Hands-on Introduction to Electronic Structure and Thermodynamics Calculations of Real Materials

Materials Computation Center
University of Illinois at Urbana-Champaign

Sponsored by
National Science Foundation
Frederick Seitz Materials Research Laboratory
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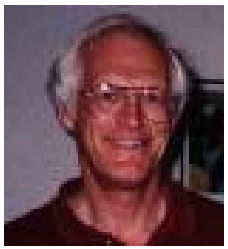
College of Engineering

Hands-on Introduction to Electronic Structure and Thermodynamics Calculations of Real Materials

- **Fundamental theory → Real Materials**
- **Week 1 - Hands-on introduction to Electronic Structure**
  - **First Principles methods for electronic Structure Density Functional Theory, Actual Codes**
- **Week 2 - Thermodynamics Calculations of Real Materials**
  - **Thermodynamics of alloys from first principles electronic structure calculations**

Hands-on Introduction to Electronic Structure
June 14-17



- **Richard M. Martin – UIUC**
  - Introduction and Overview
  - Density Functional theory, Pseudopotentials, TBPW

- **Donald R. Hamann – Bell Labs and Rutgers**
  - Introduction to the plane wave code ABINIT
  - Response functions, Examples

- **Miguel Pruneda – Inst. de Ciencia de Materials Barcelona**
  - Introduction to the local orbital code SIESTA
  - Examples

1867 ™

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NSF

Week 2: *Ab Initio* Thermodynamics *via* Cluster Expansions

D.D. Johnson, MSE
U. of Illinois

G. Hart, Physics
Northern Arizona U.

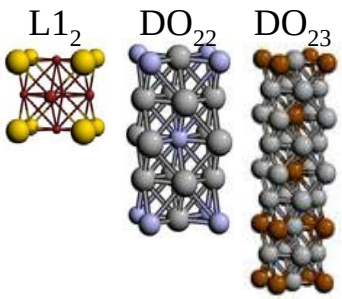
D. Morgan, MSE
U. of Wisconsin

A. Van der Walle, MSE
Northwestern

A. Van der Ven, MSE
U. of Michigan

Predict* energy of *any atomic arrangement* σ** by **fitting to a few *DFT structural energies.

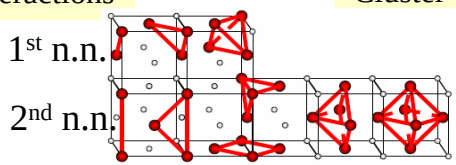
$$N \text{ structures} \xrightarrow{DFT} E^{\sigma} \xrightarrow{CE} V_i \xrightarrow{Monte\ Carlo} \text{Thermodynamics}$$

