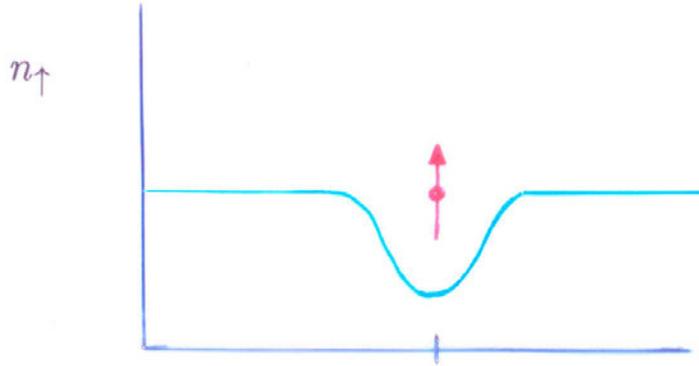
Estimate of size: sphere of radius r_0 contains unit charge:

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

Electrostatic potential at centre of uniformly charged sphere of radius r_0 is $\sim (1/r_0)$:$\longrightarrow V_x \sim (n_\uparrow)^{\frac{1}{3}}$
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: $\longrightarrow$ Good agreement with H-F eigenvalues and eigenfunctions

1960's-1970's: vast numbers of electron band structures calculated using $V_{\mathrm{x}}^{\mathrm{Sl}}$ or $\alpha V_{\mathrm{x}}^{\mathrm{Sl}}$ ($\alpha \sim \frac{2}{3}$, "Xα 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.,

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

This form led Slater[15] 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 $U^{\text{exchg}}(\mathbf{r})$, given by

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

This procedure, gross and *ad hoc* though it is, is actually followed in many band structure calculations. There have been some controversies[16] 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.

SCF-SW-Xα Method (J. C. Slater, K. H. Johnson, J. W. D. Connolly, ...):

"Muffin-tin approximation":
Potential spherically symmetrical inside spheres, constant outside
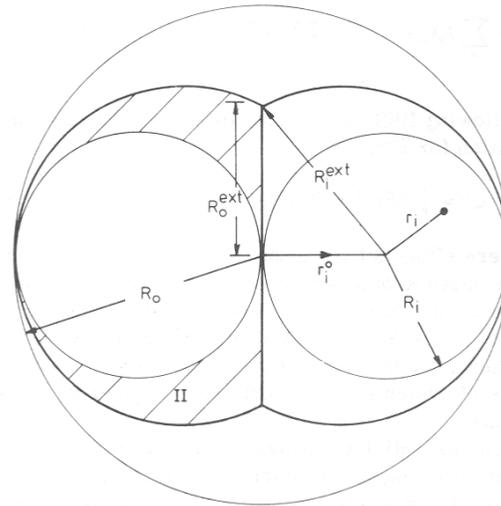
FIG. 1. Choice of cells for a diatomic molecule. R_i and R_i^{ext} denote muffin-tin and external radii, respectively, and $\vec{r}_i^{\,0}$ is the center point of the ith cell. Region II is that part of a cell outside the muffin-tin and is shown hatched for one cell. The cells have cylindrical symmetry about the molecular axis.

"Self-consistent", but MT approximation invoked every iteration for both potential and charge

Carbon dimer C_2 unbound, bond angle in H_2O molecule 180°, ...

Great hilarity in the world of quantum chemistry

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 $E[n]$:

$$E[n] \geq E_{GS}$$
$$E[n_{GS}] = E_{GS}$$

Proof:

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

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, $\psi(\vec{r}_1, \vec{r}_2, ... \vec{r}_N)$, **M. Levy** (1979) defined the functional

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

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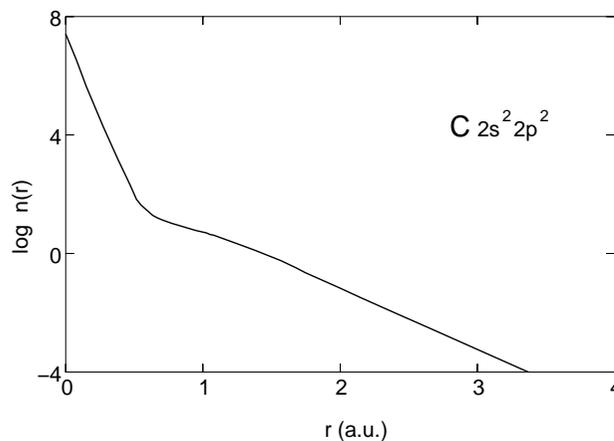
Density $n(r)$ is rather featureless, in molecules and solids close to a superposition of atomic densities.

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:

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

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

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

[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").

- **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.

- There is no *systematic* way to improve the results.

Beryllium dimer Be$_2$: 4 valence electrons ($2\sigma_g^2, 2\sigma_u^2$), same occupancy of bonding, antibonding orbitals

"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 Be$_2$, which should have a dissociation energy less than 1.2 kcal/mol, the experimental D_0 for Mg$_2$ .. 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 Be$_2$ 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, substanial 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)
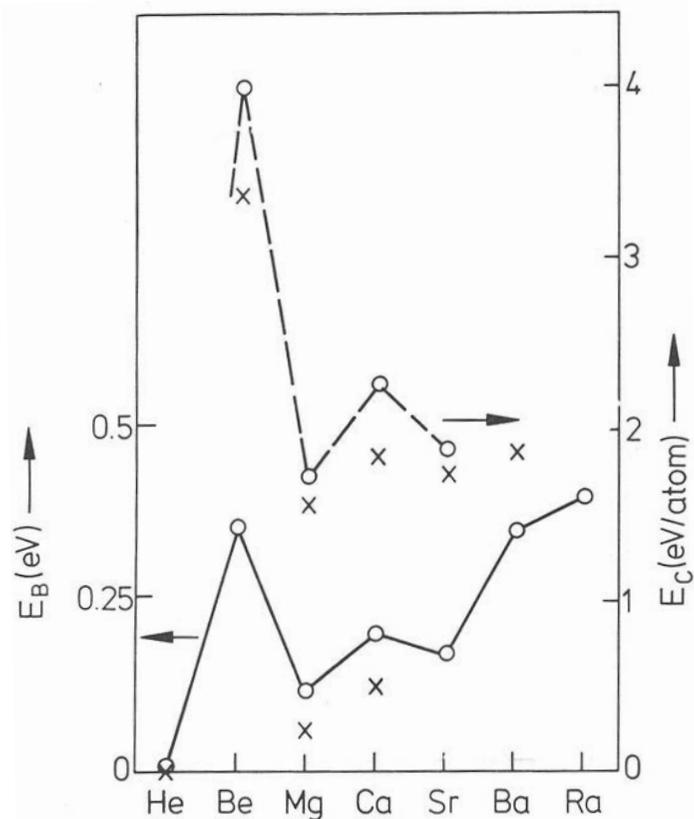
"It is perfectly obvious to any solid state physicist that Be$_2$ must be more strongly bound than Mg$_2$".

V. Heine (private communication)

"Jones was the first theoretician to suggest that Be$_2$ had a potential minimum near 2.45 Å, ... All other *ab initio* calculations to that date (1979) had predicted a minimum near 4.5 Å, 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)

P$_8$: Simulated annealing of cube (O_h) to wedge (C_{2v})

(ca. 40 kcal/mol more stable)
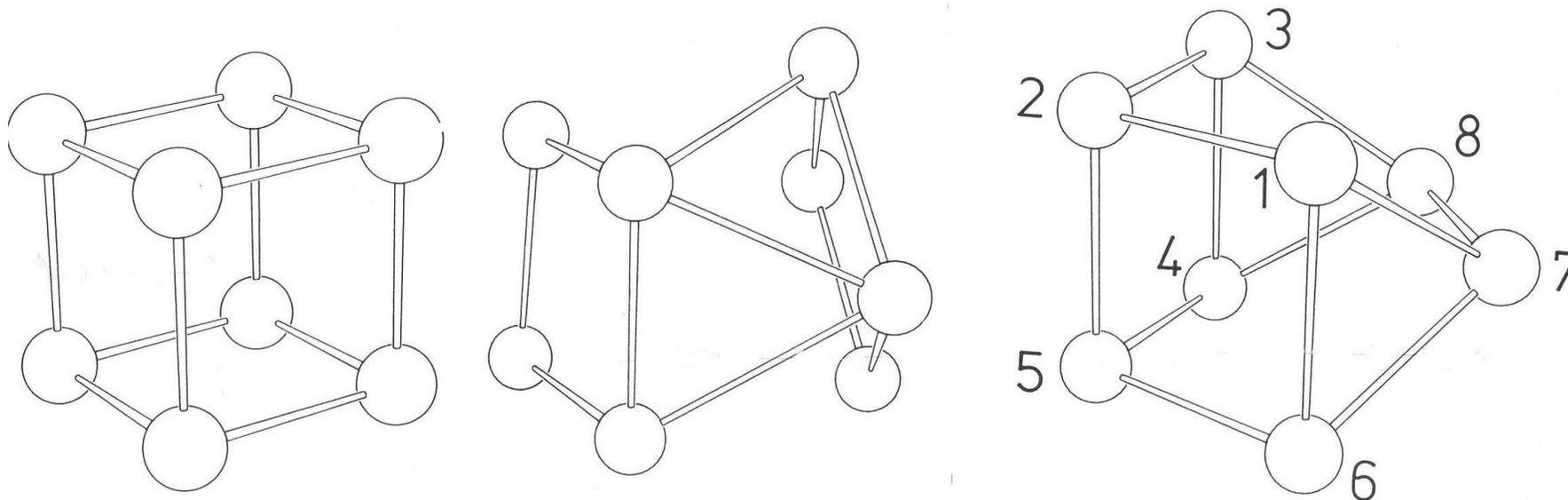
Local spin density approximation – solid state view (late 1980's)

"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
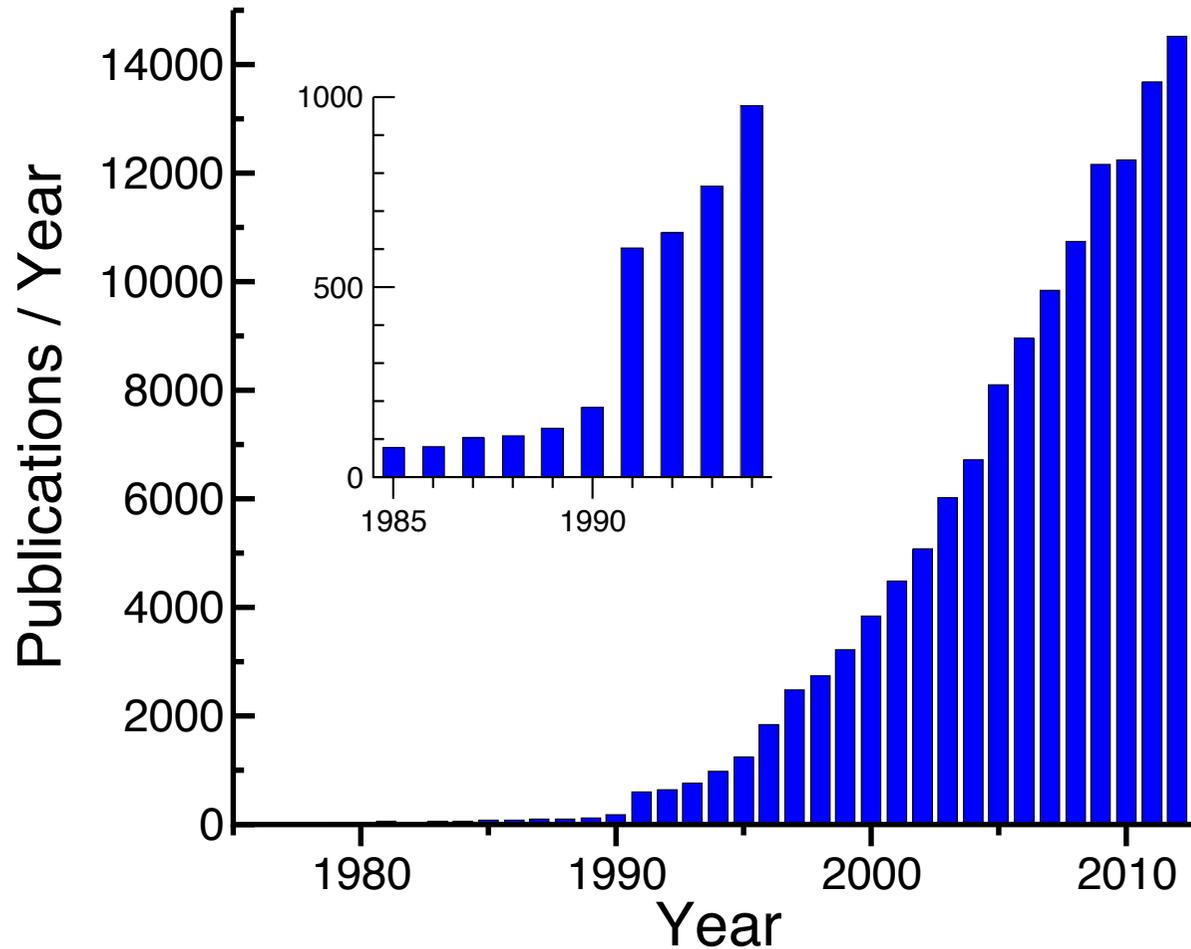
Figure 2: Number of publications per year (1975-2012) on topics **"density functional"** and **"DFT"**, according to ISI Web of Knowledge (May 2012). Inset shows data near 1990 on an expanded scale [**Ph. Mavropoulos, Φ.** $Mαυρόπουλος$ (private communication)]

