First Principles Calculations for Condensed Matter and Nanoscience

International Center for Materials Research
University of California at Santa Barbara

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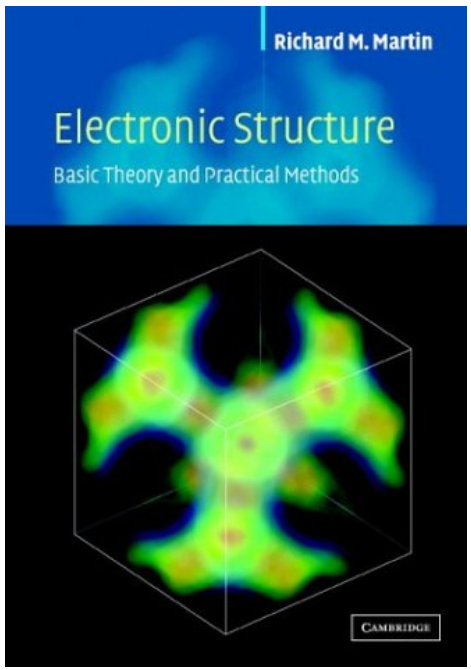
Density Functional theory

Today – Introduction – overview and accomplishments
Tomorrow – Behind the functionals – limits and challenges

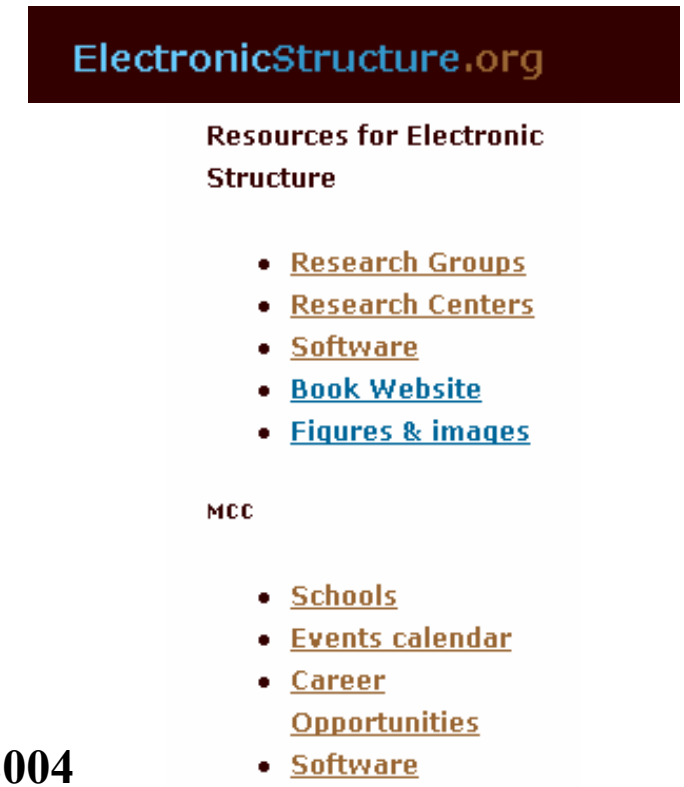
Density Functional theory
Introduction

Richard M. Martin

Based upon



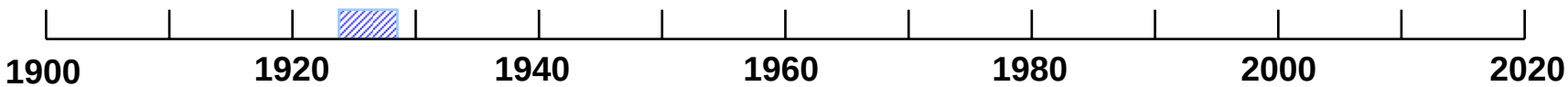
Cambridge University Press, 2004



A long way in 80 years

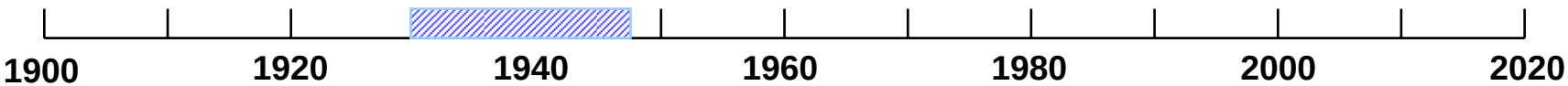
- L. de Broglie – Nature 112, 540 (1923).

- 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
Greatest Revolution of the 20th Century

- Bloch theorem – 1928
- 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
- First understanding of semiconductors – 1930's
- Invention of the Transistor – 1940's
  - Bardeen – student of Wigner
  - Shockley – student of Slater

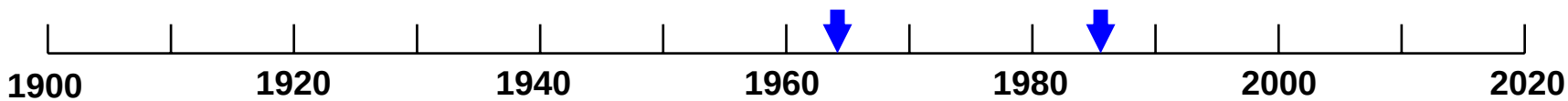


The Basic Methods of Electronic Structure

- 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 – Multiple Scattering (KKR) – 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 Most Modern Calculations
Density Functional Theory

- Hohenberg-Kohn; Kohn-Sham - 1965
- Car-Parrinello Method – 1985
- Improved approximations for the density functionals
  - Generalized Gradient Approximations, . . .
- Evolution of computer power
- Nobel Prize for Chemistry, 1998, Walter Kohn
- Widely-used codes –
  - ABINIT, VASP, CASTEP, ESPRESSO, CPMD, FHI98md, SIESTA, CRYSTAL, FPLO, WEIN2k, . . .



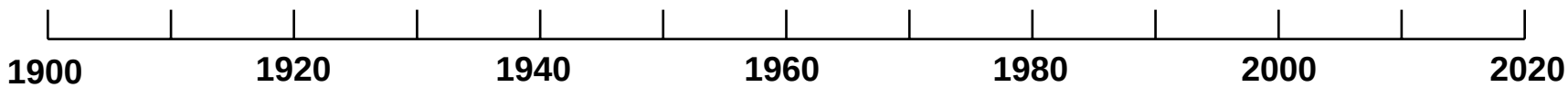
Most Cited Papers in APS Journals

- From Physics Today, June, 2005
- 11 papers published since 1893 with > 1000 citations in APS 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.