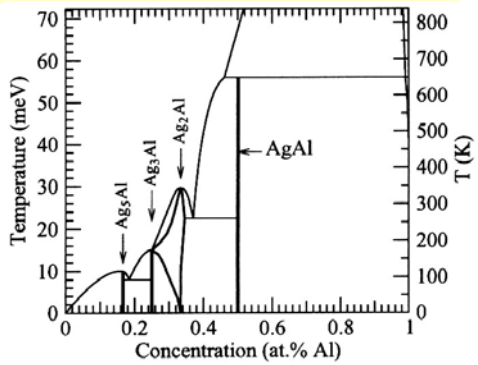


$$E^{\sigma} = \sum_i V_i \Phi_i^{\sigma}$$

Effective Interactions

Cluster correlations



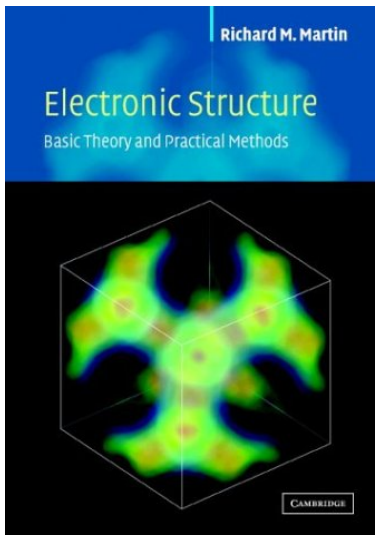


Introduction and Overview
Density Functional theory, Pseudopotentials

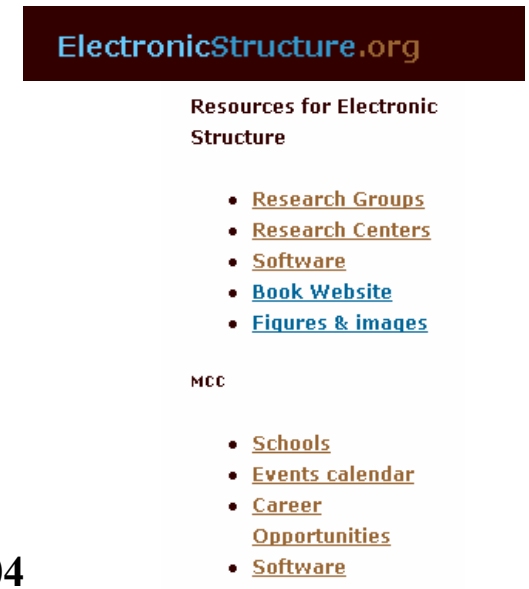
- **Richard M. Martin – UIUC**

Lecture at Summer School
Hands-on introduction to Electronic Structure
Materials Computation Center
University of Illinois – June, 2005

Based upon



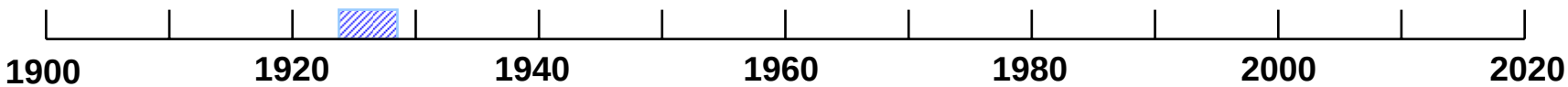
Cambridge University Press, 2004



A long way in 80 years

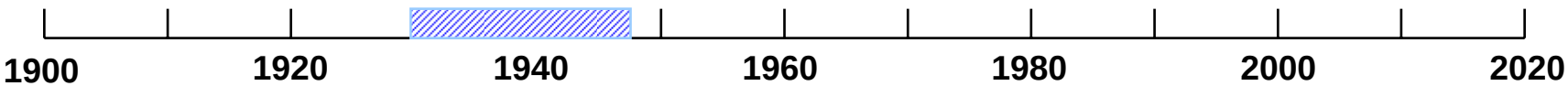
- L. de Broglie – Nature 112, 540 (1923).

- 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

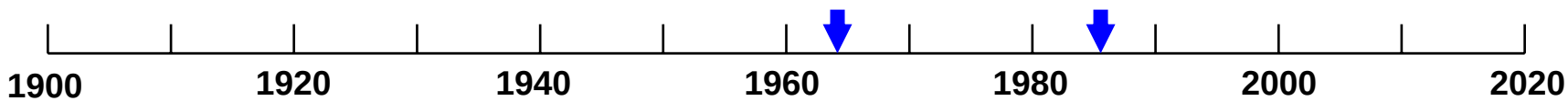


The Basic Methods of Electronic Structure

- 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, . . .



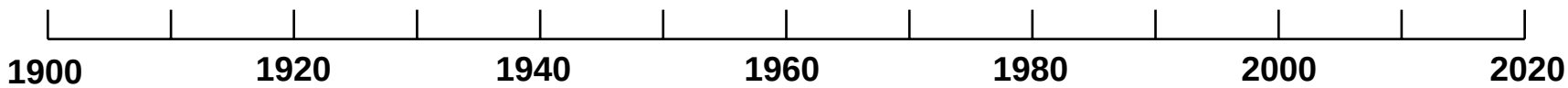
Most Cited Papers in APS Journals

- 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

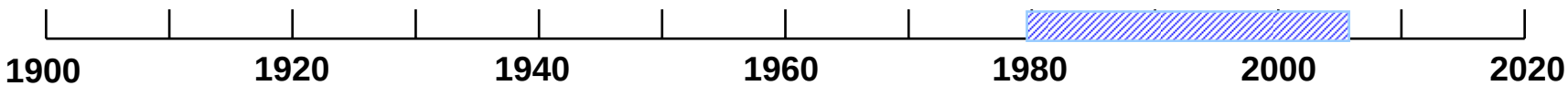
Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction 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.



