Importance of Materials Science

NOMAD — NOVEL MATERIALS DISCOVERY

Max Planck Society

MRS MATERIALS RESEARCH SOCIETY®

Advancing materials.
Improving the quality of life.

Importance of Materials Science

NOMAD — NOVEL MATERIALS DISCOVERY

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Topological Insulators

Metals

Super-conductors

Materials Science
quo vadis

Development of Research Paradigms

Jim Gray (Jan. 11. 2007): The 4th Paradigm, Data Intensive Discovery, edited by Hey, Tansley, and Tolle, Microsoft Research

Wikipedia: disappeared 2007; declared dead in absentia 2012 (aged 68)
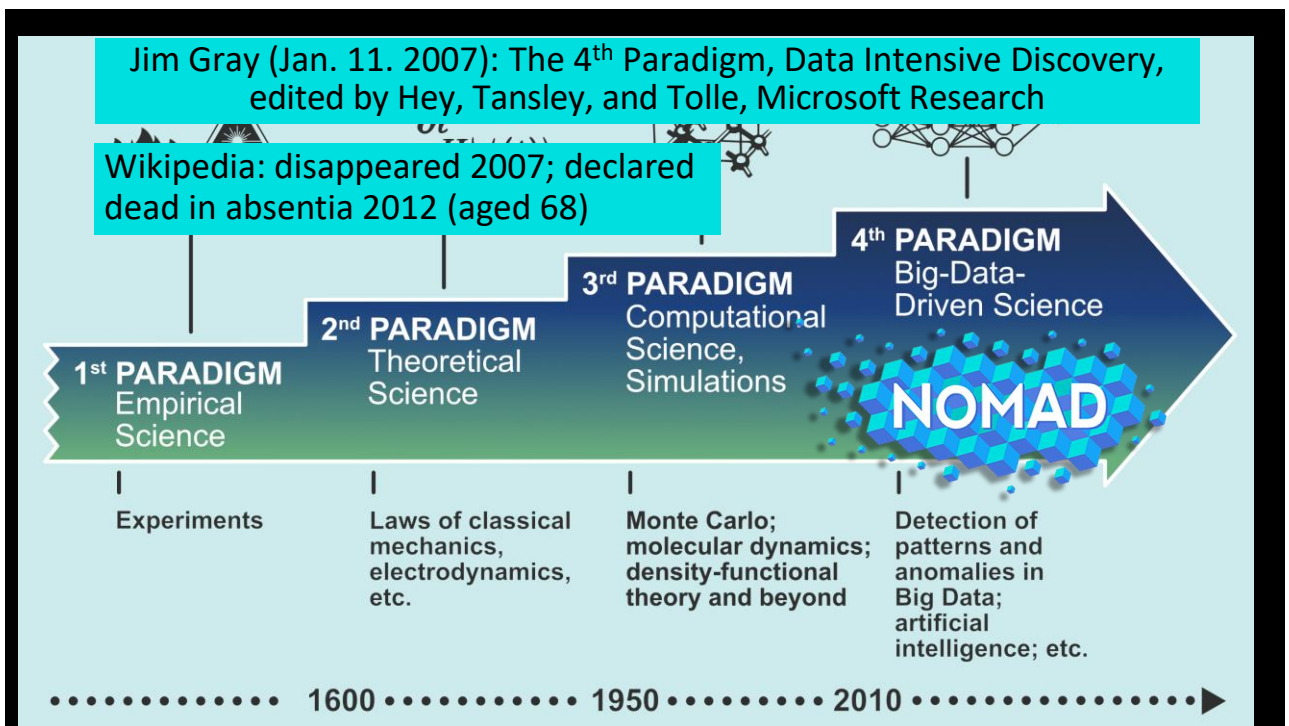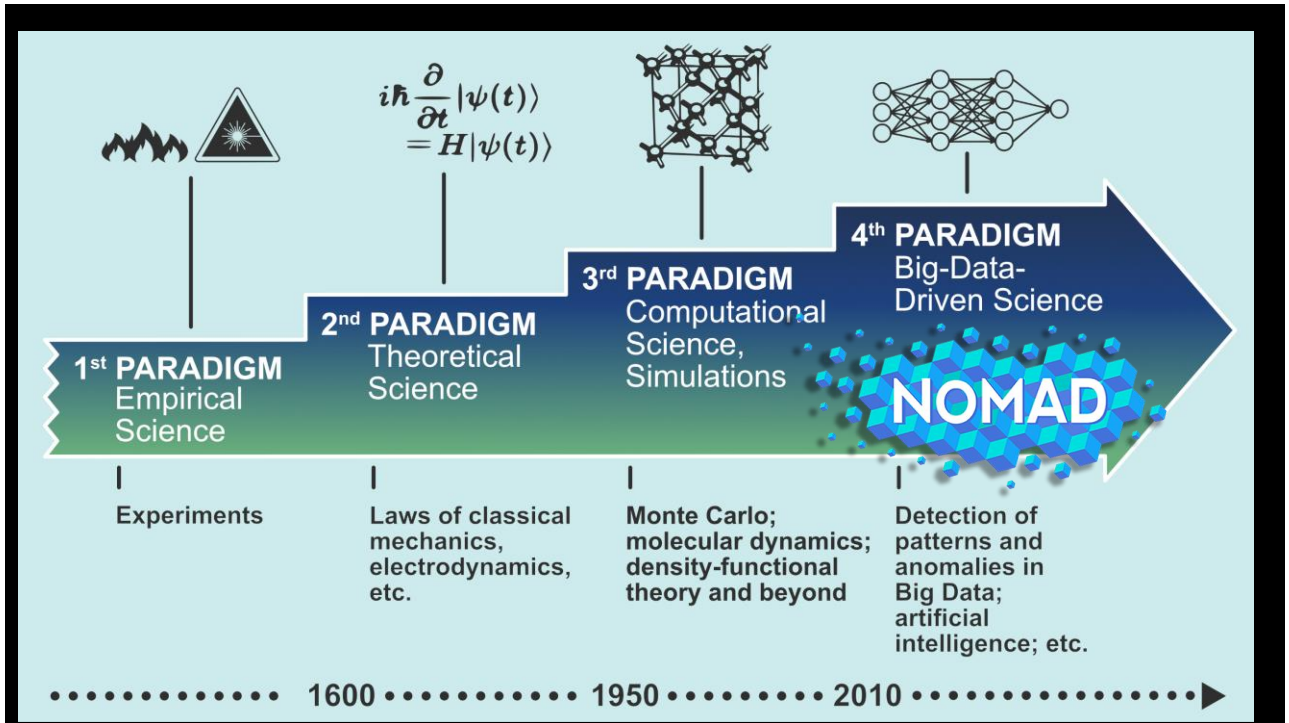
High-Throughput Screening
in Computational (and Experimental) Materials Science

