First-Principles Computational Materials Physics

Part I: Fundamentals of First-principles Calculations

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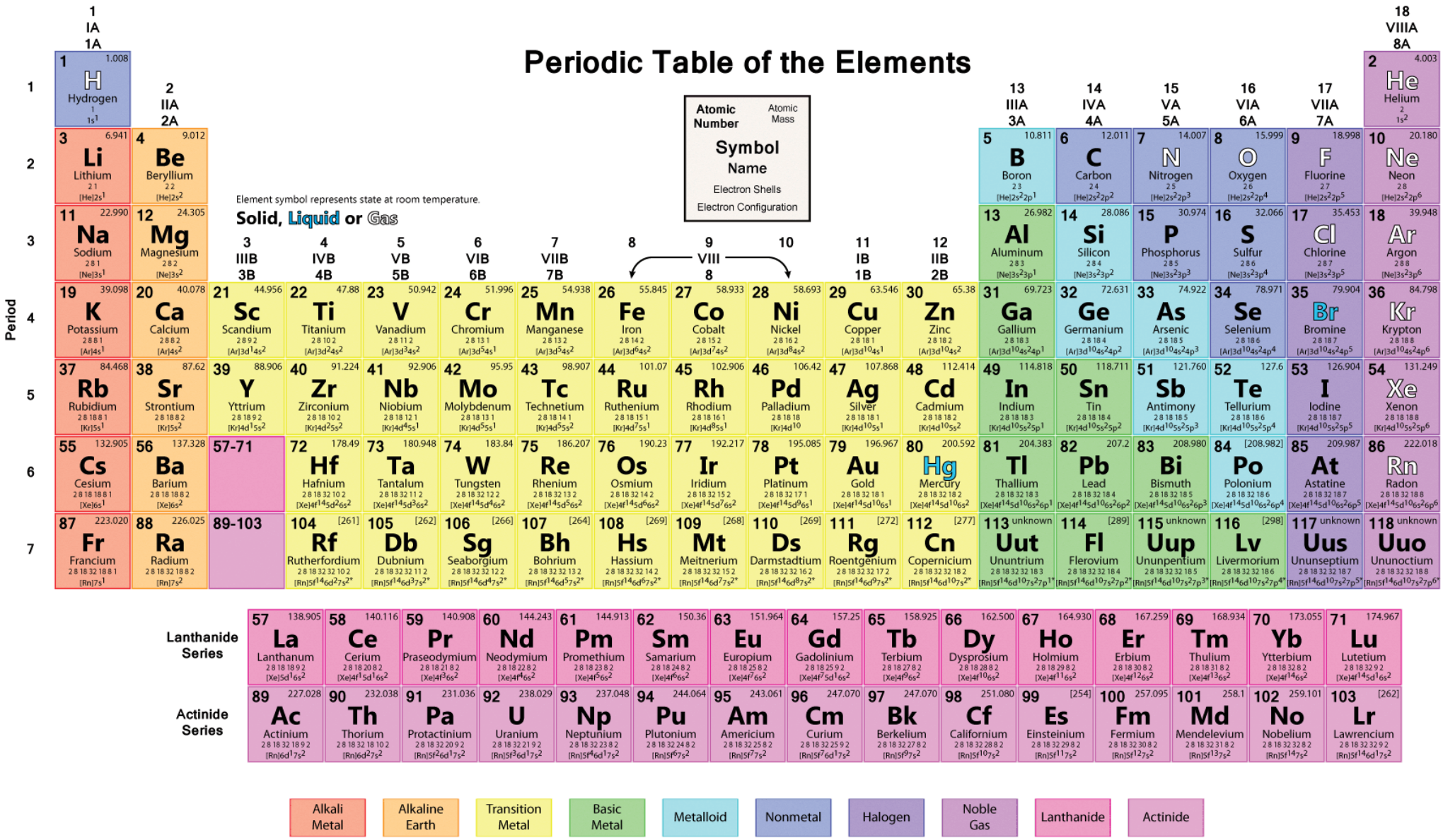
Chapter 1 Introduction to First-Principles Calculations

1.1 What is first-principles calculation

This course is about calculating the properties of materials (solid phase) from first-principles (*ab initio*), by directly or indirectly solving the Schrödinger equation that describes the motion of the electrons in the Coulomb potentials of the nuclei and of each other. By first-principles *(ab initio*), we meant empirical parameter-free calculations; that is, calculations in which the only input is the atomic numbers of the atoms and the macroscopic constraints (pressure, temperature, etc).



[from Internet]

Table 3 Crystal structures of the elements

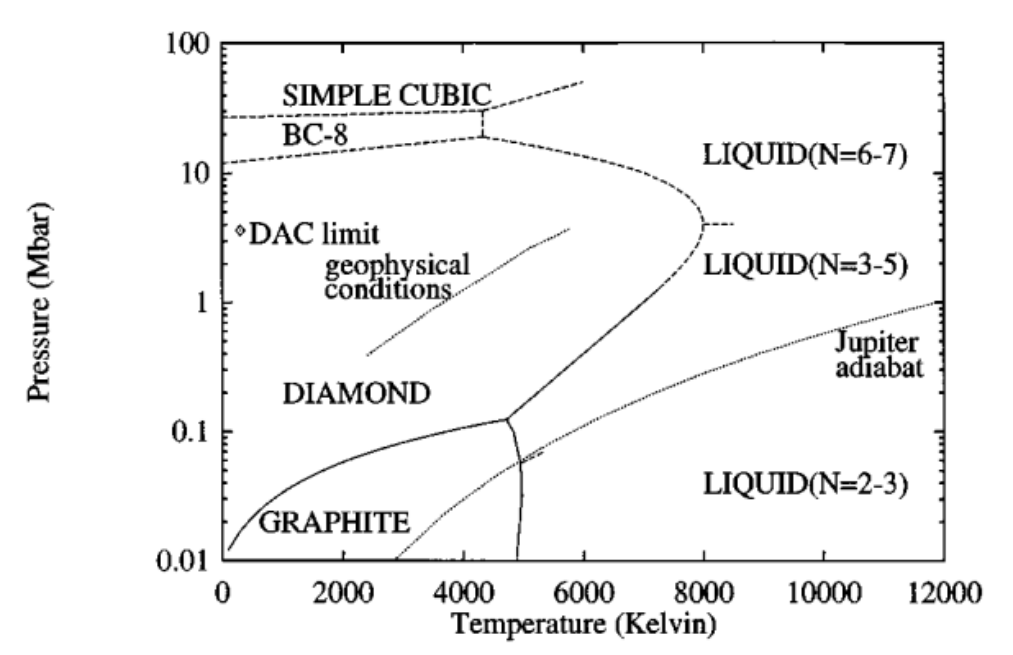
The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

