FIRESIDE CHATS FOR LOCKDOWN TIMES

Introduction to DFT (Part I)

Nicola Marzari, EPFL

OUTLINE

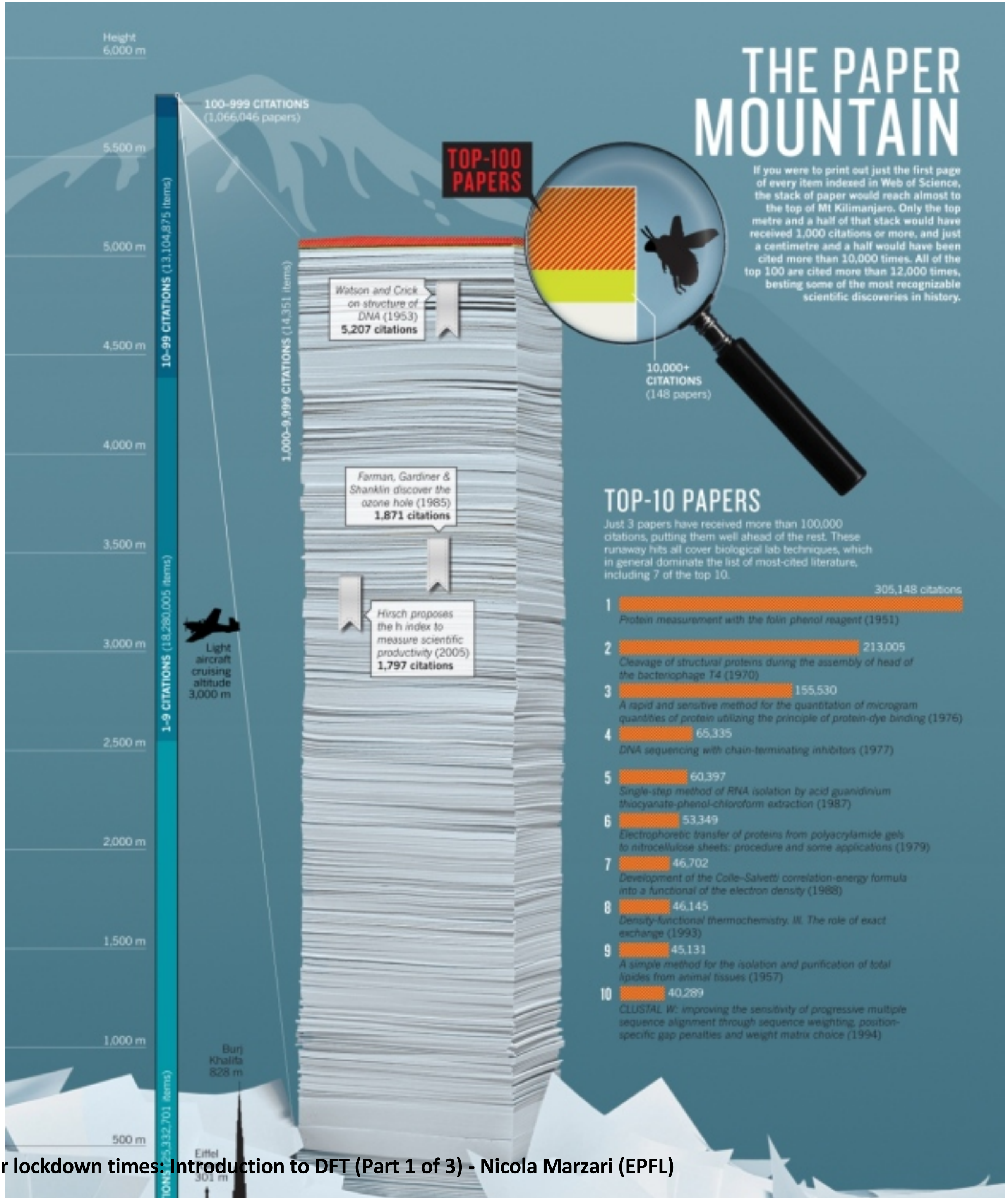
- What is density-functional theory? (Part I)
- What does it take to perform these calculations? (Part II)
- Why is it relevant for science and technology? (Part III)
- What can it do? and cannot do? (Part III)

(to keep in touch, info in the Learn section of the Materials Cloud website, and https://bit.ly/3eqighg)

THE TOP 100 PAPERS:

12 papers on density-functional theory in the top-100 most cited papers in the entire scientific literature, ever.

NATURE, OCT 2014



If you were to print out just the first page of every item indexed in Web of Science, the stack of paper would reach almost to the top of Mt Kilimanjaro. Only the top metre and a half of that stack would have received 1,000 citations or more, and just a centimetre and a half would have been cited more than 10,000 times. All of the top 100 are cited more than 12,000 times, besting some of the most recognizable scientific discoveries in history.

TOP-10 PAPERS

Just 3 papers have received more than 100,000 citations, putting them well ahead of the rest. These runaway hits all cover biological lab techniques, which in general dominate the list of most-cited literature, including 7 of the top 10.

1	305,148 citations	*Protein measurement with the folin phenol reagent* (1951)
2	213,005	*Cleavage of structural proteins during the assembly of head of the bacteriophage T4* (1970)
3	155,530	*A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding* (1976)
4	65,335	*DNA sequencing with chain-terminating inhibitors* (1977)
5	60,397	*Single-step method of RNA isolation by acid guanidinium thiocyanate-phenol-chloroform extraction* (1987)
6	53,349	*Electrophoretic transfer of proteins from polyacrylamide gels to nitrocellulose sheets: procedure and some applications* (1979)
7	46,702	*Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density* (1988)
8	46,145	*Density-functional thermochemistry. III. The role of exact exchange* (1993)
9	45,131	*A simple method for the isolation and purification of total lipides from animal tissues* (1957)
10	40,289	*CLUSTAL W: improving the sensitivity of progressive multiple sequence alignment through sequence weighting, position-specific gap penalties and weight matrix choice* (1994)

MOST CITED PAPERS IN THE HISTORY OF APS

	Journal	# cites	Title	Author(s)
1	PRL (1996)	78085	Generalized Gradient Approximation Made Simple	Perdew, Burke, Ernzerhof
2	PRB (1988)	67303	Development of the Colle-Salvetti Correlation-Energy …	Lee, Yang, Parr
3	PRB (1996)	41683	Efficient Iterative Schemes for Ab Initio Total-Energy …	Kresse and Furthmuller
4	PR (1965)	36841	Self-Consistent Equations Including Exchange and Correlation …	Kohn and Sham
5	PRA (1988)	36659	Density-Functional Exchange-Energy Approximation ...	Becke
6	PRB (1976)	31865	Special Points for Brillouin-Zone Integrations	Monkhorst and Pack
7	PRB (1999)	30940	From Ultrasoft Pseudopotentials to the Projector Augmented …	Kresse and Joubert
8	PRB (1994)	30801	Projector Augmented-Wave Method	Blochl
9	PR (1964)	30563	Inhomogeneous Electron Gas	Hohenberg and Kohn
10	PRB (1993)	19903	Ab initio Molecular Dynamics for Liquid Metals	Kresse and Hafner
11	PRB (1992)	17286	Accurate and Simple Analytic Representation of the Electron …	Perdew and Wang
12	PRB (1990)	15618	Soft Self-Consistent Pseudopotentials in a Generalized …	Vanderbilt
13	PRB (1992)	15142	Atoms, Molecules, Solids, and Surfaces - Applications of the …	Perdew, Chevary, …
14	PRB (1981)	14673	Self-Interaction Correction to Density-Functional Approx. …	Perdew and Zunger
15	PRB (1986)	13907	Density-Functional Approx. for the Correlation-Energy …	Perdew
16	RMP (2009)	13513	The Electronic Properties of Graphene	Castro Neto et al.
17	PR (1934)	12353	Note on an Approximation Treatment for Many-Electron Systems	Moller and Plesset
18	PRB (1972)	11840	Optical Constants on Noble Metals	Johnson and Christy
19	PRB (1991)	11580	Efficient Pseudopotentials for Plane-Wave Calculations	Troullier and Martins
20	PRL (1980)	10784	Ground-State of the Electron-Gas by a Stochastic Method	Ceperley and Alder

Apr 2019

SOME OPTIMISM

3 Technologies That Could Create Trillion-Dollar Markets Over the Next Decade

By Greg Satell Updated April 21, 2019 9:00 a.m. ET

Yet today, we’re in the midst of a materials revolution. Powerful simulation techniques, combined with increased computing power and machine learning, are enabling researchers to automate much of the discovery process, vastly accelerating the development of new materials

BARRON’S (April 2019)

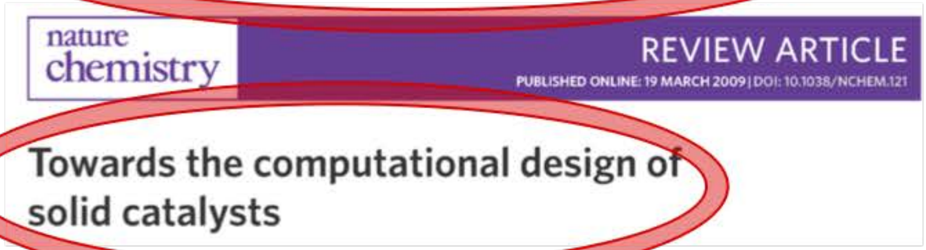
MORE OPTIMISM


nature materials

REVIEW ARTICLE

PUBLISHED ONLINE: 20 FEBRUARY 2013 | DOI: 10.1038/NMAT3568

The high-throughput highway to computational materials design


nature chemistry

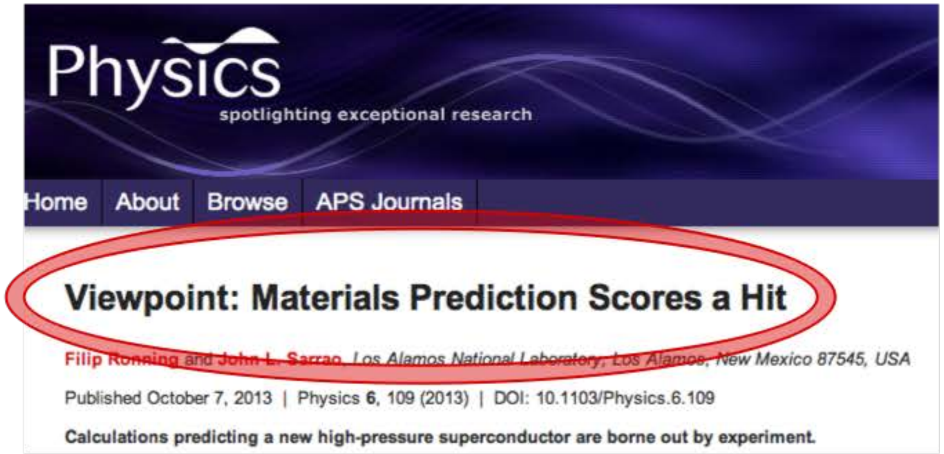
REVIEW ARTICLE

PUBLISHED ONLINE: 19 MARCH 2009 | DOI: 10.1038/NCHEM.121

Towards the computational design of solid catalysts


LETTERS

Where are nature's missing structures?