Examples of Modern Calculations

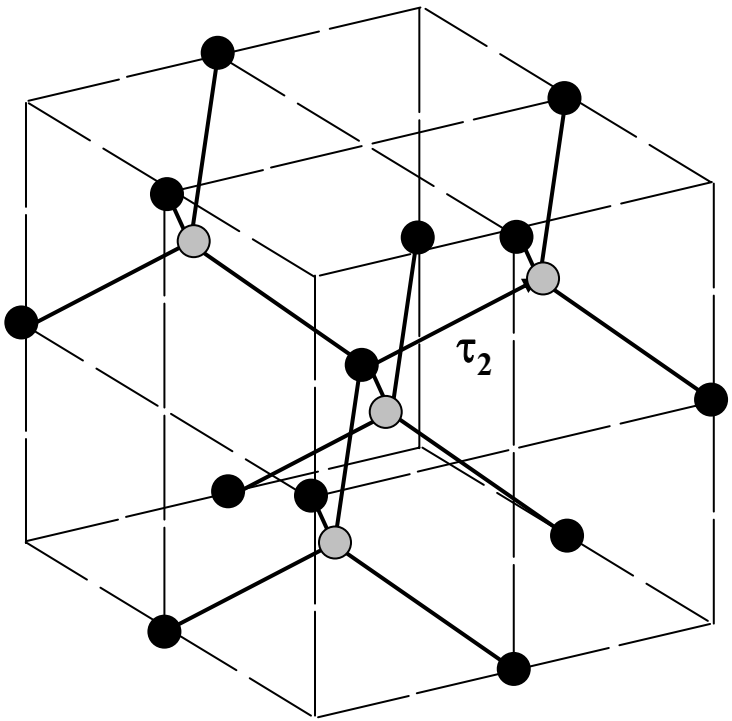
- Properties of crystals – many calculations are now "routine"
  - Definitive tests of the theory – comparisons with experiments
- Calculations for complex systems
  - Theory provides key role along with experiments
  - Understanding
  - Predictions
  - Direct simulation of atomic scale quantum phenomena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