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Consider as many compounds a possible, typically $O(10^3) - O(10^5)$

Sharing
Advances Science

Needs for a FAIR,
Efficient Research-
Data Infrastructure

Recycle the "waste"!
Enable re-purposing.

property 1
property 2
property 3
property 4
property 5

$O(10^1) - O(10^2)$ compounds selected

Findable **A**ccessible **I**nteroperable **R**eusable
M. D. Wilkinson et al., Scientific Data **3**, 160018 (2016)

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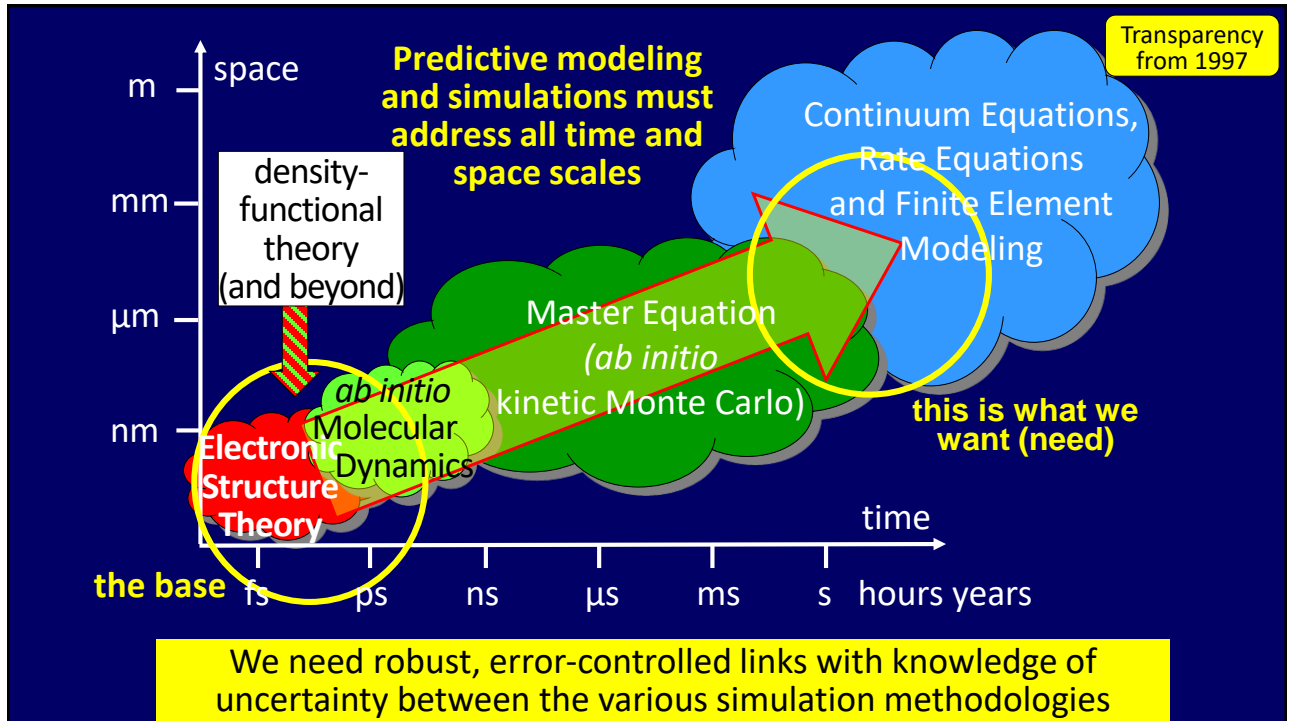
NOVEL MATERIALS DISCOVERY

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Topological
Insulators

metals

Super-
conductors

The NOMAD Repository
>50 Mio. Total-Energy Calculations

Predictive modeling and simulations must address all time and space scales

this is what we want (need)

We need robust, error-controlled links with knowledge of uncertainty between the various simulation methodologies