Physics

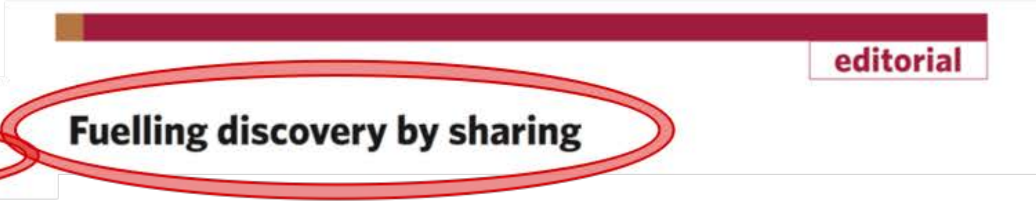
spotlighting exceptional research

Viewpoint: Materials Prediction Scores a Hit

Filip Ronning and John L. Sarrao, *Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

Published October 7, 2013 | Physics **6**, 109 (2013) | DOI: 10.1103/Physics.6.109

Calculations predicting a new high-pressure superconductor are borne out by experiment.


editorial

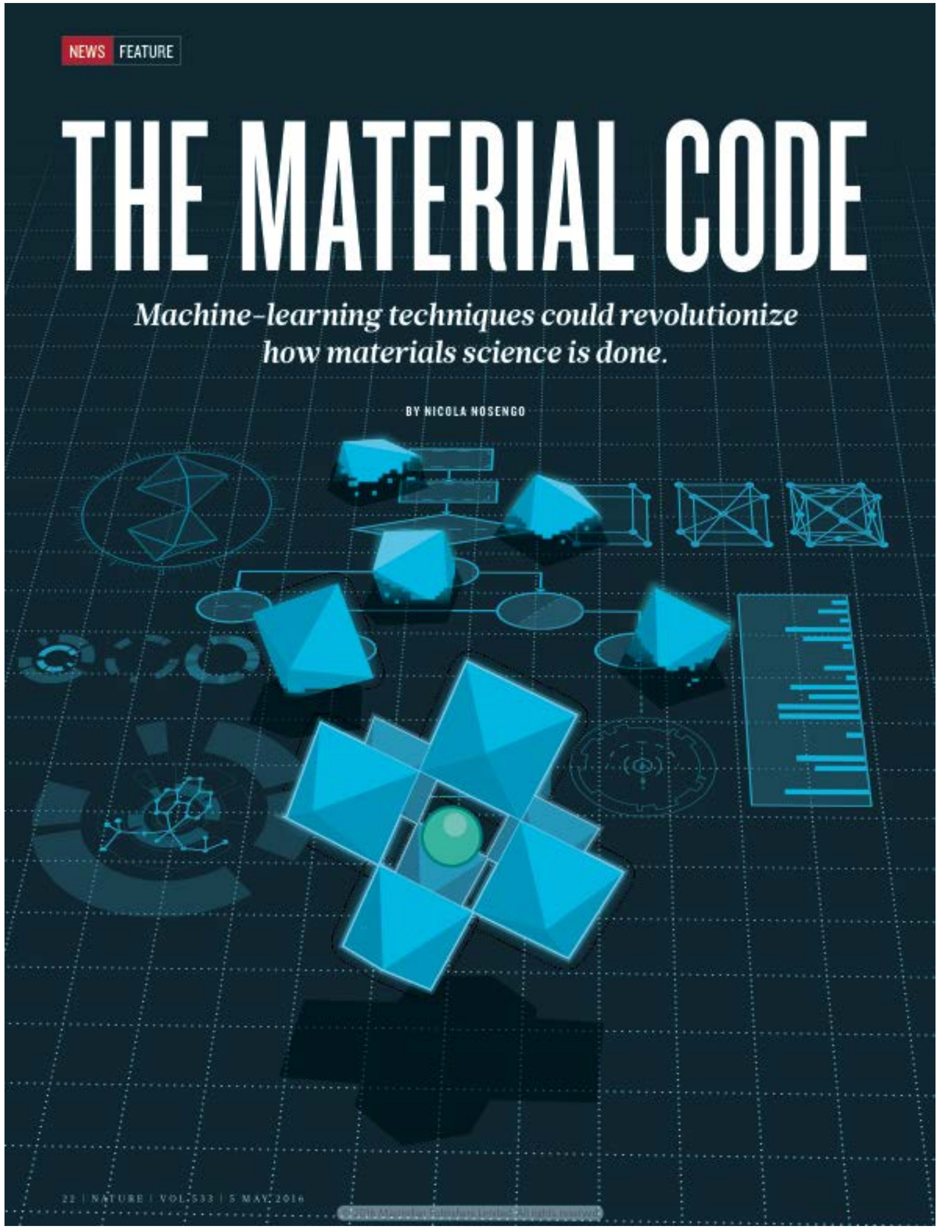
Fuelling discovery by sharing


Gordon Research Conferences

7:40 pm - 9:30 pm **Structural Predictions at Extreme Conditions: Are Experiments Still Necessary?**

Discussion Leader: **John Tse** (University of Saskatoon)

EVEN A CELLPHONE CAN DO IT



NEWS FEATURE

THE MATERIAL CODE

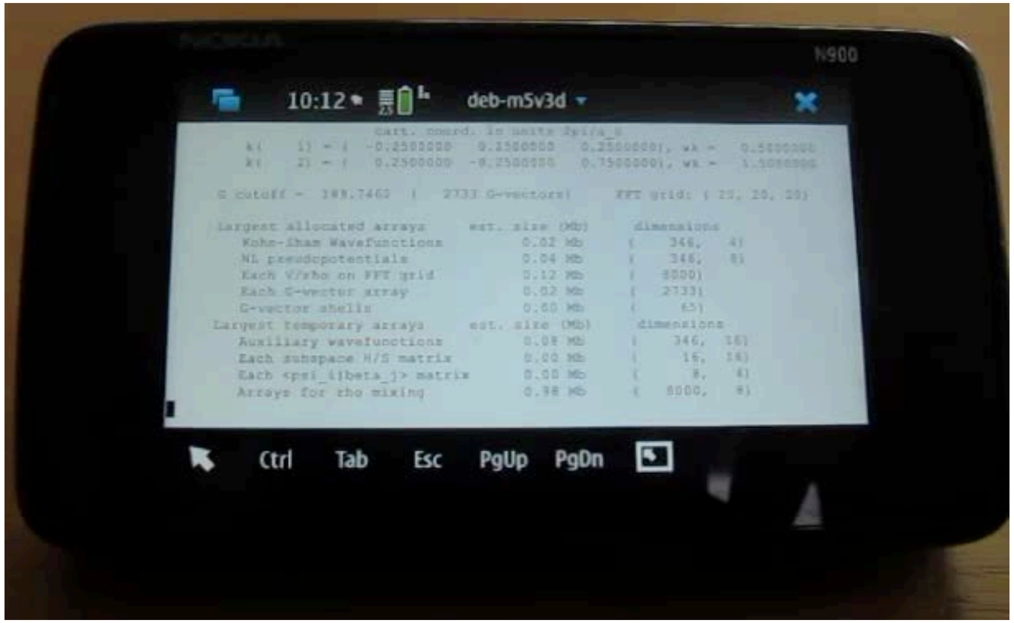
Machine-learning techniques could revolutionize how materials science is done.