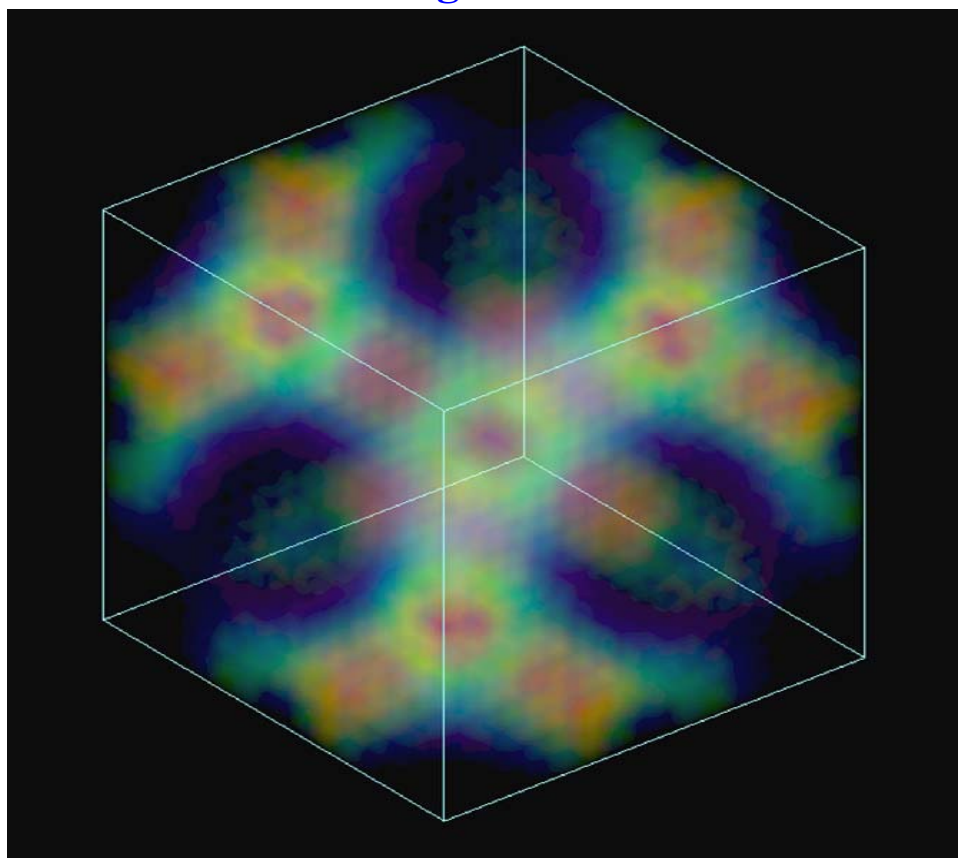


Examples of Modern Calculations

Electron density in silicon

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



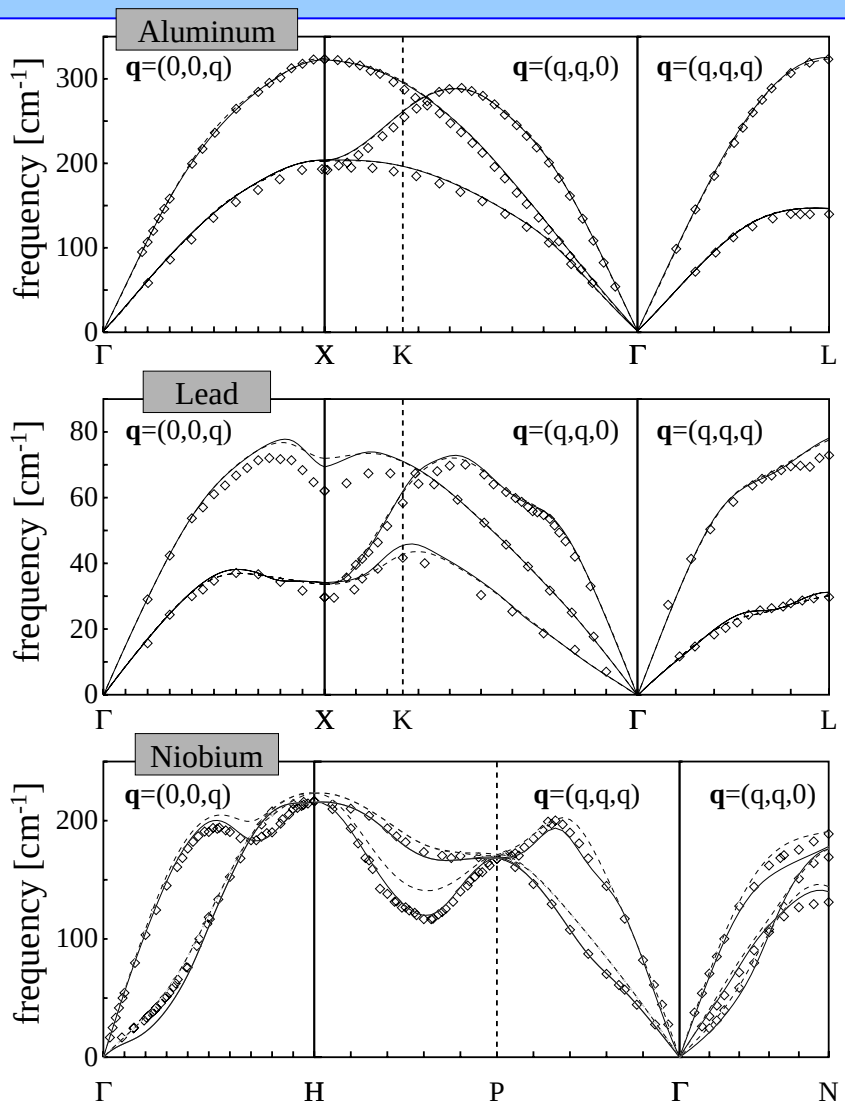