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: $^2P\ [1s^22s^22p^5] \longrightarrow {}^2S\ [1s^22s2p^6]$; $\qquad 2s_\downarrow \longrightarrow 2p_\downarrow$

- 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}

Adiabatic coupling 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):

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

Writing ($\lambda = e^2$)

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

and integrating over the coupling constant λ

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

$\longrightarrow$ expression for E_{xc} in terms of fluctuations in the system, $\chi^\lambda(\mathbf{r}, \mathbf{r}', i\omega)$, $n^\lambda(\mathbf{r})$

Exchange-correlation energy, xc-hole: O. Gunnarsson, B. I. Lundqvist, PRB **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}
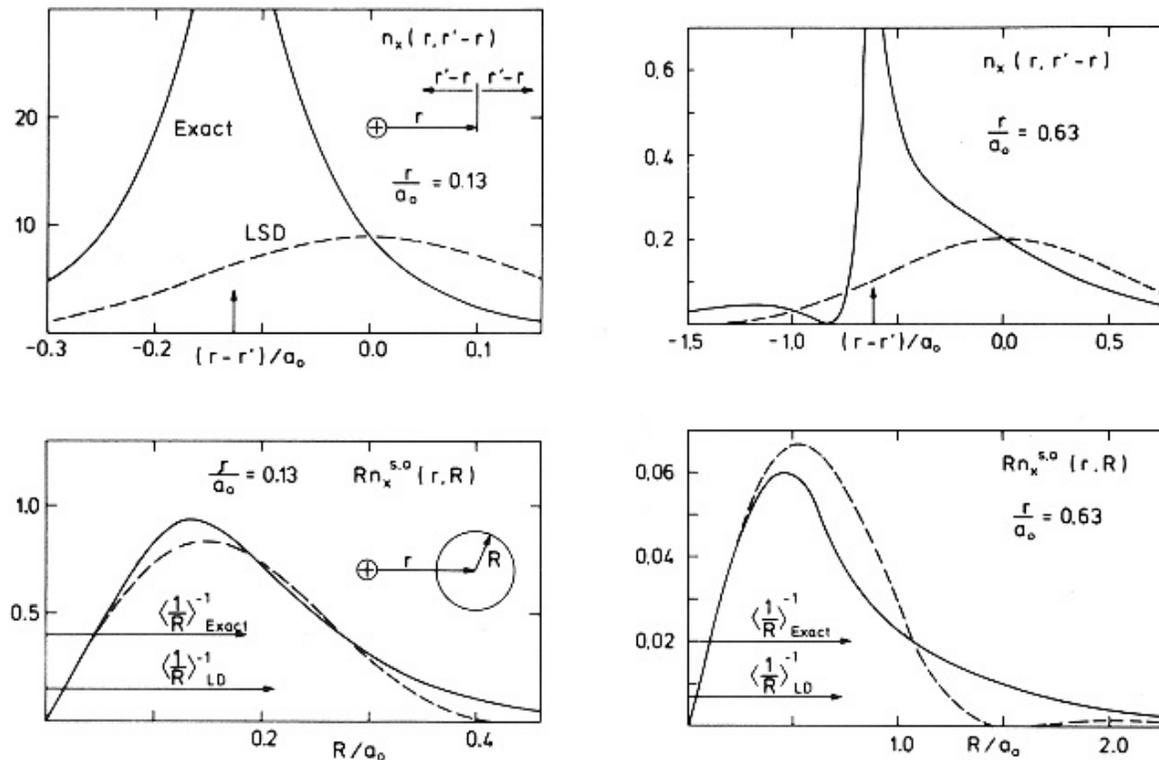
LSD results; general trends

Structural, elastic, vibrational properties

- lattice constants with 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)

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

Exchange energy ε_X:

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

$$\varepsilon_X = \varepsilon_X^{LD}\left[1 - \frac{\beta}{2^{1/3}A_X}\frac{x^2}{1 + 6\beta x \; \mathrm{arcsinh}(x)}\right],$$

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

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

Correlation energy ε_C:

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

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

where

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

$\longrightarrow$ **"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."

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"

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."

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 Xα 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?

Progress after 1990

134000 publications since 1990.

TD-DFT, "van der Waals" (dispersion) forces, DF perturbation theory, "strongly corre-lated" systems, DMRG, ...

Approximations for E_{xc}

"Jacob's ladder" of approximations, according to J. P. Perdew

Improve LSD by incorporating **exact constraints** successively
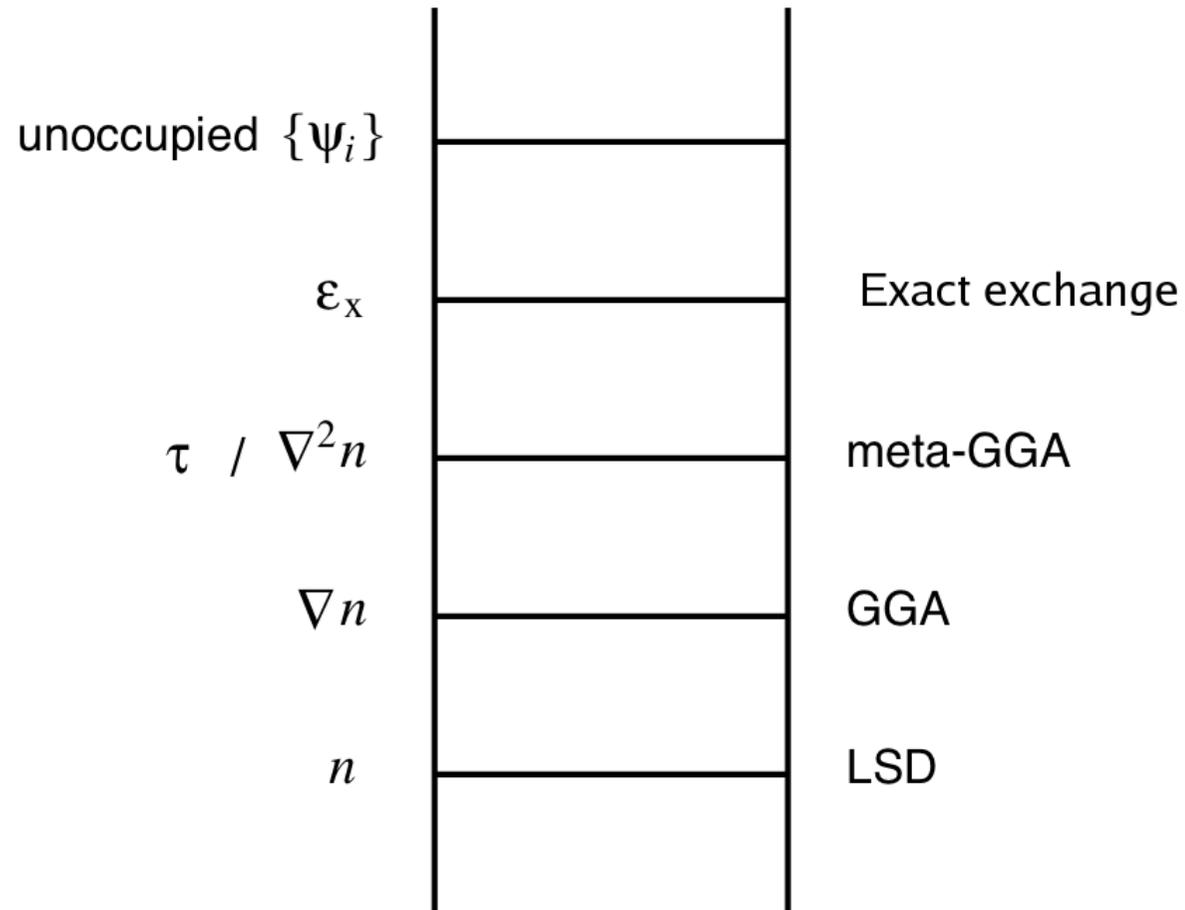
"And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven: and behold the angels of God ascending and descending on it." Genesis 28:12 (King James Version).

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

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

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

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

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

- In the slowly varying limit ($t \to 0$), H is given by the second-order GA

- In the rapidly varying limit ($t \to \infty$), $H \to -\varepsilon_C^{LD}$, and correlation vanishes

- It cancels logarithmic singularity of ε_C^{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_{XC}^{GGA} vanishes exponentially far outside an atom, $V_{XC}^{GGA}(\vec{r} \to 0) \to -\infty$).

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

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

Other schemes:

- Hybrid Schemes: Combination of HF and DF Scheme

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

  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 approach:

- 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 [**Y. Zhao, D. G. Truhlar**, J. Chem. Phys. **125**, 194101 (2006)]

Formation of protein molecules under prebiotic conditions: "iron-sulphur world" of Wächtershäuser.
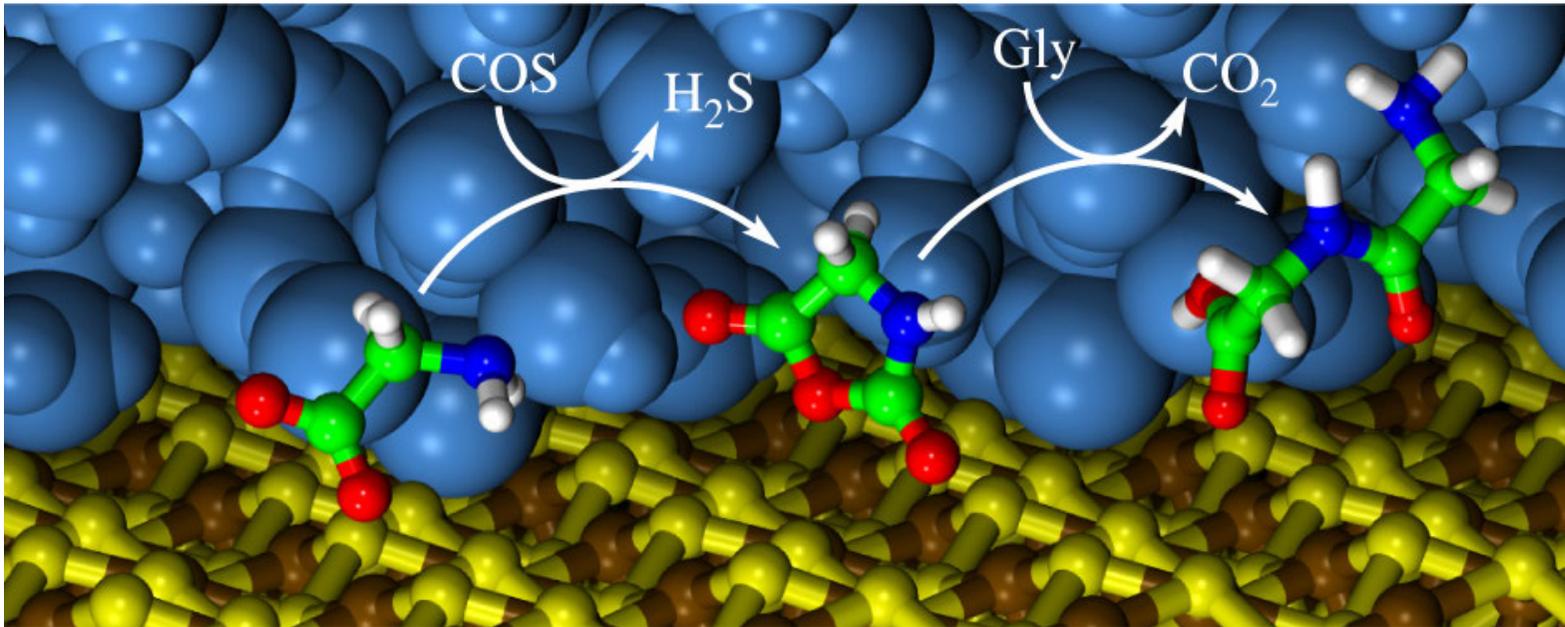
Reactions of N-carboxy anhydrides (a form of activated amino acids) in H_2O under high P, T in the presence of FeS_2 surface (72 atoms)

$\longrightarrow$ 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).

