

Computational Design of Materials

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Course Objectives

- Intelligently apply **computational methods** to the design of materials
- Effectively **design materials** to yield desirable functionality
- **Interpret experimental data** based on theoretical modeling and simulations
- **Design experiments** to yield deeper insights for materials discovery

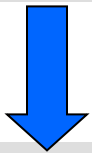
Core Issue: How to implement a meaningful simulation for the design of materials?

Materials properties charts: Scalings in Mechanical Strength vs. Density

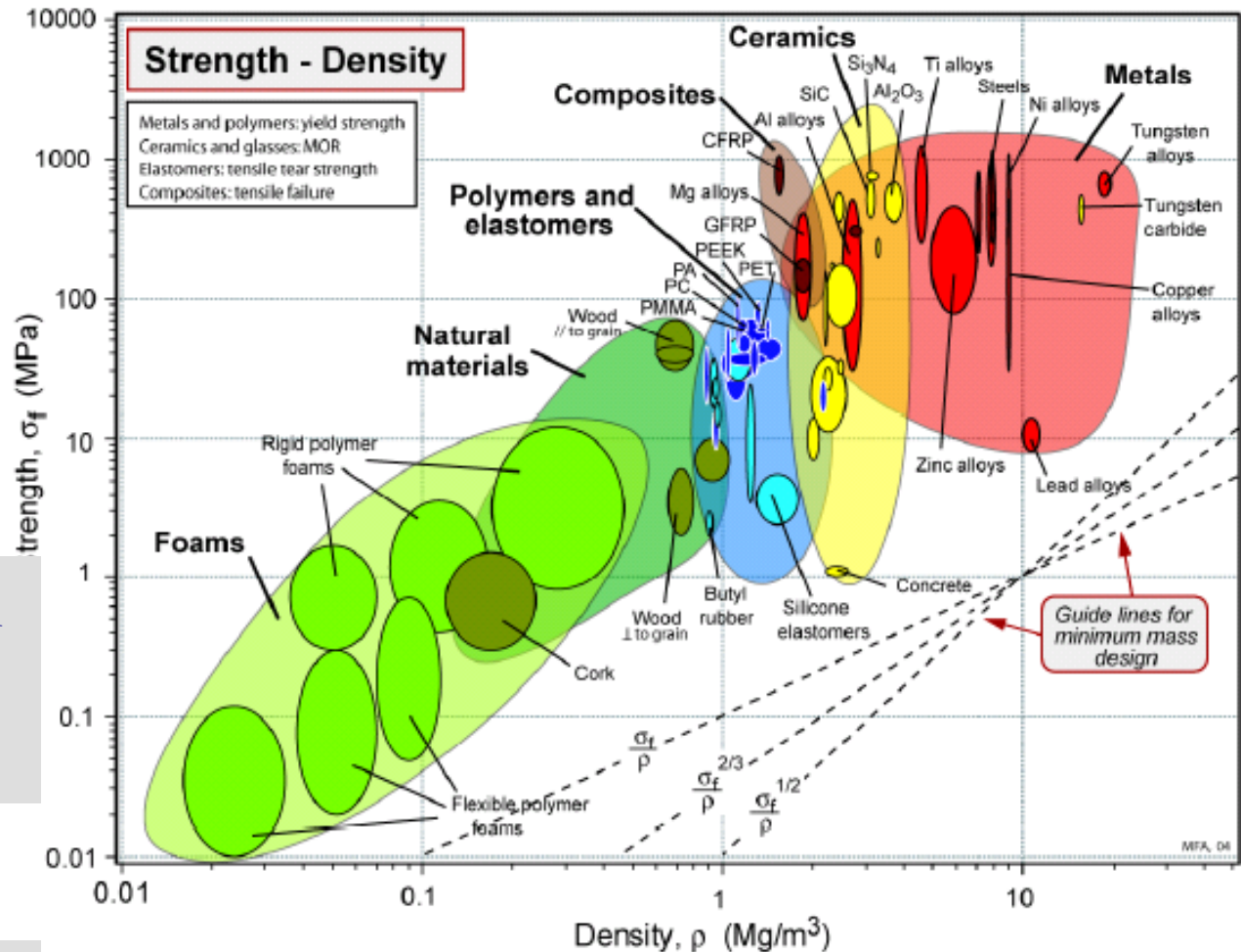
Materials look very different

Materials properties vary by many orders of magnitude

Composition/chemical bonding
Microstructure



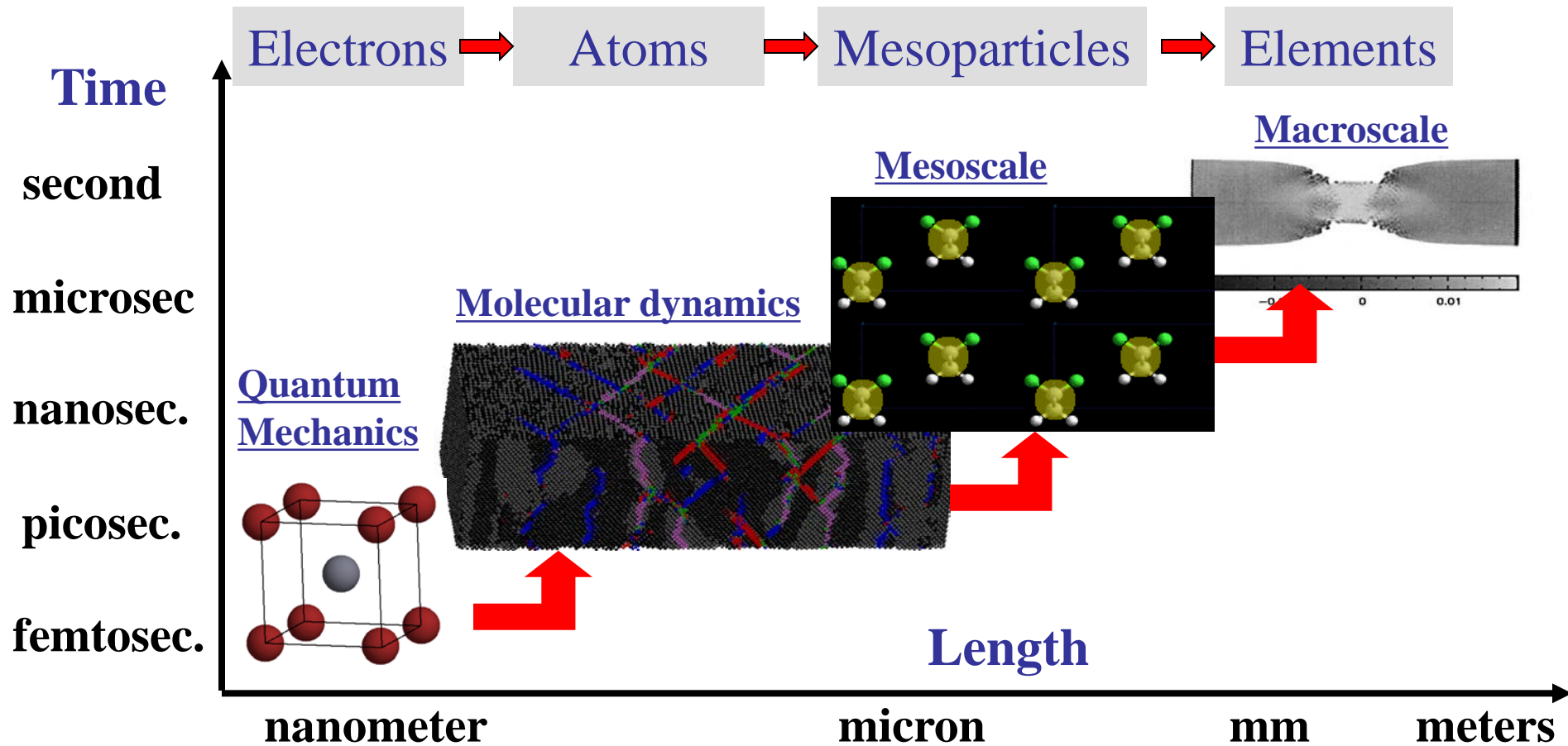
A variety of mechanisms govern materials behavior



Materials Selection in Mechanical Design (3rd edition)
by MF Ashby, Butterworth Heinemann, 2005

Objectives of multiscale modeling of materials

- **Understand** the molecular level origins of materials behavior
- **Predict** the behavior of materials from first principles



Ultimate: design new materials with improved performance

Strengths and limitations of different materials modeling approaches

Quantum Mechanical modeling

- Solve Schrodinger eqn. (SE) $\hat{H}\Phi = E\Phi$ for electrons.
- General for different materials, accurate (chemical reaction, bond breaking, *etc*)
- Very expensive; $N < 1000$

Empirical Atomistic (Molecular Dynamic) modeling

- Solve Newton eqn. $m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{f}_i = - \frac{dV_{tot}(\mathbf{r}_i)}{d\mathbf{r}_i}$
- $V_{tot}(\mathbf{r})$ unknown; constructed by fitting to data in analytical form
- Faster than QM cal.; $N \sim 10^5$ to 10^7

Continuum Mechanical Modeling with Finite-Element Method

- Solve continuous displacement field $\mathbf{u}(\mathbf{x})$ for given Hooke's Law $\sigma_{ij} = C_{ijkl} \varepsilon_{kl}$ by minimizing the elastic energy $E = \frac{1}{2} \int \sigma_{ij} \varepsilon_{ij} dv$; $\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j}$
- No microscopic physics contained in the model; no discrete lattice
- Very cheap; microns to meters for real engineering structures!