BY NICOLA NOSENGO

22 | NATURE | VOL 533 | 5 MAY 2016

Nature, May 2016

It's a strong contender for the geekiest video ever made: a close-up of a smartphone with line upon line of numbers and symbols scrolling down the screen. But when visitors stop by Nicola Marzari's office, which overlooks Lake Geneva, he can hardly wait to show it off. "It's from 2010," he says, "and this is my cellphone calculating the electronic structure of silicon in real time!"



```
                    cart. coord. in units 2pi/a_0
        k(    1) = (  -0.2500000   0.2500000   0.2500000), wk =   0.5000000
        k(    2) = (   0.2500000  -0.2500000   0.7500000), wk =   1.5000000

     G cutoff =  189.7462  (   2733 G-vectors)     FFT grid: ( 20, 20, 20)

     Largest allocated arrays     est. size (Mb)     dimensions
        Kohn-Sham Wavefunctions         0.02 Mb     (    346,    4)
        NL pseudopotentials             0.04 Mb     (    346,    8)
        Each V/rho on FFT grid          0.12 Mb     (   8000)
        Each G-vector array             0.02 Mb     (   2733)
        G-vector shells                 0.00 Mb     (     65)
     Largest temporary arrays     est. size (Mb)     dimensions
        Auxiliary wavefunctions         0.08 Mb     (    346,   16)
        Each subspace H/S matrix        0.00 Mb     (     16,   16)
        Each <psi_i|beta_j> matrix      0.00 Mb     (      8,    4)
        Arrays for rho mixing           0.98 Mb     (   8000,    8)
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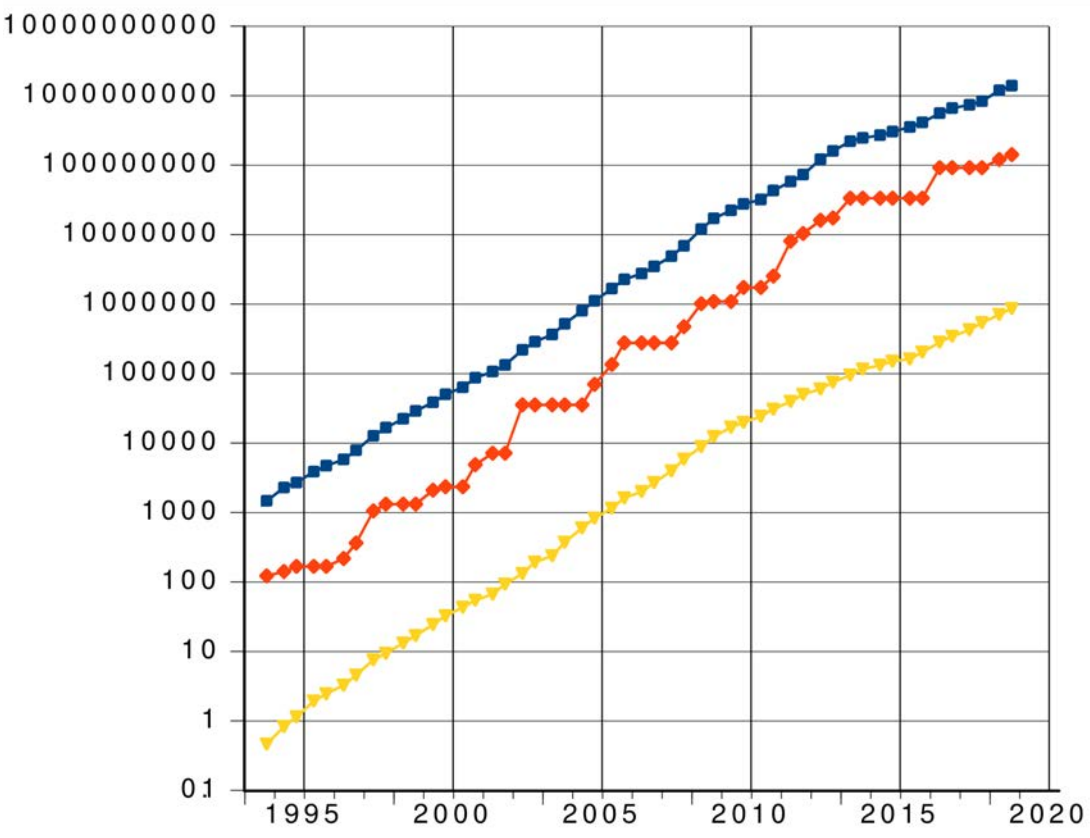
THE BUSINESS MODEL OF COMPUTATIONAL SCIENCE: THROUGHPUT CAPACITY DOUBLING EVERY 16 MONTHS

Computing power 1993-2019 (TOP 500 – Wikipedia)



Sum of the top 500 supercomputers

Number 1

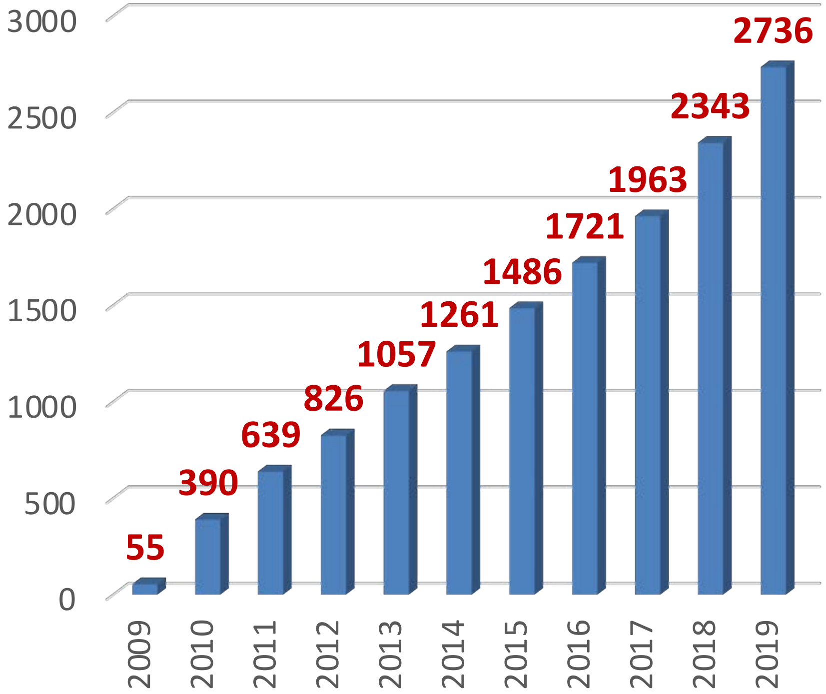
Number 500

If brick-and-mortar laboratories were to follow this pace, an experiment that took **one year in 1988** would take **one second in 2020** (32-million-fold in 32.5 years)

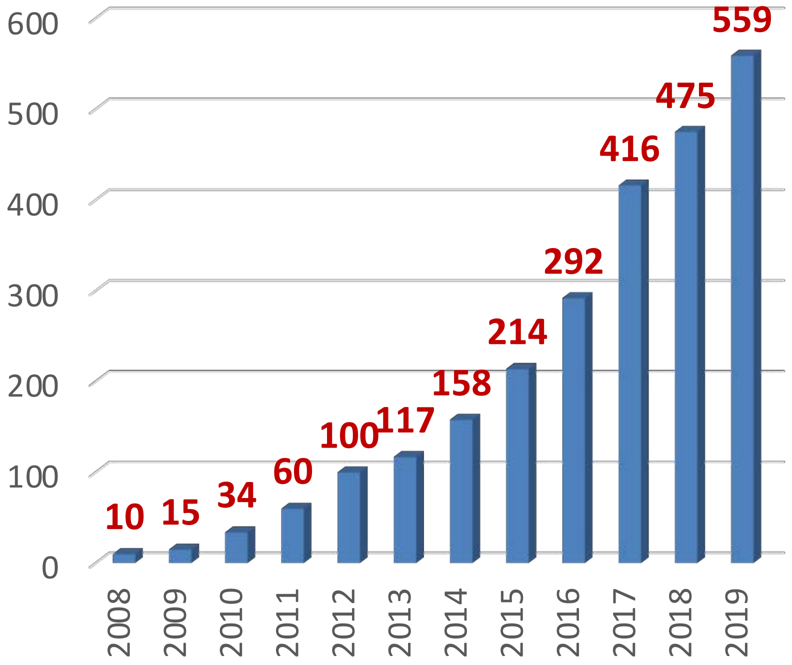
SOFTWARE AS A SCIENTIFIC INSTALLATION

Papers/year using some open-source software

www.quantum-espresso.org



www.wannier.org



QUANTUM MECHANICS IN 5 MINUTES

When is a particle like a wave ?

Wavelength • momentum = Planck constant

$$\Updownarrow$$

$$\lambda \bullet p = h$$

(h = 6.626 x 10^{-34} J s = 2π a.u.)

When is a particle like a wave ?

Wavelength • momentum = Planck constant

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$$\lambda \bullet p = h$$

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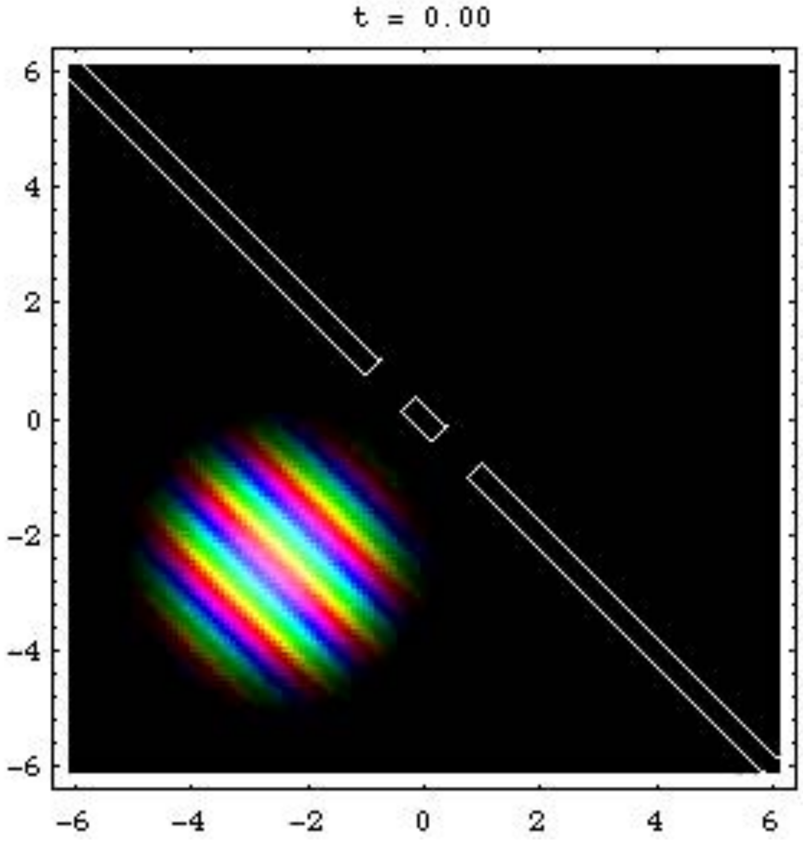


http4://www.kfunigraz.ac.at/imawww/vqm/

AROSA (GRISONS), 27th DECEMBER 1925

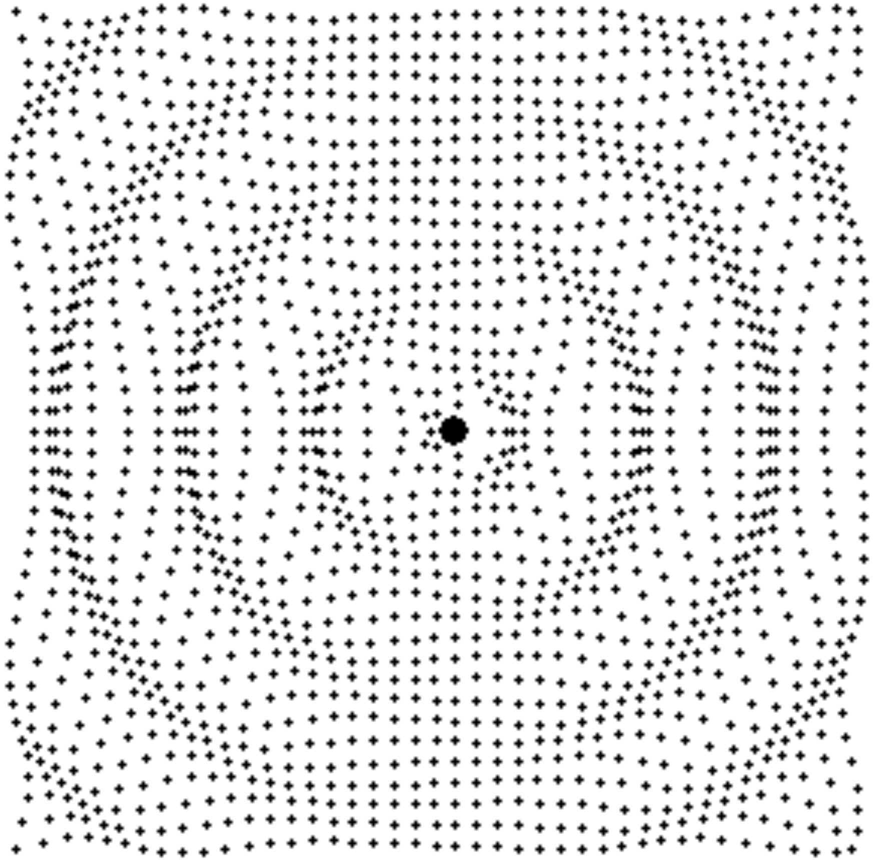
At the moment I am struggling with a new atomic theory. I am very optimistic about this thing and expect that if I can only… solve it, it will be very beautiful.

Erwin Schrödinger

AROSA (GRISONS), 27th DECEMBER 1925

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V(\vec{r},t)\Psi(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

It’s an information challenge



We need to know the amplitude (a complex number) at every point and at every instant