Modeling Materials Properties and Functions:
The Many-Body Schrödinger Equation

$$(\hat{T}^e + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

With:
$$\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_1}, \cdots \mathbf{R_M})$$

$$\hat{T}^e = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m} \qquad \hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_I^2}{2M_I}$$

$$\hat{V}^{e-e} = \frac{1}{2}\frac{1}{4\pi\epsilon_0} \sum_{k\neq k'}^{N,N} \frac{e^2}{|\mathbf{r_k} - \mathbf{r_{k'}}|}$$

$$\hat{V}^{ion-ion} = \frac{1}{2}\frac{1}{4\pi\epsilon_0} \sum_{I\neq I'}^{M,M} \frac{Z_I Z_{I'}}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

$$\hat{V}^{e-ion}(\mathbf{r_k}, \mathbf{R_I}) = \sum_{k=1}^{N}\sum_{I=1}^{M} \mathbf{v_I^{ion}}(|\mathbf{R_I} - \mathbf{r_k}|)$$

We know the operators and the interactions. We can write them down. *No open questions here!*

6

Modeling Materials Properties and Functions: The Many-Body Schrödinger Equation

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$$\hat{V}^{e-ion}(\mathbf{r_k}, \mathbf{R_I}) = \sum_{k=1}^{N} \sum_{I=1}^{M} \mathbf{v}_I^{ion}(|\mathbf{R_I} - \mathbf{r_k}|)$$

???

We know the operators and the interactions. We can write them down. *No open questions here!*

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_1}, \cdots \mathbf{R_M}) = \sum_{\nu} \Lambda_\nu(\{\mathbf{R_I}\}) \Phi_{\nu\,\{\mathbf{R_I}\}}(\{\mathbf{r_k}\})$$

Where Φ_ν are solutions of the "electronic Hamiltonian":

$$H^e_{\{\mathbf{R_I}\}} \Phi_{\nu,\{\mathbf{R_I}\}}(\{\mathbf{r_k}\}) = E^e_{\nu,\{\mathbf{R_I}\}} \Phi_{\nu,\{\mathbf{R_I}\}}(\{\mathbf{r_k}\})$$

$$H^e = T^e + V^{e-e} + V^{e-ion}$$

The Schrödinger equation of the electrons is determined by $\{\mathbf{R}_I, Z_I\}_{I=1}^{M}, N$

frequently (commonly) applied approximations:

- neglect non-adiabatic coupling (terms of order m/M_I)
- keep only Λ_0

⟹ the dynamics of electrons and nuclei decouple

Some Limits of the
Born-Oppenheimer Approximation

The BO Approximation does not account for correlated dynamics of ions and electrons. For example:

- polaron-induced superconductivity
- dynamical Jahn-Teller effect at defects in crystals
- some phenomena of diffusion in solids
- temperature dependence of band gaps
- non-adiabaticity in molecule-surface scattering and chemical reactions
- relaxation and transport of charge carriers (e^- or h)
- etc.

Some Limits of the
Born-Oppenheimer Approximation

The BO Approximation does not account for correlated dynamics of ions and electrons. For example:

- polaron-induced superconductivity
- dynamica
- some phe
- temperat
- non-adia
- relaxatio
- etc.

These limits can be severe. Nevertheless, we will use the BO approximation in the following.

How can we solve:

$$H^e_{\{\mathbf{R_I}\}} \Phi_{\nu, \{\mathbf{R_I}\}}(\mathbf{r_k}) = E^e_{\nu, \{\mathbf{R_I}\}} \Phi_{\nu, \{\mathbf{R_I}\}}(\mathbf{r_k})$$

$$H^e = T^e + V^{e-e} + V^{e-ion}$$

The Total Energy

e.g. from DFT
(see later)

a classical term

$$E_0 = E_0^e + \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{\substack{I,J \\ I\neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} Z_{v_I} Z_{v_J}$$

+ quantum mechanical corrections for lattice vibrations

$<\Lambda_0|\ T^{\text{ion}}|\Lambda_0>$

$\dfrac{E^{\text{tot}}}{N}$

$a_0+\Delta a$

cohesive energy

zero point energy

a_0 lattice parameter

The total energy per atom without zero-point vibrations as a function of the inter-atomic distance: the *Born-Oppenheimer surface*.

The *measured* inter-atomic distance is the average over the positions of vibrating atoms.

Density-Functional Theory
The Hohenberg-Kohn Theorem (1964)

$H^e\ \Phi = E\ \Phi$

$$n(\mathbf{r}) = n[\Phi]$$
$$= <\Phi|\sum_i \delta(\mathbf{r}-\mathbf{r}_i)|\Phi>$$

$\Phi^{(1)}$ $\Phi^{(2)}$ $\Phi^{(3)}$
$\Phi^{(4)}$ $\Phi^{(5)}$ $\Phi^{(6)}$
$\Phi^{(7)}$ $\Phi^{(8)}$ $\Phi^{(9)}$
$\Phi^{(10)}$ $\Phi^{(11)}$ $\Phi^{(12)}$
$\Phi^{(13)}$

$n^{(1)}$
$n^{(2)}$
$n^{(4)}$ $n^{(3)}$
$n^{(7)}$ $n^{(5)}$ $n^{(6)}$
$n^{(8)}$ $n^{(9)}$
$n^{(10)}$ $n^{(12)}$
$n^{(11)}$
$n^{(13)}$

$E = Min\ E_{\text{v}}\,[n(\text{r})]$

Set of non-degenerate ground-state wave functions Φ of arbitrary N-electron Hamiltonians.

Set of particle densities $n(\mathbf{r})$ of non-degenerate N-electron ground states.

The dashed arrow is not possible (reductio ad absurdum). Thus, there is a one-to-one correspondence between Φ_N and $n(r)$.