Contents of this Course

How computational methods are applied to modern design of materials for desired functionality

One overview on methodology and five design categories to be covered:

0. Principles of computational materials design
1. Computational design of materials for desired mechanical properties
2. Computational design of semiconductor systems
3. Computational design of metal systems
4. Computational design of catalytic materials
5. Computational design of energy-related Materials

Contents of this Course

How computational methods are applied to the design of materials to yield the desired functionality?

Methods to be Covered:

- first-principles approaches
- molecular dynamics (MD) simulations
- kinetic Monte Carlo (kMC) simulations
- continuum elasticity theory

Extensive Examples:

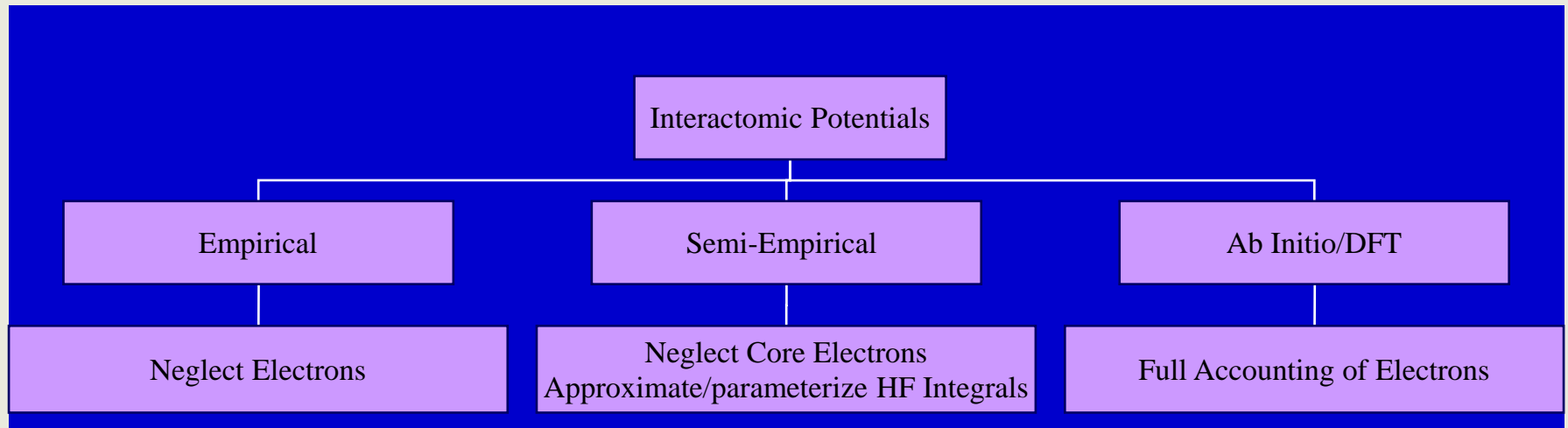
- problems in energetic and kinetic parameters of complex structures
- materials for energy conversion, storage, and environmental protection
- those related to mechanical strength of materials

0: Principles of computational materials design

- Kohn-Sham (**KS**) density functional theory (**DFT**)
- Car-Parrinello *ab initio* molecular dynamics
- Nudged elastic band (**NEB**) method for atomistic rate processes
- Kinetic Monte Carlo simulations
- Multi-scale materials modeling: sequential approaches
- Multi-scale materials modeling: concurrent approaches

Computational Approach to Materials Science Invoking Interparticle Potentials

- **Empirical**
 - ✓ Model potentials for inter-atomic interactions
 - ✓ Low accuracy and relatively poor predictability
- **Semi-empirical**
 - ✓ Input parameters in the model potentials determined quantum mechanically
 - ✓ Better accuracy and reasonable predictability
- **Quantum mechanical (first-principles)**
 - ✓ No models (at least on a formal level)
 - ✓ Highest accuracy and predictability



Materials Discovery by Quantum Design

Philosophy:

Using quantum mechanical principles, devise **kinetic pathways** to form novel materials that possess intriguing properties of technological significance.

“Uncovering nature’s hidden rules of making”

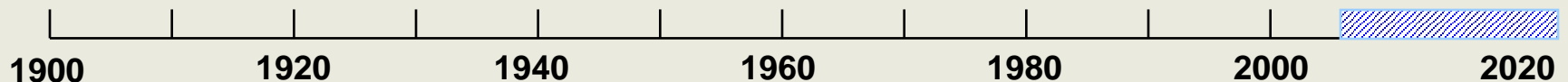
Quantum Mechanics \longrightarrow Technology Challenges for the 21st Century

- **Challenges for science**

- Create new materials and systems by design
- Scientific progress built upon **discoveries** of new materials – Fullerenes, nanotubes, and graphene (single layer 2D crystals, **10/2004** in Science Magazine).
- Build upon **discoveries** of self-assembled systems
- Make progress in **understanding biological systems** starting from the fundamental equations of quantum mechanics

- **Outstanding issues for computation**

- **Bridging** the time and length scales
- **Length** – from atoms to nano to macroscopic size
- **Time** – picoseconds to milliseconds



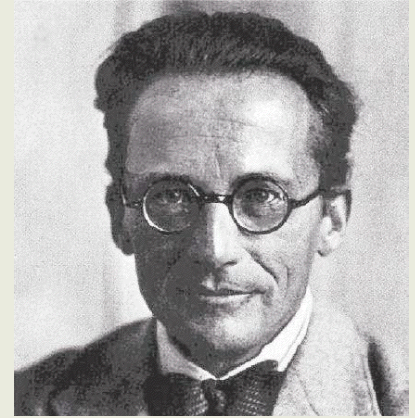
Density Functional Theory (DFT)

- P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.*, **136**, B 864 (1964).
- W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.* **140**, A 1133 (1965).

An 85-year long way

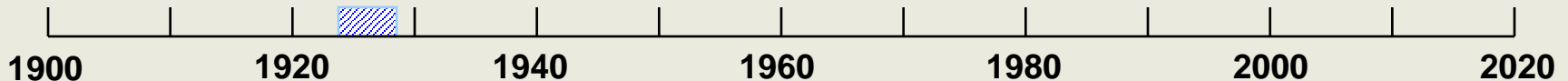


- **L. de Broglie**
Nature 112, 540 (1923).



- **E. Schrodinger – 1925**

- **Pauli exclusion Principle - 1925**
- **Fermi statistics - 1926**
- **Thomas-Fermi approximation – 1927**
- **First density functional – Dirac – 1928**
- **Dirac equation – relativistic quantum mechanics - 1928**

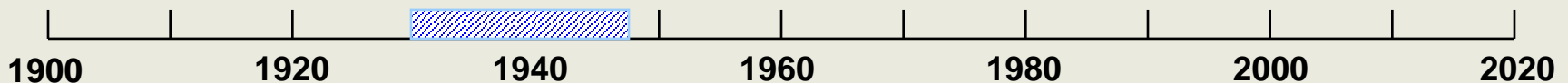


Quantum Mechanics → Technology

The Greatest Revolution of the 20th Century

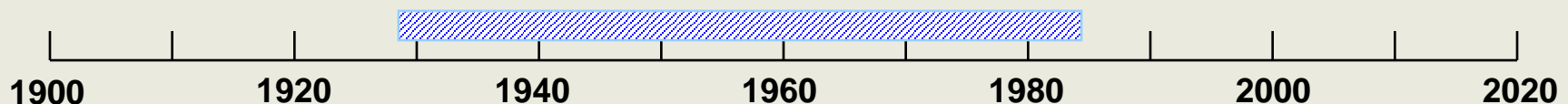
- Bloch theorem – 1928
- First understanding of semiconductors – 1930's
 - Wilson - Implications of band theory - Insulators/metals –1931
 - Wigner- Seitz – Quantitative calculation for Na – 1935
 - Slater - Bands of Na - 1934 (proposal of APW in 1937)
 - Bardeen - Fermi surface of a metal - 1935
- Invention of the Transistor – 1940' s
 - Bardeen – student of Wigner
 - Shockley – student of Slater

APW: Augmented Plane Waves



The Basic Methods of Electronic Structure

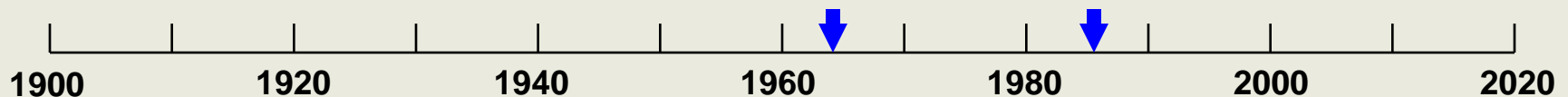
- Hylleras – Numerically exact solution for H_2 – 1929
 - Numerical methods used today in modern efficient methods
- Slater – Augmented Plane Waves (APW) - 1937
 - Not used in practice until 1950' s, 1960' s – electronic computers
- Herring – Orthogonalized Plane Waves (OPW) – 1940
 - First realistic bands of a semiconductor – Ge – Herrman, Callaway (1953)
- Koringa, Kohn, Rostocker (KKR) Multiple Scattering – 1950' s
 - The “most elegant” method - Ziman
- Boys – Gaussian basis functions – 1950' s
 - Widely used, especially in chemistry
- Phillips, Kleinman, Antoncik, – Pseudopotentials – 1950' s
 - Hellman, Fermi (1930' s) – Hamann, Vanderbilt, ... – 1980' s
- Andersen – Linearized Muffin Tin Orbitals (LMTO) – 1975
 - The full potential “L” methods – LAPW,