H^1 4K hcp 3.75 6.12																	He^4 2K hcp 3.57 5.83
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N_2)	O complex (O_2)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21	← Crystal structure → ← *a* lattice parameter, in Å → ← *c* lattice parameter, in Å →										Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl_2)	Ar 4K fcc 5.31
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br_2)	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I_2)	Xe 4K fcc 6.13
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 *ABAC*	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —
Fr —	Ra —	Ac fcc 5.31															

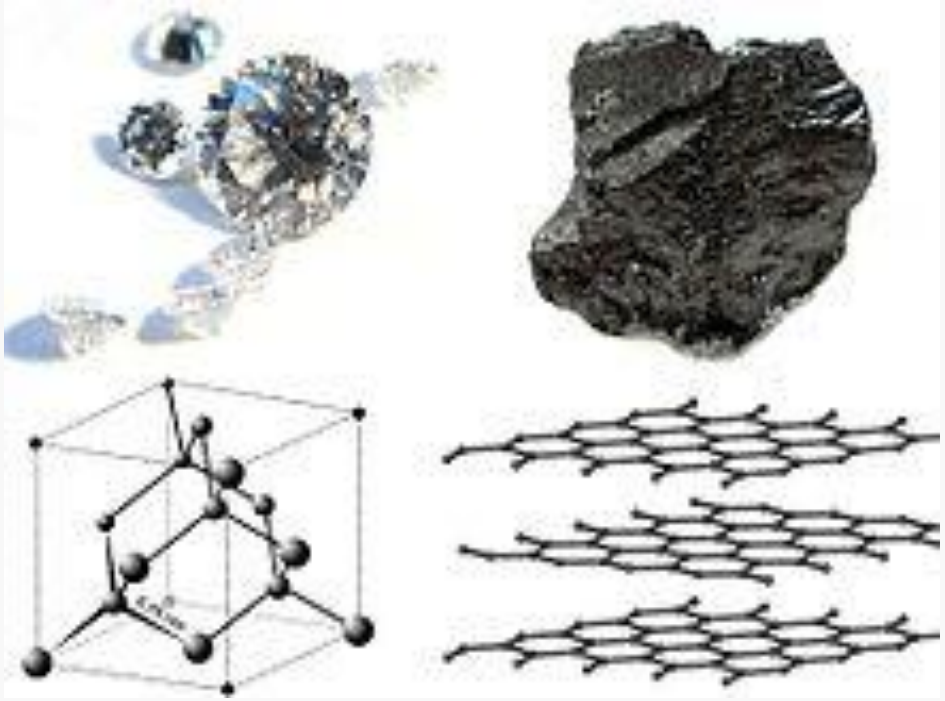
Ce fcc 5.16	Pr hex. 3.67 *ABAC*	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55
Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 *ABAC*	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —

[from Kittel's book]

Phase diagram of carbon



Carbon allotropes: diamond and graphite



[from Martin's book, p. 28]

[from Internet]

Diamond

Diamond anvil cell

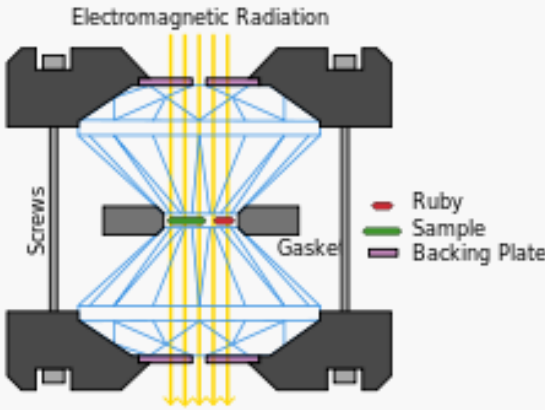


Table 3 Isothermal bulk modulii and compressibilities at room temperature

After K. Gschneidner, Jr., Solid state physics **16**, 275–426 (1964); several data are from F. Birch, in *Handbook of physical constants*, Geological Society of America Memoir **97**, 107–173 (1966). Original references should be consulted when values are needed for research purposes. Values in parentheses are estimates. Letters in parentheses refer to the crystal form. Letters in brackets refer to the temperature:

[a] = 77 K; [b] = 273 K; [c] = 1 K; [d] = 4 K; [e] = 81 K.

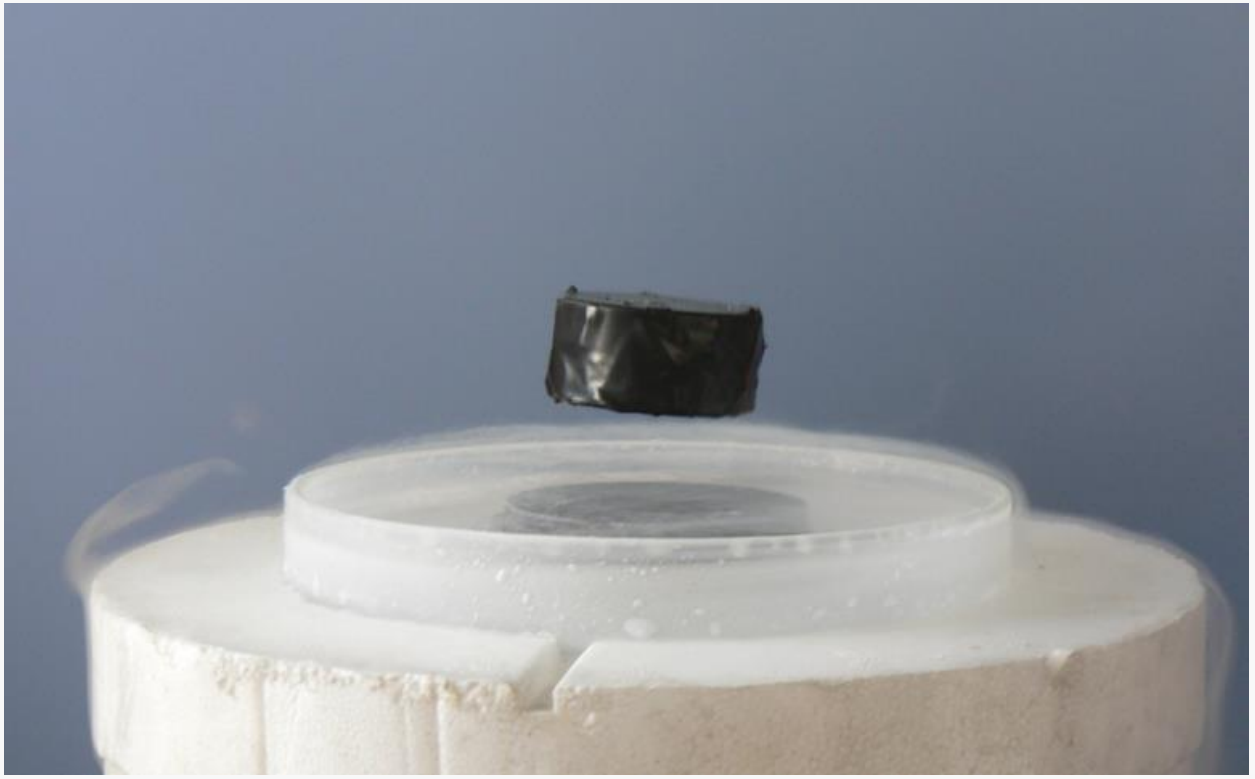
Bulk modulus in units 10^{12} dyn/cm² or 10^{11} N/m²
Compressibility in units 10^{-12} cm²/dyn or 10^{-11} m²/N