Common problem with personal computers: Long wait after switching on. Why?

Random access memory (RAM) is "volatile" [contents vanish if no power]

Non-volatile memory? Yes, USB sticks (Si/SiO$_2$ arrays), DVD-RAM (Ge$_2$Sb$_2$Te$_5$ alloy)

2008: Blu-ray Disc (BD) wins battle against HD-DVD to succeed DVD-RW optical memories

"Phase change (PC) memories"

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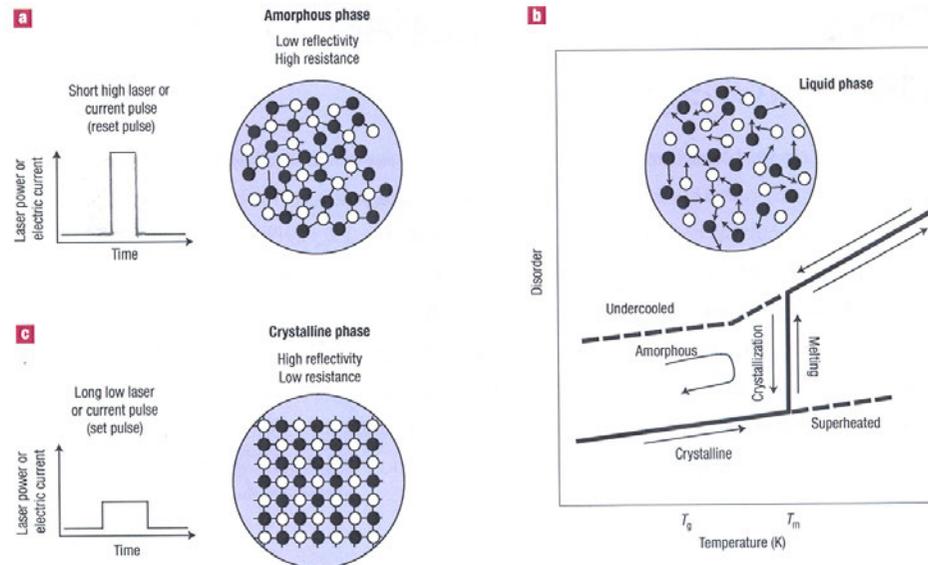
M. Wuttig and N. Yamada, Nature Mater. **6**, 824 (2007)

"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

Simulation of structural phase transitions: $Ge_2Sb_2Te_5$:

Strategy:

- Simulation of 460 atoms (102 Ge, 102 Sb, 256 Te), 52 vacancies (initially in NaCl structure)
- Melt (3000 K), cool to MP (900 K, 42 ps) data collection 21 ps
- Cool to 300 K (139 ps), data collection 21 ps, quench to 100 K (74 ps)
- DF/MD simulations, CPMD program
- Evaluate pair correlation functions, structure factors $S(Q)$, diffusion constants, order parameters, ...
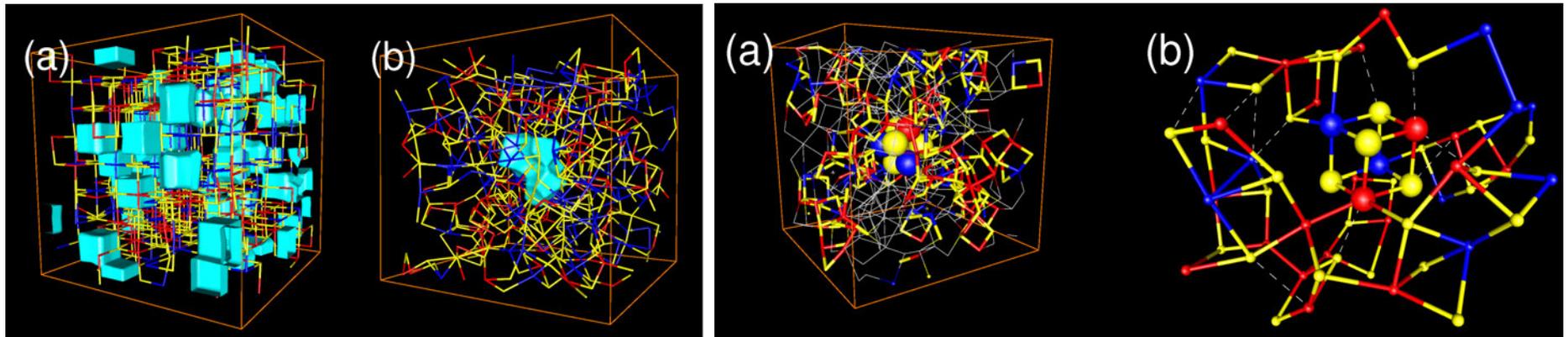
Crystallization of $Ge_2Sb_2Te_5$:   460 atoms, 600 K

J. Kalikka, J. Akola, R. O. Jones (2013, in progress)

Four simulations with different starting structures:

- 1.25 ns (400 000 time steps) complete
- Three further simulations at 700 ps to test sensitivity to initial structure
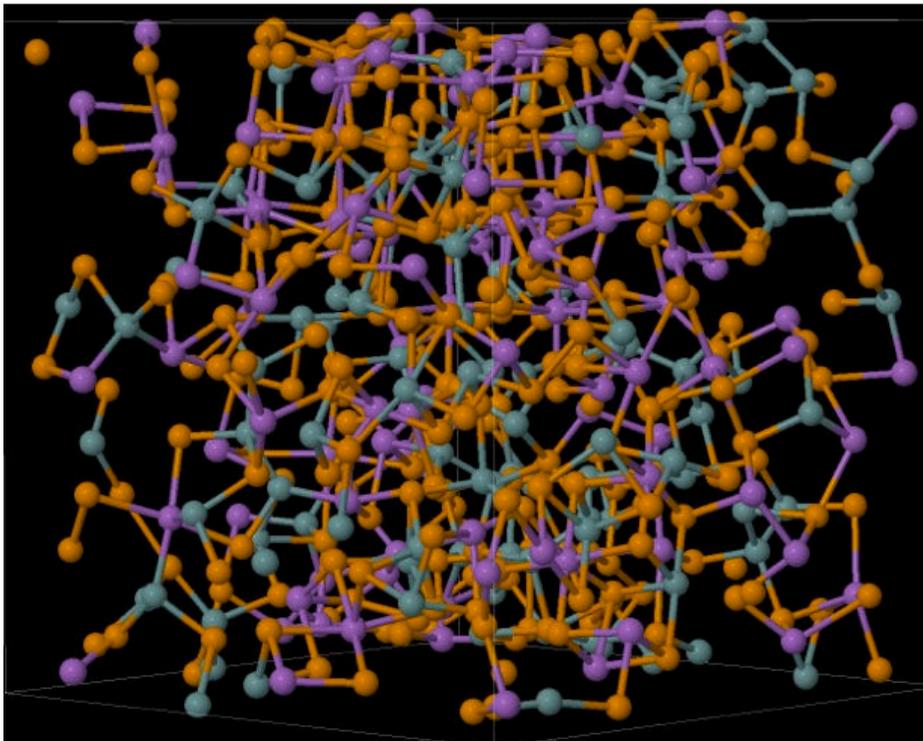
215 ps
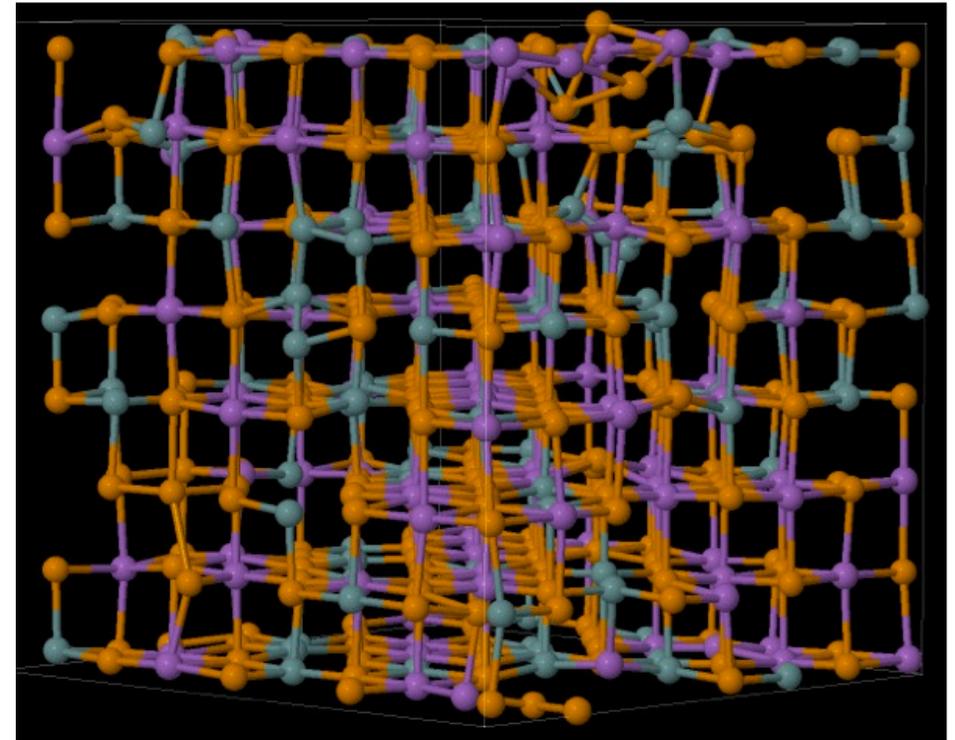
1045 ps

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 individuals over dating back to the 1920's. (**Fermi, Dirac, Bloch, Slater, Wigner, Schwinger, Kohn, Pople, ...** and MANY others)

DF calculations with **molecular dynamics**
can probe the energy hypersurfaces $E(R_I)$ in complicated systems: energy minima (structure) and barriers.

The relationship between the **Structure** and **Properties** of a system means that we are making steps to **understand 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 ↑ Mott ↓")

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

N. C. Handy (ACS National Meeting, Orlando, FL, March 2002):

73.

UNDERSTANDING ELECTRON CORRELATION. *Nicholas Handy*, Department of Chemistry, University of Cambridge, Lensfield Road, Camridge, 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.

Linus Pauling, Stockholm. 10 December 1954

Talk to students.

Young men & women: On behalf of my colleagues, as well as myself, I thank you for your kind demonstration of friendship & respect.

I am reminded of my own students in California. They are much like you — I have observed that students, young people, are much the same all over the world — and that scientists are the same. There is a world-wide brotherhood of youth & of science.

Perhaps, as one of the older generation, I should preach a little sermon to you — "~~Dearly beloved, we are gathered here tonight to think of higher things, to help overcome the temptations of the flesh~~", but I do not propose to do so. I shall, instead, give you a word of advice about how to behave toward your elders.

When an old & distinguished person speaks to you, listen to him carefully & with respect — but do not believe him. Never put your trust in anything but your own intellect. Your elder, no matter whether he has gray hair or has lost his hair, no matter whether he is a Nobel laureate — may be wrong. The world progresses, year by year, century by century, as the

TELEGRAM

TELEGRAFVERKET

De med grova linjer inramade delarna ifyllas av telegrafen. Anvisningar, se baksidan.

Klass	Nr	Ord	Datum	Kl.	Avsänt
					sign. kl.

Tj-anm. och via

Adress

members of the younger generation find out what was wrong among the things that their elders said. So you must always be skeptical – always think for yourself.