In Si the black and grey atoms are identical

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

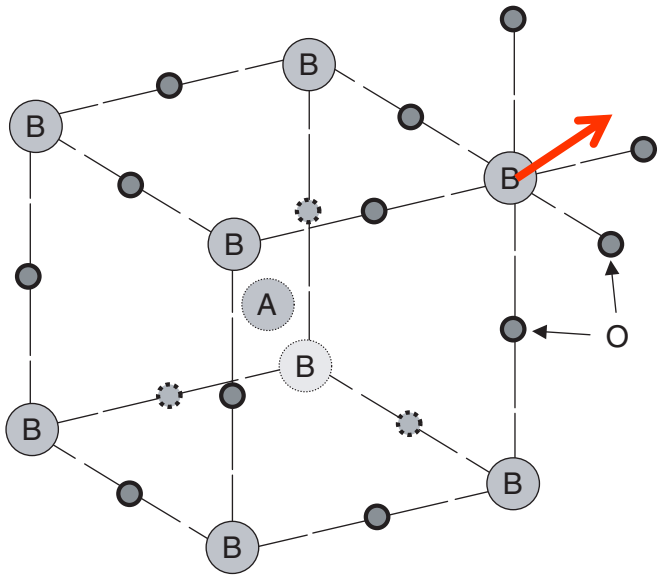


De Gironcoli [732]

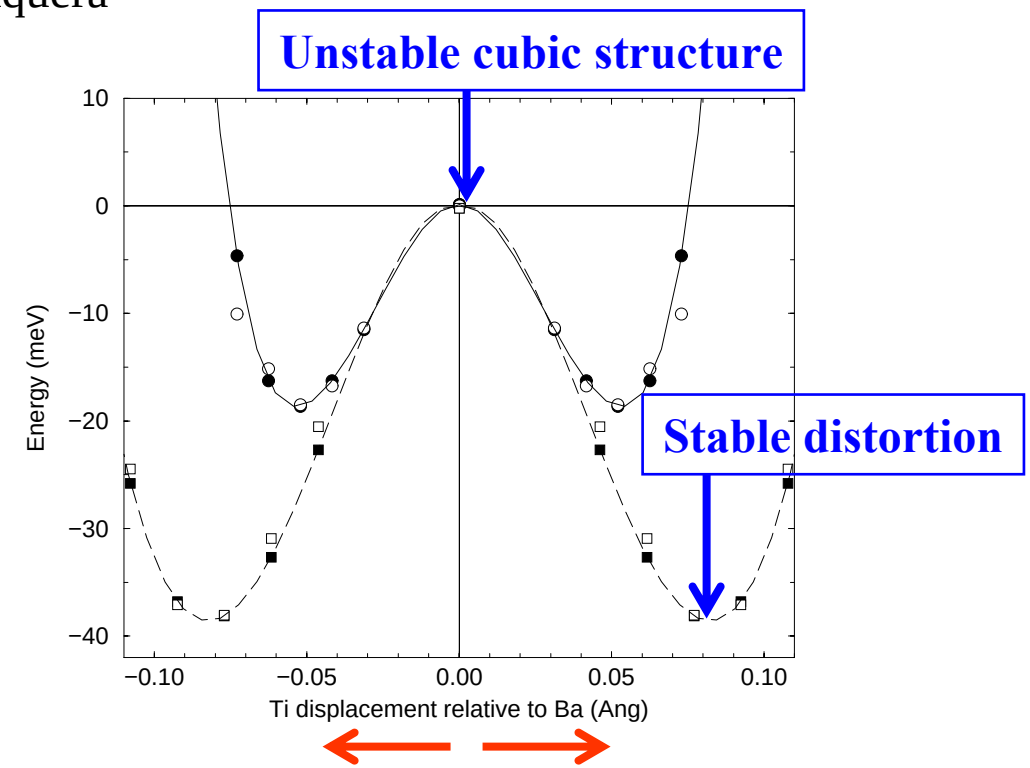
S. de Gironcoli, Phys.Rev B 51, 6773 (1995)