H [d]																	He [d]
0.002																	0.00
500																	1168
Li	Be											B	C [d]	N [e]	O	F	Ne [d]
0.116	1.003											1.78	4.43	0.012			0.010
8.62	0.997											0.562	0.226	80			100
Na	Mg											Al	Si	P (b)	S (r)	Cl	Ar [a]
0.068	0.354											0.722	0.988	0.304	0.178		0.013
14.7	2.82											1.385	1.012	3.29	5.62		79
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga [b]	Ge	As	Se	Br	Kr [a]
0.032	0.152	0.435	1.051	1.619	1.901	0.596	1.683	1.914	1.86	1.37	0.598	0.569	0.772	0.394	0.091		0.018
31.	6.58	2.30	0.951	0.618	0.526	1.68	0.594	0.522	0.538	0.73	1.67	1.76	1.29	2.54	11.0		56
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (g)	Sb	Te	I	Xe
0.031	0.116	0.366	0.833	1.702	2.725	(2.97)	3.208	2.704	1.808	1.007	0.467	0.411	1.11	0.383	0.230		
32.	8.62	2.73	1.20	0.587	0.366	(0.34)	0.311	0.369	0.553	0.993	2.14	2.43	0.901	2.61	4.35		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg [c]	Tl	Pb	Bi	Po	At	Rn
0.020	0.103	0.243	1.09	2.00	3.232	3.72	(4.18)	3.55	2.783	1.732	0.382	0.359	0.430	0.315	(0.26)		
50.	9.97	4.12	0.92	0.50	0.309	0.269	(0.24)	0.282	0.359	0.577	2.60	2.79	2.33	3.17	(3.8)		
Fr	Ra	Ac															
(0.020)	(0.132	(0.25)															
(50.)	(7.6)	(4.)															

Ce (γ)	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0.239	0.306	0.327	(0.35)	0.294	0.147	0.383	0.399	0.384	0.397	0.411	0.397	0.133	0.411
4.18	3.27	3.06	(2.85)	3.40	6.80	2.61	2.51	2.60	2.52	2.43	2.52	7.52	2.43
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
0.543	(0.76)	0.987	(0.68)	0.54									
1.84	(1.3)	1.01	(1.5)	1.9									

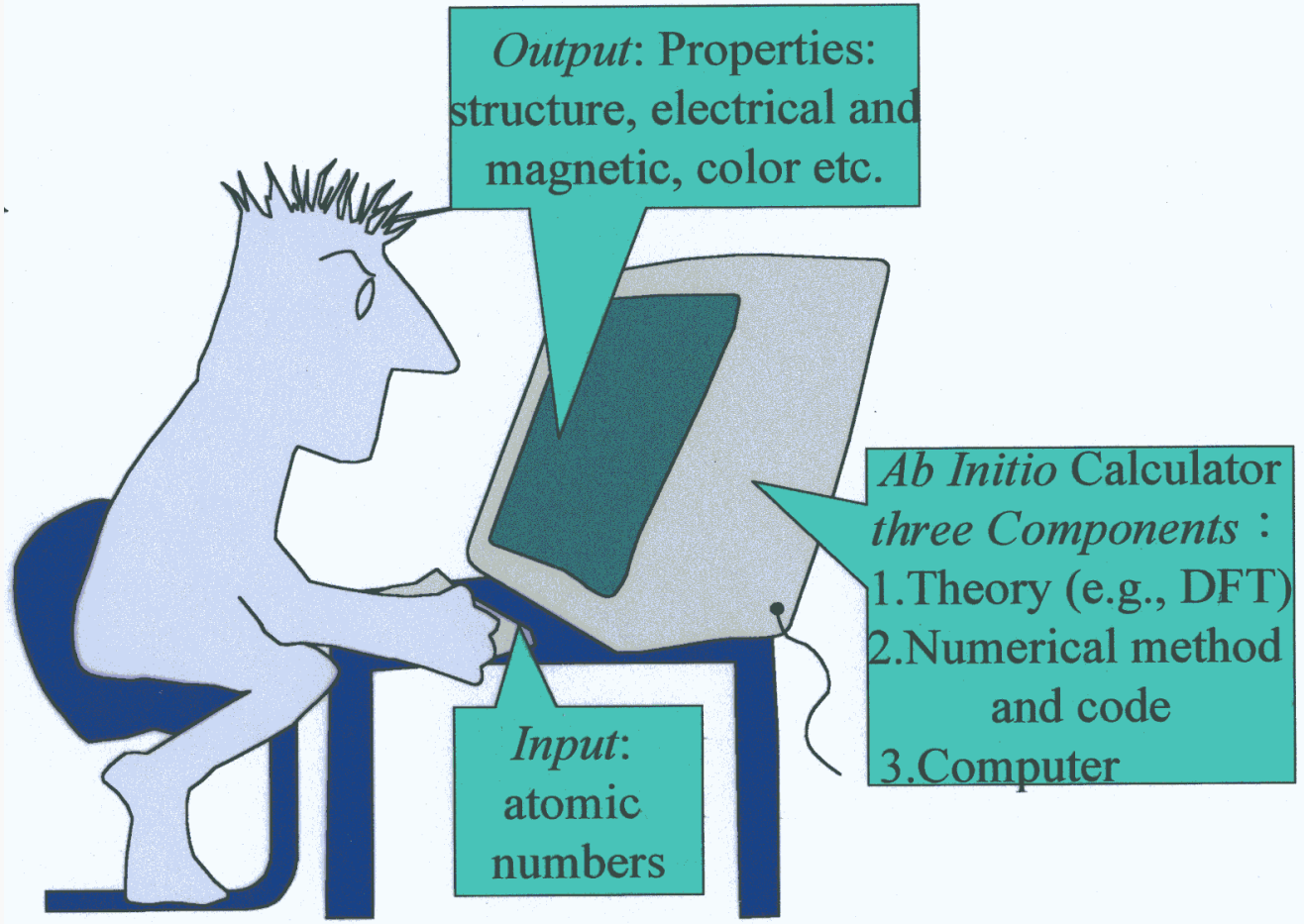
[from Kittel's book]

A metal becomes superconducting below T_c and floats in a magnetic field.