Density Functional Theory
The Basis of Most Modern Calculations

Hohenberg-Kohn; Kohn-Sham – 1965

Defined a new approach to the many-body interacting electron problem

- **Today**
  - **Brief statement of the Hohenberg-Kohn theorems and the Kohn-sham Ansatz**
  - **Overview of the solution of the Kohn-Sham equations and the importance of pseudopotentials in modern methods**
- **Tomorrow**
  - **Deeper insights into the Hohenberg-Kohn theorems and the Kohn-sham Ansatz**
  - **The nature of the exchange-correlation functional**
  - **Understanding the limits of present functionals and the challenges for the future**

The Fundamental Hamiltonian

Interacting electrons in an external potential

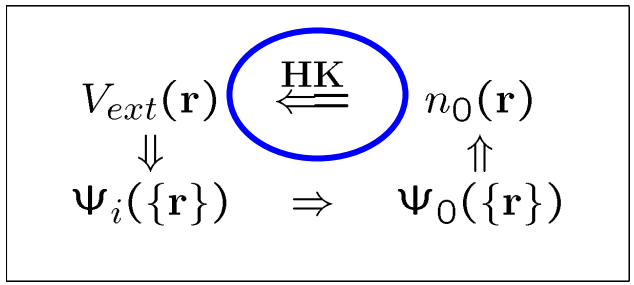
$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

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

- 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 basis of most modern calculations
Density Functional Theory (DFT)

- Hohenberg-Kohn (1964)



- All properties of the many-body system are determined by the ground state density $n_0(r)$

- Each property is a functional of the ground state density $n_0(r)$ which is written as $f[n_0]$

- A functional $f[n_0]$ maps a function to a result: $n_0(r) \rightarrow f$

The Kohn-Sham Ansatz

- Kohn-Sham (1965) – Replace original many-body problem with an independent electron problem – that can be solved!
- The ground state density is required to be the same as the exact density

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

$$\begin{array}{ccccccc} V_{ext}(\mathbf{r}) & \overset{HK}{\Longleftarrow} & n_0(\mathbf{r}) & \overset{KS}{\Longleftrightarrow} & n_0(\mathbf{r}) & \overset{HK_0}{\Longrightarrow} & V_{KS}(\mathbf{r}) \\ \Downarrow & & \Uparrow & & \Uparrow & & \Downarrow \\ \Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) & & \psi_{i=1,N_e}(\mathbf{r}) & \Leftarrow & \psi_i(\mathbf{r}) \end{array}$$

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

The Kohn-Sham Ansatz II

- From Hohenberg-Kohn the ground state energy is a functional of the density $E_0[n]$, minimum at $n = n_0$
- From Kohn-Sham

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

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

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional!

- **The new paradigm – find useful, approximate functionals**

The Kohn-Sham Equations

- Assuming a form for $E_{xc}[n]$
- Minimizing energy (with constraints) → Kohn-Sham Eqs.

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

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

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

Constraint – required Exclusion principle for independent particles

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

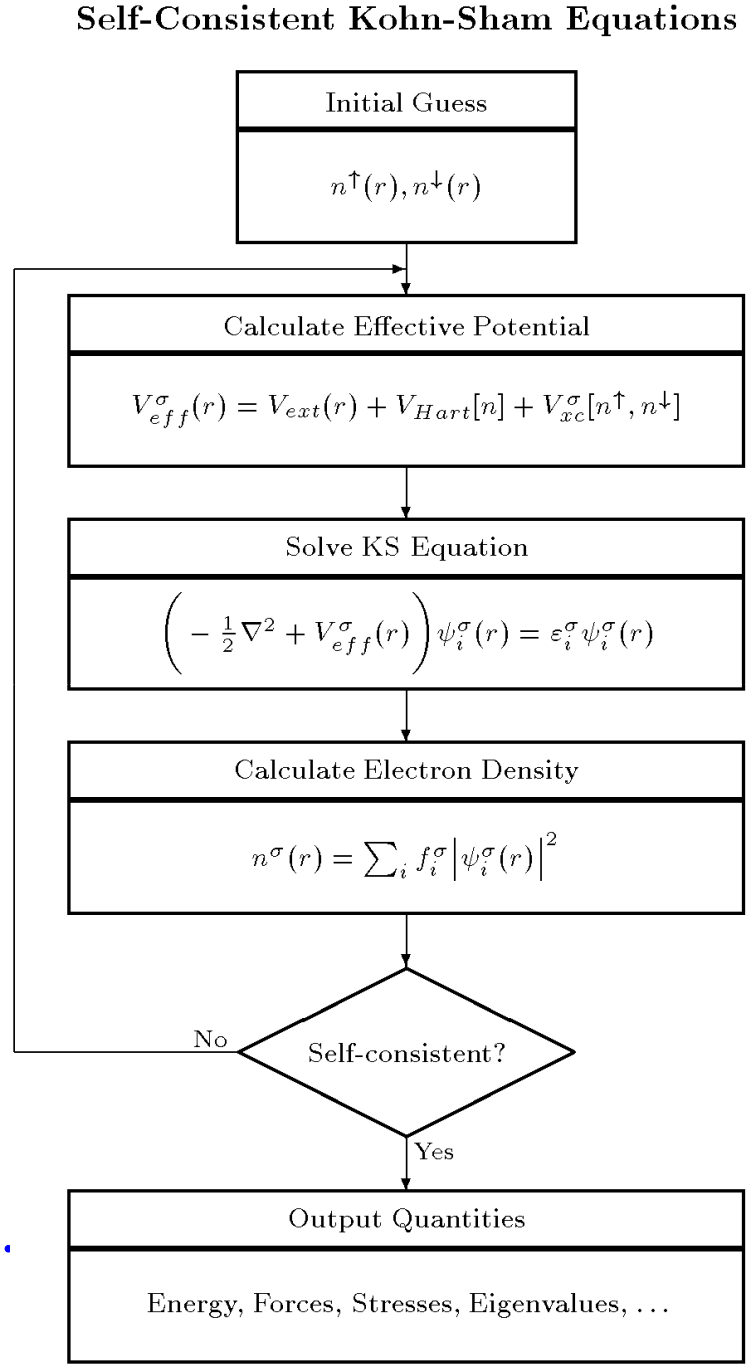
$$(-\frac{1}{2}\nabla^2 + V_{KS}^\sigma(\mathbf{r}), -\varepsilon_i^\sigma)\psi_i^\sigma(\mathbf{r}) = 0 \qquad (3)$$

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

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

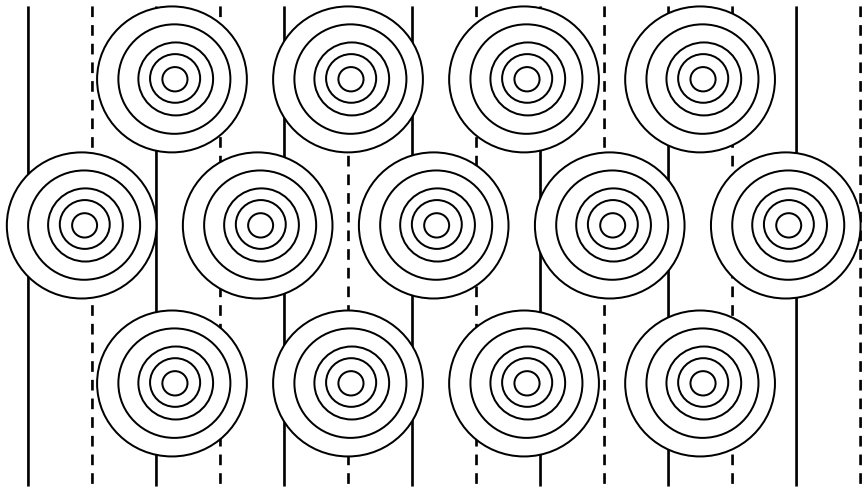
Solving Kohn-Sham Equations

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



Calculations on Materials
Molecules, Clusters, Solids, ….