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



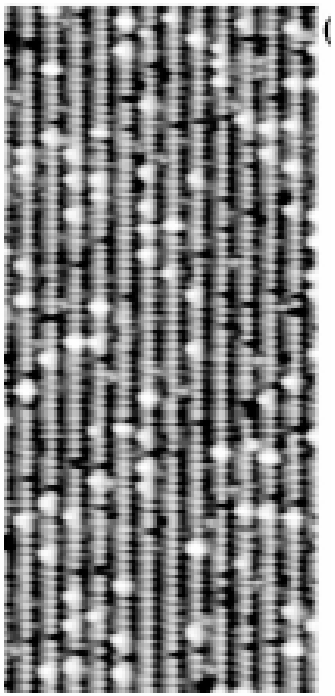
Perovskite structure



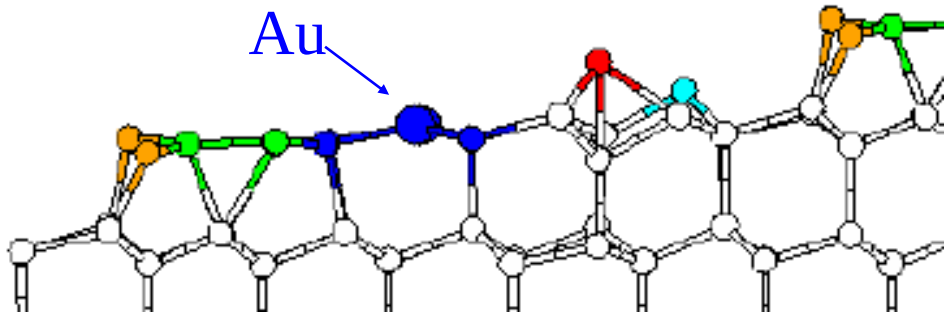
Many calculations done with ABINIT, . . .

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)

