

Density Functional Theory

DFT-I

(5 hp)

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Learning outcomes

On completion of the course, the student should be able to:

- account for the fundamental background of Density Functional Theory (DFT).
- explain how electron correlation is defined and how it is approximated within DFT and compare these approximations to other correlated methods.
- explain the Hohenberg-Kohn theorems and their application.
- account for the Kohn-Sham equation and density functionals, such as Slater's X-alpha and the Local Density Approximation (LDA).
- illustrate the difference between more modern functionals such as the PBE and B3LYP functionals and earlier functionals, such as the LDA functional.
- identify the areas within computational physics where DFT generally performs well and also areas where the theory fails in predicting properties of bulk materials or molecules.
- to be able to determine, from a physical context, whether or not the properties of a certain material can be studied by means of DFT or any other correlated method, and if so, select the method which is more suitable.

Outline of the course

- Recapitulation of quantum mechanics
- Hartree, Hartree-Fock and Thomas-Fermi-Dirac theory
- DFT: Hohenberg-Kohn theorems & Kohn-Sham equation
- Exchange-correlation functionals
- Basis sets and electronic structure calculations
- Success of DFT in applications in different disciplines
- Shortcomings of DFT with standard exchange-correlation functionals
- Correlated electrons: DFT+U and DFT+DMFT
- Band gap problem: Hybrid functionals & GW method
- Time-dependent DFT
- Van der Waals interactions

Mode of examination

Written report

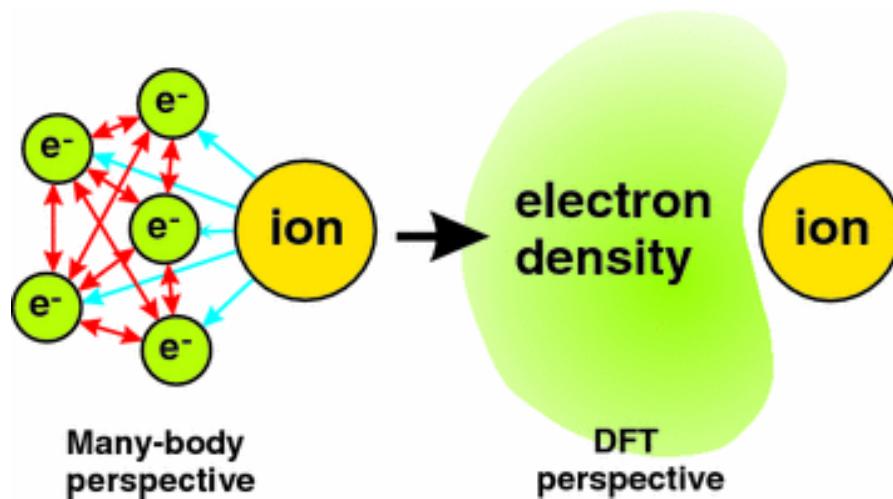
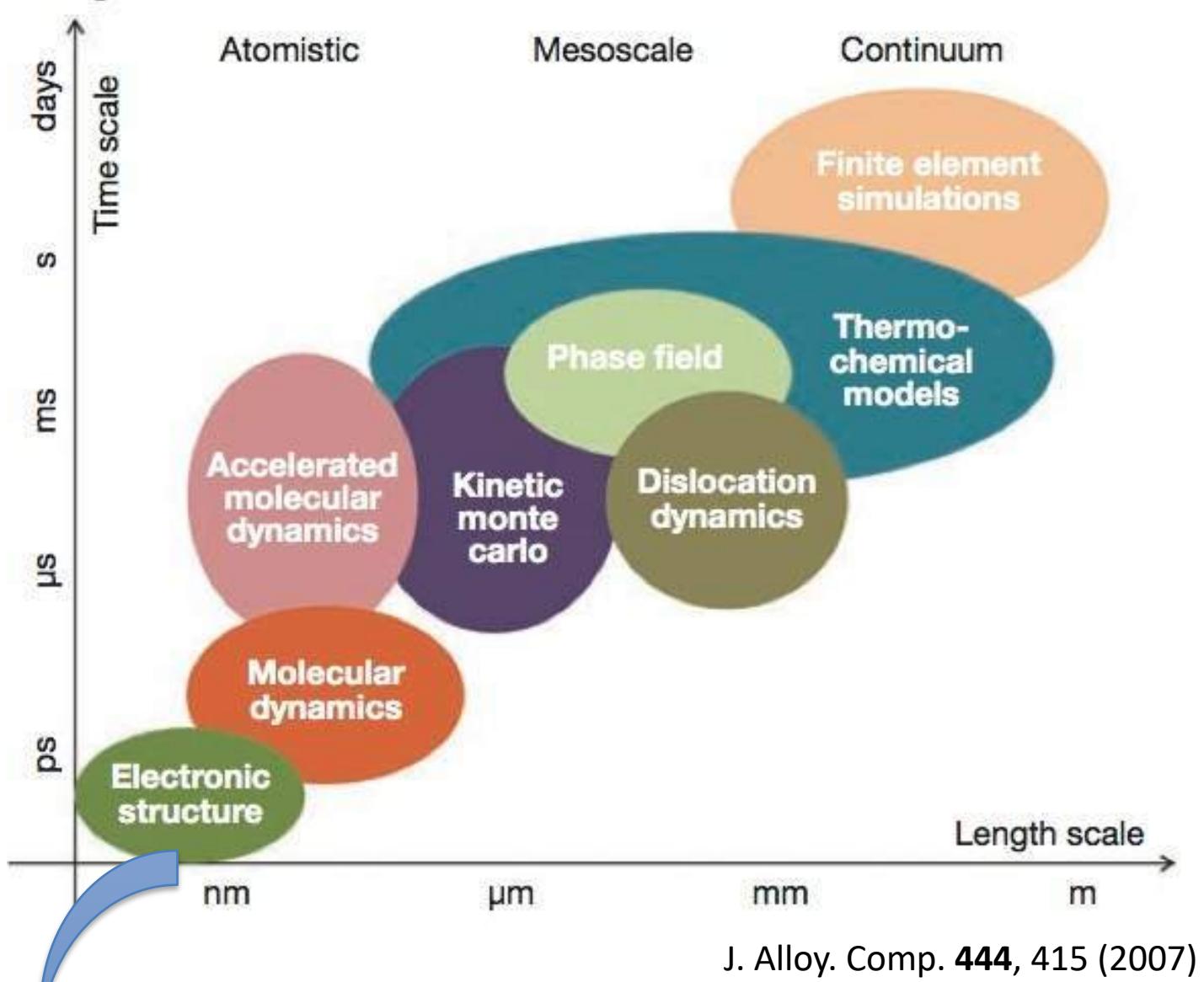
Oral presentation