[from Internet]

Cartoon of first-principles (*ab initio*) calculations



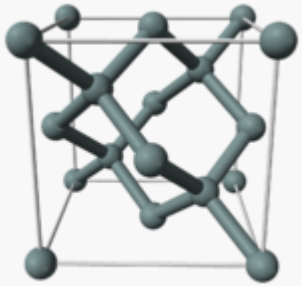
The calculation is really a “computer experiment”, as we can make intricate changes in the “experimental conditions” and measure our “observables” in arbitrarily minute details. It can make materials-specific predictions and also provide first-principles parameters for otherwise empiral models.

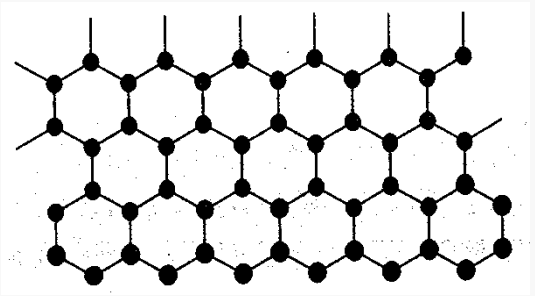
1.2 Significances of first-principles calculation

Today, due to fast computers, efficient algorithms, advanced quantum theory, first-principles calculations have become essential to understand the intricate phenomena in condensed mater systems, to search for and/or design for new materials with desired properties.

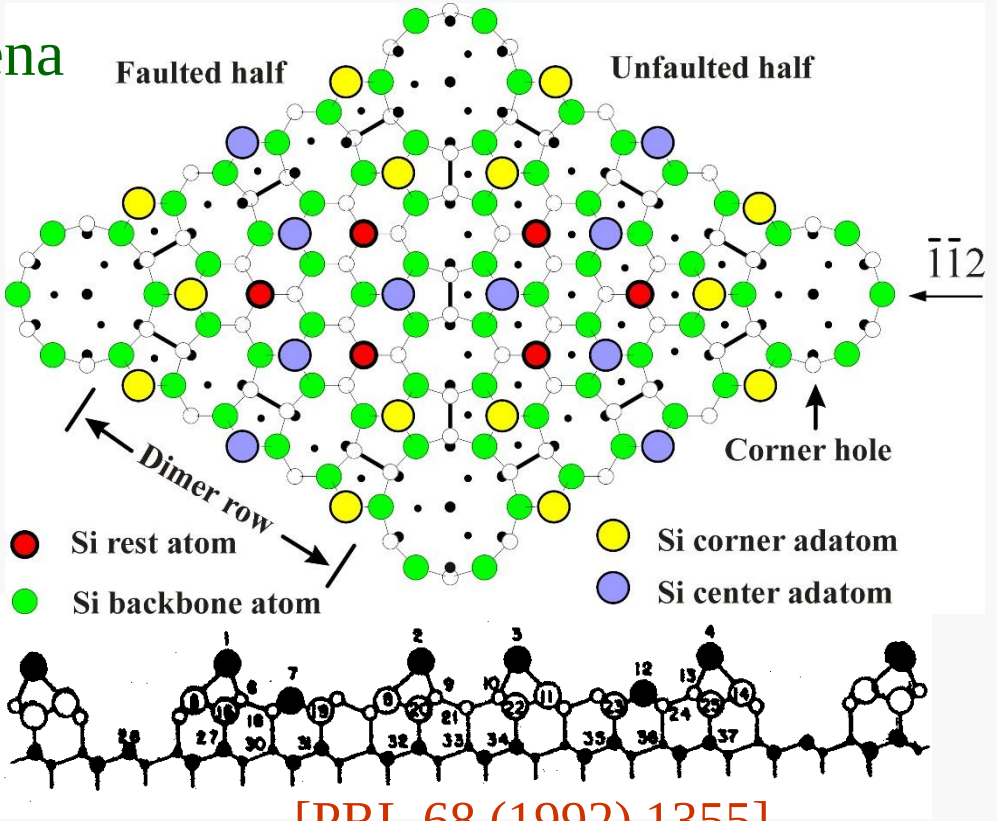
Understanding of complex phenomena

Si (111) surface





Si (111) surface reconstruction



[PRL 68 (1992) 1355]

Materials characterization

Another example, the structure of Au_{20}^- *determined jointly* by photoelectron spectroscopy and *ab initio* calculations