Basis of Modern Calculations

Density Functional Theory

- Hohenberg-Kohn; Kohn-Sham - 1965
- Car-Parrinello Method – 1985
- Improved approximations for the density functionals
 - Generalized Gradient Approximations (**GGA**), . . .
- Evolution of computer power
- Nobel Prize for Chemistry, 1998, Walter Kohn
- Widely-used codes –The most obvious distinction is between these codes is to target molecular systems or those that use periodic boundary conditions (PBCs) to treat the physics of extended systems.
 - **ABINIT**, **VASP**, **CASTEP**, **ESPRESSO**, **CPMD**, **FHI98md**, **SIESTA** (Order-N), **CRYSTAL**, **FPLO**, **WEIN2k**, . . .



Most Cited Papers in APS Journals (till 2003)

- 11 papers published in APS journals since 1893 with > 1000 citations (citations in APS journals, ~5 times as many references in all science journals)

Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
PR 140, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR 136, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB 23, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL 45, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR 108, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL 19, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB 12, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR 124, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP 57, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP 54, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB 13, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, *Physical Review*; PRB, *Physical Review B*; PRL, *Physical Review Letters*; RMP, *Reviews of Modern Physics*.

From Physics Today, June, 2005

Most Cited Papers in APS Journals till 01/24/2012

1. Title: DEVELOPMENT OF THE COLLE-SALVETTI CORRELATION-ENERGY FORMULA INTO A FUNCTIONAL OF THE ELECTRON-DENSITY
Author(s): LEE CT; YANG WT; PARR RG
Source: PHYSICAL REVIEW B Volume: 37 Issue: 2 Pages: 785-789 DOI: 10.1103/PhysRevB.37.785 Published: JAN 15 1988
Times Cited: 34,807 (from Web of Science)

[FIND IT @ HARVARD](#)

2. Title: Generalized gradient approximation made simple
Author(s): Perdew JP; Burke K; Ernzerhof M
Source: PHYSICAL REVIEW LETTERS Volume: 77 Issue: 18 Pages: 3865-3868 DOI: 10.1103/PhysRevLett.77.3865 Published: OCT 28 1996
Times Cited: 20,312 (from Web of Science)

[FIND IT @ HARVARD](#) [[View abstract](#)]

3. Title: SELF-CONSISTENT EQUATIONS INCLUDING EXCHANGE AND CORRELATION EFFECTS
Author(s): KOHN W; SHAM LJ
Source: PHYSICAL REVIEW Volume: 140 Issue: 4A Pages: 1133-8 Published: 1965
Times Cited: 18,412 (from Web of Science)

[FIND IT @ HARVARD](#)

4. Title: Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set
Author(s): Kresse G; Furthmüller J
Source: PHYSICAL REVIEW B Volume: 54 Issue: 16 Pages: 11169-11186 DOI: 10.1103/PhysRevB.54.11169 Published: OCT 15 1996
Times Cited: 11,059 (from Web of Science)

[FIND IT @ HARVARD](#) [[View abstract](#)]

5. Title: SPECIAL POINTS FOR BRILLOUIN-ZONE INTEGRATIONS
Author(s): MONKHORST HJ; PACK JD
Source: PHYSICAL REVIEW B Volume: 13 Issue: 12 Pages: 5188-5192 DOI: 10.1103/PhysRevB.13.5188 Published: 1976
Times Cited: 10,981 (from Web of Science)

[FIND IT @ HARVARD](#)

6. Title: ACCURATE AND SIMPLE ANALYTIC REPRESENTATION OF THE ELECTRON-GAS CORRELATION-ENERGY
Author(s): PERDEW JP; WANG Y
Source: PHYSICAL REVIEW B Volume: 45 Issue: 23 Pages: 13244-13249 DOI: 10.1103/PhysRevB.45.13244 Published: JUN 15 1992
Times Cited: 9,679 (from Web of Science)

[FIND IT @ HARVARD](#) [[View abstract](#)]

7. Title: SELF-INTERACTION CORRECTION TO DENSITY-FUNCTIONAL APPROXIMATIONS FOR MANY-ELECTRON SYSTEMS
Author(s): PERDEW JP; ZUNGER A
Source: PHYSICAL REVIEW B Volume: 23 Issue: 10 Pages: 5048-5079 DOI: 10.1103/PhysRevB.23.5048 Published: 1981
Times Cited: 9,049 (from Web of Science)

[FIND IT @ HARVARD](#)

8. Title: ATOMS, MOLECULES, SOLIDS, AND SURFACES - APPLICATIONS OF THE GENERALIZED GRADIENT APPROXIMATION FOR EXCHANGE AND CORRELATION
Author(s): PERDEW JP; CHEWARY JA; VOSKO SH; et al.
Source: PHYSICAL REVIEW B Volume: 46 Issue: 11 Pages: 6671-6687 DOI: 10.1103/PhysRevB.46.6671 Published: SEP 15 1992
Times Cited: 8,848 (from Web of Science)

[FIND IT @ HARVARD](#) [[View abstract](#)]

9. Title: SOFT SELF-CONSISTENT PSEUDOPOTENTIALS IN A GENERALIZED EIGENVALUE FORMALISM
Author(s): VANDERBILT D
Source: PHYSICAL REVIEW B Volume: 41 Issue: 11 Pages: 7892-7895 DOI: 10.1103/PhysRevB.41.7892 Published: APR 15 1990
Times Cited: 8,822 (from Web of Science)

[FIND IT @ HARVARD](#)

10. Title: Note on an approximation treatment for many-electron systems
Author(s): Møller C; Plesset MS
Source: PHYSICAL REVIEW Volume: 46 Issue: 7 Pages: 6618-6622 DOI: 10.1103/PhysRev.46.618 Published: OCT 1934
Times Cited: 8,788 (from Web of Science)

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Most Cited Papers in APS Journals till 01/24/2012

11. Title: **INHOMOGENEOUS ELECTRON GAS**
Author(s): HOHENBERG P; KOHN W
Source: PHYSICAL REVIEW B Volume: 136 Issue: 3B Pages: 8664-6 DOI:
10.1103/PhysRev.136.8664 Published: 1964
Times Cited: 8,708 (from Web of Science)

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12. Title: **DENSITY-FUNCTIONAL APPROXIMATION FOR THE CORRELATION-ENERGY OF THE INHOMOGENEOUS ELECTRON-GAS**
Author(s): PERDEW JP
Source: PHYSICAL REVIEW B Volume: 33 Issue: 12 Pages: 8822-8824
DOI: 10.1103/PhysRevB.33.8822 Part: Part 2 Published: JUN 15 1986
Times Cited: 8,542 (from Web of Science)

[FIND IT](#)  HARVARD

13. Title: **From ultrasoft pseudopotentials to the projector augmented-wave method**
Author(s): Kresse G; Joubert D
Source: PHYSICAL REVIEW B Volume: 59 Issue: 3 Pages: 1758-1775 DOI:
10.1103/PhysRevB.59.1758 Published: JAN 15 1999
Times Cited: 7,848 (from Web of Science)

[FIND IT](#)  HARVARD [ View abstract]

14. Title: **GROUND-STATE OF THE ELECTRON-GAS BY A STOCHASTIC METHOD**
Author(s): CEPERLEY DM; ALDER BJ
Source: PHYSICAL REVIEW LETTERS Volume: 45 Issue: 7 Pages: 566-569
DOI: 10.1103/PhysRevLett.45.566 Published: 1980
Times Cited: 7,209 (from Web of Science)

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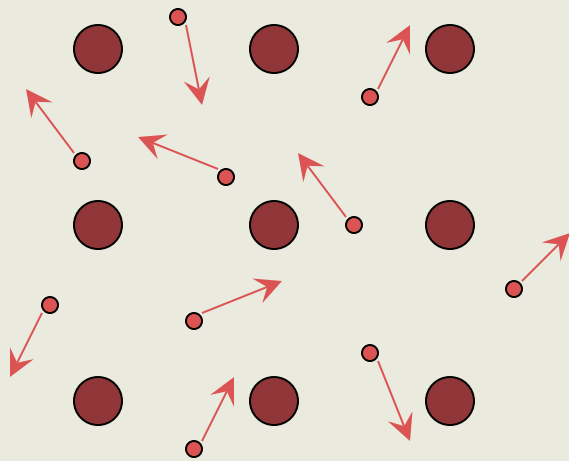
15. Title: **ATOMIC FORCE MICROSCOPE**
Author(s): BINNIG G; QUATE CF; GERBER C
Source: PHYSICAL REVIEW LETTERS Volume: 56 Issue: 9 Pages: 930-933
DOI: 10.1103/PhysRevLett.56.930 Published: MAR 3 1986
Times Cited: 7,132 (from Web of Science)