Density Functional Theory

The energy of the ground state of a many-electron system :

$$E_0 (\{\mathbf{R}_I\}) = \text{Min}_\Phi <\Phi|H^e|\Phi>$$

Hohenberg and Kohn (1964):   The functional

$$n(\mathbf{r}) = n[\Phi] = <\Phi| \sum_i \delta(\mathbf{r}-\mathbf{r}_i) |\Phi>$$
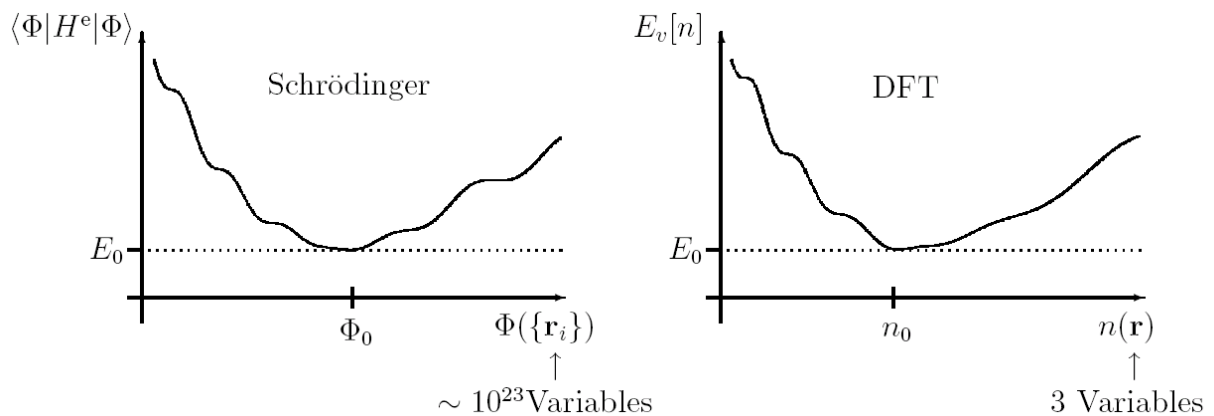
can be inverted, *i.e.,*

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N,}) = \Phi[n(\mathbf{r})] \ .$$

This implies:

$$E_0 (\{\mathbf{R}_I\}) = \text{Min}_{n(\mathbf{r})} E_{\{\mathbf{R}\}} [n]$$

Density-Functional Theory
The Hohenberg-Kohn Theorem (1964)

The Hohenberg-Kohn-Sham Ansatz of Density-Functional Theory

- Kohn-Sham (1965): Replace the original many-body problem by an independent electron problem **that can be solved!**

$$E_v[n] \;=\; T_s[n] \;+\; \int v(\mathbf{r})\,n(\mathbf{r})\,d^3\mathbf{r} \;+\; E^{\text{Hartree}}[n] \;+\; E^{\text{xc}}[n]$$

- With $T_s[n]$ the kinetic energy functional of independent electrons, and $E^{\text{xc}}[n]$ the "unknown" functional.

- The challenge is to find useful, approximate xc functionals.

The existence of a one-to-one relationship does not imply that the exact xc functional can be written down as a closed mathematical expression. In fact, it is "just an algorithm": $n(\mathbf{r}) \rightarrow \{\boldsymbol{R}_I, Z_I\}, N \;\rightarrow\; H^{\text{e}} \rightarrow E^{\text{e}}, \Phi_N$

Walter Kohn passed away April 19, 2016 at the age of 93
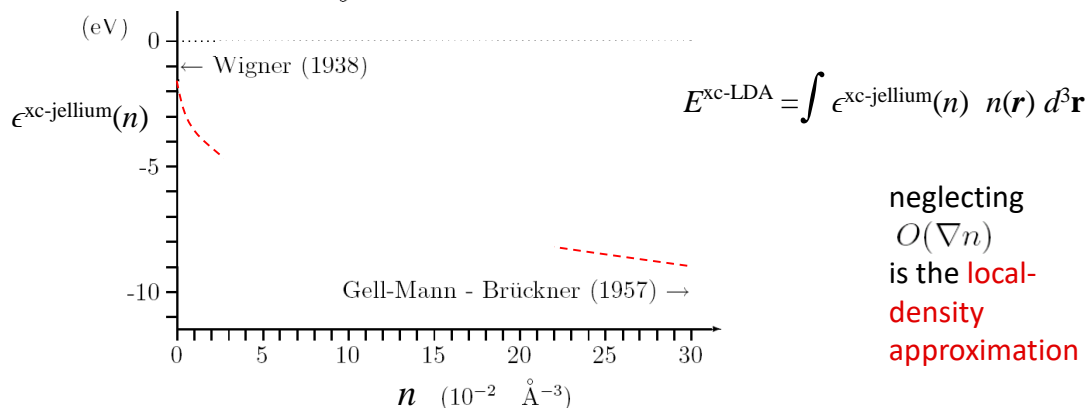
I started with DFT
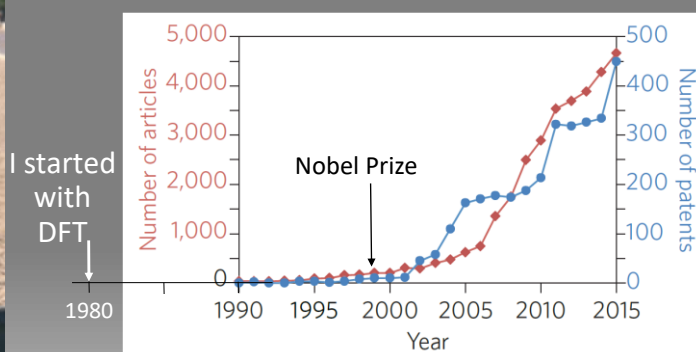
Number of articles and patents in materials science including the term "density functional theory" published per year during the past 25 years.