$$\Psi = \Psi(\vec{r}, t)$$

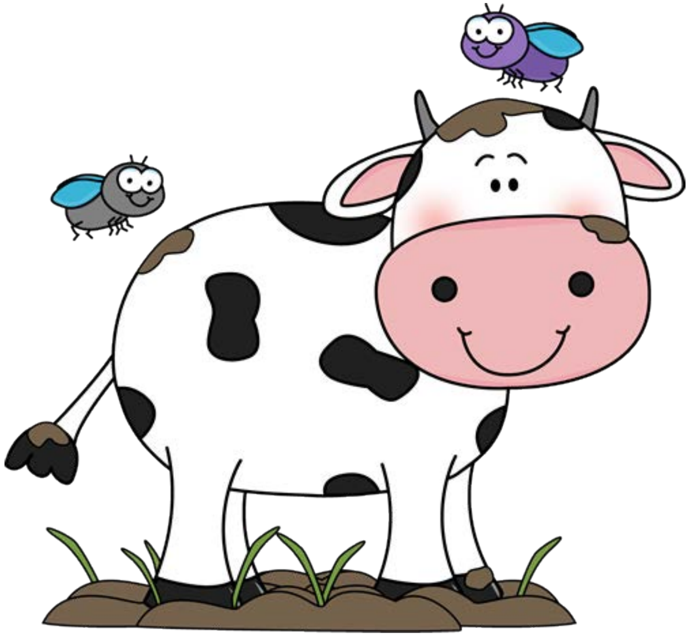
Time-independent potential → Ψ(x,t)=φ(x)f(t)

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\varphi(\vec{r})=E\varphi(\vec{r})}$$

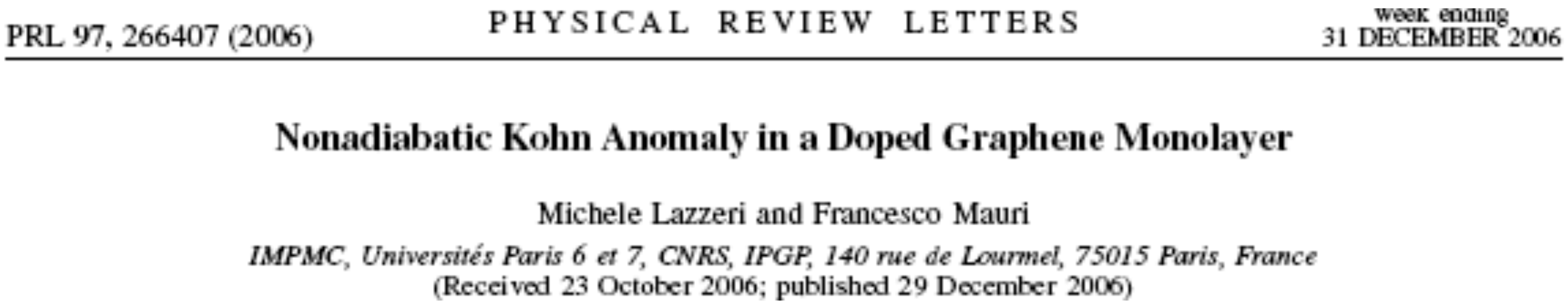
$$\boxed{i\hbar\frac{d}{dt}f(t)=Ef(t)}$$

Already an approximation

- We treat only the electrons as quantum particles, in the field of the fixed (or slowly varying) nuclei $E(\vec{R}_i) \quad = \quad \min_\psi E(\vec{R}_i, \psi)$
- This is generically called the adiabatic or Born-Oppenheimer approximation
- Adiabatic means that there is no coupling between different electronic surfaces; B-O no influence of the ionic motion on one electronic surface.



A Born-Oppenheimer violation



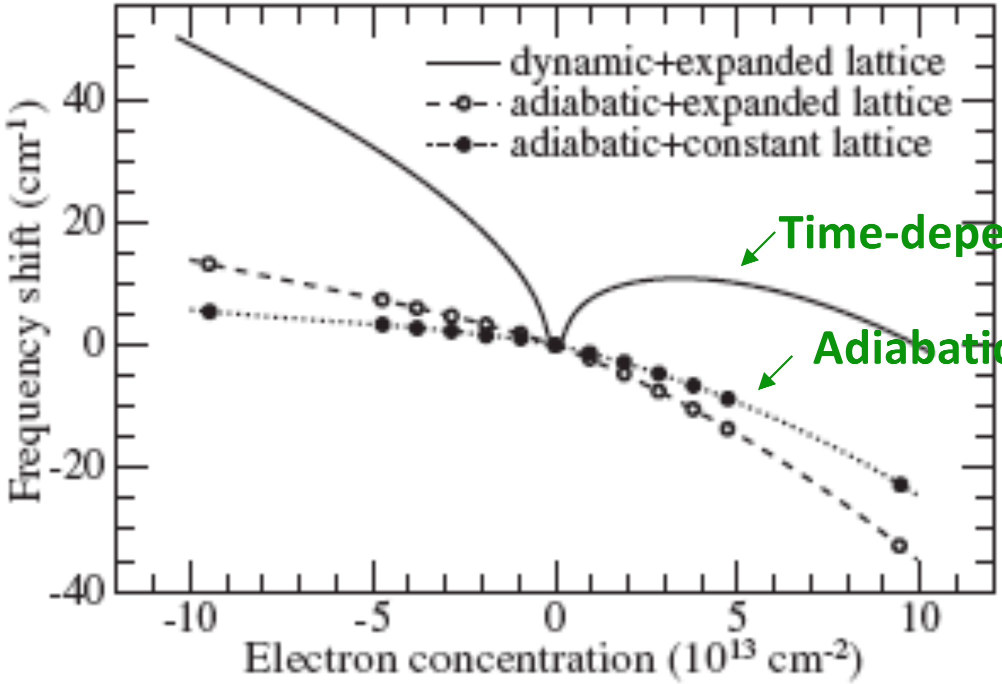
PRL 97, 266407 (2006) PHYSICAL REVIEW LETTERS week ending 31 DECEMBER 2006

Nonadiabatic Kohn Anomaly in a Doped Graphene Monolayer

Michele Lazzeri and Francesco Mauri

IMPMC, Universités Paris 6 et 7, CNRS, IPGP, 140 rue de Lourmel, 75015 Paris, France

(Received 23 October 2006; published 29 December 2006)



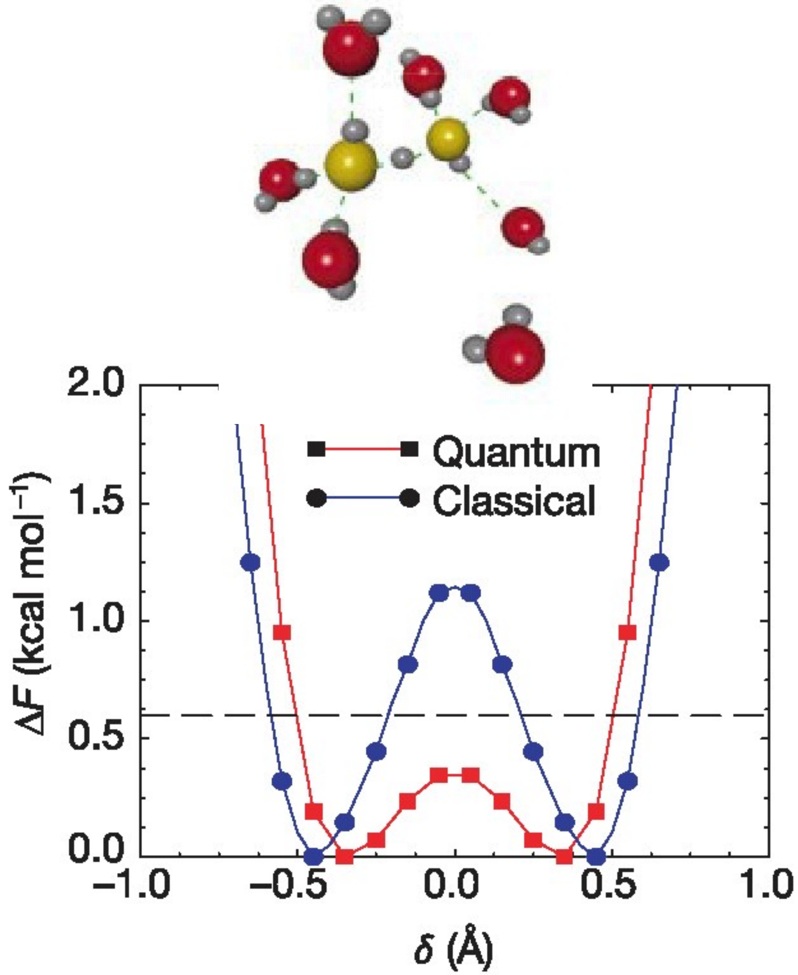
Time-dependent DFT

Adiabatic (BO) DFT

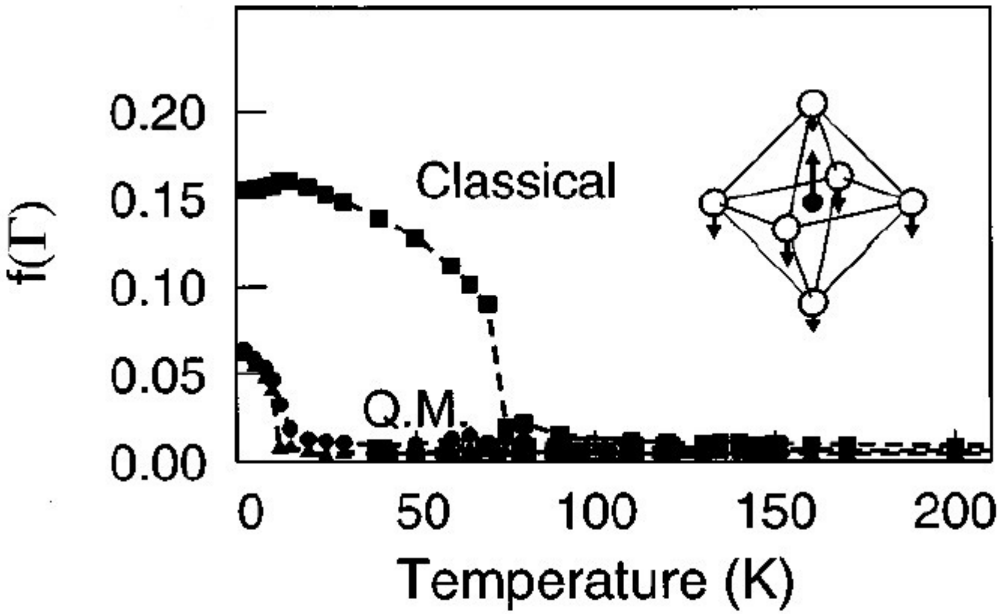
Shift of phonon frequency with doping of a single graphene layer

Strong coupling between electron and nuclear coordinates for phonons with $\mathbf{q} = 2\,\mathbf{k}_F$ (Kohn anomaly)

Quantum effects in the nuclear motion: tunnelling

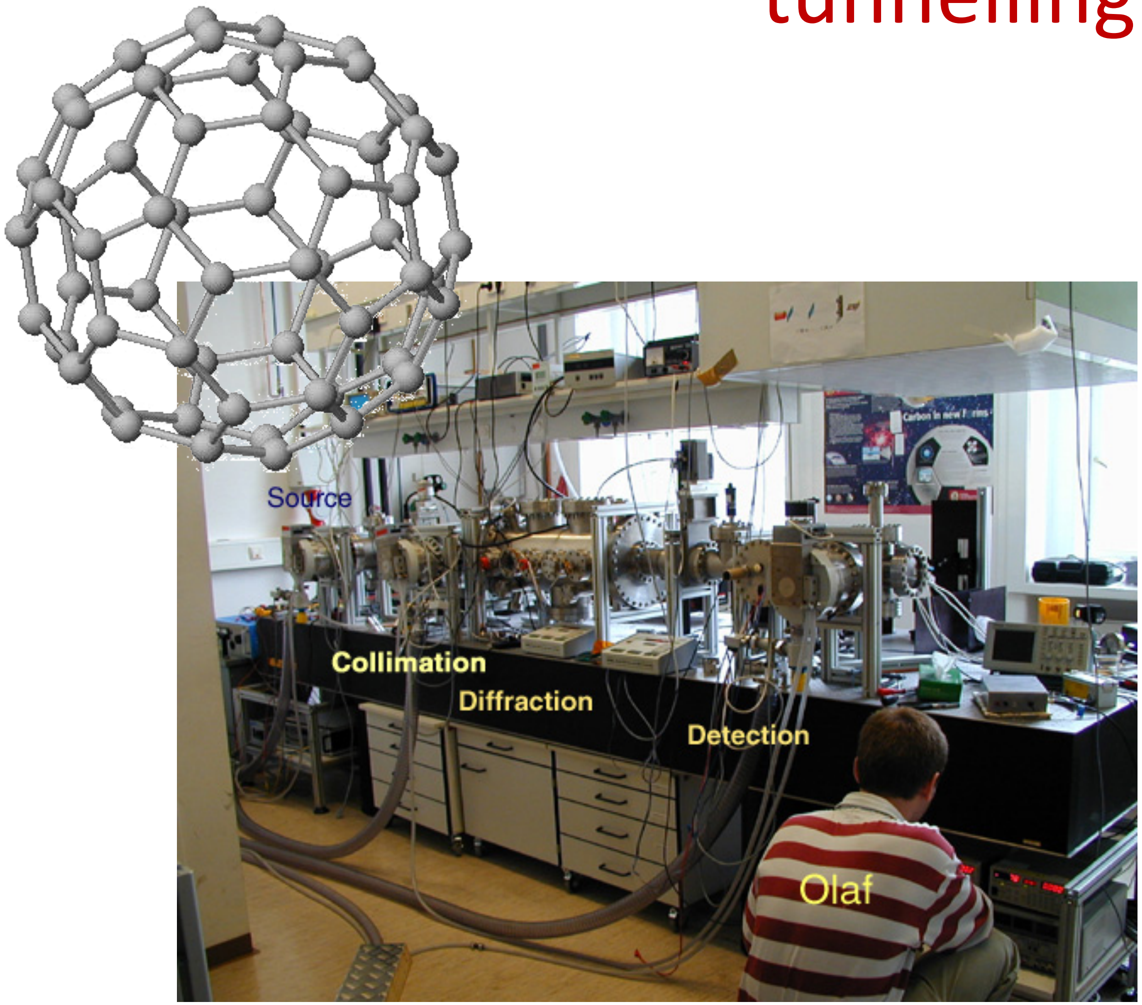


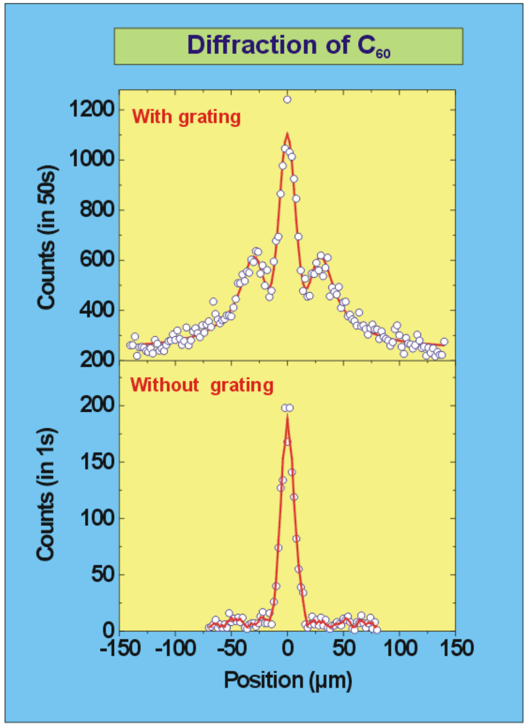
Hydrated hydroxide diffusion (Tuckerman, Marx, and Parrinello)



Quantum paraelectricity in $SrTiO_3$ (Vanderbilt)

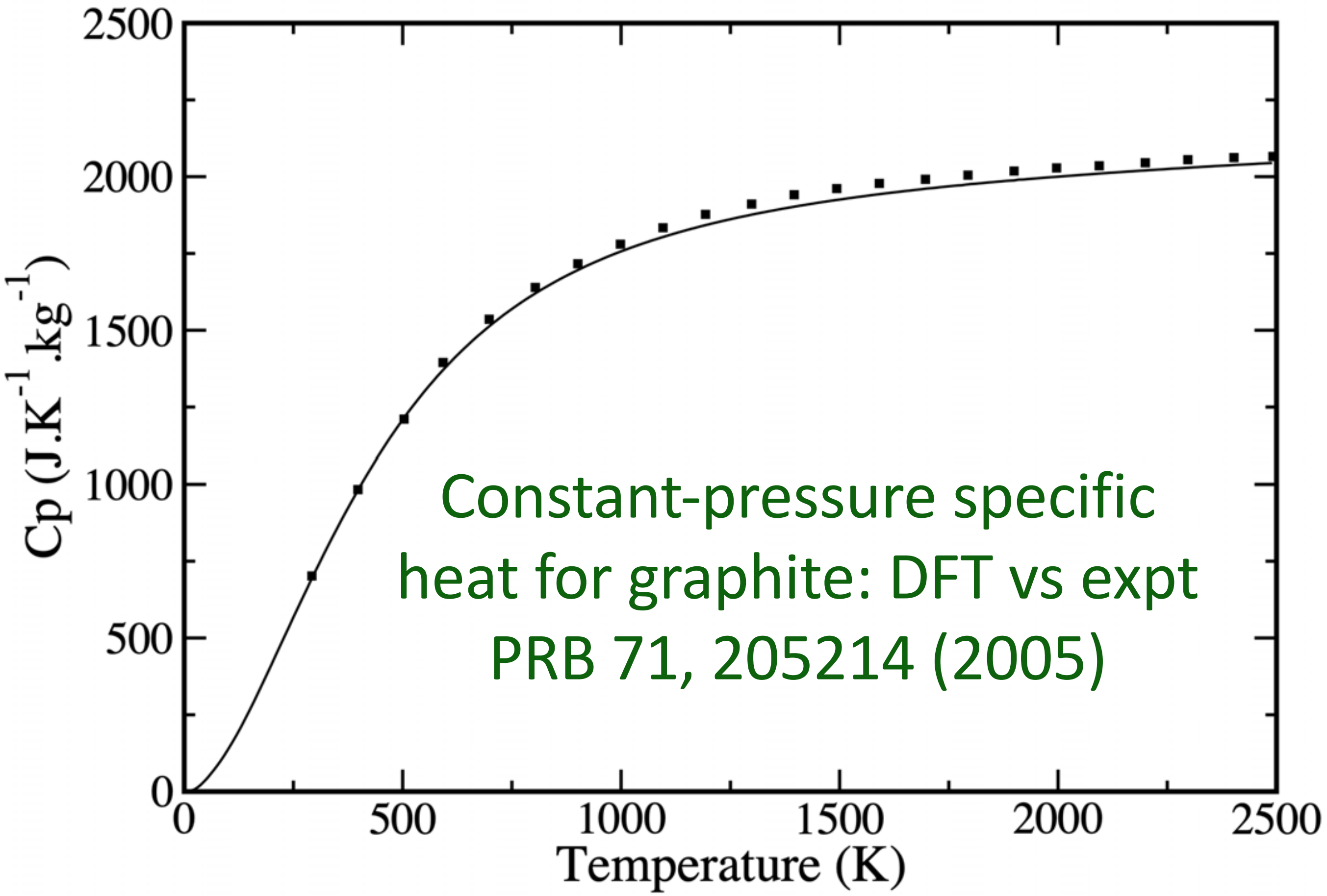
Quantum effects in the nuclear motion: tunnelling





http://www.quantum.univie.ac.at/research/c60/

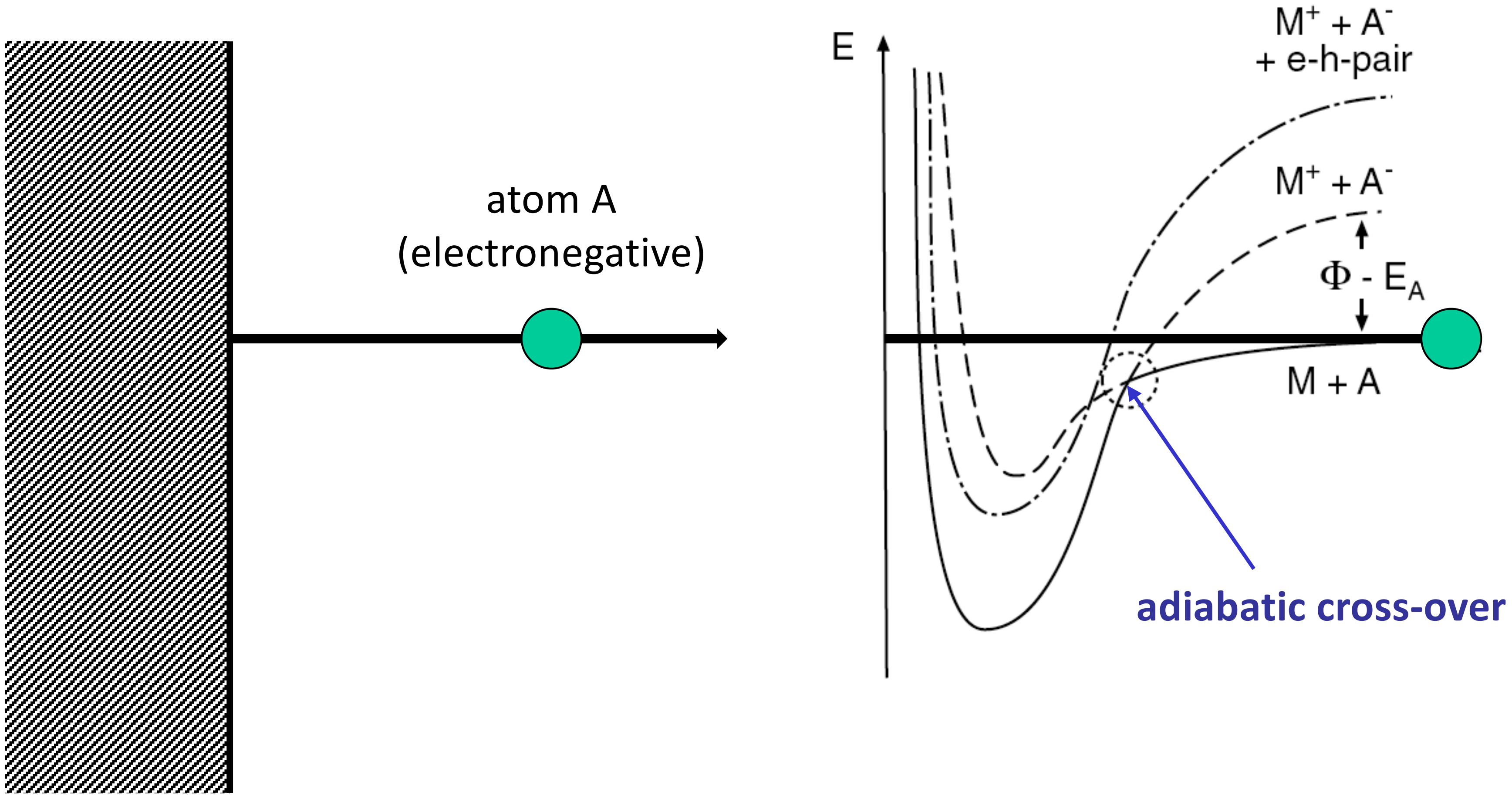
Quantum effects in the nuclear motion: Bose-Einstein statistics



Constant-pressure specific heat for graphite: DFT vs expt
PRB 71, 205214 (2005)

“Potential energy surface” for atom A deposited on a metal M

metal M (low work function)



E. Hasselbrink, Current Opinion in Solid State and Materials Science 10, 192 (2006)

Energy of a collection of atoms

$$\widehat{H} = \hat{T}_e + \hat{V}_{e-N} + \hat{V}_{e-e} + T_N + V_{N-N}$$

- $\hat{T}_e$: quantum kinetic energy of the electrons (1-body operator)
- $\hat{V}_{e-N}$: electrons in the field of all the nuclei (1-body)
- $\hat{V}_{e-e}$: electron-electron interactions (2-body)

$$\hat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2 \qquad \hat{V}_{e-N} = \sum_i \left[\sum_I V\left(\vec{R}_I - \vec{r}_i\right) \right] \qquad \hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

- T_N: classical kinetic energy of the nuclei
- $V_{N\text{-}N}$: classical electrostatic nucleus-nucleus repulsion

The electronic wave function becomes an informational challenge

$$\psi(\vec{r}_1,\ldots,\vec{r}_n)$$

"… the full specification of a single wave function of neutral iron is a function of 78 variables. It would be rather crude to restrict to 10 the number of values of each variable … even so, full tabulation would require 10^{78} entries."

Douglas R Hartree