Literature

A chemist's guide to density functional theory
by Wolfram Koch & Max C. Holthausen

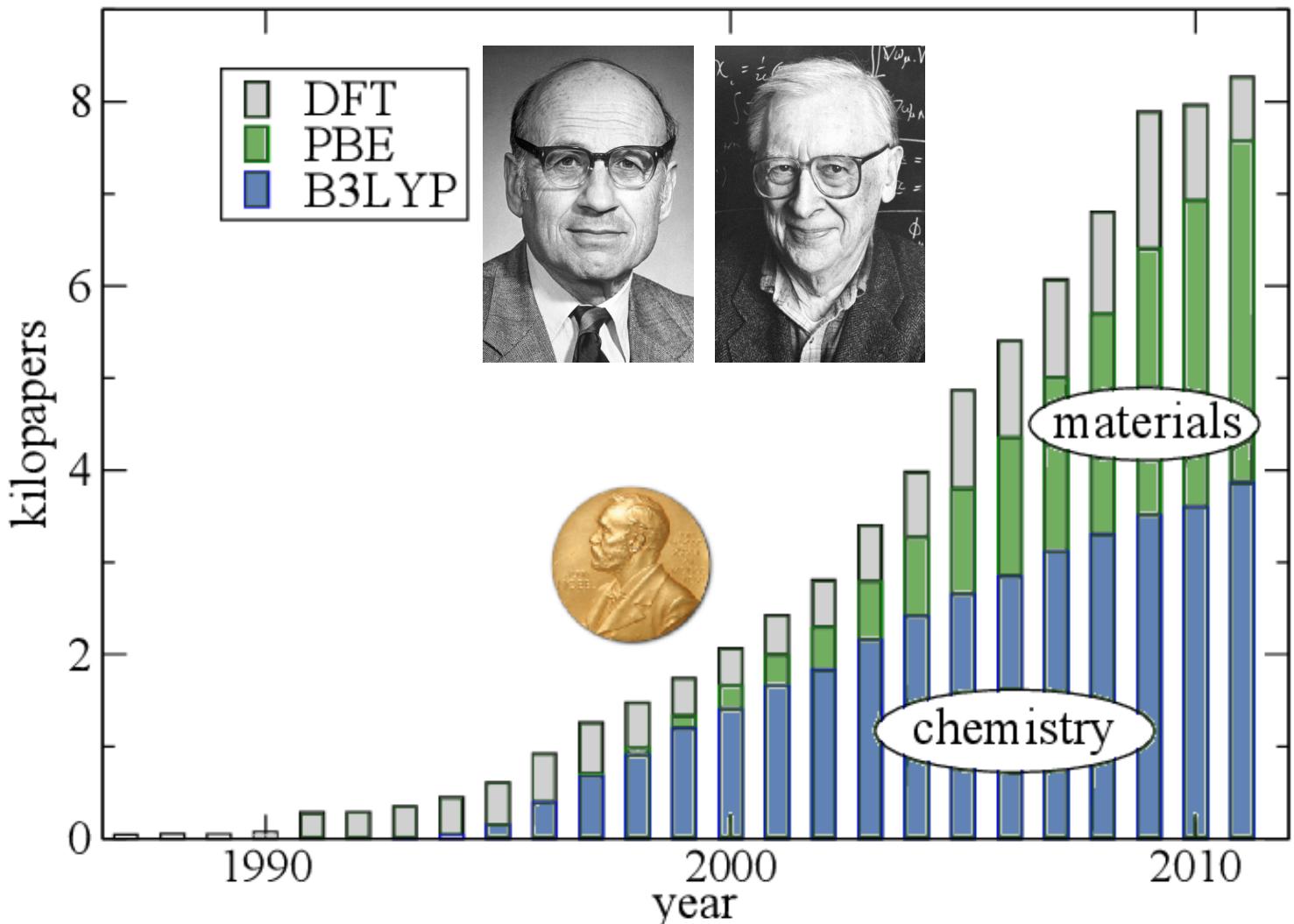
Modern quantum mechanics (introduction to advanced electronic structure theory) by Attila Szabo & Neil S. Ostlund

Bridging length and time scales



Courtesy: Springer

Success of DFT



Burke, J. Chem. Phys. (2012)

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry."