Walter Kohn at West Beach Santa Barbara at age 75

The xc Functional

T_s, E^{Hartree}, and E^{xc} are all ***universal*** functionals in $n(\mathbf{r})$, i.e., they are independent of the special system studied. (general theory: see the work by Levy and Lieb)
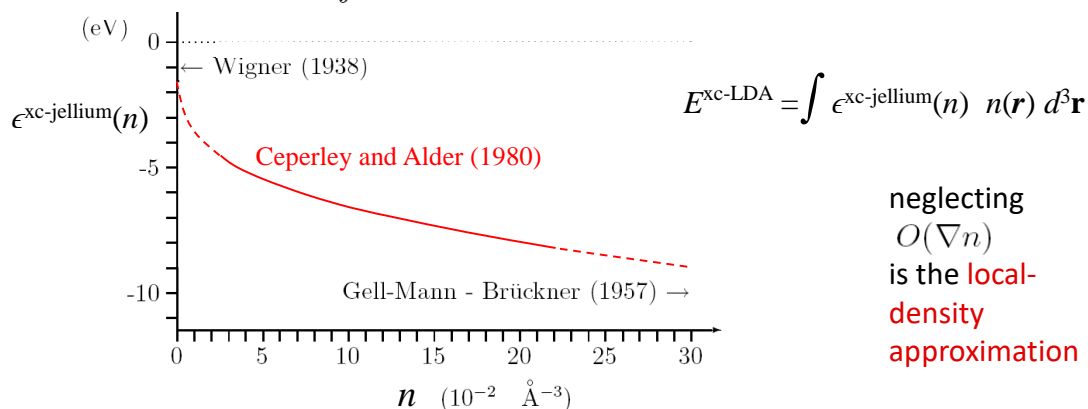
$$E^{\text{xc}}[n] \ = \ \int \epsilon^{\text{xc}}[n]n(\mathbf{r})d^3\mathbf{r} \ = E^{\text{xc}-\text{LDA}}[n] + O(\nabla n)$$

$$E^{\text{xc-LDA}} = \int \epsilon^{\text{xc-jellium}}(n) \ n(\boldsymbol{r}) \ d^3\mathbf{r}$$

neglecting
$O(\nabla n)$
is the local-density approximation

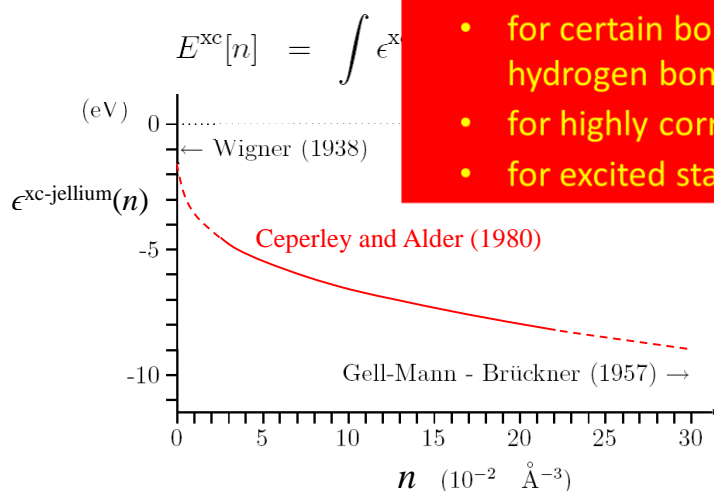## The xc Functional

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neglecting
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The xc Functional

T_s, E^{Hartree}, and E^{xc} are all **uni** of the special system studied.

Approximate xc functionals have been very successful but there are problems
- for certain bonding situations (vdW, hydrogen bonding, certain covalent bonds)
- for highly correlated situations, and
- for excited states.

$$E^{\mathrm{xc}}[n] = \int \epsilon^{\mathrm{xc}} \cdots$$

(eV)

$\epsilon^{\mathrm{xc\text{-}jellium}}(n)$

← Wigner (1938)

Ceperley and Alder (1980)

Gell-Mann - Brückner (1957) →

n $(10^{-2}\ \text{Å}^{-3})$

neglecting $O(\nabla n)$ is the local-density approximation

Perdew's Dream: Jacob's Ladder in Density-Functional Theory

The exchange-correlation functional

our favorite

accuracy

5	unoccupied $\psi_i(\mathbf{r})$,	EX + cRPA, as given by ACFD
4	occupied $\psi_i(\mathbf{r})$,	hybrids (B3LYP, PBE0, HSE, …)
3	$\tau(\mathbf{r})$,	meta-GGA (e.g., **SCAN**)
2	$\nabla n(\mathbf{r})$,	Generalized Gradient Approximation
1	$n(\mathbf{r})$,	Local-Density Approximation

$\tau(\mathbf{r})$: Kohn-Sham kinetic-energy density

EX: exact exchange: $E_x = -\dfrac{1}{2} \sum_{}^{occ} \iint d\mathbf{r}\, d\mathbf{r}' \dfrac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$

cRPA : random-phase approximation for correlation

ACFD : adiabatic connection fluctuation dissipation theorem

Bohm, Pines (1953); Gell-Mann, Brueckner (1957); Gunnarsson, Lundqvist (1975, 1976); Langreth, Perdew (1977); X. Ren, P. Rinke, C. Joas, and M. S., Invited Review, Mater. Sci. 47, 21 (2012)