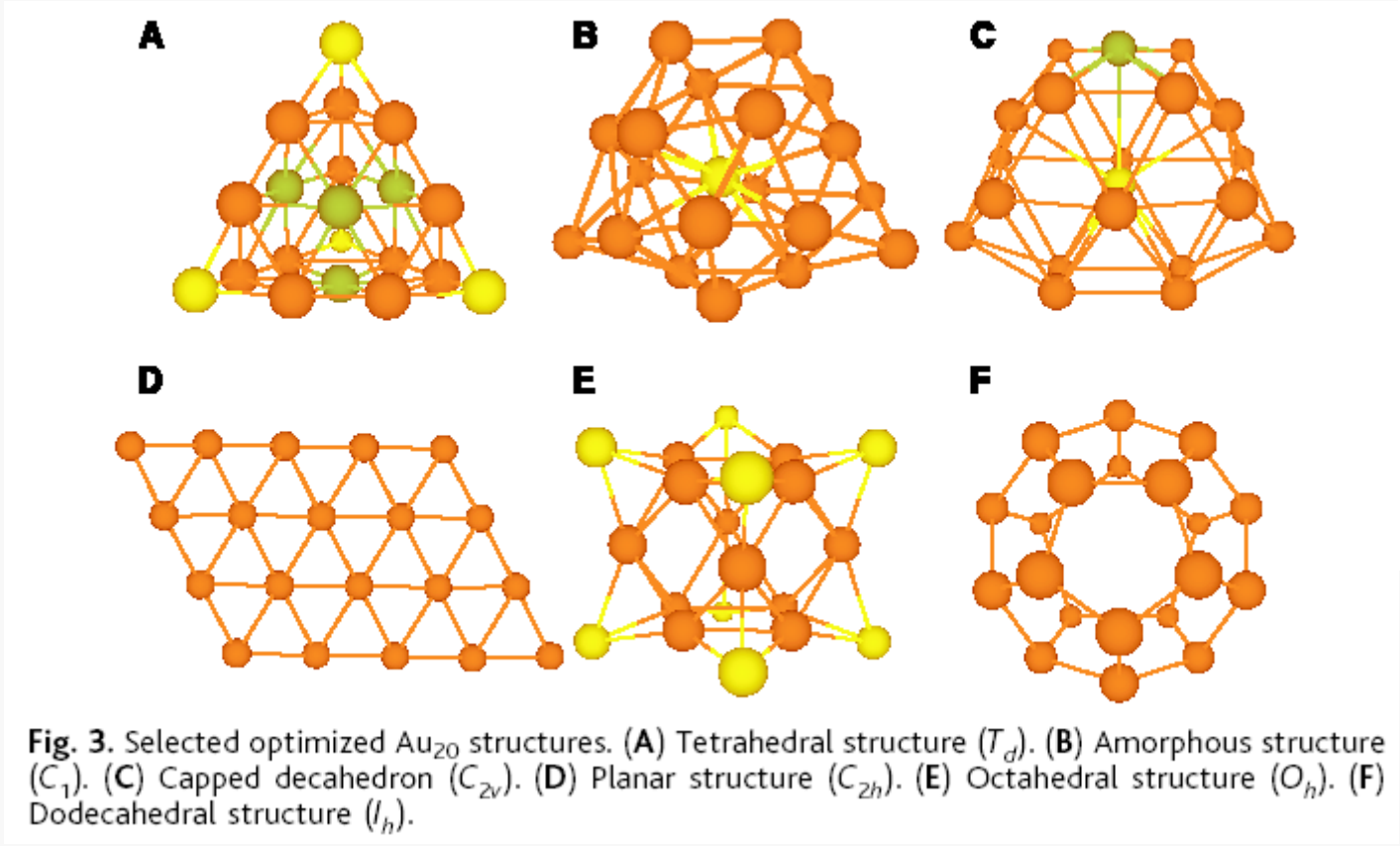
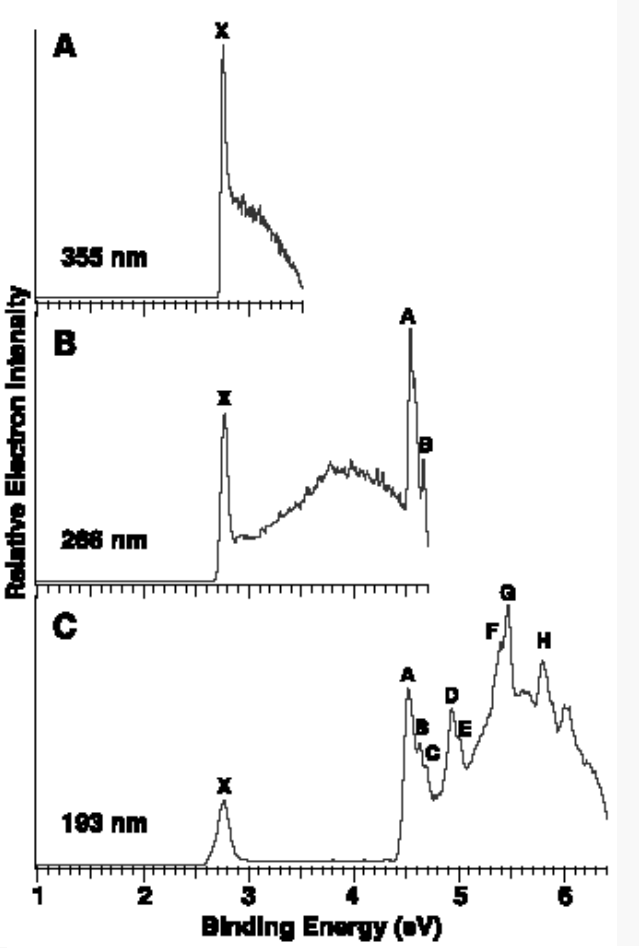
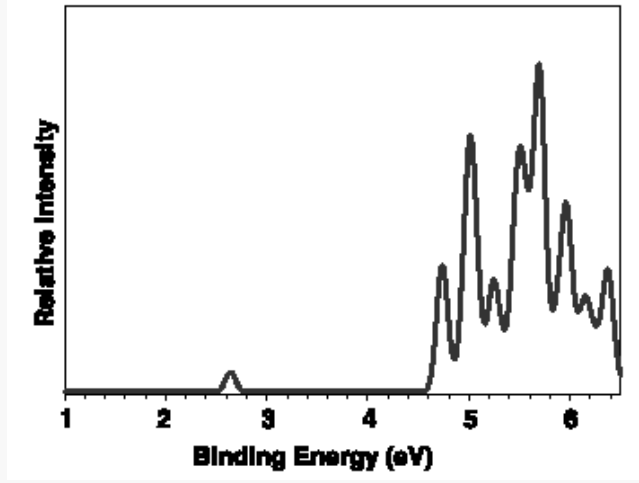


Fig. 3. Selected optimized Au_{20} structures. (**A**) Tetrahedral structure (T_d). (**B**) Amorphous structure (C_1). (**C**) Capped decahedron (C_{2v}). (**D**) Planar structure (C_{2h}). (**E**) Octahedral structure (O_h). (**F**) Dodecahedral structure (I_h).

[Science 299, 864 (2003) 1355]

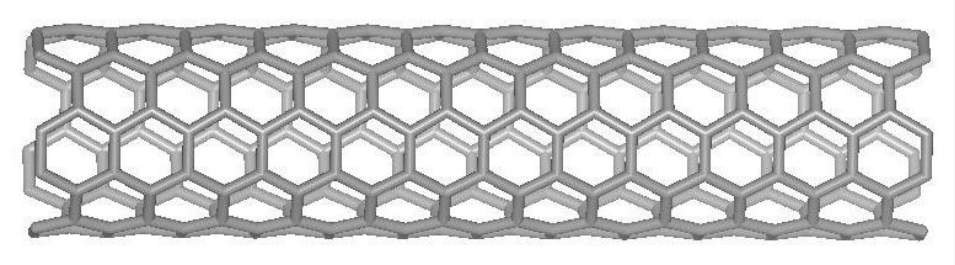




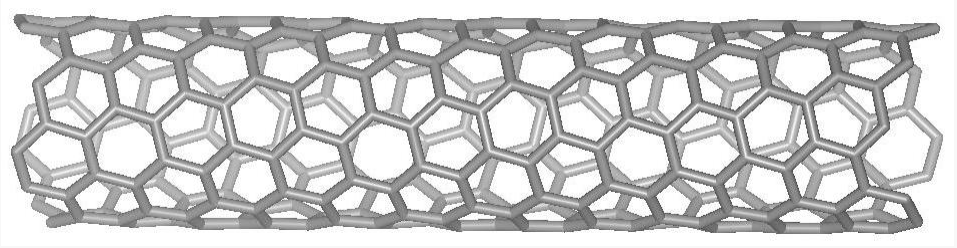
Materials prediction/design

Carbon nanotubes

(Iijima, 1991)