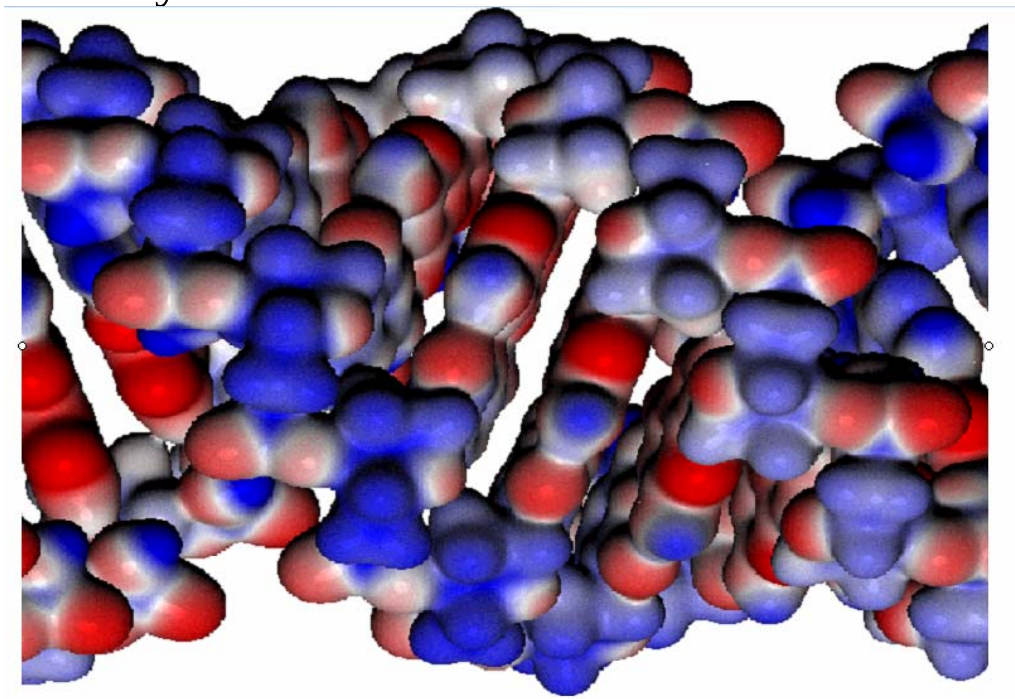


Theoretical prediction – using SIESTA code - of structure in very good agreement with experiment– done later!
Sanchez-Portal and R. M. Martin, Surf. Sci. 532, 655 (2003)

Explains one-dimensional metallic bands observed by photoemission

Examples of Modern Calculations

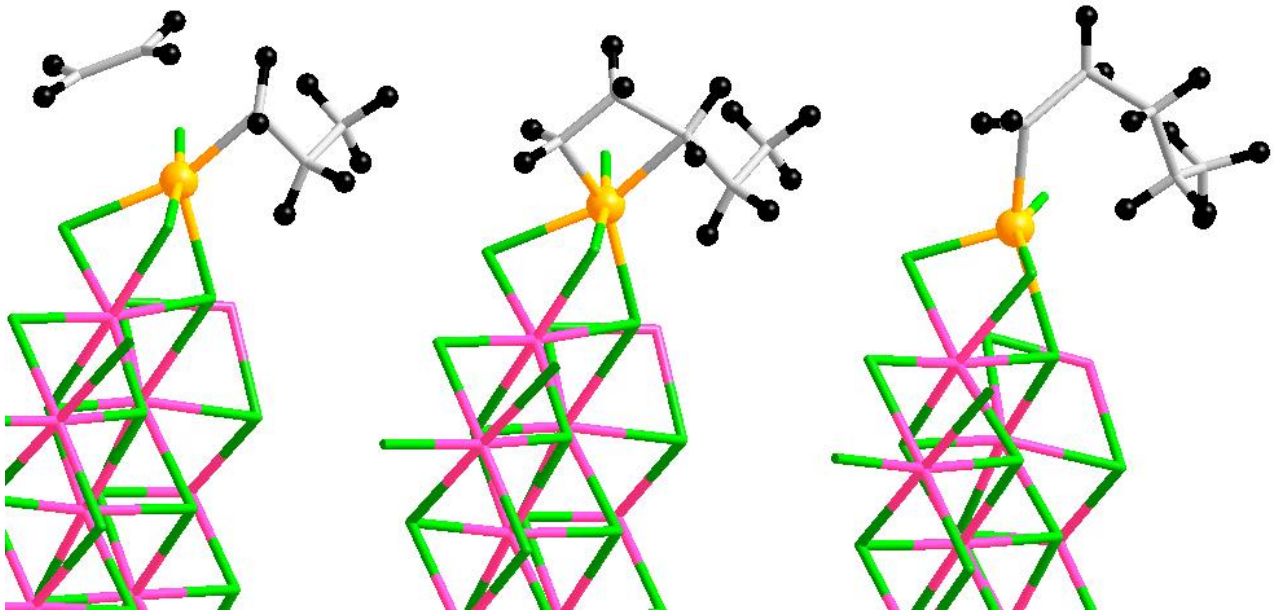
- **Simulations of DNA with the SIESTA code**
- Machado, Ordejon, Artacho, Sanchez-Portal, Soler
- Self-Consistent Local Orbital O(N) Code
- Relaxed atoms – dynamical simulations – on a workstation



Iso-surfaces of valence charge

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.