Perdew's Dream: Jacob's Ladder in Density-Functional Theory
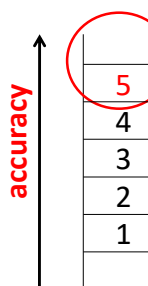
The exchange-correlation functional

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		our favorite	
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4	occupied $\psi_i(\mathbf{r})$,	hybrids (B3LYP, PBE0
3	$\tau(\mathbf{r})$,	meta-GGA (e.g.
2	$\nabla n(\mathbf{r})$,	Generalized
1	$n(\mathbf{r})$,	Loc

Functionals of level 1 and 2 suffer from severe self-interaction errors.
Functionals of level 1, 2, 3, & 4 are lacking the long-range vdW tails.
With "Level 5 plus" validation (error estimation) is becoming possible.

$\tau(\mathbf{r})$:

$$\iint d\mathbf{r}\, d\mathbf{r}' \frac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

...ation for correlation

...tion fluctuation dissipation theorem

Bohm ...s (1953... ...Brueckner (1957); Gunnarsson, Lundqvist (1975, 1976); Langreth, Perdew (1977); X. Ren, P. Rinke, C. J... ...nd M. S., Invited Review, Mater. Sci. 47, 21 (2012)

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The First (Convincing) DFT Calculations

Stability of crystals and crystal phase transitions
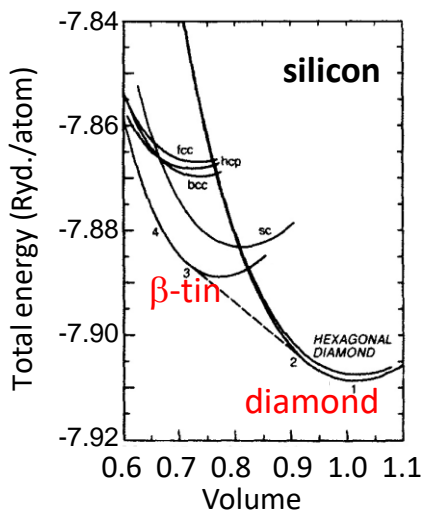
M. T. Yin and M. L. Cohen PRB 26 (1982) < and PRL 1980 >

Approximations: LDA, pseudopotentials, neglect of relativistic effects.

see also:
V.L. Moruzzi, J.F. Janak, and A.R. Williams Calculated Electronic Properties of Metals; Pergamon (1978)

Valence-Electron Density of Semiconductors
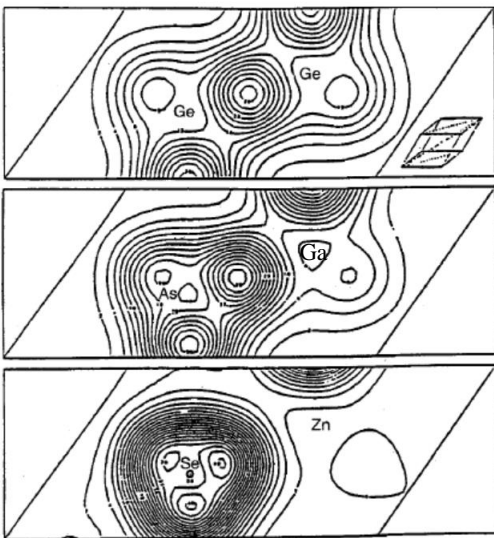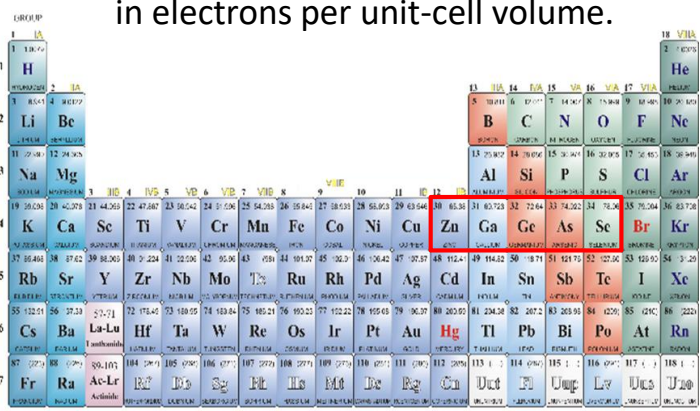

a) Ge (top),
b) GaAs (middle), and
c) ZnSe (lower)

in electrons per unit-cell volume.