Text

There are, of course, exceptional circumstances: when you are taking an examination, it is smart to answer the questions not by saying what you think is right, but rather what you think the Professor thinks is right. Arrhenius discovered that there is danger in being too original in one's Doctor's thesis.

You will have some great problems to solve – The greatest of all is the problem of war & peace. I believe that this problem has been solved, by the hydrogen bomb – that there will never

Avsändarens namn, adress och telefonnummer (avtelegraferas icke).

Avgift	sign.

Bl. 201
(1947)

Litografiska AB Norrköping 14/3 52. 4,000,000

THANK YOU !!

Sources of error in LSD calculations: Exchange energy

The exchange energy can be expressed in terms of exchange integrals (Φ_i, Φ_j are HF orbitals)

$$I_{ij} = e^2 \int d\mathbf{r} \int d\mathbf{r}' \frac{\Phi_i^*(\mathbf{r})\Phi_j(\mathbf{r})\Phi_i(\mathbf{r}')\Phi_j^*(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid}$$

I_{ij} depends strongly on the nodal structure of Φ_i and Φ_j (if Φ_i and Φ_j have different l and m-quantum numbers, the integrand oscillates and I_{ij} is reduced).

Fluorine atom:$s_\downarrow \longrightarrow p_\downarrow$ orbital

$$1s^2 2s(\uparrow\downarrow)2p(\uparrow\uparrow\uparrow\downarrow\downarrow) \to 1s^2 2s(\uparrow)2p(\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow)$$

$$\Delta E_x = -\frac{9}{25}G^2(2p, 2p) + \frac{2}{3}G^1(2p, 2s)$$

$$G^k(i,j) = e^2 \int_0^\infty dr\, r^2 \int_0^\infty dr'(r')^2 \frac{r_<^k}{r_>^{k+1}}\phi_i(r)\phi_j(r)\phi_i(r')\phi_j(r')$$

($\phi_i(r)$ is radial part of $\Phi_i(\mathbf{r})$)

First term: Exchange interaction between a p electron with $m = -1$ and two p electrons with $m = 1$ and 0 (two nodal planes). Second term: interaction between an s electron and two p electrons (one nodal plane). Realistic values for Slater integrals $\longrightarrow \Delta E_x \sim 6$ eV.

Orbitals in first row atoms
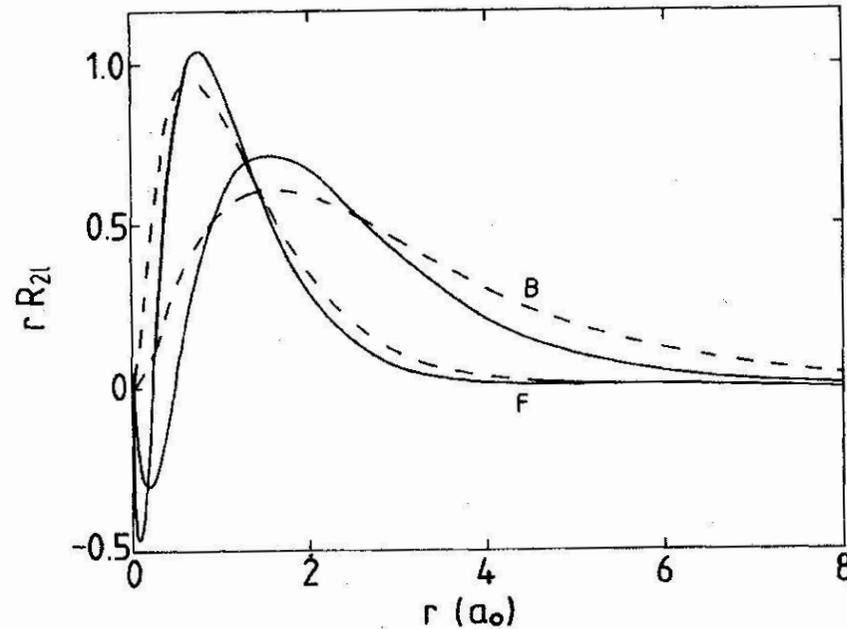
FIG. 1. Valence orbitals from density-functional calculations for B and F. The solid curves represent the $2s$ orbitals, the dashed curves the $2p$ orbitals.

If radial parts of $s-$ and $p-$orbitals are assumed to be *identical* (neglecting small nonspherical corrections), LSDX $\longrightarrow \Delta_{sp} = 0$ on sp transfer, i.e. LSDX prediction for Δ_{sp} differs from HF by 6 eV. The deviation between the LSD result and experiment is 2.6 eV.

Conclusions from model calculations (see notes):

- If we occupy the orbitals with the minimum number of nodal planes consistent with the Pauli principle, trends in interelectronic exchange energies are reproduced well by LSDX. The absolute value is overestimated in most systems. (e.g. $\triangle_{sp}$ in Be - C).

- Transfer energy to a state with additional node(s) often underestimated substantially by LSDX. (e.g. $\triangle_{sp}$ in O-F).

Iron series atoms: $\Delta_{sd} = E([core]3d^{n-1}4s^1) - E([core]3d^{n-2}4s^2)$
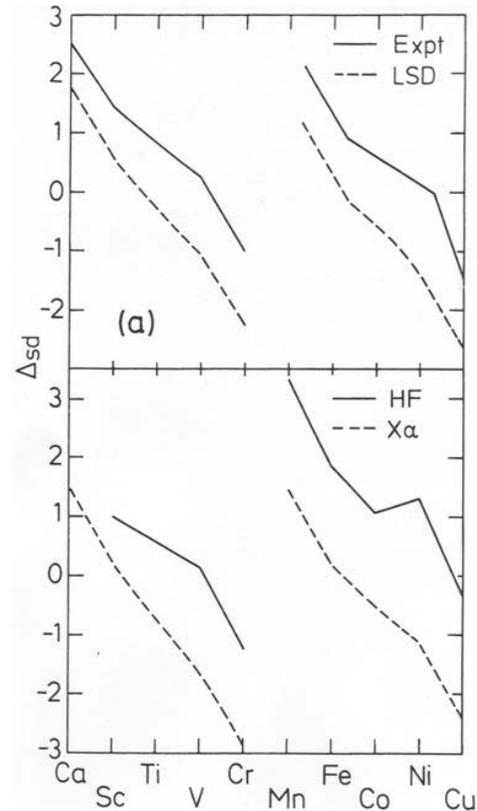
Trends and break in the middle (filling of spin-up d-shell) described well by LSDX and LSD approximations.

Mn atom: $[core]3d(\uparrow\uparrow\uparrow\uparrow\uparrow)4s(\uparrow\downarrow) \rightarrow [core]3d(\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow)4s(\uparrow)$:

(only) spin down valence electron is transferred from a $4s \longrightarrow 3d$ orbital. Expect similar results for HF and LSD, but difference of about 2 eV, due to exchange between $3d$ electron and $3s3p$ core.

Crystalline? What is a "crystal" ?: Periodicity? Order?

D. Shechtman, I. Blech, D. Gratias, J. Cahn, *Metallic phase with long-range orientational order and no translational symmetry*, Phys. Rev. Lett. **53**, 1951 (1984)

$Al_{14}Mn_{86}$ alloy with icosahedral point group symmetry $m\bar{3}\bar{5}$ (a **"quasicrystal"**)

Dan Shechtman Nobel Prize for Chemistry 2011
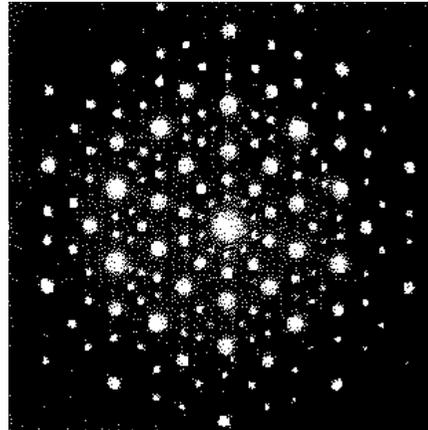
International Union of Crystallography, Acta Cryst. **A48**, 922-946 (1992), see p. 928.

"crystal": any solid having an essentially discrete diffraction diagram,
"aperiodic crystal": any crystal in which three-dimensional lattice periodicity can be considered to be absent.

Crystalline structure: implies order, not periodicity

Number of "wrong bonds": 500 K, 600 K, 600 K (648 atoms), 700 K (times in ps)
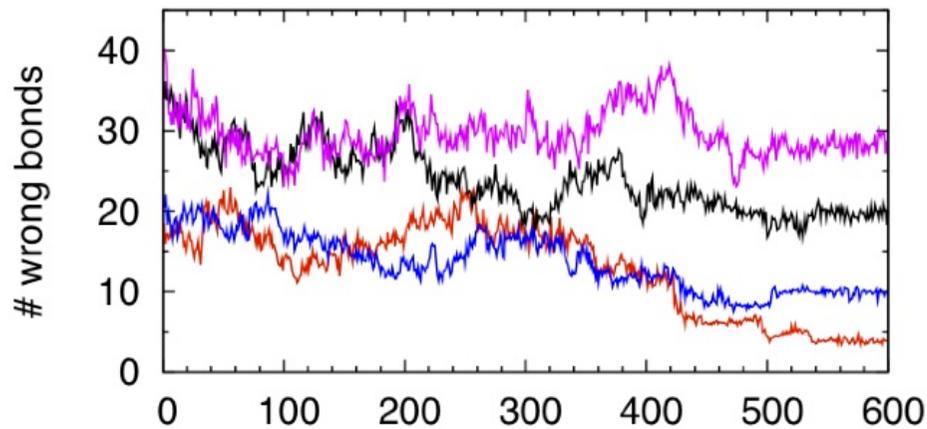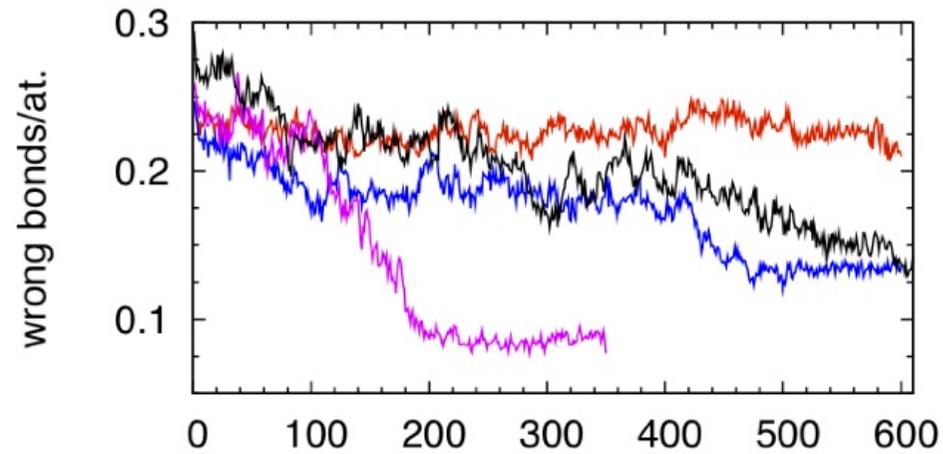
600 K
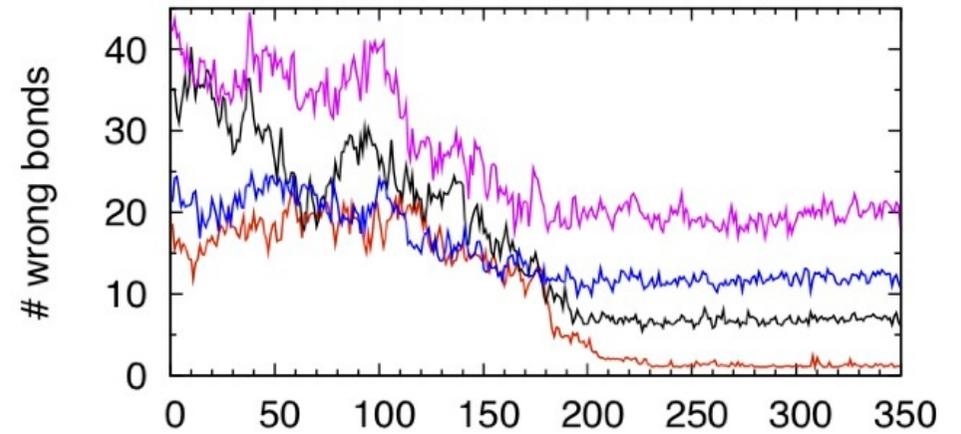
700 K