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Many-Electron Systems

Electron: ● Nucleus: ●

Many-electron problem



electron-electron interaction
electron-nucleus interaction

- Born-Oppenheimer Approximation
 - Allows the equation of motion for electrons and nuclei to be treated separately
- Quantum mechanical description of the electronic states
 - Quantum chemistry (Hartree, Hartree-Fock, CI)
 - Quantum Monte-Carlo
 - Perturbation theory
 - **Density functional theory**

The basis of Density Functional Theory (DFT)

The Fundamental Hamiltonian

Interacting electrons in an external potential

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$- \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- Only one small term: The kinetic energy of the nuclei
- If we omit this term, the nuclei are a fixed external potential acting on the electrons
- The final term is essential for charge neutrality – but is a classical term that is added to the electronic part

The Hohenberg-Kohn Theorems

- Theorem I: For any system of electrons in an external potential $V_{ext}(\mathbf{r})$, that potential is determined uniquely, except for a constant, by the ground state density $n(\mathbf{r})$.
$$n(\vec{r}) \rightarrow V_{ext}(\vec{r}) + \text{constant}$$

Corollary I: Since the hamiltonian is thus fully determined, except for a constant shift of the energy, the full many-body wavefunction and all other properties of the system are also completely determined!

$$\mathbf{n}_0(\mathbf{r}) \rightarrow \mathbf{V}_{ext}(\mathbf{r}) + c$$

$$\rightarrow \mathbf{H} \rightarrow \Psi$$

→ All properties based on the wavefunction and total energy

Proof by Variational Principle

Proof of Theorem I:

Suppose that there were two different external potentials $V_{ext}^{(1)}(\mathbf{r})$ and $V_{ext}^{(2)}(\mathbf{r})$ with the same ground state density $n(\mathbf{r})$. The two external potentials lead to two different hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, which have different ground state wavefunctions, $\Psi^{(1)}$ and $\Psi^{(2)}$, which are hypothesized to have the same density $n(\mathbf{r})$. Then:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle. \quad (6)$$

which leads to *Note* : $H_1 = H_2 + (V_{ext}^{(1)} - V_{ext}^{(2)})$

$$E^{(1)} < E^{(2)} + \int d^3r \{ V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r}) \} n(\mathbf{r}). \quad (7)$$

But changing the labels leads to

$$E^{(2)} < E^{(1)} + \int d^3r \{ V_{ext}^{(2)}(\mathbf{r}) - V_{ext}^{(1)}(\mathbf{r}) \} n(\mathbf{r}). \quad (8)$$

which is a contradiction!

$$E^{(1)} < E^{(2)} + \int dr^3 \{ V^{(1)}(r) - V^{(2)}(r) \} n(r)$$
$$E^{(1)} > E^{(2)} + \int dr^3 \{ V^{(1)}(r) - V^{(2)}(r) \} n(r)$$

The Hohenberg-Kohn Theorems

- Theorem II: A universal functional for the energy $E[n]$ of the density $n(\mathbf{r})$ can be defined for all electron systems. The exact ground state energy is the global minimum for a given $V_{ext}(\mathbf{r})$, and the density $n(\mathbf{r})$ which minimizes this functional is the exact ground state density.

Corollary II: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. Excited states of the electrons must be determined by other means.

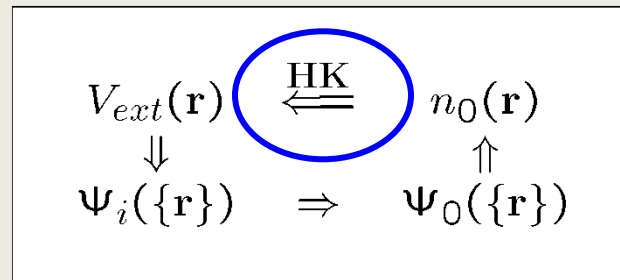
A functional $E[n(r)]$ maps a function $n(r)$ to a property $E: n(r) \rightarrow E$

Minimizing $E[n]$ for a given $V_{ext}(r) \rightarrow n_0(r)$ and E

In principle, one can find all other properties, which are functionals of $n_0(r)$.

The basis of Density Functional Theory (DFT)

- Hohenberg-Kohn (1964)

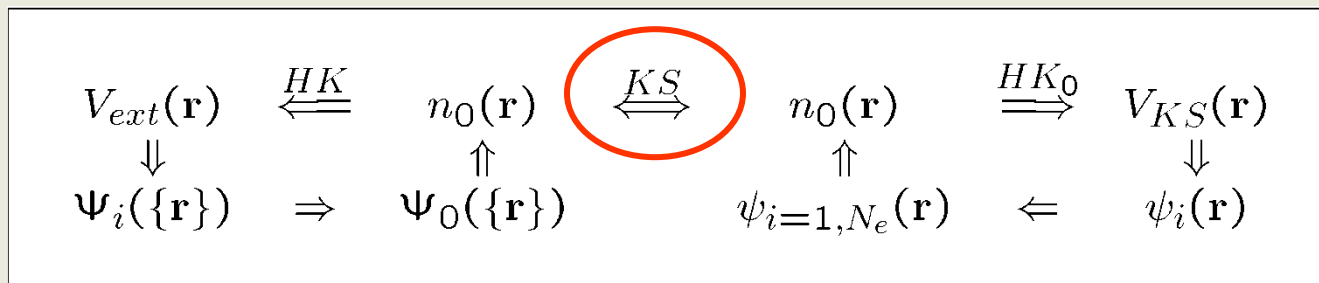


- All properties of the many-body system are determined by the ground state density $n_0(\mathbf{r})$
- Each property is a functional of the ground state density $n_0(\mathbf{r})$ which is written as $f[n_0]$

The Kohn-Sham Ansatz

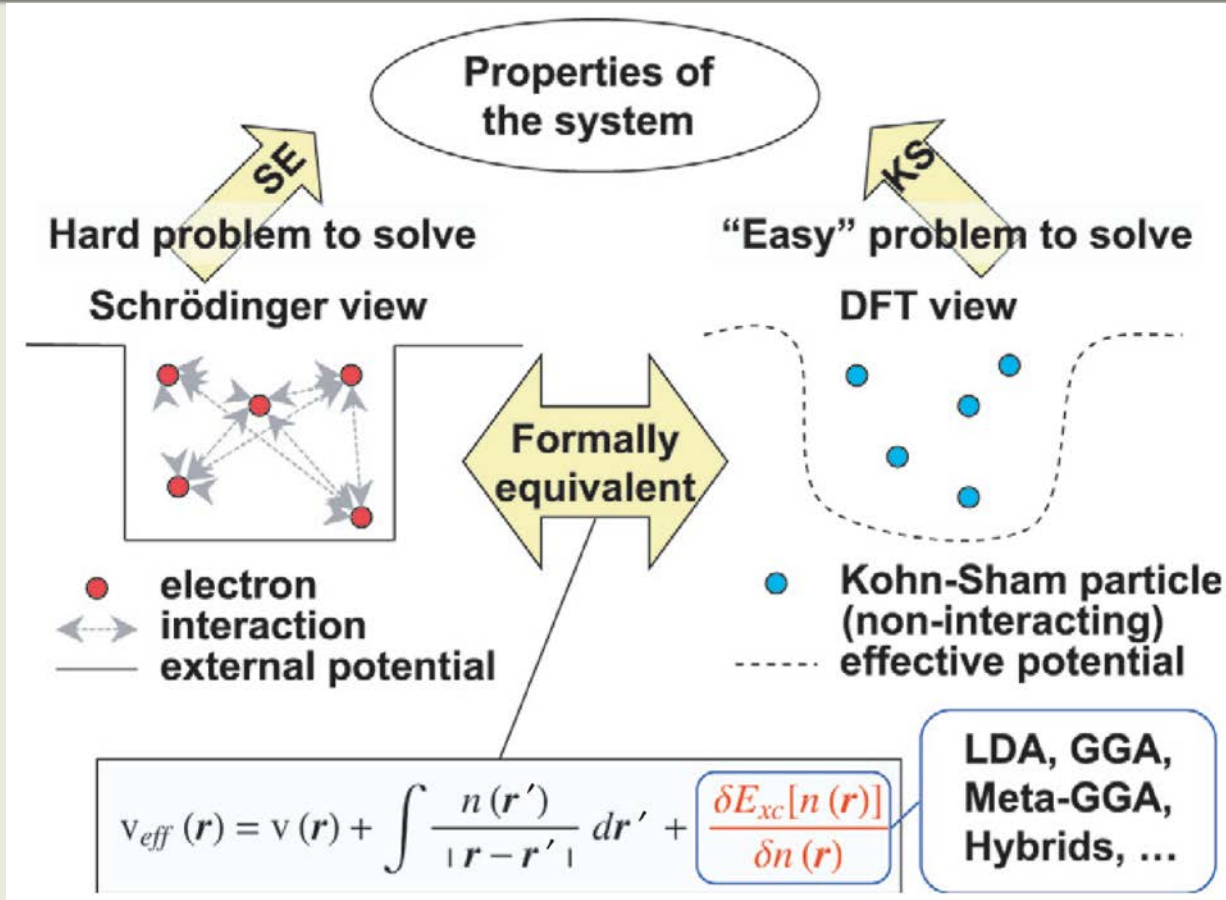
- Kohn-Sham (1965) – Replace original **many-body problem** with an **independent electron problem**, which can be solved!