V. L. Moruzzi, J. F. Janak, and A. R. Williams
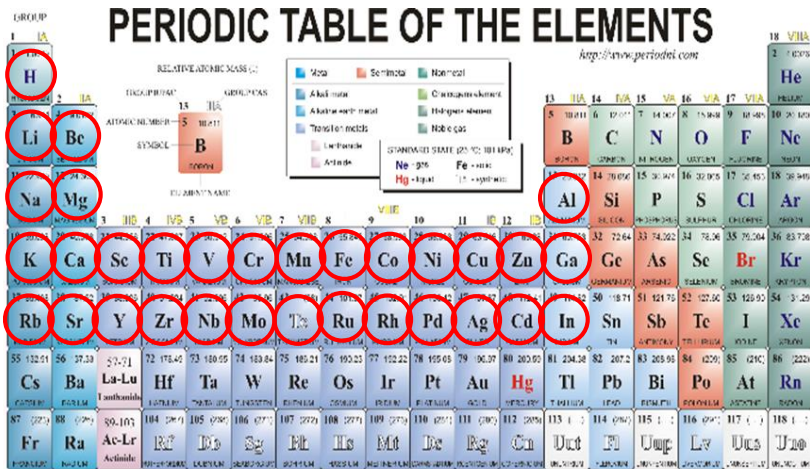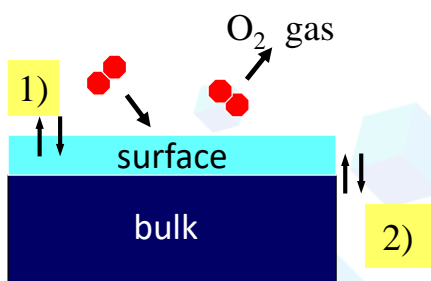## Calculated Electronic Properties of Metals
Pergamon Press (1978)

Approximations:
LDA,
'muffin-tin' approximation,
neglect of relativistic effects.

Ab initio Atomistic Thermodynamics

Surface in contact with a one-component gas phase – Example: O_2 @ Pd

$$\gamma_{\text{surf.}} = 1/A \left[G(N_O, N_{Pd}) - N_O \mu_O - N_{Pd} \mu_{Pd} \right]$$

O_2 gas

N_O = # of O atoms in the system
N_{Pd} = # of Pd atoms (substrate) in the system

Concept of thermodynamic reservoirs:

1) The environment can give and take O atoms at an energy $\mu_O = \tfrac{1}{2} \mu_{O_2}$

$$\mu_O (T, p) = \tfrac{1}{2} \mu_{O_2} (T, p^0) + \tfrac{1}{2} k_B T \ln(p/p^0)$$

2) Also the bulk of the substrate is practically of infinite size and acts as a reservoir for the Pd atoms: $\mu_{Pd} = g_{Pd}{}^{bulk}$

surface

bulk

Ab initio Atomistic Thermodynamics

Surface in contact with a one-component gas phase – Example: O_2 @ Pd

$$\gamma_{\text{surf.}} = 1/A \left[G(N_O, N_{Pd}) - N_O \mu_O - N_{Pd} \mu_{Pd} \right]$$

O_2 gas

N_O = # of O atoms in the system

1)

C. M. Weinert and M. Scheffler, Mat. Sci. Forum 10-12, 25 (1986).
E. Kaxiras et al. Phys. Rev. Lett. 56, 2819 (1986).
M. Scheffler and J. Dabrowski, Phil. Mag. A 58, 107-121 (1988).
E. Kaxiras et al., Phys. Rev. B 35, 9625 (1987).
X.-G. Wang et al., Phys. Rev. Lett. 81, 1038 (1998).
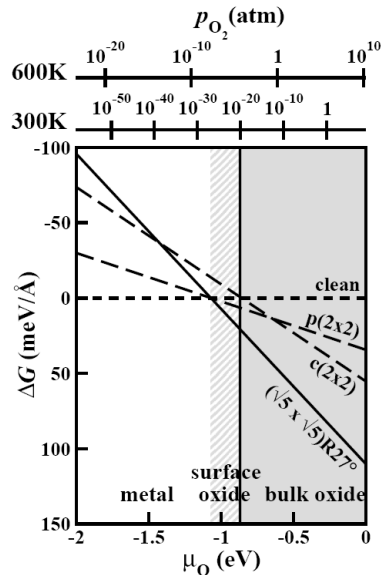*K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002).*

2) Also the bulk of the substrate is practically of infinite size and acts as a reservoir for the Pd atoms: $\mu_{Pd} = g_{Pd}{}^{bulk}$

8/27/2019

Oxide Formation on Pd(100)

p(2x2) O/Pd(100)
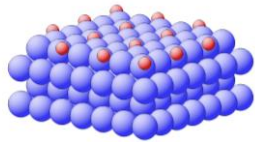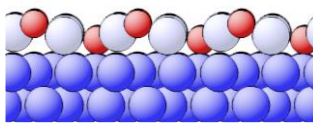
(√5 x √5)R27°

M. Todorova et al.,
Surf. Sci. 541, 101 (2003);
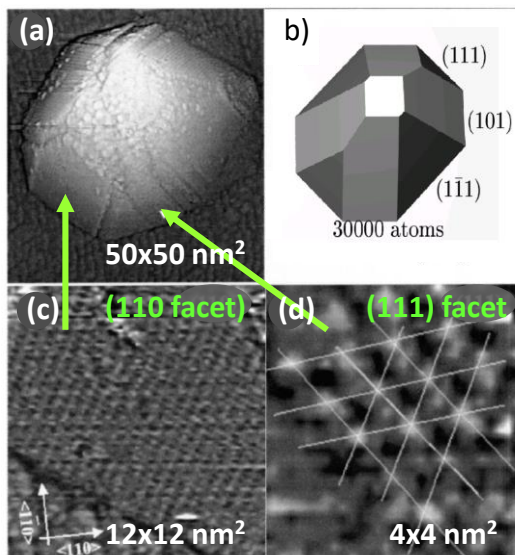K. Reuter and M. Scheffler,
Appl. Phys. A 78, 793 (2004)

A more general approach, including anharmonic vibrations: *Grand canonical replica exchange molecular dynamics*.