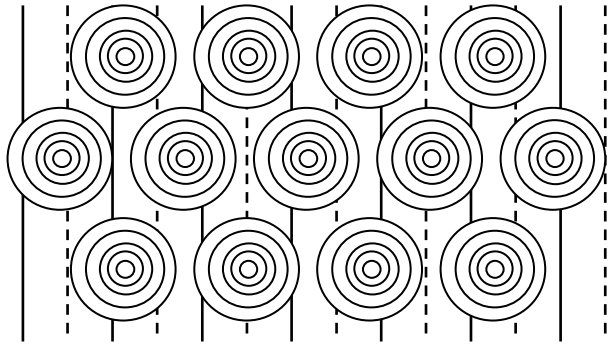
- Basic problem - many electrons in the presence of the nuclei



- 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

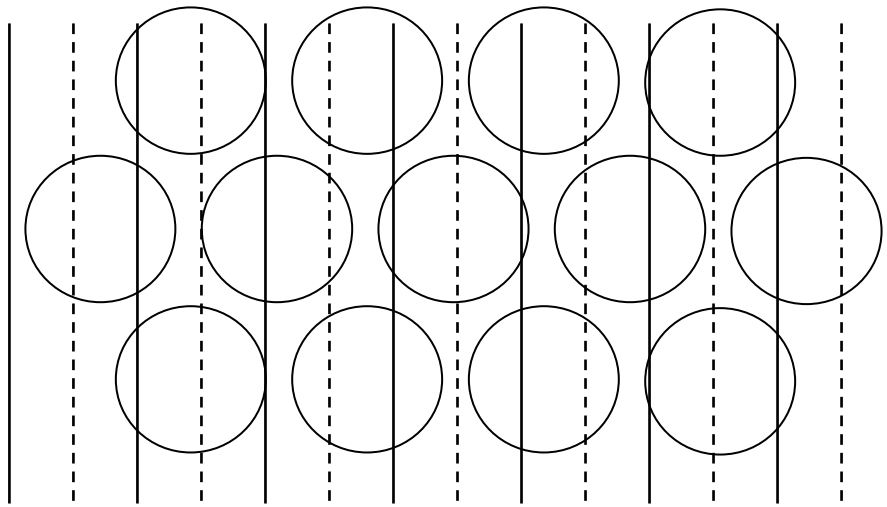
- **Plane waves**
  - The simplicity of Fourier Expansions
  - The speed of Fast Fourier Transforms
  - Requires smooth pseudopotentials



- **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

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

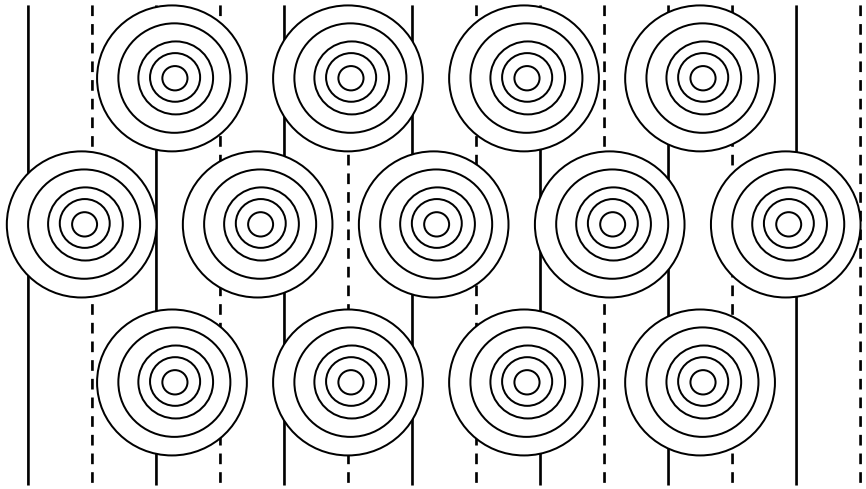
$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}) \quad (2)$$

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

- The problem is the atoms! High Fourier components!