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$



- Only the **ground state density and energy** are required to be the same as in the original many-body system

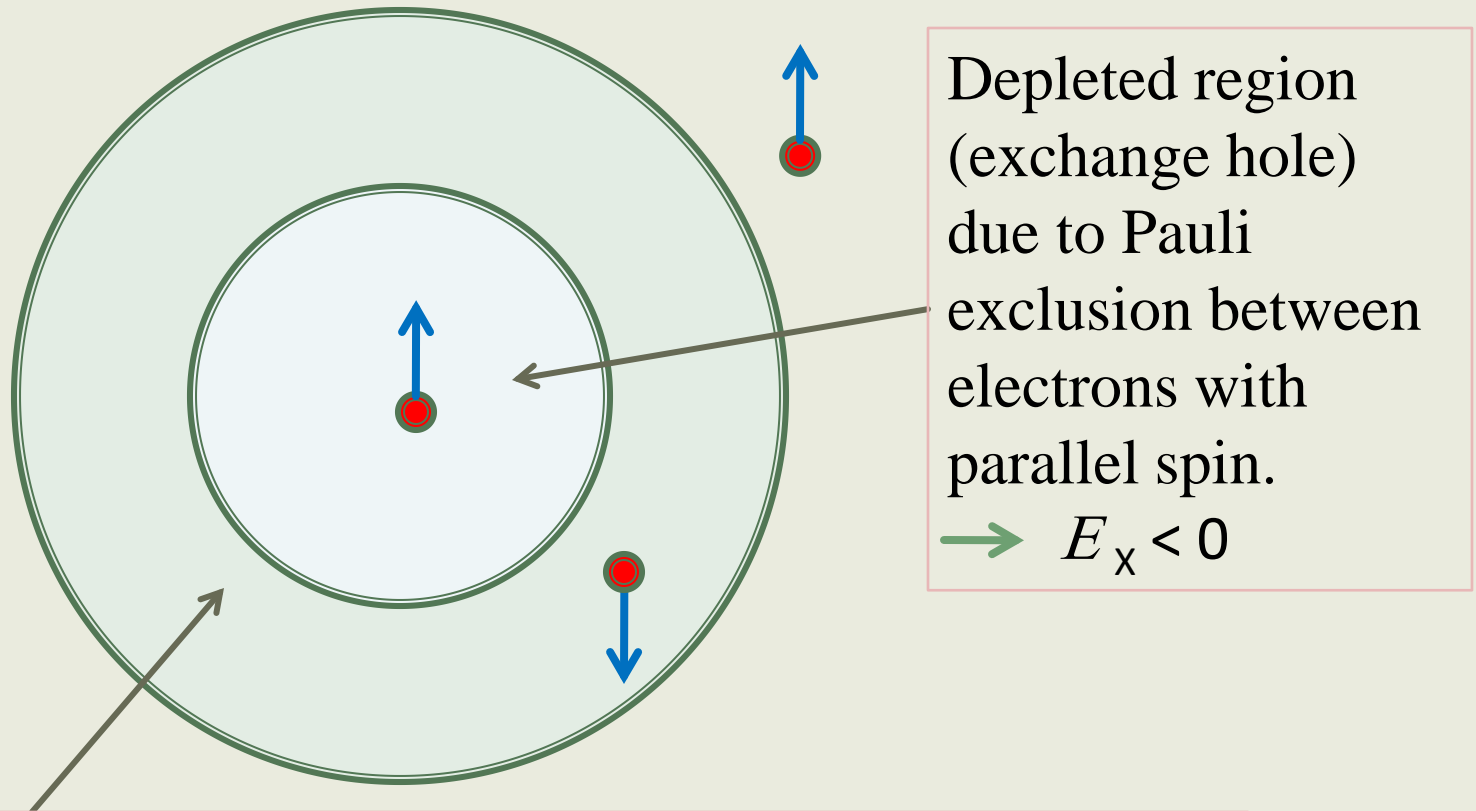
The Hohenberg-Kohn Theorems - Continued



The functional is part of the translation of the SE external potential into the KS effective potential.

Instead of solving the complicated real system of interacting electrons in an external potential $v(r)$, a much simpler equivalent fictitious system of non-interacting KS particles in an effective potential $v_{eff}(r)$ is solved.

An Explanation of Exc in Many-Electron System



Depleted region
(exchange hole)
due to Pauli
exclusion between
electrons with
parallel spin.

→ $E_x < 0$

Depleted region (correlation hole) due to the
electrostatic interaction between electrons. → $E_c < 0$

Functional $E_{xc}[n]$ in Kohn-Sham Eqs.

How to find a functional $E_{xc}[n]$? It requires information on the many-body system of interacting electrons

Climb up the Jacob's ladder

◆ Local Density Approximation (LDA)

- Uses only the electron density $n(r)$ at spatial point r to determine E_{xc} at that point. Assume the functional is the same as that of the homogeneous electron gas;
- E_{xc} has been calculated as a function of density using quantum Monte Carlo methods (Ceperley & Alder)---PZ, PW, and VWN

◆ Gradient approximations (GGA) ---PBE and PW91

- Adds the gradient of the density $|\nabla n(r)|$ as an independent variable.

Functional $Exc[n]$ in Kohn-Sham Eqs.

◆ *Meta-GGA*

- Use Laplacians of the density and/or kinetic energy densities as additional degrees of freedom.

◆ *Hyper-GGA*

- Adds an exact exchange (EXX) energy per particle calculated from the SE many-body wavefunctions with the Hartree–Fock (HF) exchange formula.

◆ **Generalized random phase approximation**

- Use EXX and exact partial correlation

Selecting a functional

There are no guarantees when selecting functionals. Following are some useful guidelines:

- It is useful to perform a calculation with at least two different types of functional in order to get a rough estimate of the accuracy.
- Currently available functionals are sometime inadequate for computation of surface properties and for systems where van der Waals interactions are important. It is also well know the inability of LDA and GGA functionals to reproduce the experimental valence–conduction band gap in semiconductors and insulators.
- Spin polarized calculations are crucial in getting reasonable results for defects in insulators. But watch out present functionals tend to delocalize spin densities too much.
- Always keep in mind that DFT calculations with presently available functionals do not always give the correct answer (see CO on Pt(111)).

The Kohn-Sham Equations (KSE)

- Assuming a form for $\mathbf{E}_{xc}[\mathbf{n}]$
- Minimizing energy (with constraints) \rightarrow **Kohn-Sham Eqs.**

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

$$E_{KS} = \frac{1}{2} \sum_{\sigma} \sum_{i=1} |\nabla \psi_i^{\sigma}|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n].$$

Constraint – required
Exclusion principle for
independent particles

$$\frac{\delta E_{KS}}{\delta \psi_i^{\sigma*}(\mathbf{r})} = 0, \quad (1)$$

$$\langle \psi_i^{\sigma} | \psi_j^{\sigma'} \rangle = \delta_{i,j} \delta_{\sigma,\sigma'}. \quad (2)$$

$$\left(-\frac{1}{2}\nabla^2 + V_{KS}^{\sigma}(\mathbf{r}), -\varepsilon_i^{\sigma}\right) \psi_i^{\sigma}(\mathbf{r}) = 0 \quad (3)$$

$$\begin{aligned} V_{KS}^{\sigma}(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r}, \sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + \underline{V_{xc}^{\sigma}(\mathbf{r})} \quad (4) \end{aligned}$$

Eigenvalues are approximation to the energies to add or subtract electrons –electron bands