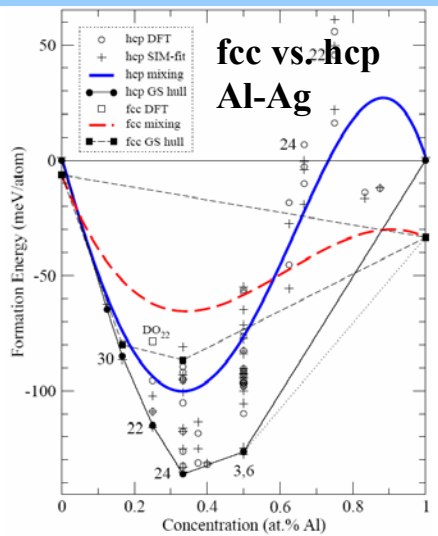
π-complex – Transition – insertion

Adds one ethelyne unit to polymer

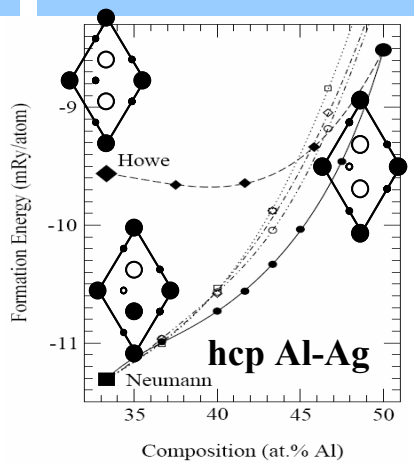
Week 2: *Ab Initio* Thermodynamics *via* Cluster Expansions

With DFT based CE: $E^{\sigma} = \sum_i V_i \Phi_i^{\sigma}$ ***We can predict/interpret:***

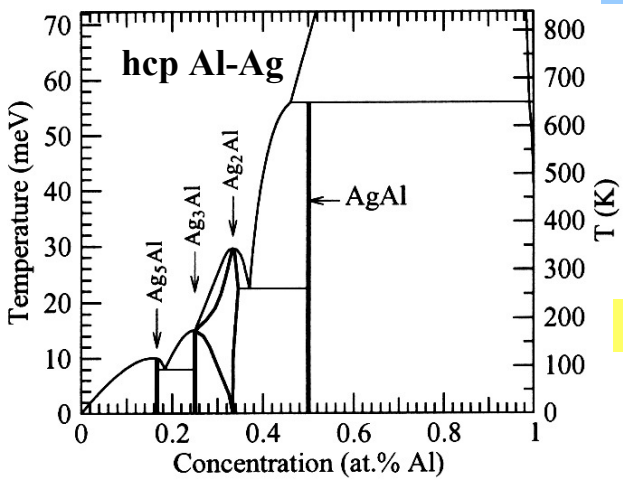
Energies of Disordered and Ordered Phases



Off-Stochiometric Phases

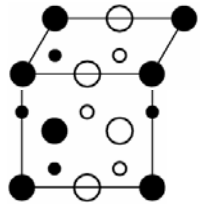


Phases Diagrams
Long- and Short- Range Order

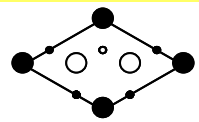


(Meta-)Stable Phases

ground state AlAg



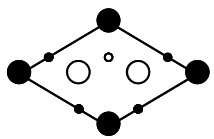
metastable AlAg

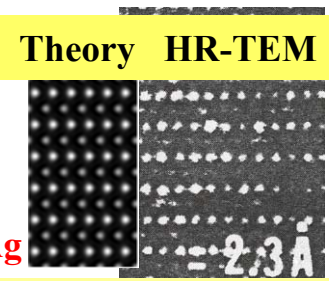


Zarkevich and Johnson, *PRB* 67, 064104 (2003).

Interpret Experimental Data

Theory **HR-TEM**





metastable hcp Al-Ag

Zarkevich and Johnson, *Acta Mater.* 50, 2443 (2002).

Conclusions

- **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**