Plane Waves

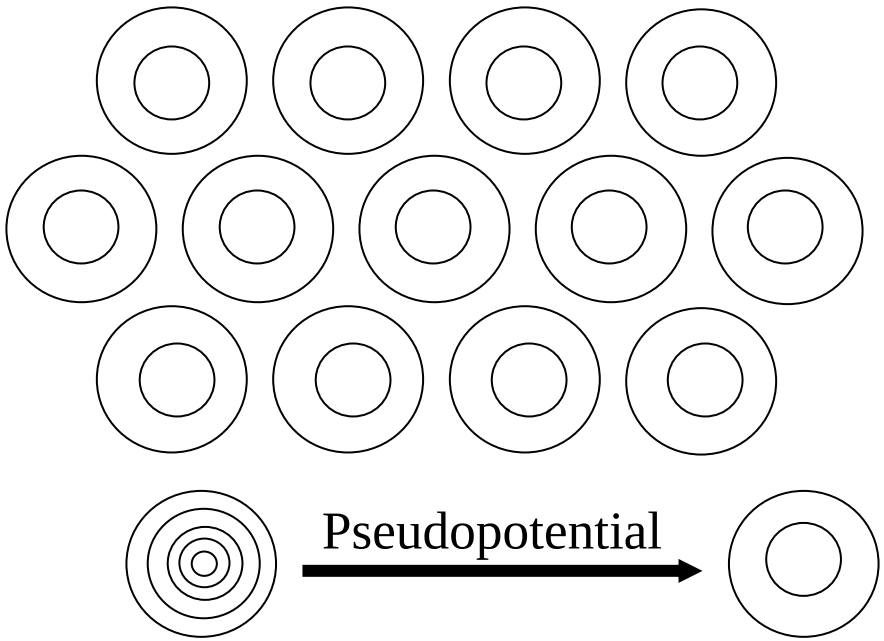
- **(L)APW method**



- 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



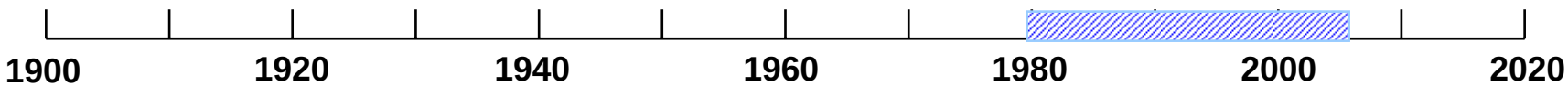
solid 2

atom 1

- 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

Examples of Modern Calculations

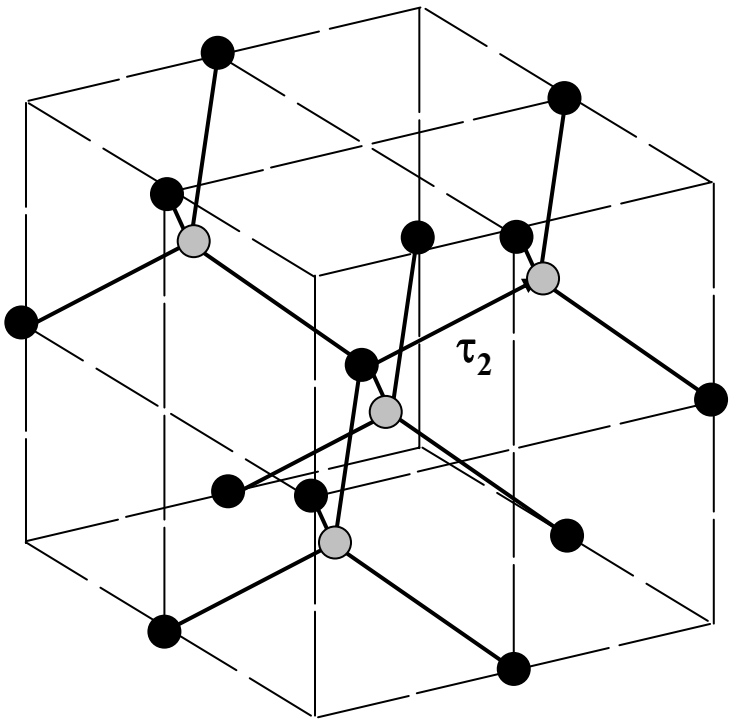
- Properties of crystals – many calculations are now "routine"
  - Definitive tests of the theory – comparisons with experiments
- Calculations for complex systems
  - Theory provides key role along with experiments
  - Understanding
  - Predictions
  - Direct simulation of atomic scale quantum phenomena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

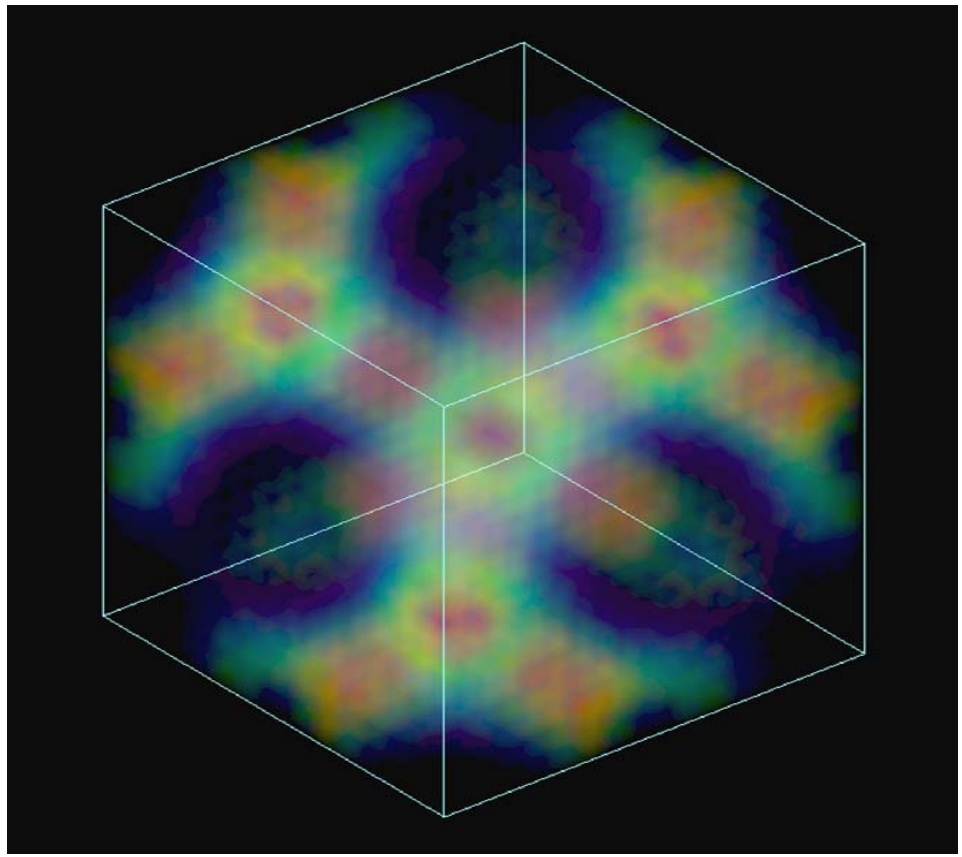


Examples of Modern Calculations

Electron density in silicon

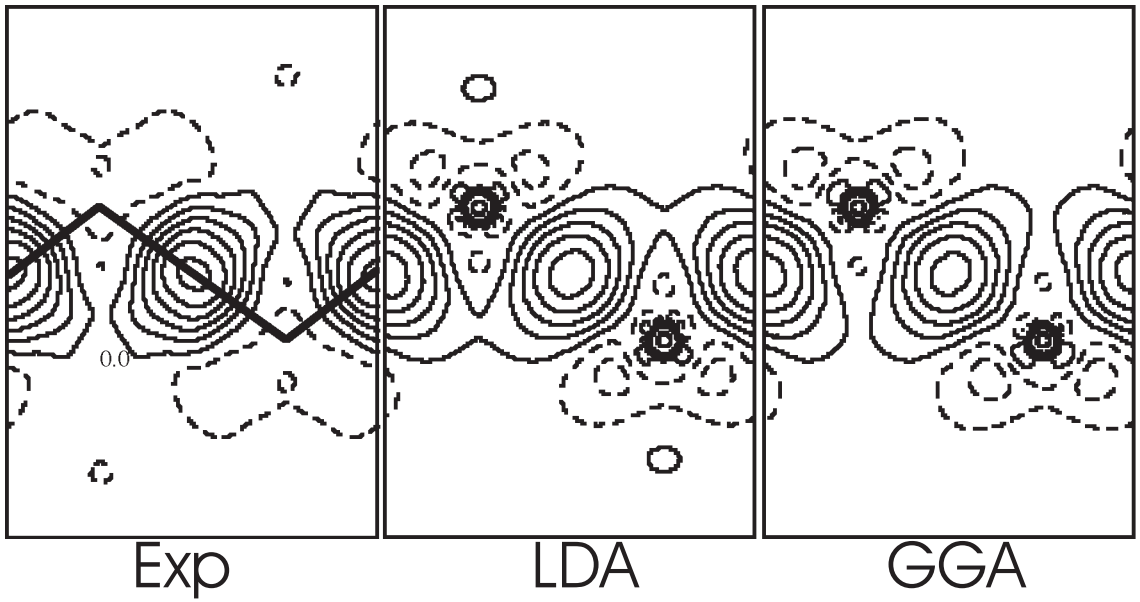
"Electronic Structure: Basic Theory and Practical Methods", R. M. Martin, Cambridge University Press, 2004 – Calculated using ABINIT