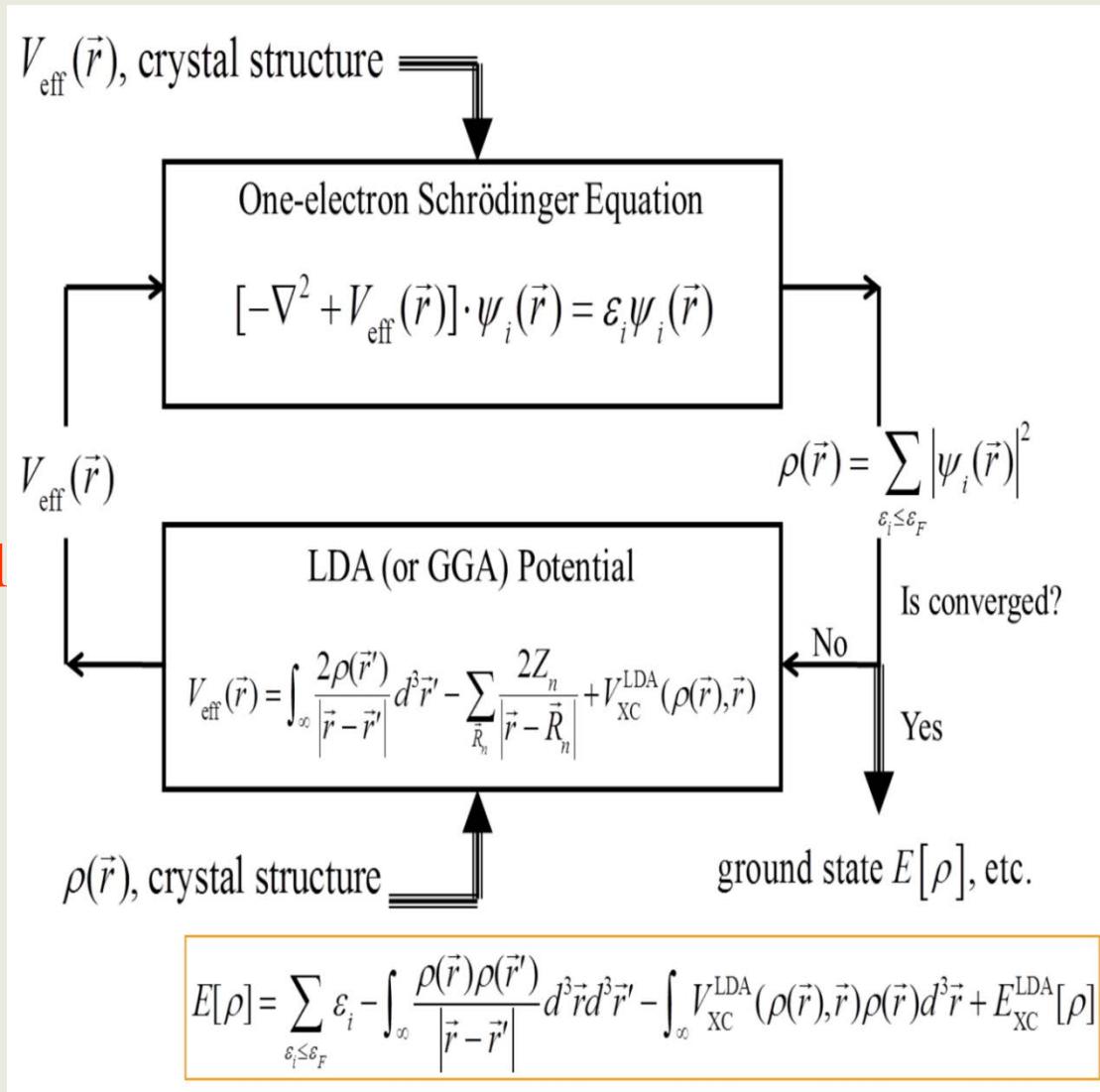
What about eigenvalues of KSE?

$$\left(-\nabla^2 + \int_{\infty} \frac{2\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' - \sum_{\vec{R}_n} \frac{2Z_n}{|\vec{r} - \vec{R}_n|} + V_{\text{xc}}(\rho, \vec{r}) \right) \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

- The only quantities that are supposed to be correct in the Kohn-Sham approach are the **density, energy, forces,**
- These are **integrated quantities**
 - Density $n(\mathbf{r}) = \sum_i |\Psi_i(\mathbf{r})|^2$
 - Energy $E_{\text{tot}} = \sum_i \varepsilon_i + F[n]$
 - Force $F_I = -dE_{\text{tot}}/dR_I$ where $R_I =$ position of nucleus I
- **What about the individual $\Psi_i(\mathbf{r})$ and ε_i ?**
 - In a non-interacting system, ε_i are the energies to add an non-interacting electron.
 - In the real interacting many-electron system, energies to add and subtract electrons are well-defined **only** at the Fermi energy.

Solving Kohn-Sham Equations

- Structure, types of atoms
- Guess for input
- Solve KSE
- New Density and Potential
- Self-consistent?
- Output:
 - Total energy, force, stress, ...
 - Eigenvalues



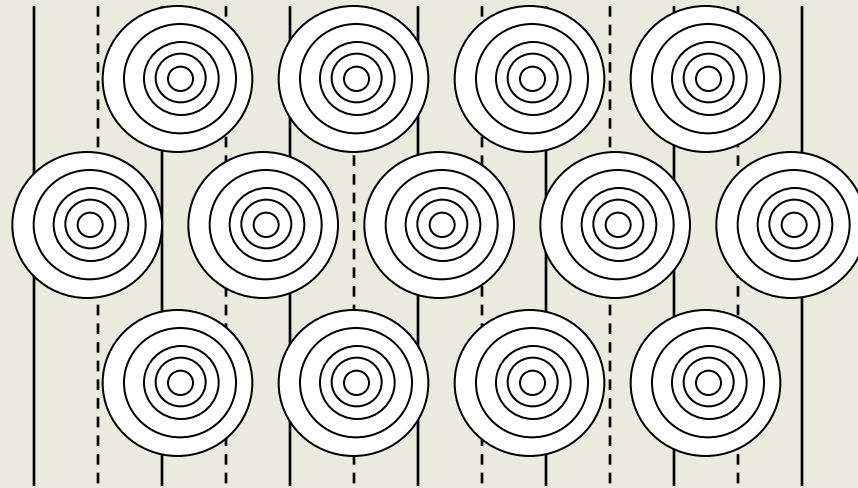
Solving Kohn-Sham Equations

What is the computational cost? Can the KSE be applied to large complex systems?

- Limiting factor – Solving the KSE.
- Solution by diagonalization scales as $(N_{\text{electron}})^3$
- Improved methods $\sim N^2$
- **Order-N** – “Linear Scaling”
Allows calculations for large systems – integration with classical methods for multiscale analysis

Calculations on Materials: Molecules, Clusters, Solids,

- Basic problem - many electrons in the presence of the nuclei



- Core states – strongly bound to nuclei – atomic-like
- Valence states – change in the material – determine the bonding, electronic and optical properties, magnetism,

The Three Basic Methods for Modern Electronic Structure Calculations

- **Plane waves**

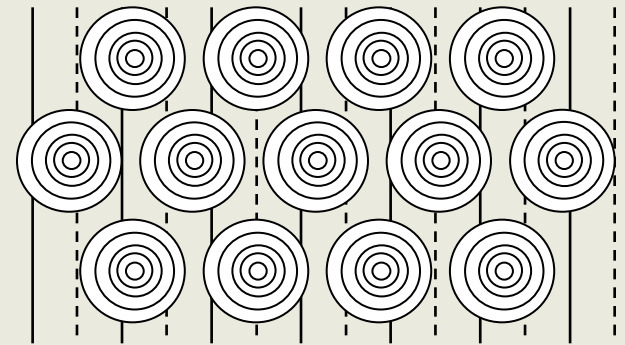
- The simplicity of Fourier Expansions
- The speed of Fast Fourier Transforms
- Requires smooth pseudopotentials

- **Localized orbitals**

- The intuitive appeal of atomic-like states
- Simplest interpretation in tight-binding form
- Gaussian basis widely used in chemistry
- Numerical orbitals used in SIESTA

- **Augmented methods**

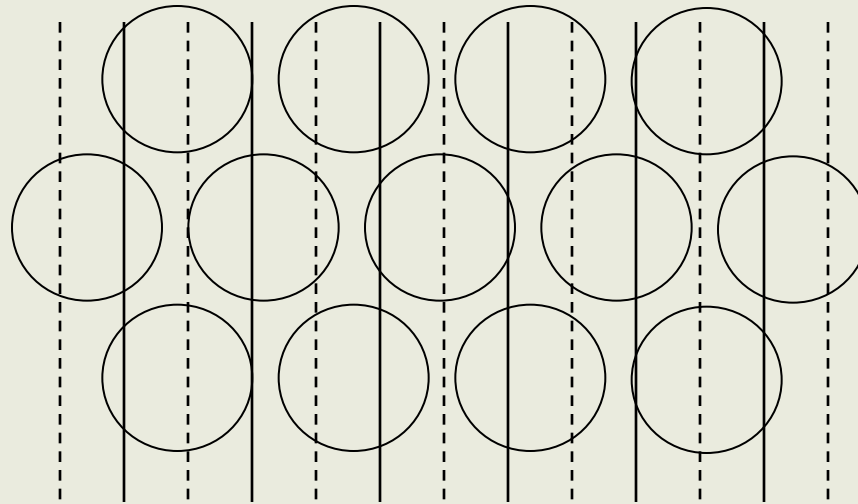
- “Best of both worlds” – also most demanding
- Requires matching inside and outside functions
- Most general form – (L)APW



**All methods agree
when done carefully!**

Plane Waves

- **The most general approach**



$$\psi_{i,\mathbf{k}}(\mathbf{r}) \propto \sum_m c_{i,m}(\mathbf{k}) \times \exp(i(\mathbf{k} + \mathbf{G}_m) \cdot \mathbf{r}) \quad (1)$$