See talk by Luca Ghiringhelli

Strained InAs Quantum Dots at GaAs(001)

G. Costantini et al. APL 82 (2003)

a) STM topography of a large island.

b) Equilibrium shape (theory: *E. Pehlke, N. Moll, M.S., Proc. 23rd ICPS (1996); Q. Liu, et al., PRB 60 (1999)*).

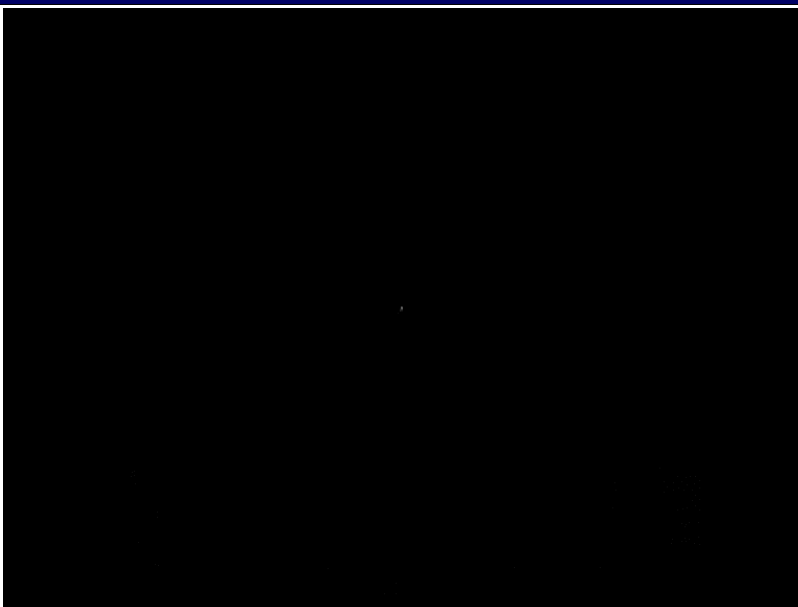c), d) High-resolution views of the (110) and (111) side facets.

Also:
*J. Marquez et al., APL 78 (2001);
Y. Temko et al., APL 83 (2003).*

Au$_{13}$ at Room Temperature
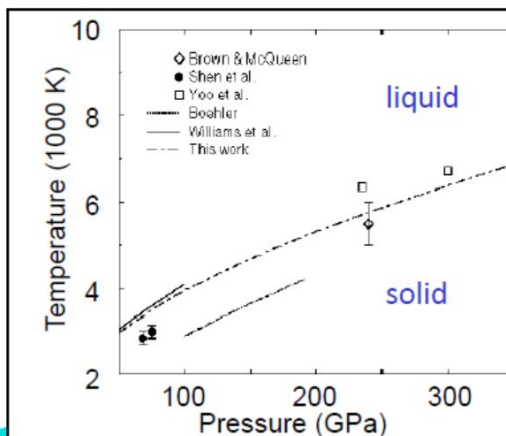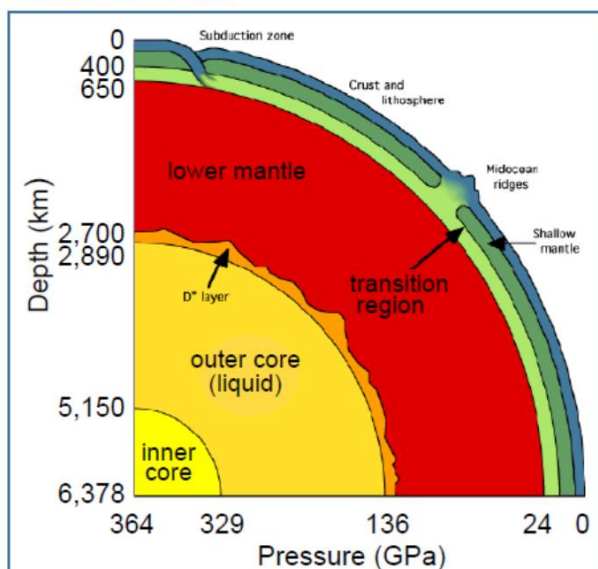### visiting many metastable structures

Ab initio molecular dynamics

Ab Initio Melting Curve of Fe as Function of Pressure

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D. Alfe, M. J. Gillan, and G. D. Price
NATURE 401 (1999)

Summary and Outlook: Interacting Electrons Determine the Properties and Function of Real Materials

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Important arenas for future theoretical work:
- Non-adiabatic effects, dissipation
- Transport (electrons, ions, heat)
- Thermodynamic phase transitions, e.g. melting
- Modeling the kinetics, e.g. of catalysts or crystal growth (self-assembly and self-organization) – in realistic environments
- Molecules and clusters (incl. bio molecules) in solvents, electrochemistry, fuel cells, external fields
- Correlated systems, e.g. f-electron chemistry
- Big-data analytics (statistical learning, compressed sensing, etc.)

The challenges:
- Find ways to control the xc approximation
- Develop methods for bridging length and time scales

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle$$

1st PARADIGM Empirical Science

2nd PARADIGM Theoretical Science

3rd PARADIGM Computational Science, Simulations

4th PARADIGM Big-Data-Driven Science

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Experiment

Detection of patterns and anomalies in Big Data; artificial intelligence; etc.

"The future is already here.
It is just unevenly distributed."

William F. Gibson (*1948),
American and Canadian
fiction writer and essayist

1600 • • • • • • • • • • • 1950 • • • • • • • • • 2010