Ge–Ge, Ge–Sb, Sb–Sb, Te–Te

The time in annealing process is crucial:

Energy surface of system (schematic)
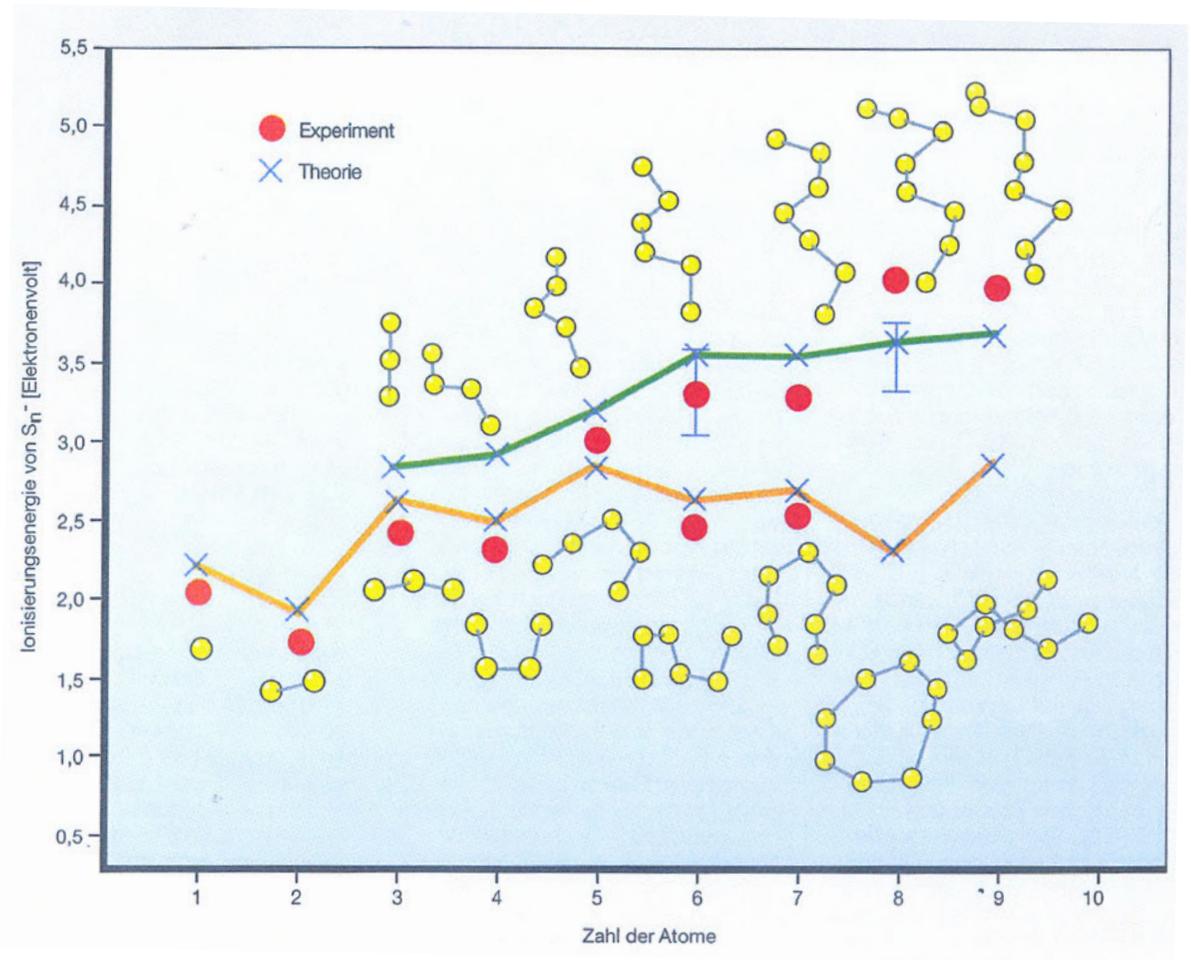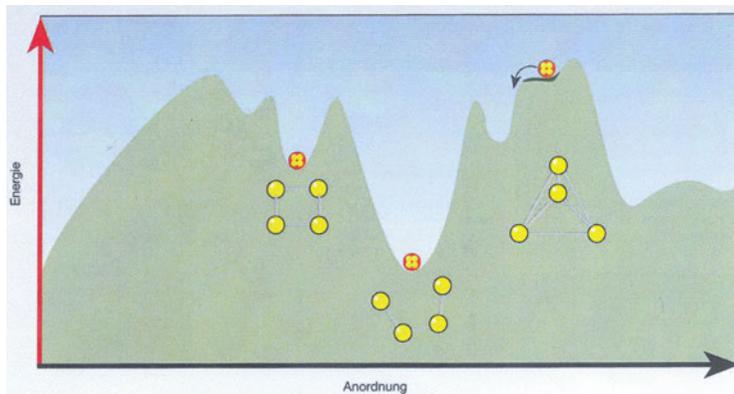
Ionization of sulphur cluster anions S_n^- generated with different cooling rates.
Rapid cooling results in chain structures for $n \geq 6$, although *much* less stable than rings

S. Hunsicker, R. O. Jones, G. Ganteför, J. Chem. Phys. **102**, 5917 (1995)

Chemical reactions:

Nucleophilic attack of lithium phenoxide on ring oligomers of BPA-PC (polycarbonate)
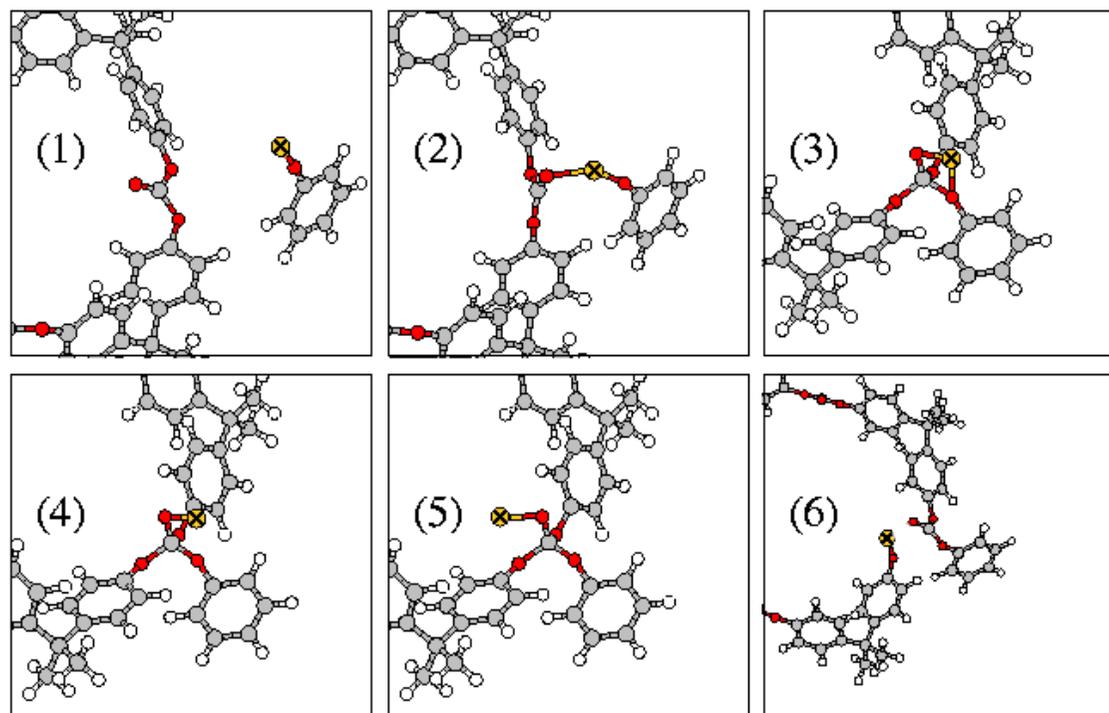
- Li still at end of chain, i.e. it remains "active" (a "living polymer").
- Reaction conserves number and type of bonds
- Energy change during reaction very small

P. Ballone, B. Montanari, R. O. Jones, J. Phys. Chem. A **104**, 2793 (2000).

Biochemistry: ATP hydrolysis to ADP

Basic energy mechanism in mammals (and elsewhere).

"The most prevalent chemical reaction in the human body and "the principal net chemical reaction occurring in the whole world"

R. D. Boyer, *Nobel Lectures*, 1997.
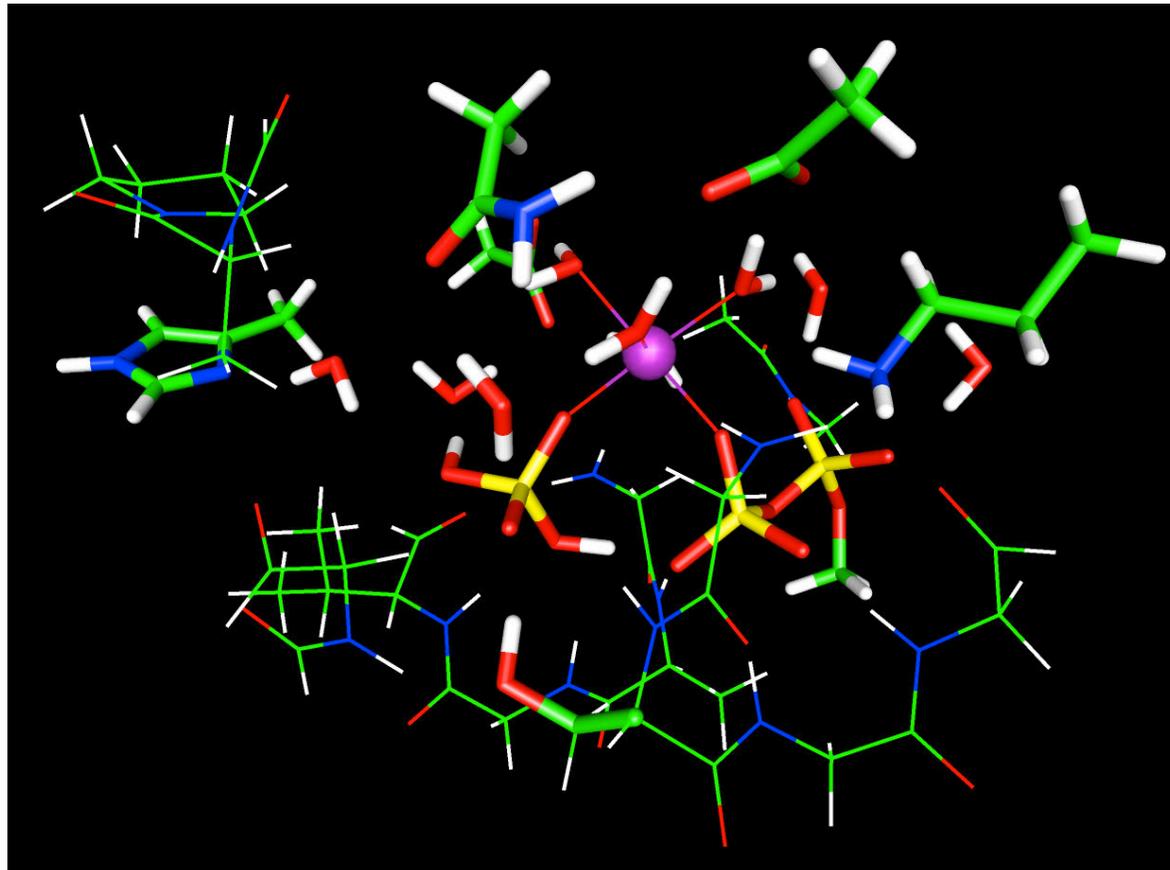
Structure of metastable GST-225:

T. Nonaka *et al.*, Thin Solid Films **370**, 258 (2000)

Switching positions of *all* Sb atoms with Te atoms gave equally good agreement with XRD data

Table 2
Calculation results of the R factors and the S values of meta-stable $Ge_2Sb_2Te_5$ with changing the vacancies of 4a site

No.	4a site (0, 0, 0)				4b site (0.5, 0.5, 0.5				R	S
	Ge	Sb	Te	Vacancy	Ge	Sb	Te	Vacancy		
1	0.444	0.444	0.111	0.000	0.000	0.000	1.000	0.000	15.33	2.38
2	0.433	0.433	0.083	0.050	0.000	0.000	1.000	0.000	14.43	2.24
3	0.422	0.422	0.056	0.100	0.000	0.000	1.000	0.000	13.57	2.10
4	0.411	0.411	0.028	0.150	0.000	0.000	1.000	0.000	12.87	2.00
5	0.400	0.400	0.000	0.200	0.000	0.000	1.000	0.000	12.51	1.94
6	0.389	0.361	0.000	0.250	0.000	0.028	0.972	0.000	12.58	1.95
7	0.378	0.322	0.000	0.300	0.000	0.056	0.944	0.000	13.19	2.04
8	0.367	0.283	0.000	0.350	0.000	0.083	0.917	0.000	14.36	2.23
9	0.356	0.244	0.000	0.400	0.000	0.111	0.889	0.000	16.05	2.49
10	0.400	0.000	0.400	0.200	0.000	0.400	0.600	0.000	12.55	1.95

"It indicates that to determine the distribution of Sb and Te by this method (XRD) is very difficult."