- **Kohn-Sham Equations in a crystal**

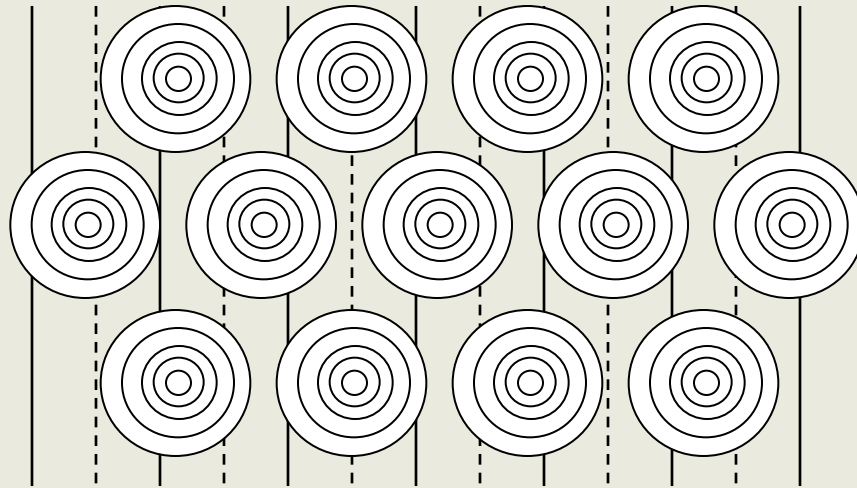
$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}) \quad (2)$$

$$H_{m,m'}(\mathbf{k}) = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}). \quad (3)$$

- **The problem is the atoms! High Fourier components!**

Plane Waves

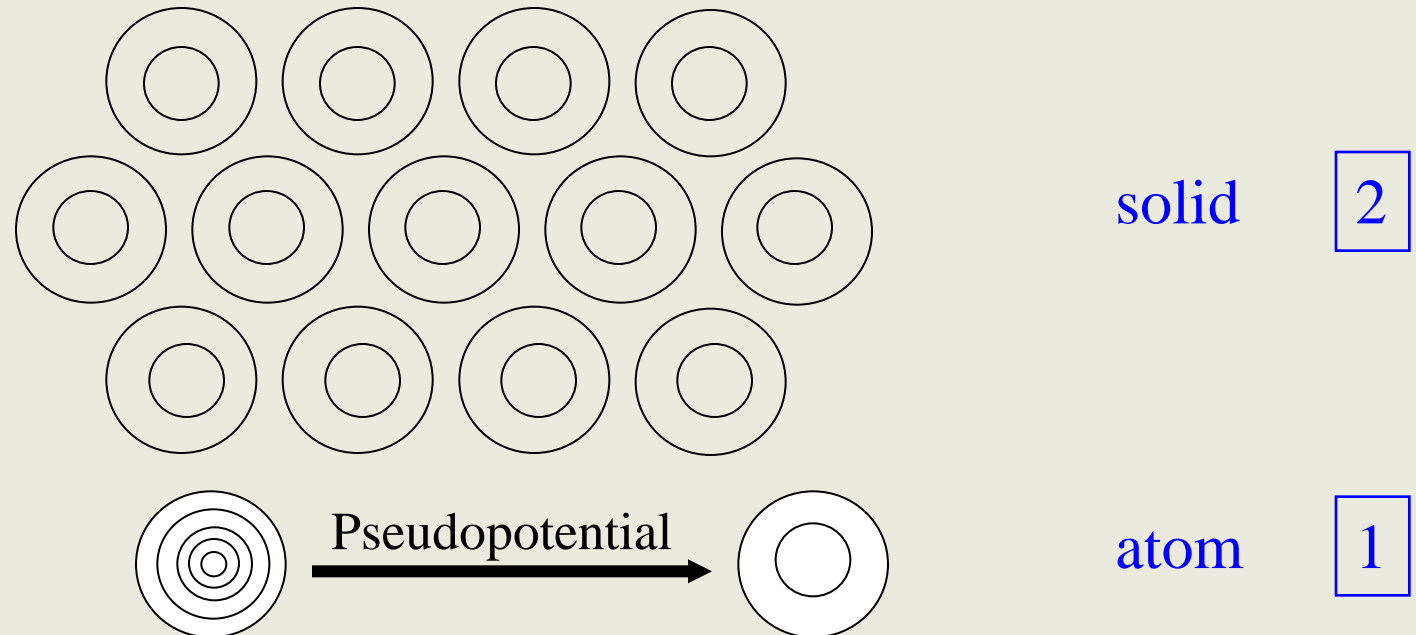
- **(L)APW method**



- **Augmentation:** represent the wave function inside each sphere in spherical harmonics
 - “Best of both worlds”
 - But requires matching inside and outside functions
 - Most general form – can approach arbitrarily precision

Plane Waves

- **Pseudopotential Method** – replace each potential



- **1** Generate **Pseudopotential** in atom (spherical) – **2** use in solid
- **Pseudopotential** can be constructed to be weak
 - Can be chosen to be smooth
 - Solve Kohn-Sham equations in solid directly in Fourier space

Pseudopotentials (PP)

- The replacement of the full all-electron (AE) potential with a PP is a compromise between **chemical transferability** (faithful reproduction of AE behavior) and **improved computational efficiency** (slowest possible spatial variability). Thus, an appropriate guideline to generate a PP is not how well it matches experiment, but how well it reproduces the results of identical AE calculations.
- The effectiveness of a given PP needs to be validated in every new chemical environment (e.g., in a metal or an oxide).
- Non-local core correction is needed to get correct spin-polarized states of first row atoms like oxygen and nitrogen.
- Mixing functionals in a calculation is a dangerous practice. An atomic PP developed within one DFT flavor should not be used in DFT calculations performed in another flavor of DFT.

Brillouin Zone Sampling

$$P = \left(\frac{1}{V_{\text{BZ}}} \right) \int_{\text{BZ}} d\mathbf{k} \sum_n p_n(\mathbf{k}) f(\epsilon_n(\mathbf{k}))$$

- Bloch's theorem transforms a problem with an infinite number of atoms and electronic states into a finite number of atoms and states in a translationally invariant unit cell but with an infinite number of wave-vectors in the Brillouin zone (BZ).
- Thus to calculate a property P , a special-point scheme is employed that uses the fewest possible \mathbf{k} points to give the most accurate approximation to the integration over the BZ. The \mathbf{k} point sampling can have a profound impact on computed properties.
- For metals, the convergence behavior of computed properties must be checked, versus the \mathbf{k} sample and occupation broadening method.

Basis Set Sufficiency

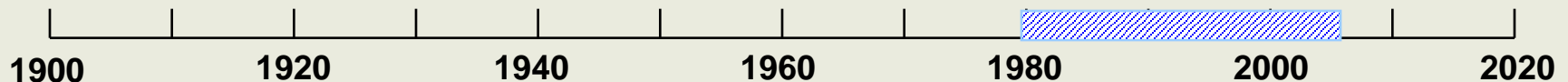
- The real space formulae for evaluating pressure and stresses contain derivatives with respect to coordinates ∇_r . Each of these derivatives introduces reciprocal lattice vectors G , which is directly dependent on the energy cutoff. Thus, pressure and stress are more sensitive to the plane wave cutoff than the energy.
- The error in the pressure is linear in the kinetic energy error (i.e., the kinetic energy in the atomic wavefunction above the cutoff). The slope of this linear dependence does depend on the atomic configuration. So one should always test some relevant configurations for convergence.
- An advantage of LCAO methods is a much smaller basis set than the plane waves basis. To simulate atoms far removed from equilibrium with LCAO may require extra variational freedom in the basis set. For unusual chemical or strained atomic configurations, it is advisable to verify whether basis augmentation is needed.
- Note that standard LCAO basis sets are not designed for weak interactions,. Special attention must be paid when simulate material systems with interplanar spacings or in computing work functions at surfaces.

Structural Relaxation

- For a DFT calculation to have predictive value, the study must be performed systematically.
- A good practice of theoretical investigation should include structural relaxation. A plausible strategy for finding the lowest energy geometry is to explore unrelaxed structures first and to relax the structure(s) with low(est) energy.

Examples of Modern Calculations

- Properties of crystals – many calculations are now “routine”
 - Definitive tests of the theory – comparisons with experiments
- Calculations for complex systems
 - Theory provides key role along with experiments
 - Understanding
 - Predictions
 - Direct simulation of atomic scale quantum phenomena
- Examples
 - Surfaces, interfaces, defects,
 - Thermodynamic phase transitions, Liquids, Melting, ...
 - Nanostructures – in real environments, ...
 - Large complex molecules – in solution,



Supercell Size

- For a molecule with a significant dipole, a molecular calculation with a supercell DFT code is constructed as a three-dimensional molecular crystal and the molecule can interact with its artificial periodic images. Note that the supercell error in the computed energy can amount to tenths of an eV.
- Supercell calculations for systems with a net charge can be done by neutralizing the net charge in the supercell with a compensating flat background density.
- Simulating two-dimensional surfaces can be constructed as a periodic array of thin slabs separated by vacuum. If the slab is polar, the electric field from the periodic array of dipole layers affects the surface. Only relatively simple correction schemes are available to fix the problem.
- Slabs in surface calculations are made as thin as possible to minimize the computational cost. The thickness needs to be checked for convergence.