Charles G. Darwin, Biographical Memoirs of Fellows of the Royal Society, 4, 102 (1958)

How to easily solve differential equations?
Use the variational principle

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \qquad E[\Psi] \geq E_0$$

If $E[\Psi]=E_0$, then Ψ is the ground-state wavefunction, and viceversa…

Hartree Equations

The Hartree equations can be obtained directly from the variational principle, once the search is restricted to the many-body wavefunctions that are written as the product of single orbitals (i.e. we are working with independent electrons)

$$\psi(\vec{r}_1,\ldots,\vec{r}_n)=\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\cdots\varphi_n(\vec{r}_n)$$

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)+\underbrace{\sum_{j\neq i}\int|\varphi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j}_{\text{Hartree operator}}\right]\varphi_i(\vec{r}_i)=\varepsilon\varphi_i(\vec{r}_i)$$

The self-consistent field

- We have *n* simultaneous 1-particle integro-differential equations
- **The Hartree operator is self-consistent.** It depends on the orbitals that are the solution of all other Hartree equations ⇒ solution must be achieved iteratively

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)+\underbrace{\sum_{j\neq i}\int|\varphi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j}_{\text{Hartree operator}}\right]\varphi_i(\vec{r}_i)=\varepsilon\varphi_i(\vec{r}_i)$$

It’s a mean-field approach

- Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the average effect of the repulsive interactions of the other electrons
- This average repulsion is the electrostatic repulsion of the average charge density of all other electrons a

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)+\underbrace{\sum_{j\neq i}\int|\varphi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j}_{\text{Hartree operator}}\right]\varphi_i(\vec{r}_i)=\varepsilon\varphi_i(\vec{r}_i)$$

Iterations to self-consistency

1) Initial guess at the orbitals
2) Construction of the Hartree operators
3) Solution of the single-particle Hartree equations (each one, Schrödinger-like)
4) With this new set of orbitals, construct the Hartree operators again
5) Iterate the procedure until it (hopefully) converges

Differential analyzer

As We May Think – Atlantic Monthly Jul 1945

- The advanced arithmetical machines of the future [...] will **perform complex arithmetical computations at exceedingly high speeds**, and they will record results in such form as to be readily available for distribution or for later further manipulation.

- Only then will mathematics be practically effective in bringing the **growing knowledge of atomistics to the useful solution of the advanced problems of chemistry, metallurgy, and biology.**

- A **memex is a device in which an individual stores all his books, records, and communications**, and which is mechanized so that it may be consulted with exceeding speed and flexibility. It is an enlarged intimate supplement to his memory.

- It consists of **a desk,** and while it can presumably be operated from a distance, it is primarily the piece of furniture at which he works. On the top are **slanting translucent screens, on which material can be projected for convenient reading. There is a keyboard, and sets of buttons and levers.**