"It revealed that $Ge_2Sb_2Te_5$ belongs to the NaCl type structure $(Fm\bar{3}m)$ with the 4a site including 20% vacancies."

Amorphous (A) to crystalline (C) transition in phase change memory materials:

Crystallization is the time-limiting, crucial process in write/erase cycle of PCM

(here $Ge_2Sb_2Te_5$, prototype "GST" alloy)

Which amorphous, which crystalline form?

Amorphous	Crystalline
"as-deposited" (AD)	equilibrium, stable (primitive hexagonal)
"melt-quenched" (MQ)	"metastable" (rock salt)
J. Akola, J. Larrucea, R. O. Jones, Phys. Rev B **83**, 094113 (2011)	**B. J. Kooi, J. T. M. de Hosson**, J. Appl. Phys. **92**, 3584 (2002)

We focus on:

- MQ (the result of most simulations)
- "metastable" crystalline structure (relevant for PCM)

Thermal expansion in Ceran cooktops (β-eucryptite, LiAlSiO$_4$):

TE close to zero over range of 1000 K, but 21 / 84 atoms in unit cell (HT, LT) !!

Are DF calculations of thermal expansion coefficients possible?

CERAN ® Elektro

CERAN Matic ®

CERAN Flam ®

CERAN ® Elektro Halogen
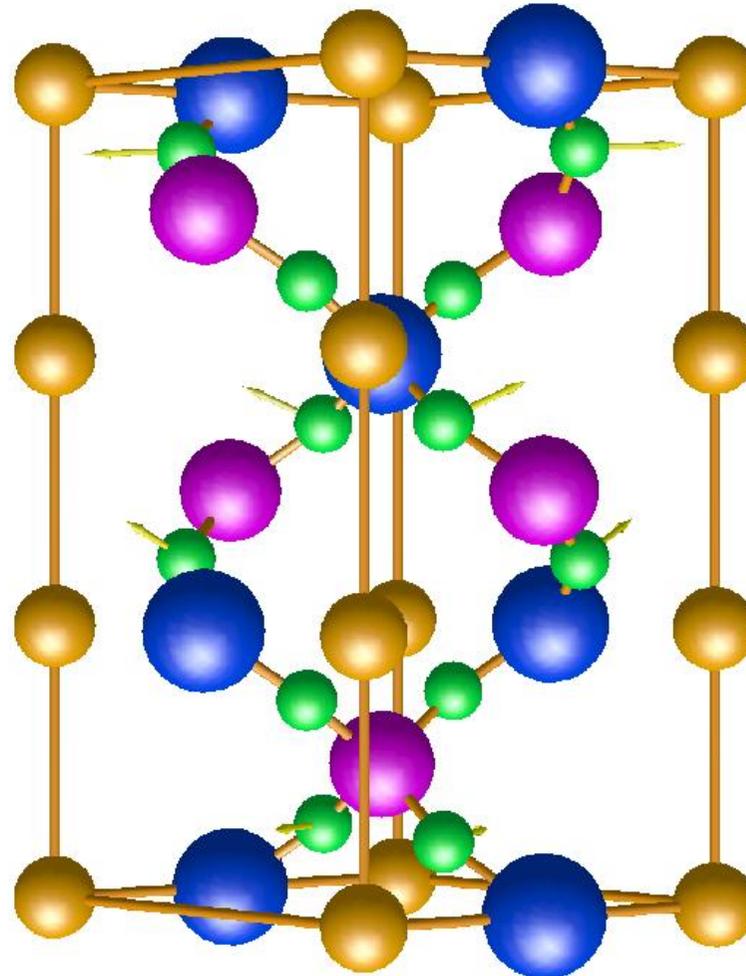
Thermal expansion:
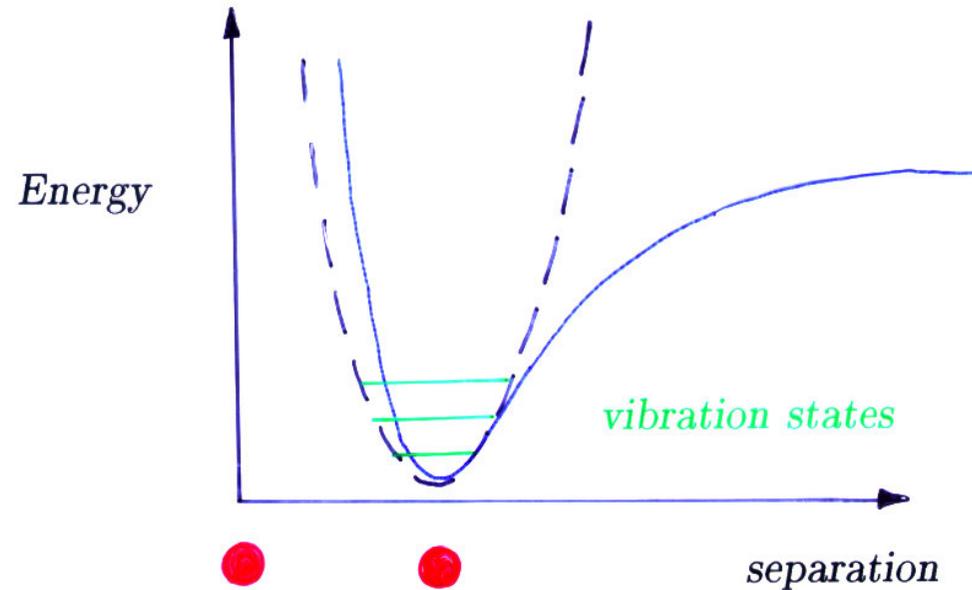
Anharmonicity $\longrightarrow$ thermal expansion [**M. Born** (1923), **E. Grüneisen** (1924)]:
[*before* quantum mechanics, but with quantum nature of phonons]

- Energy surfaces (DF calculations)
- Temperature effects

Free energy F as function of the displacement u_i and T:

$$F(u_i, T) = E(0,0) + \frac{1}{2}V\sum_{i,j} B_{ij} u_i u_j + F^*(u_i, T)$$

Thermal expansion:

Uniaxial crystals such as β-eucryptite have independent volume and axial displacements:

$$du_1 = d \ln V; \quad du_2 = d \ln(c/a)$$

Using the "quasiharmonic" approximation:

$$\alpha_a(T) = \frac{1}{3BB_{22}} \left[(B_{22} + B_{12}) \gamma_1 - (B_{11} + B_{12}) \gamma_2 \right]$$

$$\alpha_c(T) = \frac{1}{3BB_{22}} \left[(B_{22} - 2B_{12}) \gamma_1 + (2B_{11} - B_{12}) \gamma_2 \right]$$

$\omega_j(\mathbf{q})$: phonon frequencies, B: bulk modulus

$$\gamma_i(T) = - \sum_{\mathbf{q},n} \frac{\partial \omega_n(\mathbf{q})}{\partial u_i} \frac{\partial n_B(\omega_n(\mathbf{q}))}{\partial T}$$

$$n_B(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$$

Thermal expansion of β-eucryptite: Lattice constants as function of T
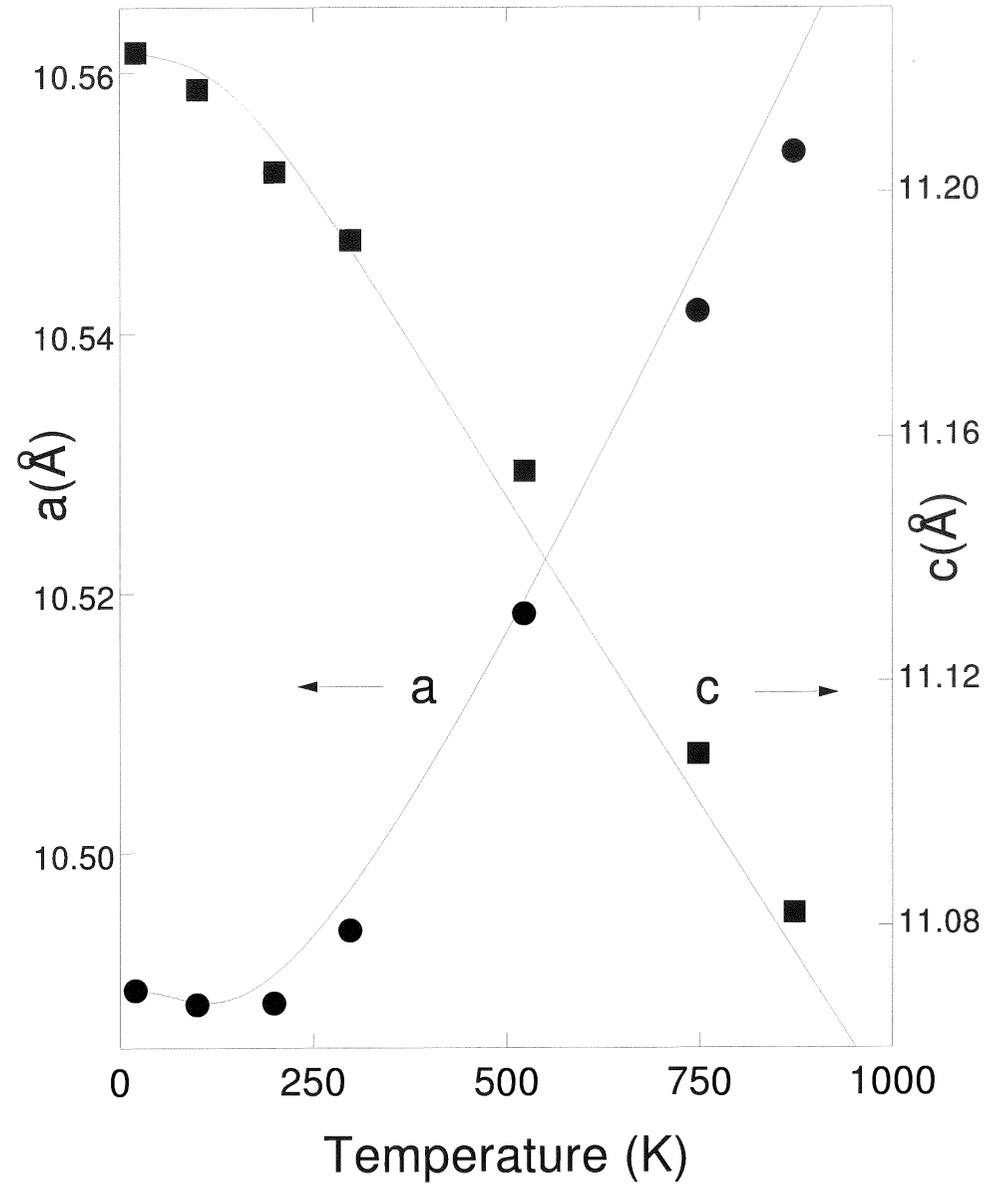
A. I. Lichtenstein, R. O. Jones, H. Xu, P. J. Heaney, Phys. Rev. B **58**, 6219 (1998)