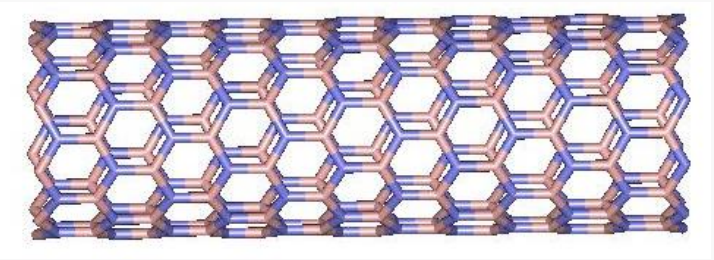


armchair (5,5) nanotube

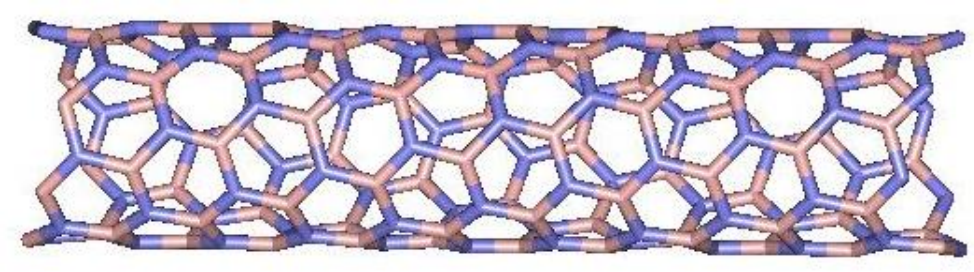


chiral (7,3) nanotube

BN nanotubes



zigzag (10,0) nanotube



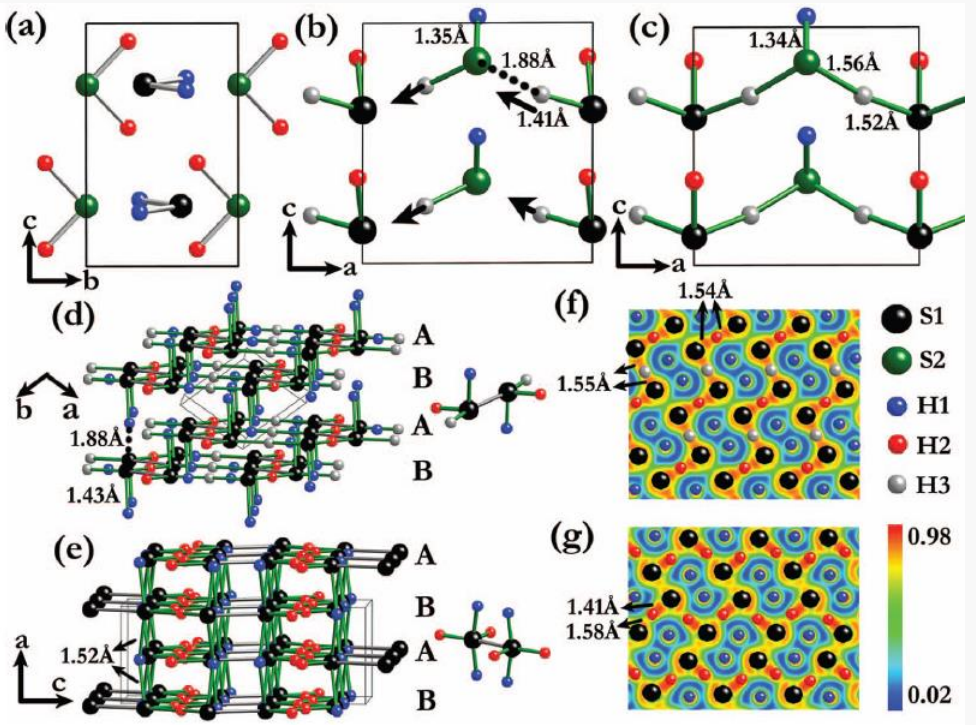
chiral (6,2) nanotube

[predicted and subsequently synthesized by Berkeley groups in the mid-90's]

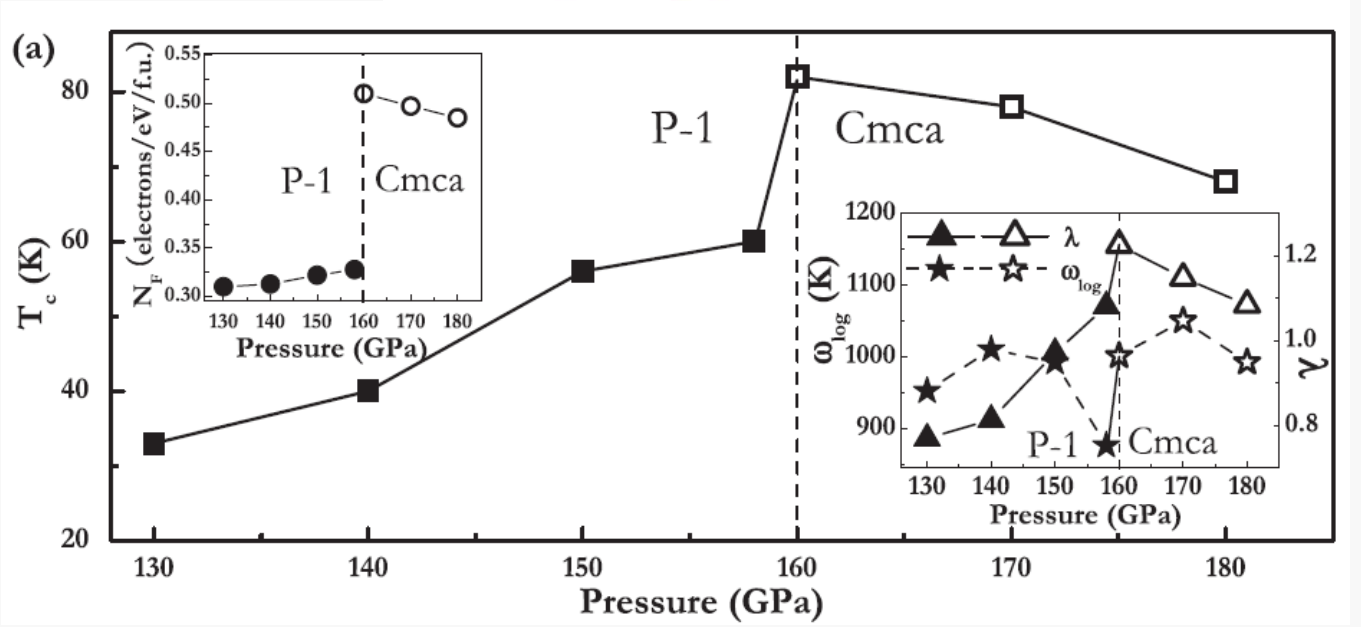
[Rubio et al., PRB 1994;
Chopra, et al., Science, 1994]