In Si the black and grey atoms are identical

Charge Density of Si – Experiment - LAPW calculations with LDA, GGA



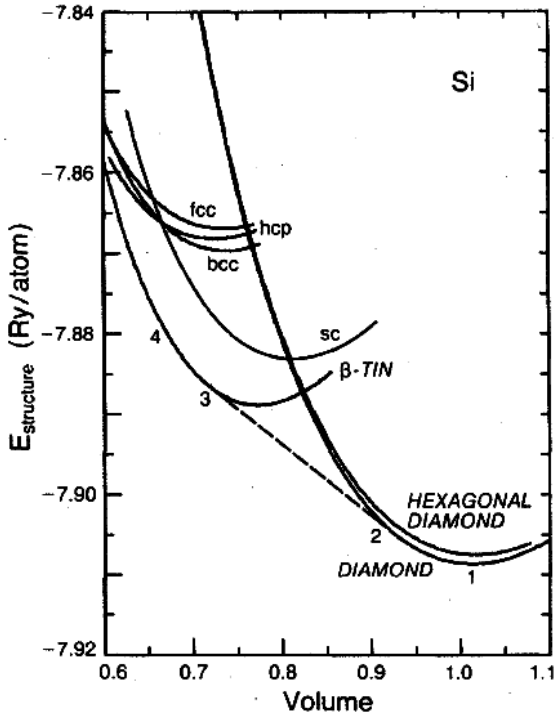
- Electron density **difference** from sum of atoms
  - Experimental density from electron scattering
  - Calculations with two different functionals
    - J. M. Zuo, P. Blaha, and K. Schwarz, J. Phys. Cond. Mat. 9, 7541 (1997).
  - Very similar results with pseudopotentials
    - O. H. Nielsen and R. M. Martin (1995)

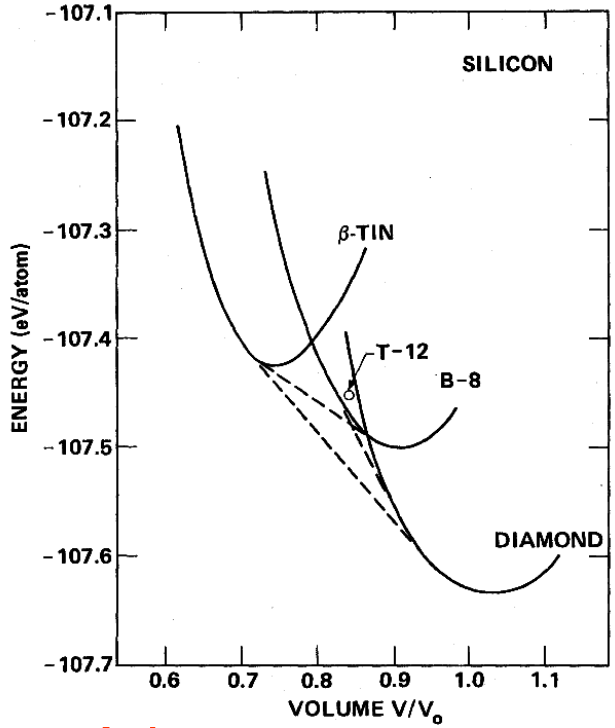
Comparisons – LAPW – PAW - - Pseudopotentials (VASP code)

Method	C		Si		CaF_2		bcc Fe		
	a	B	a	B	a	B	a	B	m
NCPP[a]	3.54	460	5.39	98	5.21	90	2.75[c]	226[c]	
PAW[a]	3.54	460	5.38	98	5.34	100			
PAW[b]	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP[b]	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW[a]	3.54	470	5.41	98	5.33	110	2.72[d]	245[d]	2.04[d]
EXP[a]	3.56	443	5.43	99	5.45	85-90	2.87[d]	172[d]	2.12[d]

- a – lattice constant; B – bulk modulus; m – magnetization
- [a]Holzwarth , *et al.*; [b]Kresse & Joubert; [c]Cho & Scheffler; [d]Stizrude, *et al.*

Phase Transitions under Pressure
Silicon is a Metal for P > 110 GPa



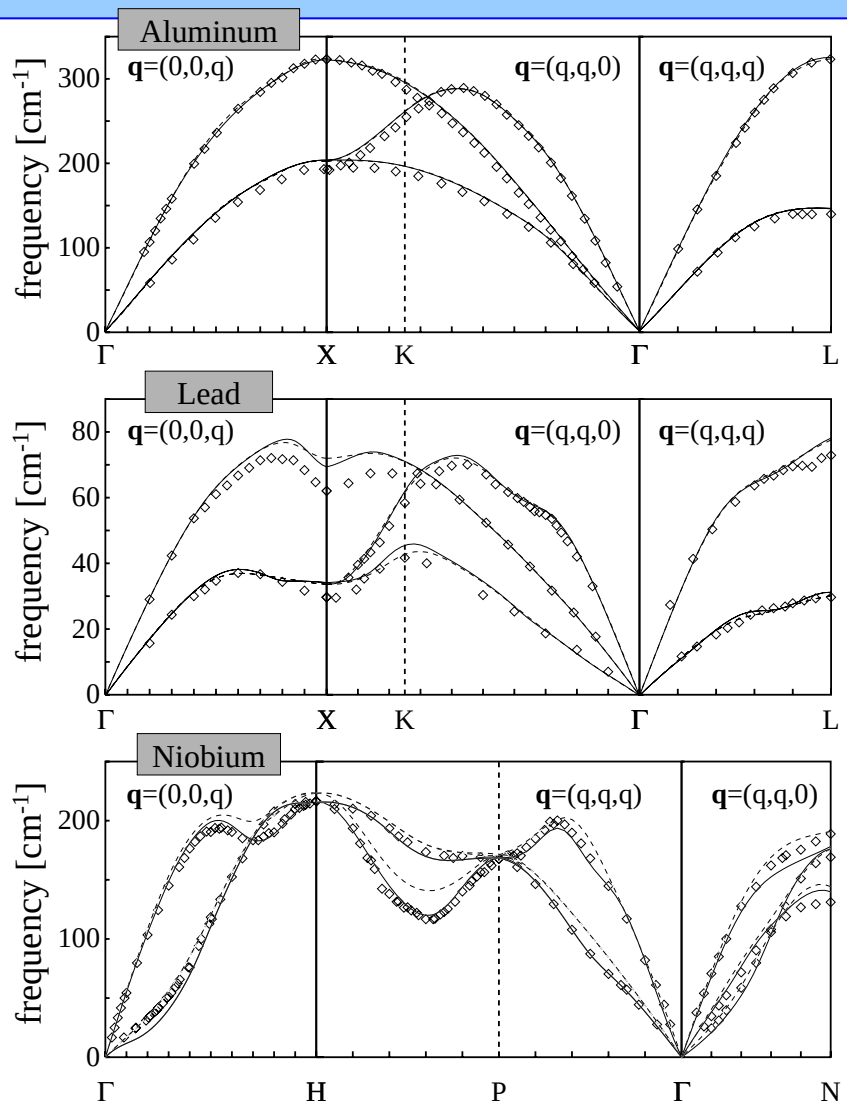


- Demonstration that pseudopotentials are an accurate "ab initio" method for calculations of materials
- Results are close to experiment!
  - M. T. Yin and M. L. Cohen, Phys. Rev. B 26, 5668 (1982).
  - R. Biswas, R. M. Martin, R. J. Needs and O. H. Nielsen, Phys. Rev. B 30, 3210 (1982).