- **Wholly new forms of encyclopedias will appear, ready made with a mesh of associative trails** running through them.

- The chemist, struggling with the synthesis of an organic compound, has **all the chemical literature before him in his laboratory, with trails following the analogies of compounds, and side trails to their physical and chemical behavior.**

Spin-Statistics

- All elementary particles are either fermions (half-integer spins) or bosons (integer)
- A set of identical (indistinguishable) fermions has a wavefunction that is totally antisymmetric by exchange

$$\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_j,\ldots,\vec{r}_k,\ldots,\vec{r}_n)=-\psi(\vec{r}_1,\vec{r}_2,\ldots,r_k,\ldots,\vec{r}_j,\ldots,\vec{r}_n)$$

- (for bosons it is totally symmetric)

Slater determinant

A totally antisymmetric wavefunction is constructed as a Slater determinant of the individual orbitals (instead of just a product, as in the Hartree approach)

$$\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n)=\frac{1}{\sqrt{n!}}\begin{Vmatrix}\varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1)\\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n)\end{Vmatrix}$$

Pauli principle

- If two states are identical, the determinant vanishes (i.e. we can’t have two electrons in the same quantum state)

Hartree-Fock Equations

The Hartree-Fock equations are, again, obtained from the variational principle: we look for the minimum of the many-electron Schroedinger equation in the class of all wavefunctions that are written as a single Slater determinant

$$\psi(\vec{r}_1,\ldots,\vec{r}_n) = \left\| Slater \right\|$$

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i)\right]\varphi_\lambda(\vec{r}_i) +$$

$$\left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j - \vec{r}_i|}\varphi_\mu(\vec{r}_j)\,d\vec{r}_j\right]\varphi_\lambda(\vec{r}_i) -$$

$$\sum_\mu \left[\int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j - \vec{r}_i|}\varphi_\lambda(\vec{r}_j)\,d\vec{r}_j\right]\varphi_\mu(\vec{r}_i) = \varepsilon\varphi_\lambda(\vec{r}_i)$$

Reduced density matrices

$$\gamma_1(r_1',r_1) =$$

$$N\int\ldots\int \Psi(r_1',r_2,r_3,r_4,\ldots,r_N)\Psi^*(r_1,r_2,r_3,r_4,\ldots,r_N)\,dr_2\,dr_3\,dr_4\ldots dr_N$$

$$\gamma_2(r_1',r_2',r_1,r_2) =$$

$$\frac{N(N-1)}{2}\int\ldots\int \Psi(r_1',r_2',r_3,r_4,\ldots,r_N)\Psi^*(r_1,r_2,r_3,r_4,\ldots,r_N)\,dr_3\,dr_4\ldots dr_N$$

A variation principle for RDMs

$$E=\int\left[\left(-\frac{1}{2}\nabla_1^2+v\left(r_1\right)\right)\gamma_1\left(r_1',r_1\right)\right]_{r_1'=r_1}dr_1+\iint\frac{1}{r_{12}}\gamma_2\left(r_1,r_2,r_1,r_2\right)dr_1\,dr_2$$

N-representability problem!

Density-functional theory

- The external potential V_{ext} and the number N of electrons completely define the quantum problem
- The wavefunctions are – in principle – uniquely determined, via the Schrödinger Equation
- All system properties follow from the wavefunctions
- The energy (and everything else) is thus a functional of V_{ext} and N

The Thomas-Fermi approach