A. I. Lichtenstein, R. O. Jones, S. de Gironcoli, S. Baroni, Phys. Rev. B **62**, 11487 (2000)

Promotion energies in atoms: Δ_{sp}

For first-row atoms

$$\Delta_{sp} = E(1s^2 2s2p^{n-1}) - E(1s^2 2s^2 2p^{n-2}) \tag{1}$$

Comparison between LSD and experiment, and between H-F and LSDX
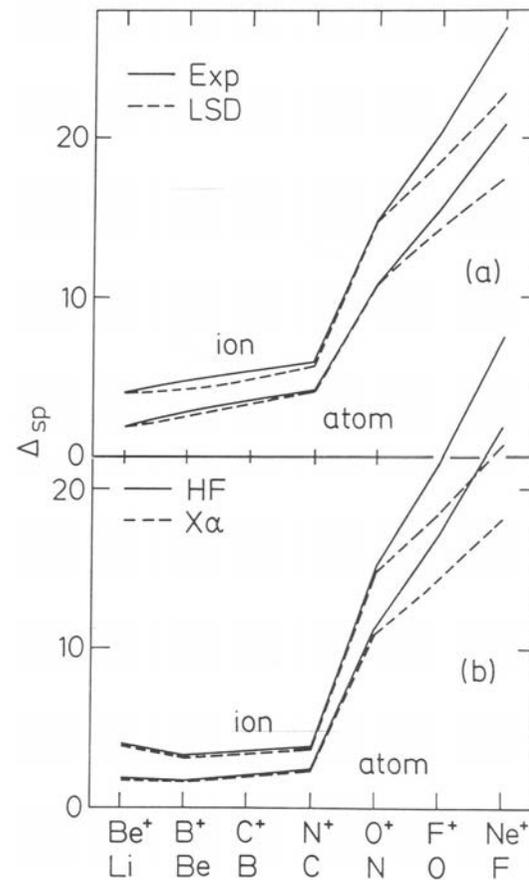
O. Gunnarsson, R. O. Jones, Phys. Rev. B **31**, 7588 (1985)

Promotion energies in atoms: Δ_{sd}

For 3d-transition element atoms

$$\Delta_{sp} = E([\text{core}]3d^{n-1}4s^1) - E([\text{core}]3d^{n-2}4s^2) \tag{2}$$

Comparison between LSD and experiment, and between H-F and LSDX
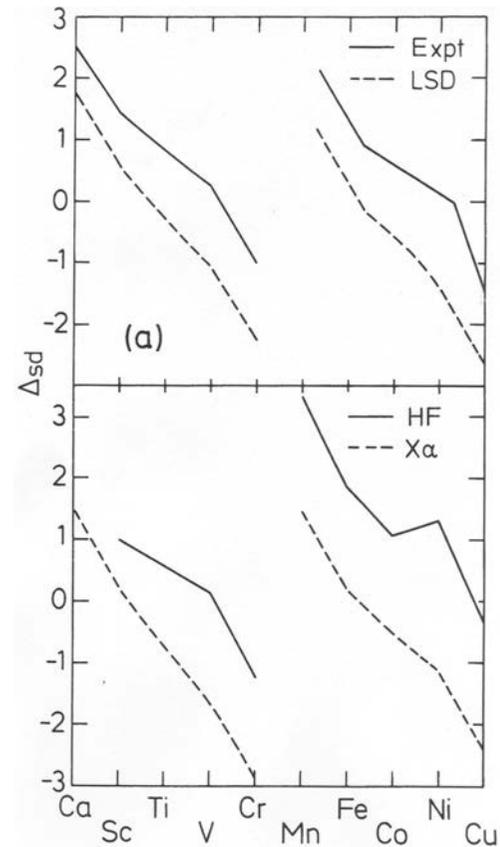
O. Gunnarsson, R. O. Jones, Phys. Rev. B **31**, 7588 (1985)

Another self-consistent solution (M. C. Escher):
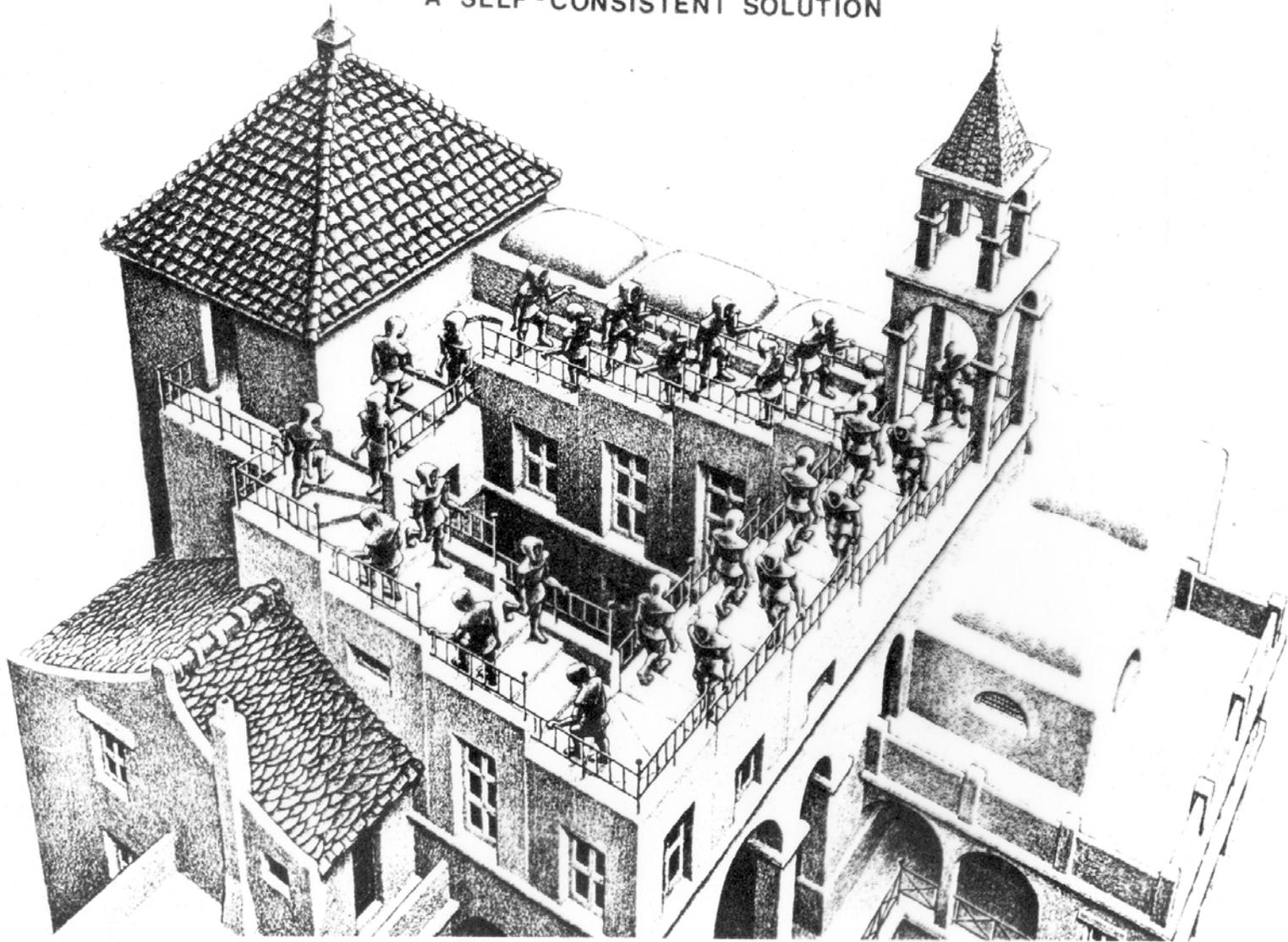
Dr. R. O. Jones

April 14, 1977

4202

Prof. R. Hoffmann
Department of Chemistry
Cornell University

Ithaca, N.Y. 14853

U S A

Dear Professor Hoffmann,

As you can see from the enclosed preprint, we have developed
an ab initio method for calculating the total energy of atomic
clusters which gives surprisingly good results for simple mole-
cules. Further details of the calculational procedure are given
in the March 15 issue of Phys. Rev. B. We have now carried out
calculations for a variety of heavier molecules, for some of
which only extended Hückel calculations have been performed
previously.

We are very encouraged by the results so far and are interested to
discover the reaction of theoretical chemists to our method.
I shall be visiting Cornell for several days in mid-June (staying
with Neil Ashcroft), and I hope that it will be possible to talk
to you then.

Yours sincerely,

(R.O. Jones)

Encl.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK 14853
U.S.A.

May 26, 1977

Dr. Robert O. Jones
Institut für Festkörperforschung
der Kernforschungsanlage Jülich GmbH
Postfach 1913
D-5170 Jülich 1
FEDERAL REPUBLIC OF GERMANY

Dear Dr. Jones:

I appreciated receiving the preprint of your work with Gunnarson
and Harris on the applications of density functional theory to diatomic.
The results you obtain are spectacular, and I certainly would like to learn
more about the method.

Unfortunately I will be away in mid-June, leaving for Orsay, France,
on June 12, and returning here only on the 30th. If I am not here when you
come, I would very much like to have my research group hear of your work,
and I have let Neil Ashcroft know about this.

Cordially yours,

Roald Hoffmann

RH/e

Ehrenfest's Theorem

P. Ehrenfest, "Bemerkung über die angenäherte Gültigkeit der klassischen Mechanik innerhalb der Quantenmechanik", Z. Physik **45**, 455-457 (1927)

Time derivative of the expectation value of a quantum mechanical operator A is given by the commutator of A with the Hamiltonian of the system H:

$$\frac{d}{dt}\langle A \rangle = \frac{i}{\hbar}\langle [H, A] \rangle$$

Example: Particle in potential $V(r)$

$$H = \frac{p^2}{2m} + V(r)$$

.

Instantaneous change in momentum p

$$\frac{d}{dt}\langle p \rangle = \frac{i}{\hbar}\langle [p, V(r)] \rangle$$

$$\frac{d}{dt}\langle p \rangle = -\langle \nabla V(r) \rangle = \langle F \rangle$$

Newton's equation of motion

Structure of metastable $Ge_2Sb_2Te_5$:

N. Yamada, MRS Bulletin **21**, 48 (1996)

"It is believed that 4(a) sites of (this) NaCl-type crystal are occupied only by Te atoms, while 4(b) sites are randomly occupied by Ge and Sb atoms or vacancies."
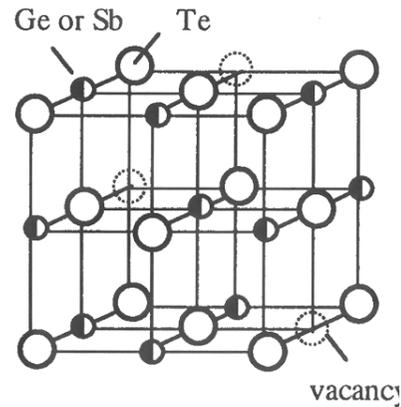

N. Yamada, T. Matsunaga, J. Appl. Phys. **88**, 7020 (2000)

Ge$_2$Sb$_2$Te$_5$: XRD and XPS measurements (SPring-8, Japan):