Examples of Modern Calculations

Phonons
Comparison of theory and experiment

- Calculated from the response function – "Density functional perturbation theory"
- Now a widely-used tool in ABINIT

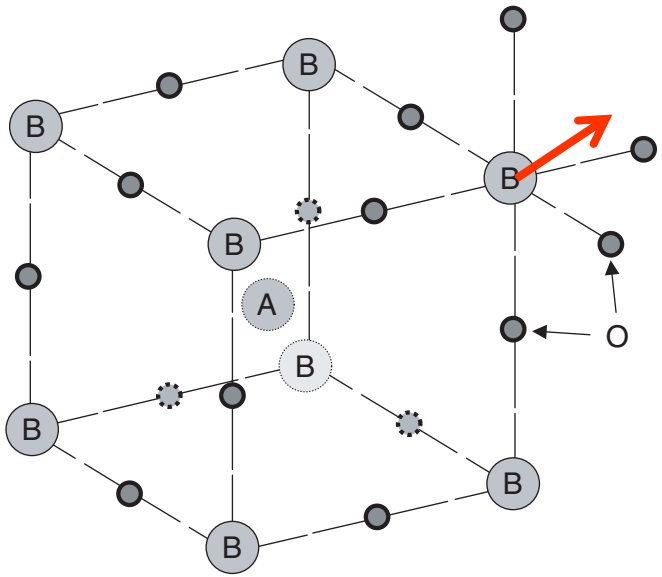


De Gironcoli, et al.

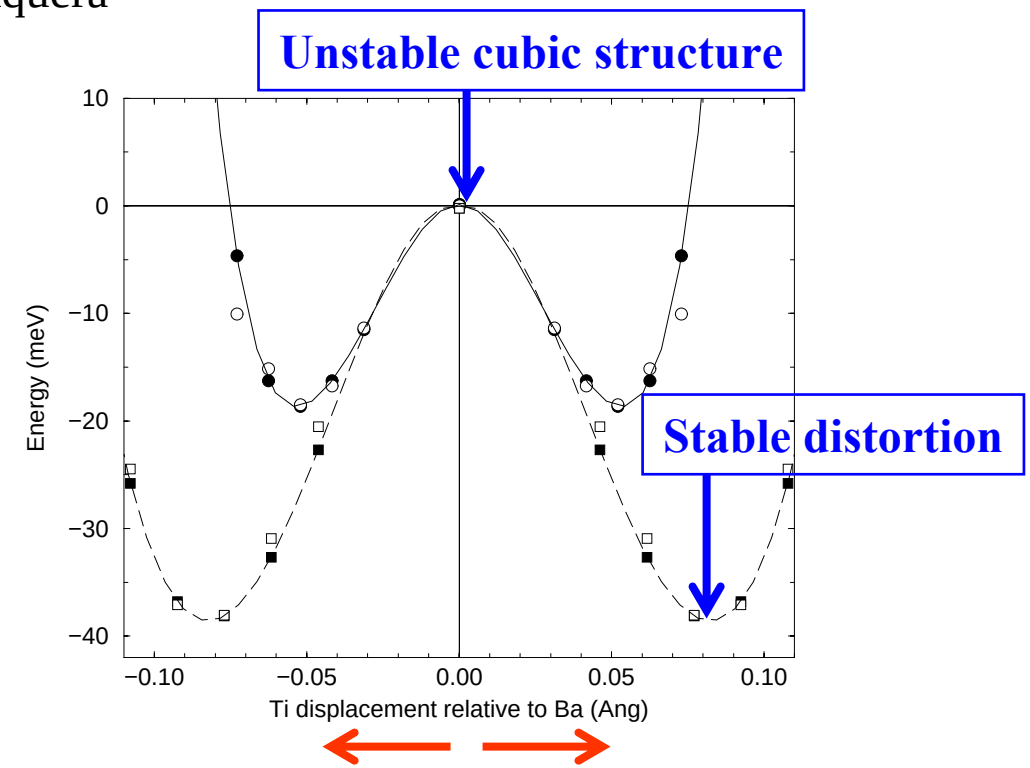
S. de Gironcoli, Phys.Rev B 51, 6773 (1995)

Examples of Modern Calculations

- **Instability and predicted ferroelectric displacement in $BaTiO_3$ - calculated with the SIESTA and LAPW codes**
  - Provided by R. Weht and J. Junquera



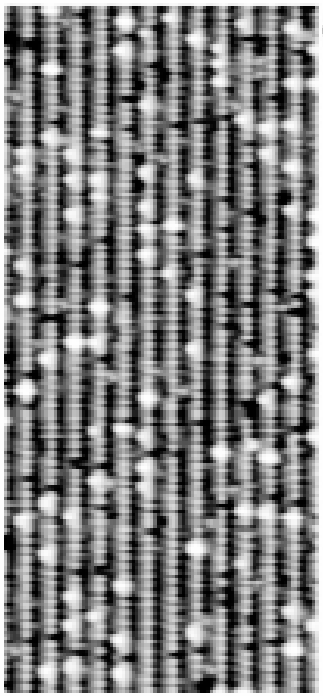
Perovskite structure



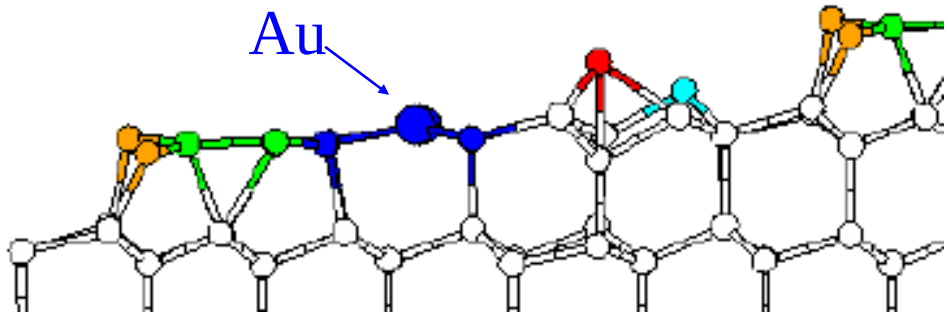
Many calculations done with ABINIT, . . .