- Let' s try to find out an expression for the energy as a function of the charge density
- E=kinetic+external+el.-el.
- Kinetic is the tricky term: how do we get the curvature of a wavefunction from the charge density ?
- Answer: local density approximation

Local-density approximation

- We take the kinetic energy density at every point to correspond to the kinetic energy density of the non-interacting homogenous electron gas

$$T(\vec{r}) = A\rho^{\frac{5}{3}}(\vec{r})$$

$$E_{Th-Fe}[\rho] = A\int \rho^{\frac{5}{3}}(\vec{r})\,d\vec{r} + \int \rho(\vec{r})v_{ext}(\vec{r})\,d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$

It’s a poor man Hartree…

- The idea of an energy functional is not justified
- It does not include exchange effects - but Dirac proposed to add the LDA exchange energy:

$$-C\int \rho(\vec{r})^{\frac{4}{3}}\, d\vec{r}$$

- It scales linearly, and we deal with 1 function of three coordinates !

The Argon atom

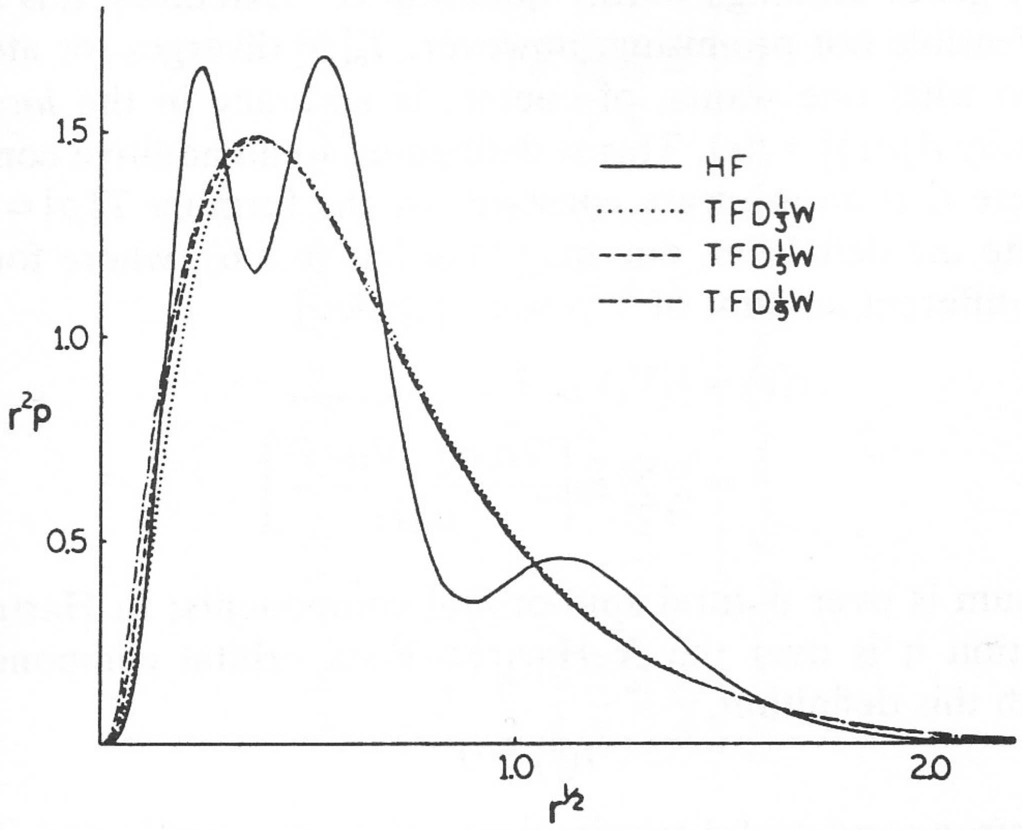


Figure 6.3 Electron density for argon from various models (after Yang 1986.)

First Hohenberg-Kohn theorem

The density as the basic variable: the external potential and the number of electrons determine uniquely the charge density, and the **charge density determines uniquely the external potential and the number of electrons.**

Proof: Let us assume, *ad absurdum*, that there exists a different potential v' with a ground state Ψ' that gives rise to the same charge density $n(\mathbf{r})$. Let E and E' be the respective ground-state energies; taking Ψ' as a trial solution for the Hamiltonian $\hat{H}$, we have the strict inequality

$$E < \langle\Psi'|\hat{H}|\Psi'\rangle = \langle\Psi'|\hat{H}'|\Psi'\rangle + \langle\Psi'|\hat{H} - \hat{H}'|\Psi'\rangle = E' + \int n(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r}$$

(if $\langle\Psi'|\hat{H}|\Psi'\rangle = E$ then Ψ' would be the ground state for H, in virtue of (1.8), but the two distinct differential equations for $\hat{H}$ and $\hat{H}'$ cannot have the same ground state). Similarly, taking Ψ as a trial solution for $\hat{H}'$, we have

$$E' < \langle\Psi|\hat{H}'|\Psi\rangle = \langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi|\hat{H}' - \hat{H}|\Psi\rangle = E - \int n(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r}$$

The universal functional $\mathrm{F}[\mathrm{n}(\vec{\mathrm{r}})]$

- The ground state density $\mathrm{n}(\vec{\mathrm{r}})$ determines the potential of the Schrödinger equation, and thus the wavefunction Ψ; we define

$$\mathrm{F}[\mathrm{n}(\vec{\mathrm{r}})] = \langle \Psi | \widehat{\mathrm{T}}_{\mathrm{e}} + \widehat{\mathrm{V}}_{\mathrm{e-e}} | \Psi \rangle$$

- It’s an emotional moment…

Second Hohenberg-Kohn theorem

The variational principle – we have an alternative to Schrödinger’s equation, expressed in terms of the charge density only!

$$E_{V_{ext}}[\mathrm{n}(\vec{\mathrm{r}})] = \mathrm{F}[\mathrm{n}(\vec{\mathrm{r}})] + \int V_{ext}(\vec{\mathrm{r}})\,\mathrm{n}(\vec{\mathrm{r}})\,d\vec{\mathrm{r}} \;\geq\; E_0$$

($\mathrm{n}(\vec{\mathrm{r}})$ determines its groundstate wavefunction, that can be taken as a trial wavefunction in this external potential)