-nobelprize.org

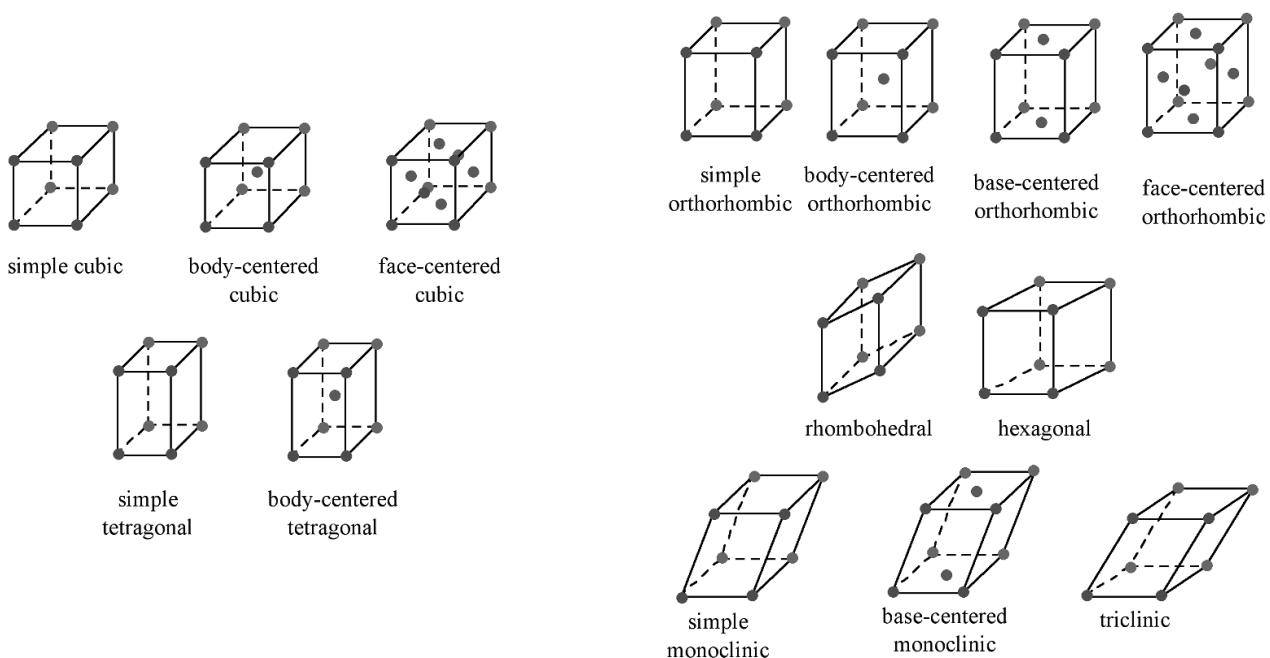
1 H₂ Hydrogen GAS	Periodic Table of the Elements																		2 He Helium GAS
3 Li Lithium BCC	4 Be Beryllium HEX																		10 Ne Neon GAS
11 Na Sodium BCC	12 Mg Magnesium HEX		Solid		Liquid		Gas												18 Ar Argon GAS
19 K Potassium BCC	20 Ca Calcium FCC	21 Sc Scandium HEX	22 Ti Titanium BCC	23 V Vanadium BCC	24 Cr Chromium BCC	25 Mn Manganese BCC	26 Fe Iron BCC	27 Co Cobalt HEX	28 Ni Nickel FCC	29 Cu Copper FCC	30 Zn Zinc HEX	31 Ga Gallium ORTHO	32 Ge Germanium FCC	33 As Arsenic RHOM	34 Se Selenium HEX	35 Br Bromine LIQUID	36 Kr Krypton GAS		
37 Rb Rubidium BCC	38 Sr Strontium FCC	39 Y Yttrium HEX	40 Zr Zirconium HEX	41 Nb Niobium BCC	42 Mo Molybdenum BCC	43 Tc Technetium HEX	44 Ru Ruthenium HEX	45 Rh Rhodium FCC	46 Pd Palladium FCC	47 Ag Silver FCC	48 Cd Cadmium HEX	49 In Indium TETRA	50 Sn Tin TETRA	51 Sb Antimony RHOM	52 Te Tellurium HEX	53 I Iodine ORTHO	54 Xe Xenon GAS		
55 Cs Cesium BCC	56 Ba Barium BCC	57-71 Lanthanides	72 Hf Hafnium HEX	73 Ta Tantalum BCC	74 W Tungsten BCC	75 Re Rhenium HEX	76 Os Osmium HEX	77 Ir Iridium FCC	78 Pt Platinum FCC	79 Au Gold FCC	80 Hg Mercury LIQUID	81 Tl Thallium HEX	82 Pb Lead FCC	83 Bi Bismuth RHOM	84 Po Polonium CUBIC	85 At Astatine UNK	86 Rn Radon GAS		
87 Fr Francium UNK	88 Ra Radium BCC	89-103 Actinides	104 Rf Rutherfordium UNK	105 Db Dubnium UNK	106 Sg Seaborgium UNK	107 Bh Bohrium UNK	108 Hs Hassium UNK	109 Mt Meitnerium UNK	110 Ds Darmstadtium UNK	111 Rg Roentgenium UNK	112 Cn Copernicium UNK	113 Nh Nihonium UNK	114 Fl Flerovium UNK	115 Mc Moscovium UNK	116 Lv Livermorium UNK	117 Ts Tennessee UNK	118 Og Oganesson UNK		

57 La Lanthanum HEX	58 Ce Cerium FCC	59 Pr Praseodymium HEX	60 Nd Neodymium HEX	61 Pm Promethium HEX	62 Sm Samarium RHOM	63 Eu Europium BCC	64 Gd Gadolinium HEX	65 Tb Terbium HEX	66 Dy Dysprosium HEX	67 Ho Holmium HEX	68 Er Erbium HEX	69 Tm Thulium HEX	70 Yb Ytterbium FCC	71 Lu Lutetium HEX
89 Ac Actinium FCC	90 Th Thorium FCC	91 Pa Protactinium TETRA	92 U Uranium ORTHO	93 Np Neptunium ORTHO	94 Pu Plutonium MONO	95 Am Americium HEX	96 Cm Curium HEX	97 Bk Berkelium HEX	98 Cf Californium HEX	99 Es Einsteinium HEX	100 Fm Fermium HEX	101 Md Mendelevium UNK	102 No Nobelium UNK	103 Lr Lawrencium UNK