Examples of Modern Calculations

Atomic scale Au wires on Si (557) surface



STM image of self-assembled atomic "wires" on a Si surface
Crain, et al, Phys Rev B 69, 125401 (2004)



Theoretical prediction – using SIESTA code - of structure in very good agreement with experiment– done later!
Sanchez-Portal and R. M. Martin, Surf. Sci. 532, 655 (2003)

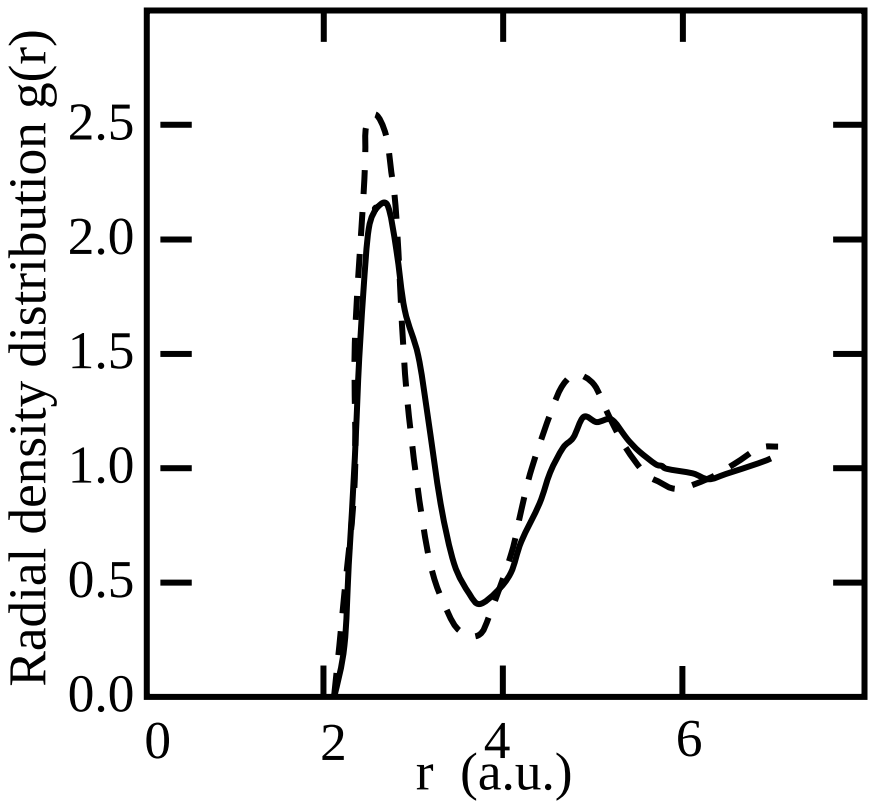
Explains one-dimensional metallic bands observed by photoemission

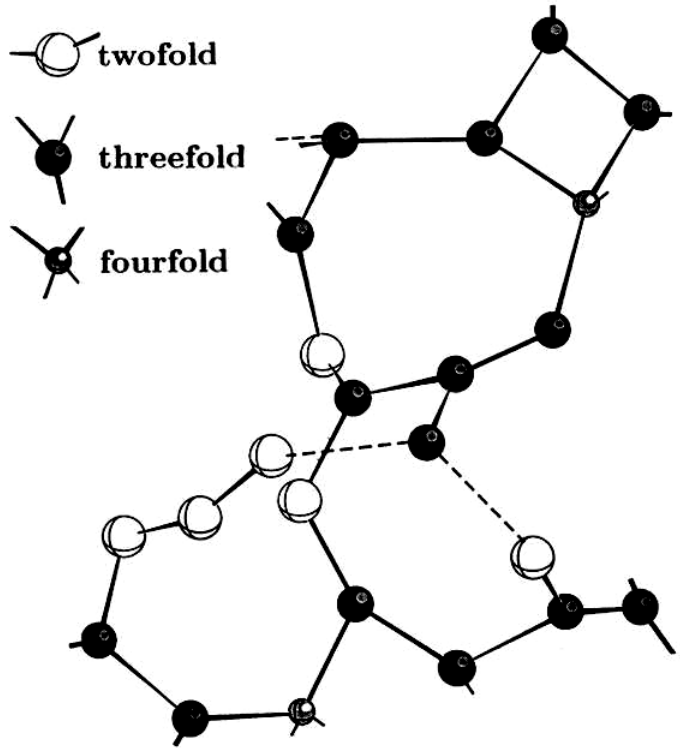
The Car-Parrinello Advance

- Car-Parrinello Method – 1985
  - Simultaneous solution of Kohn-Sham equations for electrons and Newton's equations for nuclei
  - Iterative update of wavefunctions - instead of diagonalization
  - FFTs instead of matrix operations – N lnN instead of N^2 or N^3
  - Trace over occupied subspace to get total quantities (energy, forces, density, …) instead of eigenfunction calculations
  - Feasible due to simplicity of the plane wave pseudopotential method
- A revolution in the power of the methods
  - Relaxation of positions of nuclei to find structures
  - Simulations of solids and liquids with nuclei moving thermally
  - Reactions, . . .
- Stimulated further developments - VASP, ABINIT, SIESTA, . . .

Simulation of Liquid Carbon

- Solid Line: Car-Parrinello plane wave pseudopotential method (Galli, et al, 1989-90)
- Dashed Line: TB potential of Xu, et al (1992)