XRD: S. Kohara *et al.* Appl. Phys. Lett. **89**, 201910 (2006)
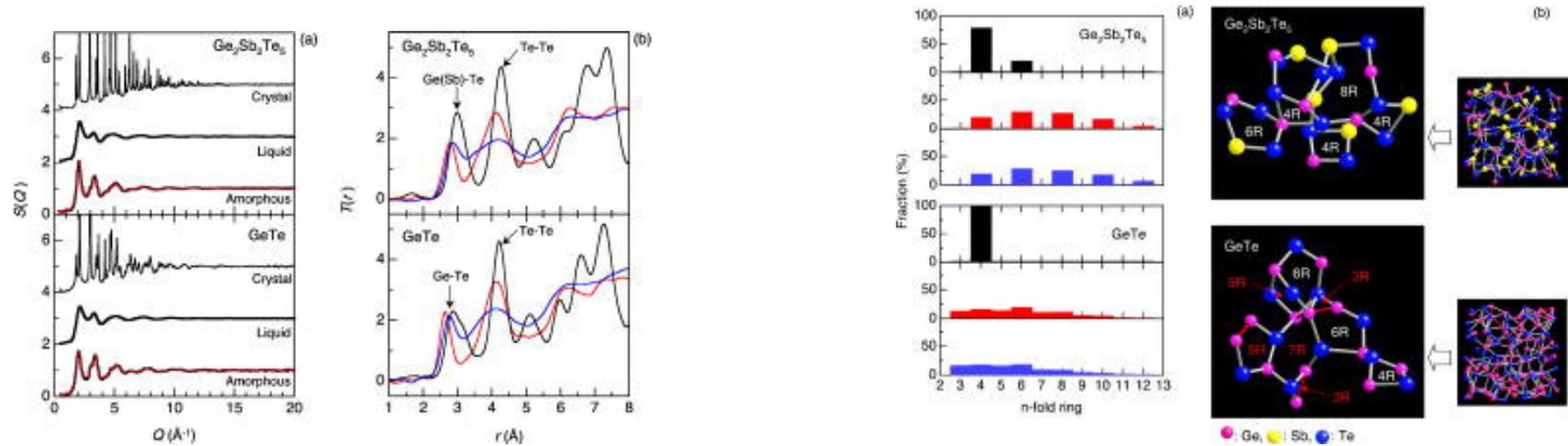
XPS: J.-J. Kim *et al.* Phys. Rev. B **76**, 115124 (2007)
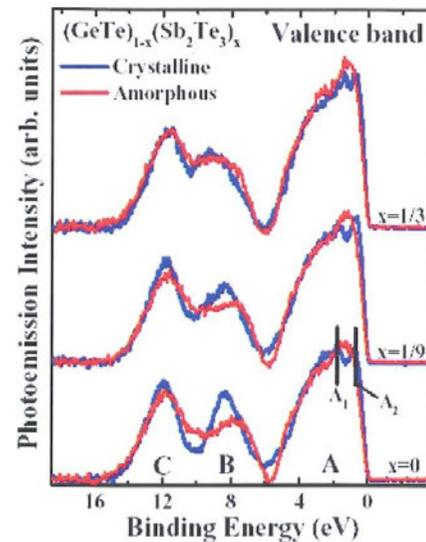
Crystallization of $Ge_2Sb_2Te_5$ with fixed seed

J. Kalikka, J. Akola, J. Larrucea , Phys. Rev. B **86**, 144113(2012)

- 460 atoms with 64 sites (13 Ge, 13 Sb, 32 Te, 6 cavities) fixed, 500 K (600 ps), 600 K (600 ps); 700 K (350 ps)

- One simulation with 648 atoms (600 K, 600 ps)

- Density changed from amorphous to crystalline (five steps) during simulation

- "Crystalline" atoms identified using directional order parameter

  P. J. Steinhardt, D. R. Nelson, M. Ronchetti, Phys. Rev. B **28**, 784 (1983)

$$\overline{Q}_\ell = \sqrt{\frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} |\overline{Q}_{\ell m}(i)|^2}$$

$$\overline{Q}_{\ell m}(i) = \frac{1}{N_b(i)} \sum_{k=0}^{N_b(i)} Q_{\ell m}(k); \quad Q_{\ell m}(i) = \frac{1}{N_i} \sum_{j=1}^{N_i} Y_{\ell m}(r_{ij})$$

  $N(i)$; number of neighbours of atom i. Average over atom i and first coordination shell
  "Crystalline" atom if $\overline{q}_4 \geq 0.6$

- "Percolation" if path of bonds from atom to its replica in next cell

Crystalline atoms and percolation:

Simulation: 460 atoms, 600 K, 100 – 600 ps in steps of 100 ps
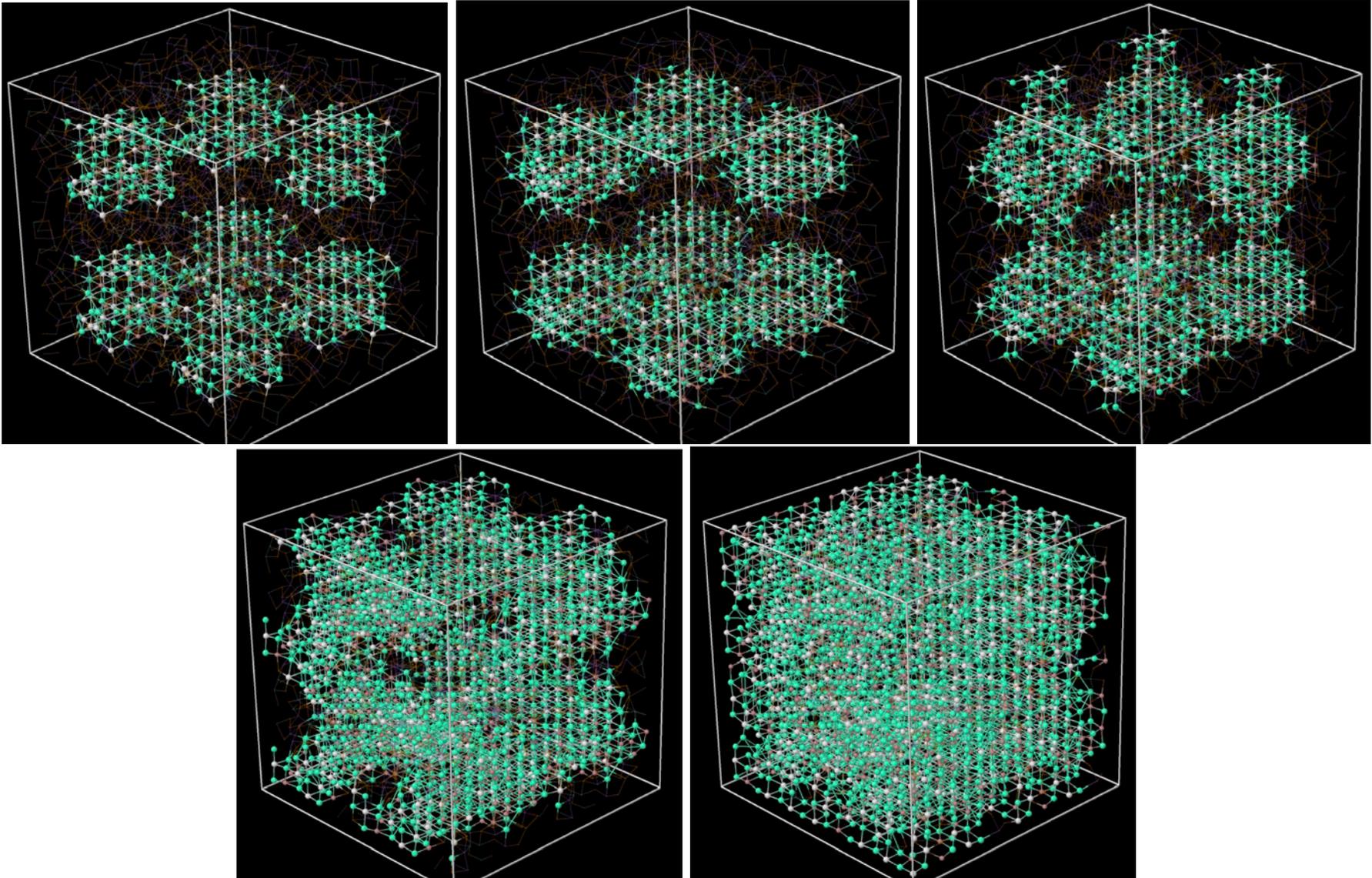
Results at 500 K, 600 K, and 700 K:

- Energy, fraction of crystalline atoms, number of $ABAB$ squares
- Size of percolating cluster
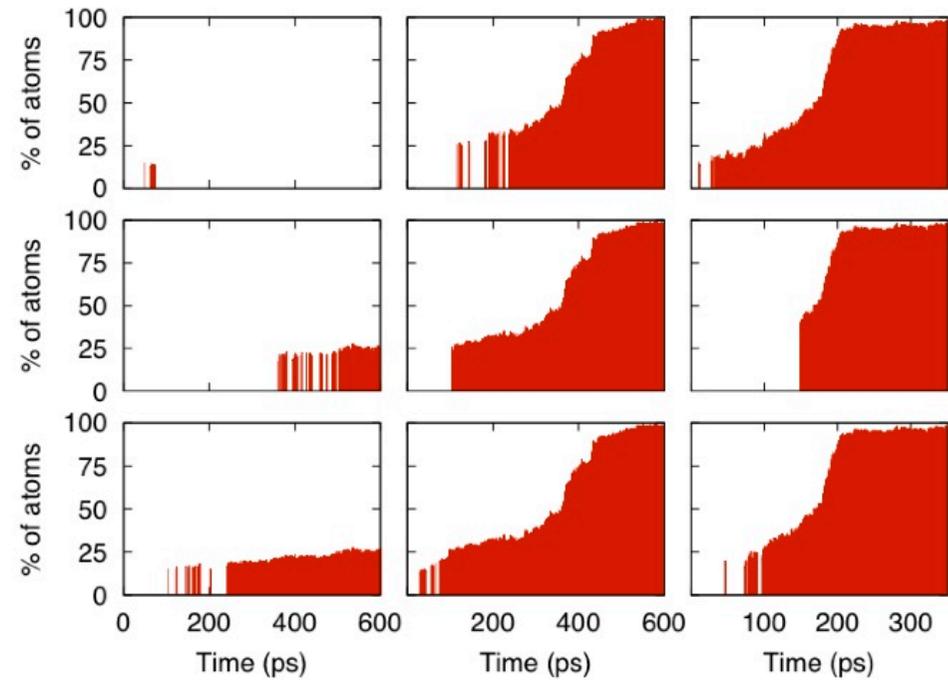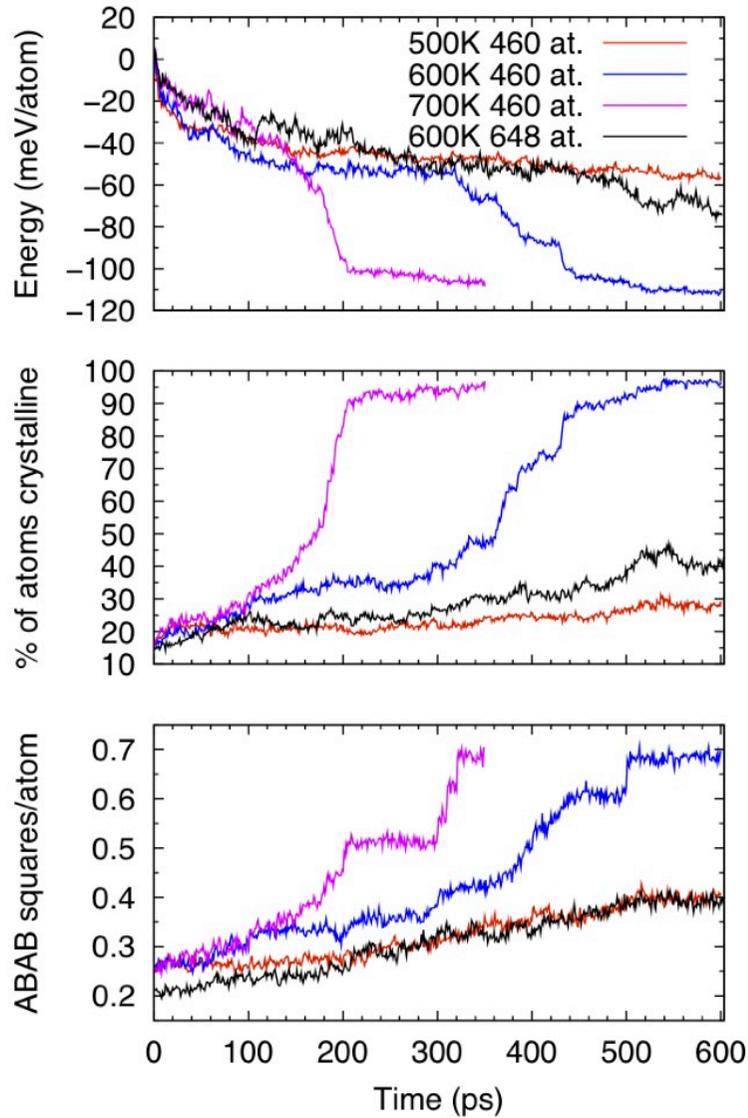
Small molecules:

Ground state of H_2 (and alkali dimers): $^1\Sigma_g^+[\sigma_g(\uparrow\downarrow)]$ bond between valence s orbitals. LSDX approximation reproduces HF, LSD agrees well with experiment.

For states with minimum number of nodal planes, LSD usually leads to moderate overestimate of E_{XC}. For states with additional nodal planes E_{XC} is often overestimated greatly. We can expect this in molecules whenever $sp-$ or sd hybridization reduces the s occupancy.

Nodal character in O_2, ozone O_3