$$\langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi|\hat{T} + \hat{V}_{e-e} + v_{ext}|\Psi\rangle = \int \rho v_{ext} + F[\rho]$$

The non-interacting unique mapping

- A reference system is introduced (the Kohn-Sham electrons)
- These electrons do not interact, and live in an external potential (the Kohn-Sham potential) such that their ground-state charge density is identical to the charge density of the interacting system

Though this be madness, yet there's method in't

- For a system of non-interacting electrons, the Slater determinant is the exact wavefunction (try it, with 2 orbitals)
- The kinetic energy of the non interacting system - called $T_s[n(\vec{r})]$ - is well defined.
- The Hartree energy $E_H[n(\vec{r})]$ is well defined.

$$E_H[n(\mathbf{r})] = \frac{1}{2}\int\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2.$$

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})]$$

Electronic total energy

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^{\star}(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\ d\mathbf{r} + E_H[n(\mathbf{r})] + \\ + E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})\ d\mathbf{r}$$

From the variational principle ⇒ Euler-Lagrange equations

$$\delta\left(F[n(\vec{r})] + \int v_{ext}(\vec{r})n(\vec{r})d\vec{r} - \mu\left(\int n(\vec{r})\,d\vec{r} - N\right)\right) = 0$$

$$\frac{\delta F[n(\vec{r})]}{\delta n(\vec{r})} + v_{ext}(\vec{r}) = \mu$$

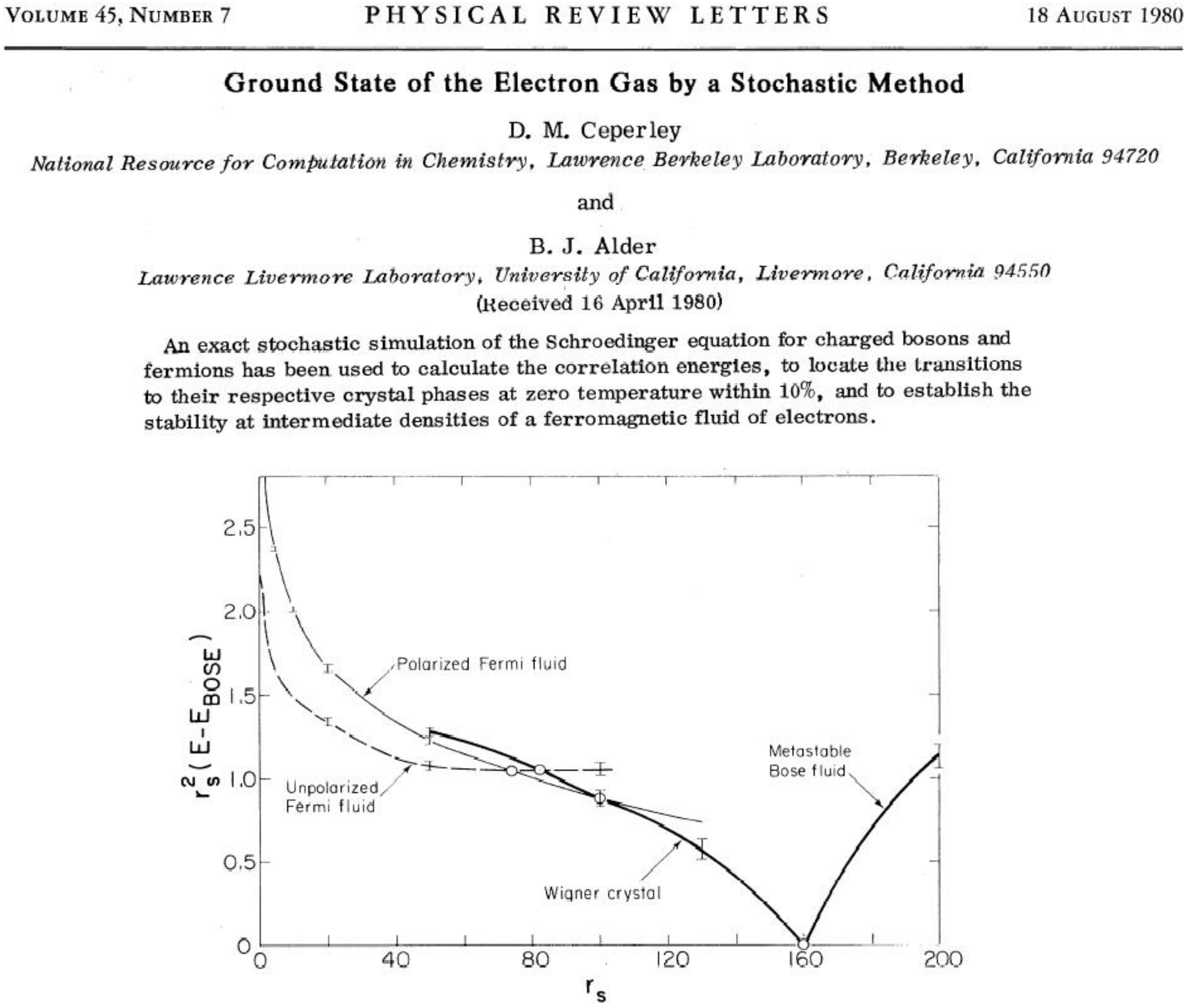
I.e. the Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r})\right] \psi_i(\mathbf{r}) = \hat{H}_{KS}\ \psi_i(\mathbf{r}) = \epsilon_i\ \psi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ d\mathbf{r}', \qquad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

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

What about E_{xc} ? LDA!



VOLUME 45, NUMBER 7 PHYSICAL REVIEW LETTERS 18 AUGUST 1980

Ground State of the Electron Gas by a Stochastic Method

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(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

In full detail…

$$\begin{aligned}E_{XC}[n(\mathbf{r})] &= \int d\mathbf{r}\; e_{XC}[n(\mathbf{r})]\, n(\mathbf{r}) \\ &\approx \int d\mathbf{r}\; [e_X^{hom}(n(\mathbf{r})) + e_C^{hom}(n(\mathbf{r}))]\, n(\mathbf{r})\end{aligned}$$

$$\begin{aligned}e_X^{hom}(n) &= -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r}) \\ e_C^{hom}(n) &= \begin{cases} -0.1423(1+1.0529\sqrt{r_s}+0.3334r_s)^{-1} & \text{if} \quad r_s \geq 1, \\ -0.0480+0.0311\,\ln r_s - 0.0116 r_s + 0.002 \quad r_s \quad \ln r_s & \\ & \text{if} \quad r_s < 1. \end{cases}\end{aligned}$$

$r_s := (4\pi n(\mathbf{r})/\mathbf{3})^{-1/3}$ Wigner-Seitz radius

[see, e.g. Perdew & Zunger, PRB **23** 5048 (1981)]

It works!

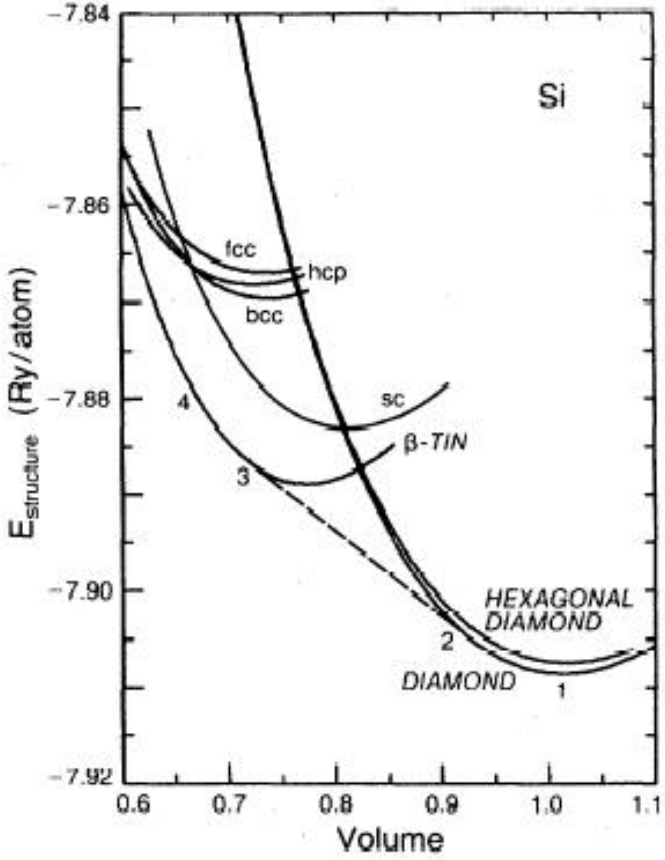

FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β-tin phase ($c/a = 0.552$).

**Yin and Cohen,
PRL 1980 and
PRB 1982**

References

Online resources

- The open-access class (videos, slides, readings) on simulations that Gerd Ceder and myself ran at MIT for 10 years: http://ocw.mit.edu/3-320S05
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