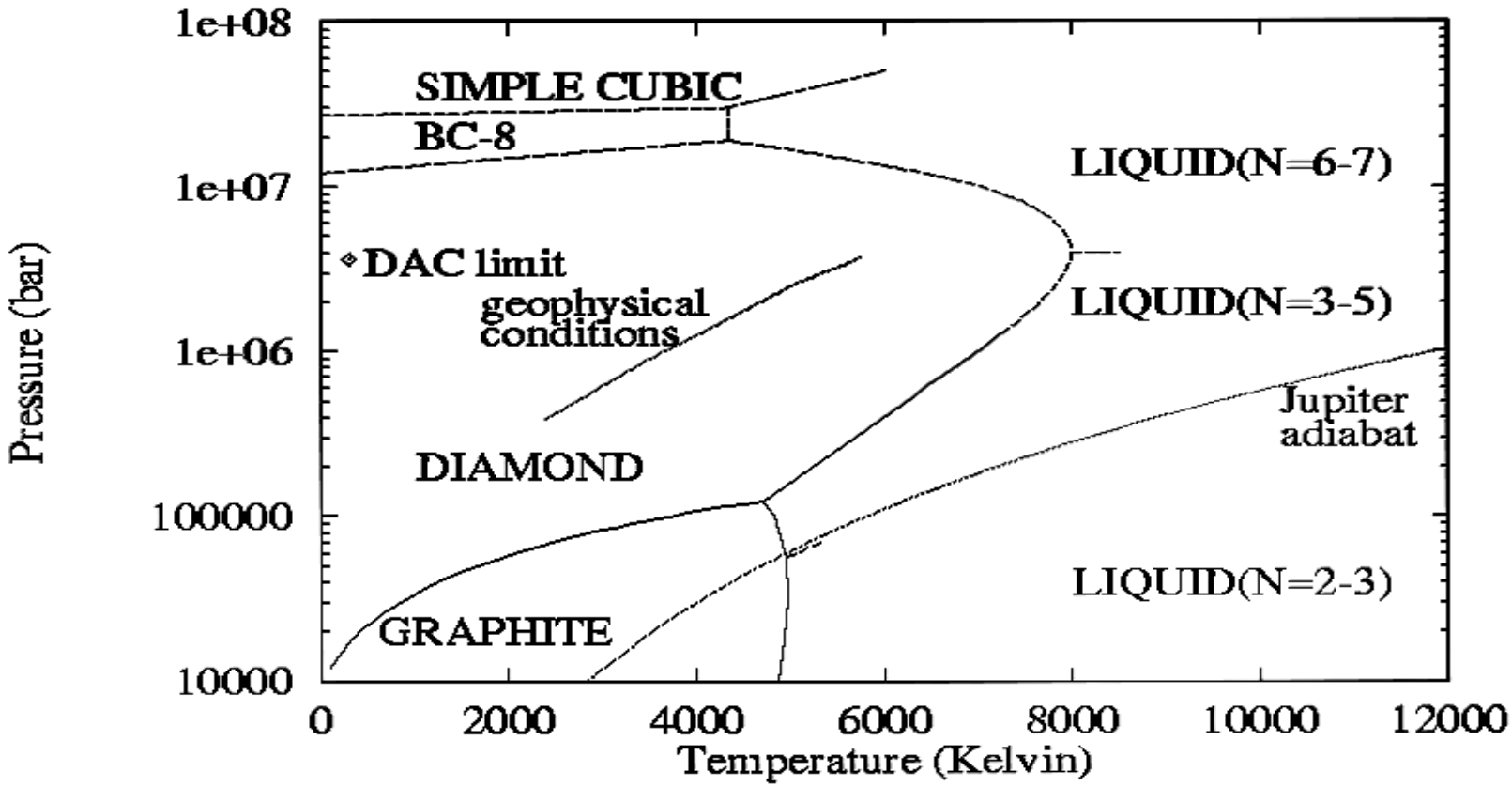




"snapshot of liquid"

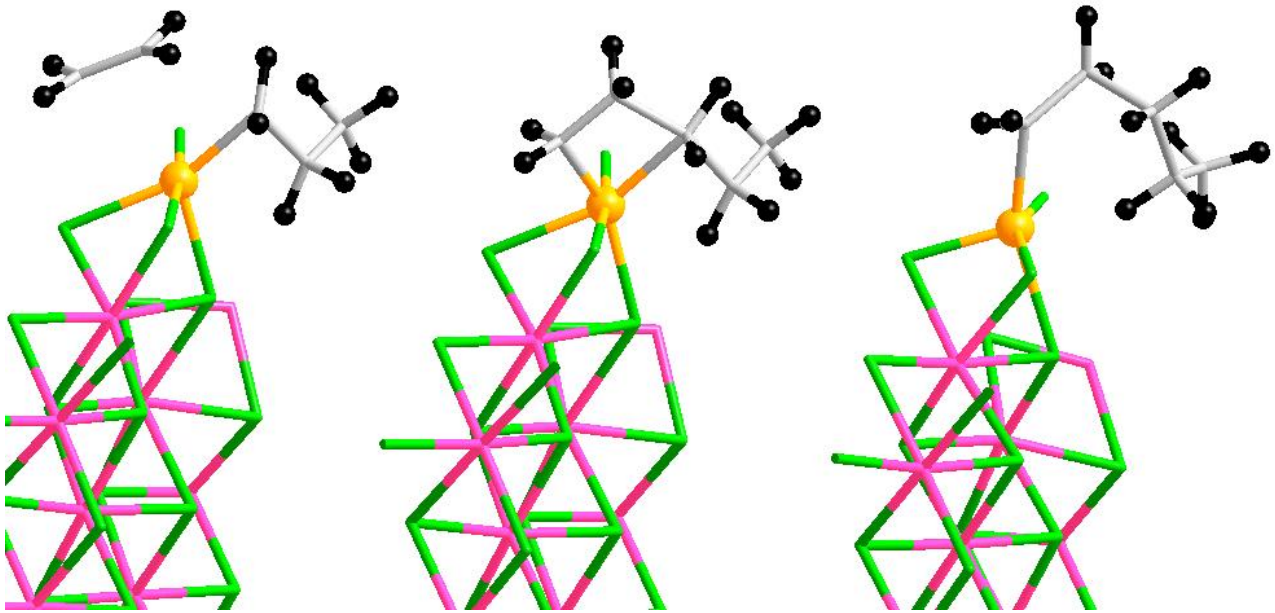
Example of Thermal Simulation

- **Phase diagram of carbon**
- **Full Density Functional "Car-Parrinello" simulation**
- **G. Galli, et al (1989); M. Grumbach, et al. (1994)**



Examples of Modern Calculations

- **Unraveling the steps in the Ziegler-Nata reaction**
  - **Industrial process for production of polyethylene**
  - Simulations with Car-Parrinello MD – plane wave pseudopotentials – M. Boero, et al.

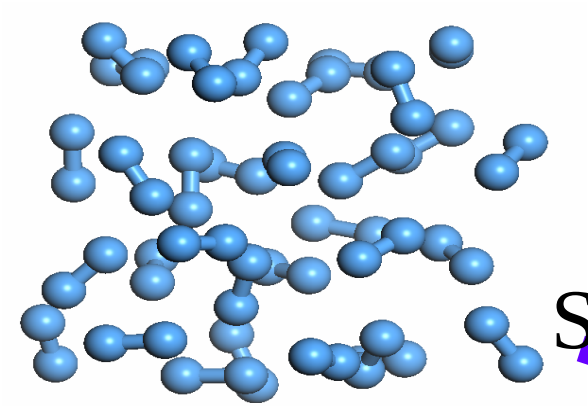


π-complex – Transition – insertion

Adds one ethelyne unit to polymer

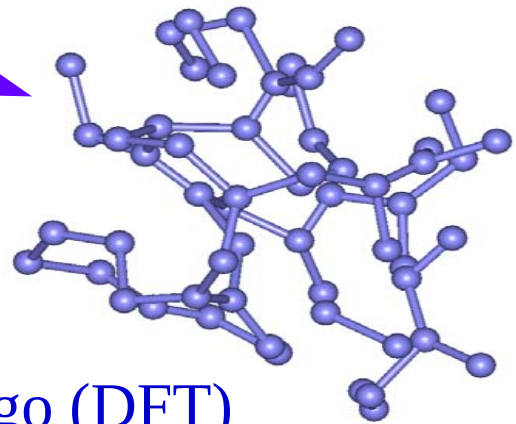
Nitrogen under pressure – Recent discoveries

- Used SIESTA code for MD simulation
- Sample structures tested using ABINIT



- Hot Molecular Liquid
- 58 Gpa 7600 K
- Nitrogen Molecules Disassociate and Reform

Squeezed & Cooled



- P > 100 Gpa and 0K
- Network solid
- Predicted > 15 years ago (DFT)
- Found experimentally in 2000
- New Prediction of Metallic N

W. D. Mattson, S. Chiesa, R. M. Martin, PRL, 2004.

Conclusions to this point

- **A long way in 80 years!**
- **Electronic Structure** is the quintessential many-body problem of quantum mechanics
  - **Interacting electrons ⟶ real materials and phenomena**
- **Density functional theory** is by far the most widely applied "*ab intio*" method used for "real materials" in physics, chemistry, materials science
  - **Approximate forms have proved to be very successful**
  - **BUT there are shortcomings and failures!**
- **Momentous time for theory**
  - **New opportunities and challenges**
  - **Requires care and understanding of limitations**