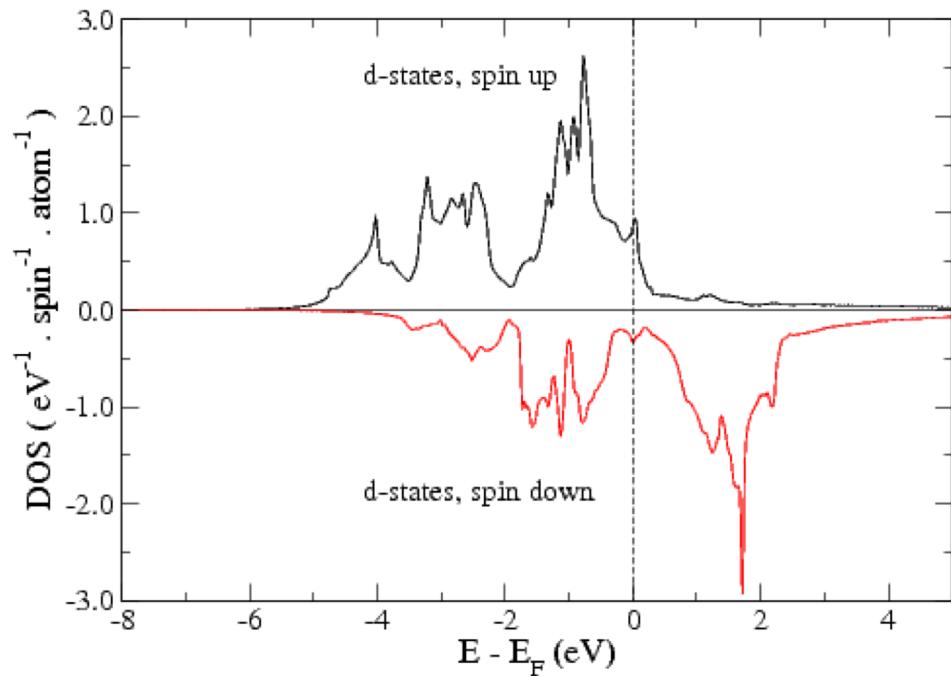
Most Stable Crystalline Structure Of Solids

CUBIC Simple Cubic FCC Face Centered Cubic ORTHO Orthorhombic TETRA Tetragonal UNK Unknown
 BCC Body Centered Cubic HEX Hexagonal RHOM Rhombohedral MONO Monoclinic

<https://sciencenotes.org/periodic-table-natural-state/>



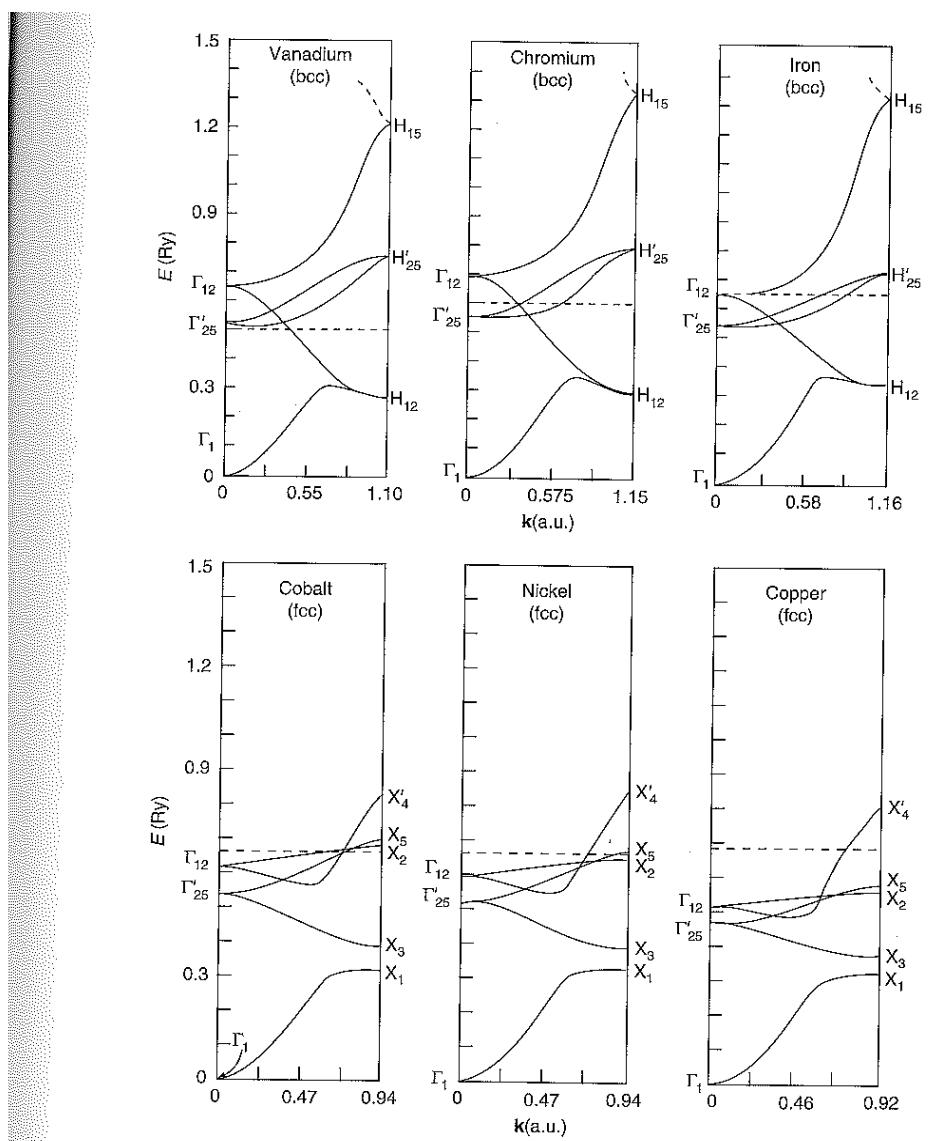
Electronic structure (DFT)