New materials prediction

Prediction of mellalization and superconductivity of dense hydrogen sulfide (2014)



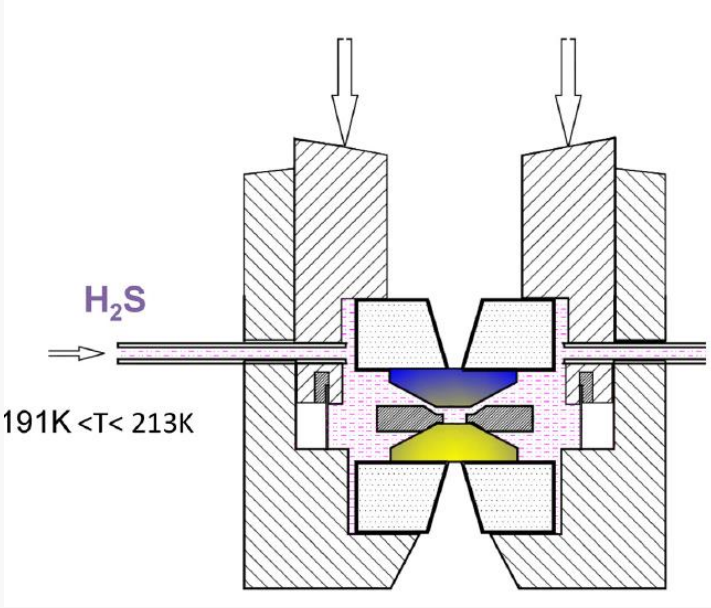
[Li, Hao, Liu, Li, Ma, JCP 140 (2014) 174712]

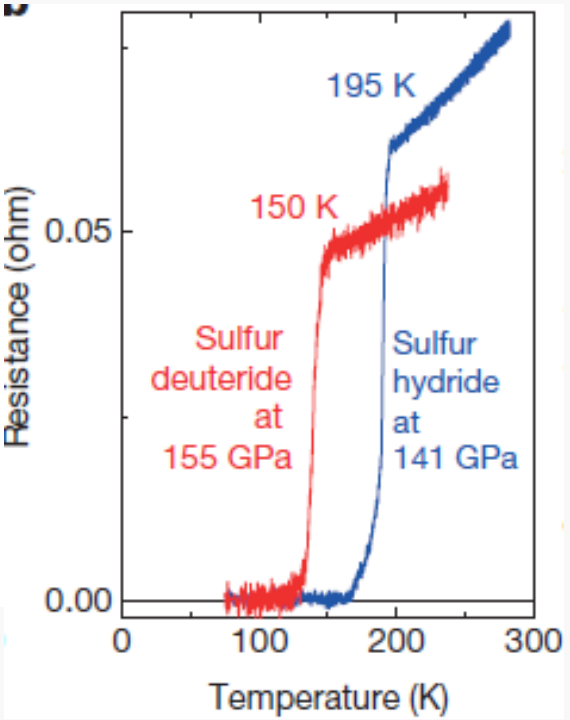


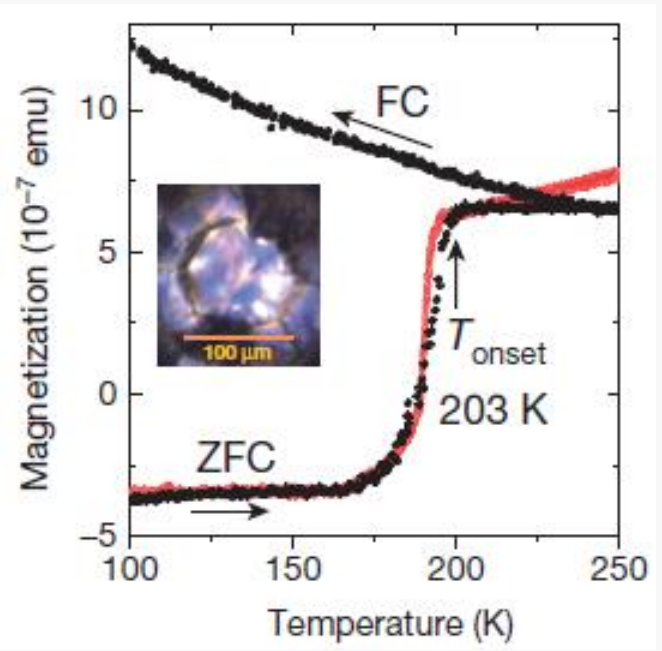
Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