When attempting to simulate properties of systems of reduced dimensionality, special attention must be paid to the manner in which **the boundary conditions are applied.**

A Case Study of Modern DFT Calculations

- **AlAs Lattice and Electronic Structure**

Recent Development

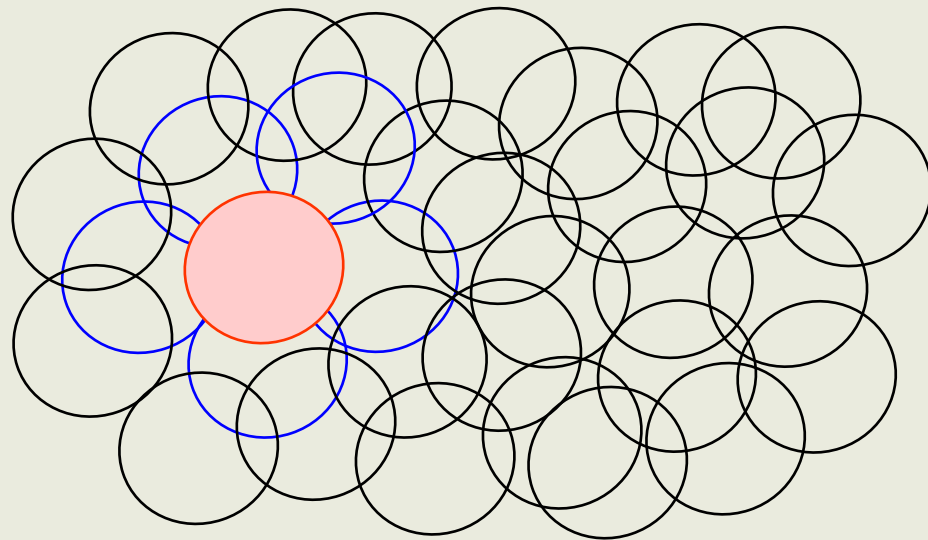
- **Improving accuracy**
 - Better approximation schemes for the exchange-correlation functional
- **Multiphysics applications**
 - Magnetoelectronics (spintronics)
 - Multiferroics (ferromagnetism, ferroelectricity, ferroelasticity and ferrotoroidicity)
- **Improving the performance to meet multiscale challenges**
 - Order- N methods

Simulations of Large Systems: Linear Scaling Order-N Method

- Fundamental Issues of locality in quantum mechanics
- Paradigm for view of electronic properties
- Practical Algorithms
- Results

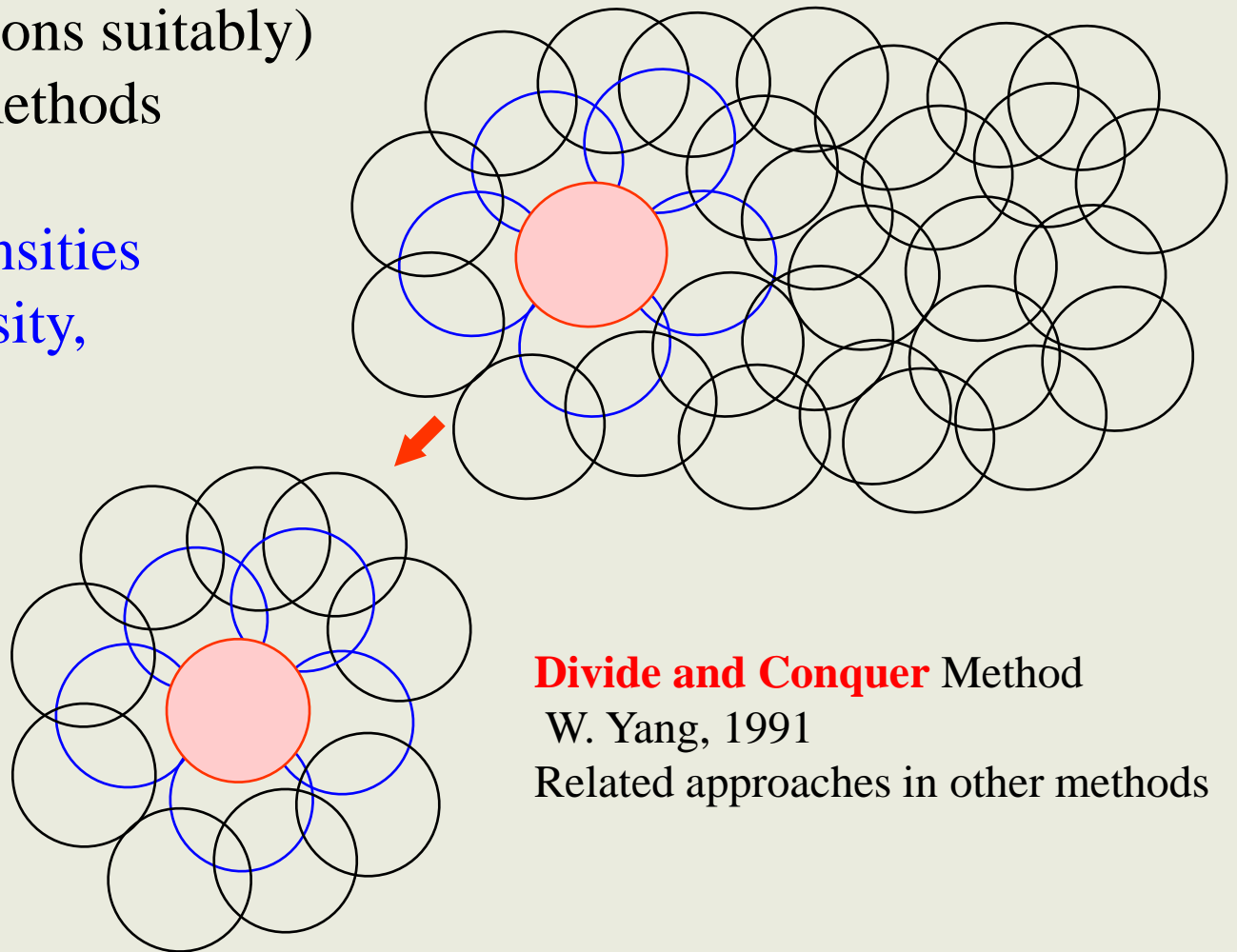
Locality in Quantum Mechanics

- V. Heine (Sol. St. Phys. Vol. 35, 1980)
“Throwing out k-space”
Based on ideas of Friedel (1954) , . . .
- Many properties of electrons in one region are independent of distant regions
- Walter Kohn
“Nearsightedness”



General idea used to create Order-N methods

- Divide System into (Overlapping) Spatial Regions.
Solve each region in terms only of its neighbors.
(Terminate regions suitably)
- Use standard methods for each region
- Sum charge densities to get total density, Coulomb terms



Divide and Conquer Method

W. Yang, 1991

Related approaches in other methods

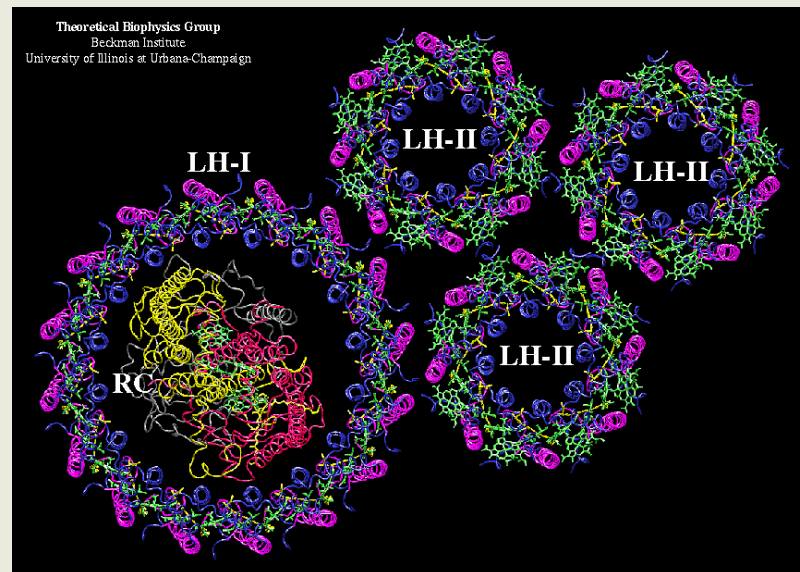
Biological Systems, . . .

- How to go beyond **empirical potentials**?
- **Solve the entire system quantum mechanically**
 - not feasible and not accurate enough now
 - need empirical adjustments for sensitive processes
- Solve electronic problem only in critical regions (e.g. catalytic sites)
 - probably still with some adjustments
 - couple to empirical methods for large scale features

Multiscale!

Space

Time



Looking Forward

- **Exciting arenas for theoretical predictions of materials design**
 - Realistic simulations under real condition
 - Molecules/clusters in solvents, . . .
 - Catalysis in real situations
 - Nanoscience and Nanotechnology
 - Biological problems
- **Beware -- understand what you are doing!**
 - Limitations of present DFT functionals
 - Use codes properly and carefully
- **Critical issues: to be able to describe relevant Time and Length Scales**

Concluding Remarks

- Density functional theory is by far the most widely applied “*ab initio*” method used in for “real materials” in physics, chemistry, materials science
- Approximate forms have proved to be very successful
- **BUT there are failures**
- No one knows a feasible approximation valid for **all problems** – especially for cases with strong electron-electron correlations