Density of states:
Ferromagnetic bcc iron

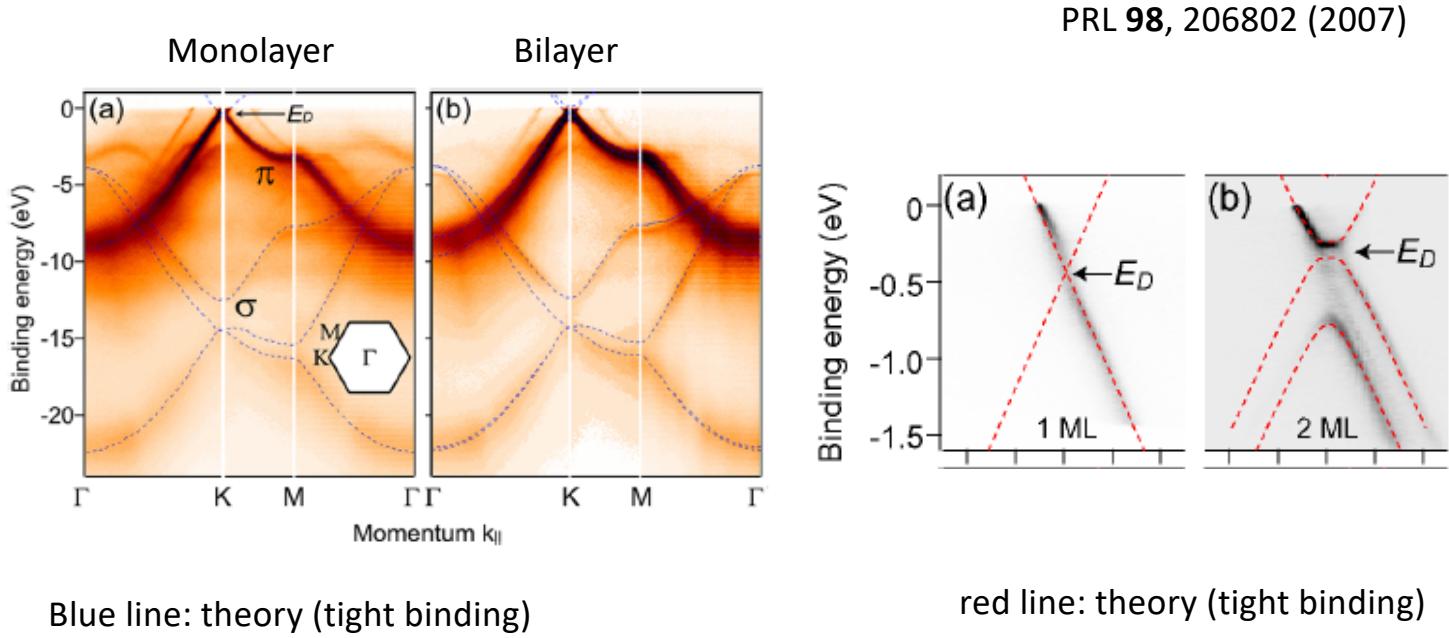
Expt: Photoemission

Band structure