A. P. Drozdov[1]*, M. I. Eremets[1]*, I. A. Troyan[1], V. Ksenofontov[2] & S. I. Shylin[2]

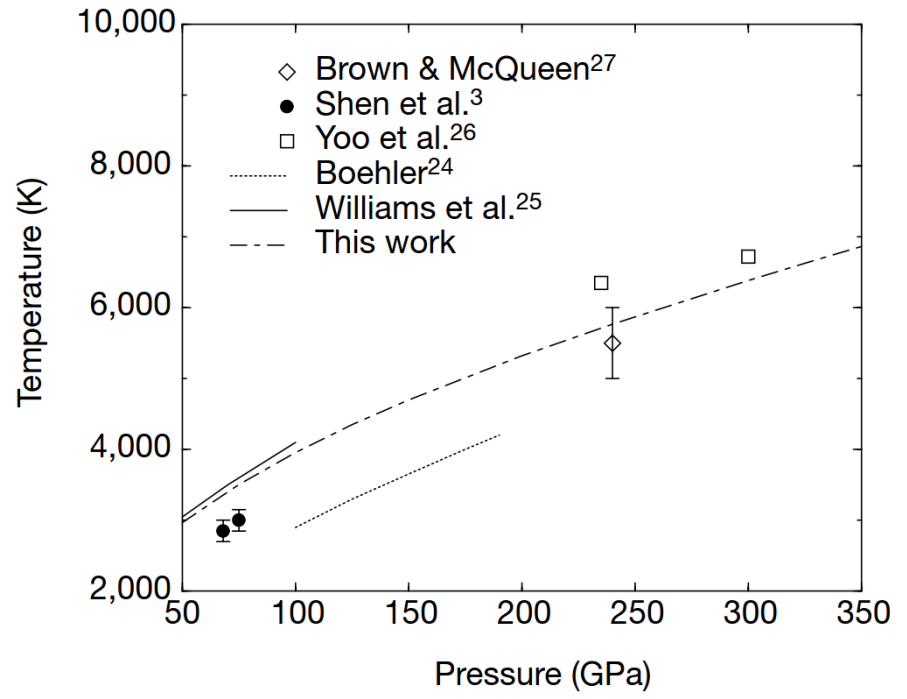
[Nature 525 (2015) 73]

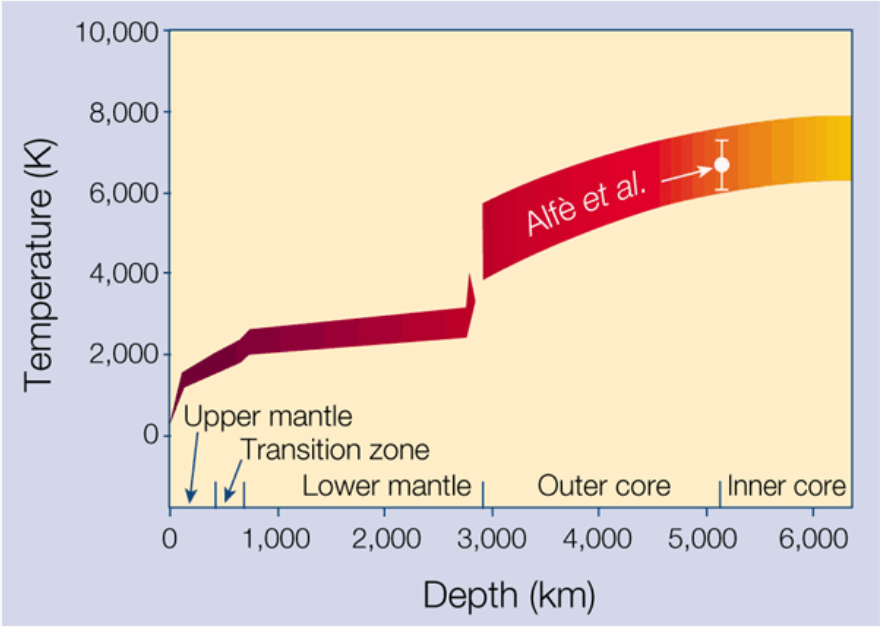






Through “computer experiments”, theoreticians can now investigate some important systems where human being cannot conduct experiments yet, such as the physical and chemical processes happening in the interior of our planet.





[*Ab initio* melting curve of iron compared with experiments.]

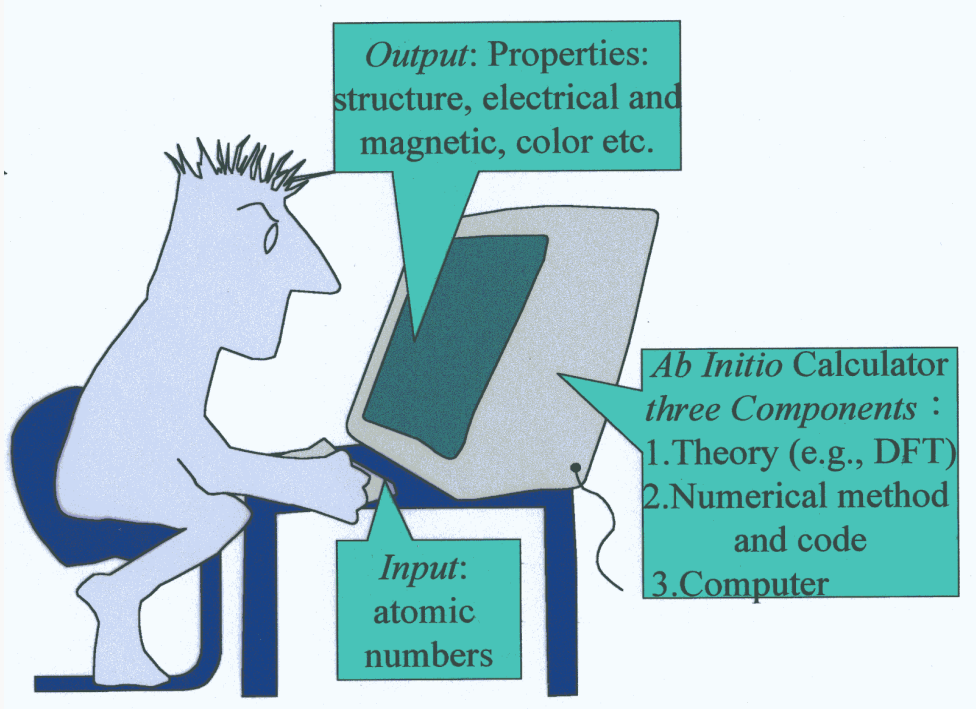
[Nature 401 (1999) 462]

1.3 Outline of this course

This lecture consists of two parts.

Part one is on the fundamentals of first-principles materials calculations. This part will cover basic concepts of crystals, theories of electrons in periodic potentials, fundamentals of density functional theory and computational (numerical) techniques.

Part two is about determination of materials properties. This part consists of several units made up of lectures and hands-on excises, given by senior researchers in field. Each unit focus on one major physical property of materials or one topic of current interest in materials physics.



Course Materials

1. Main Information Source:
   The course will be largely based on lecture notes and hand-outs.
2. Principal Reference Book
   [1] *Electronic Structure: Basic Theory and Practical Methods*
   by Richard M. Martin (Cambridge U. P., 2004).
3. Other References:
   [2] *Introduction to Solid State Physics*
   by Charles Kittel (John Wiley & Sons).
   [3] *Solid State Physics* by Neil W. Ashcroft and N. David Mermin.
   [4] *Planewaves, Pseudopotentials and the LAPW Method*
   by David J. Singh and Lars Nordstrom (2nd edition) (Springer, 2006)
   [5] *Theory of Itinerant Electron Magnetism*, J. Kübler (Oxford, 2000).