Expt: ARPES



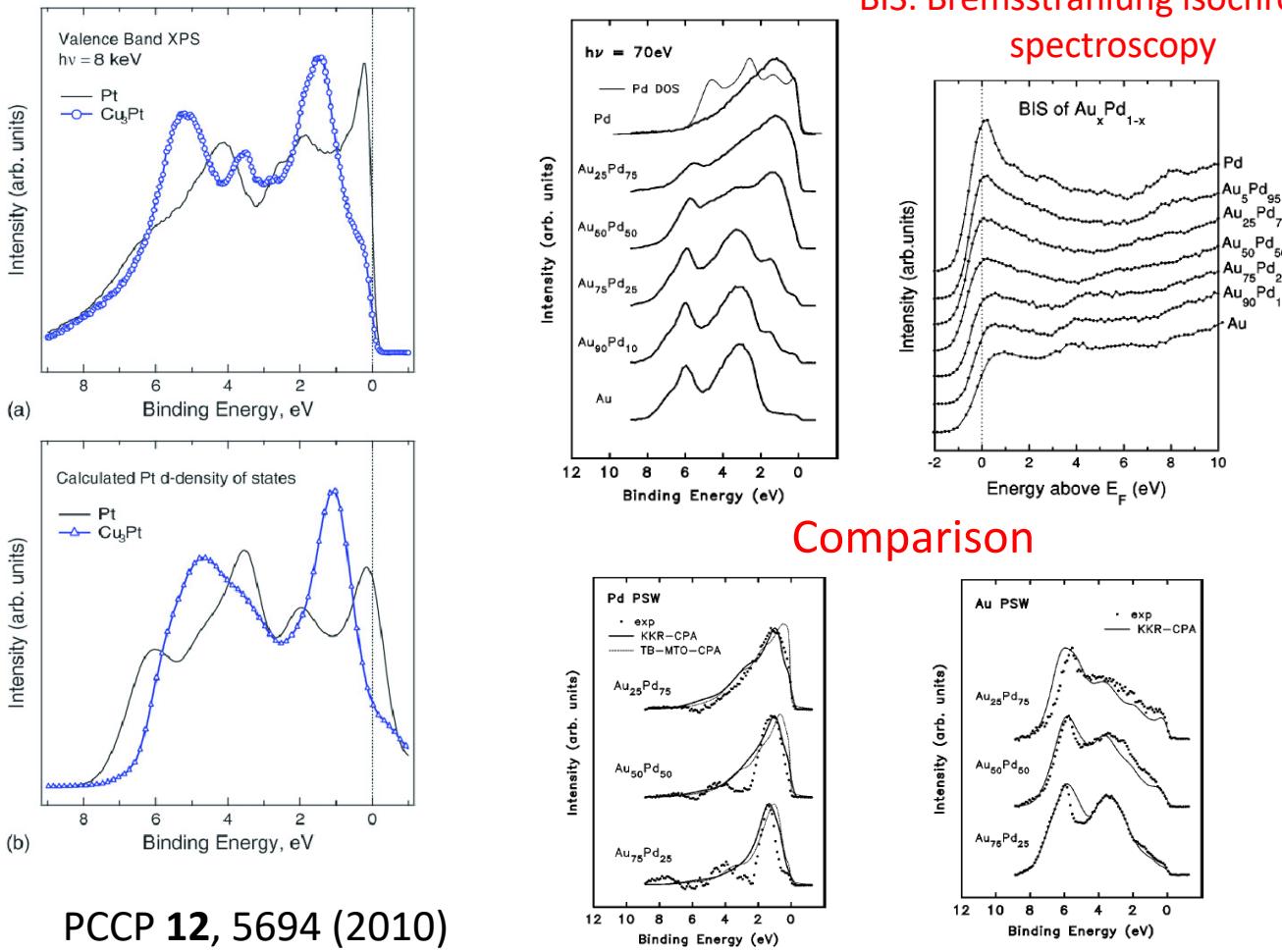
Angle resolved photoemission spectroscopy (ARPES)

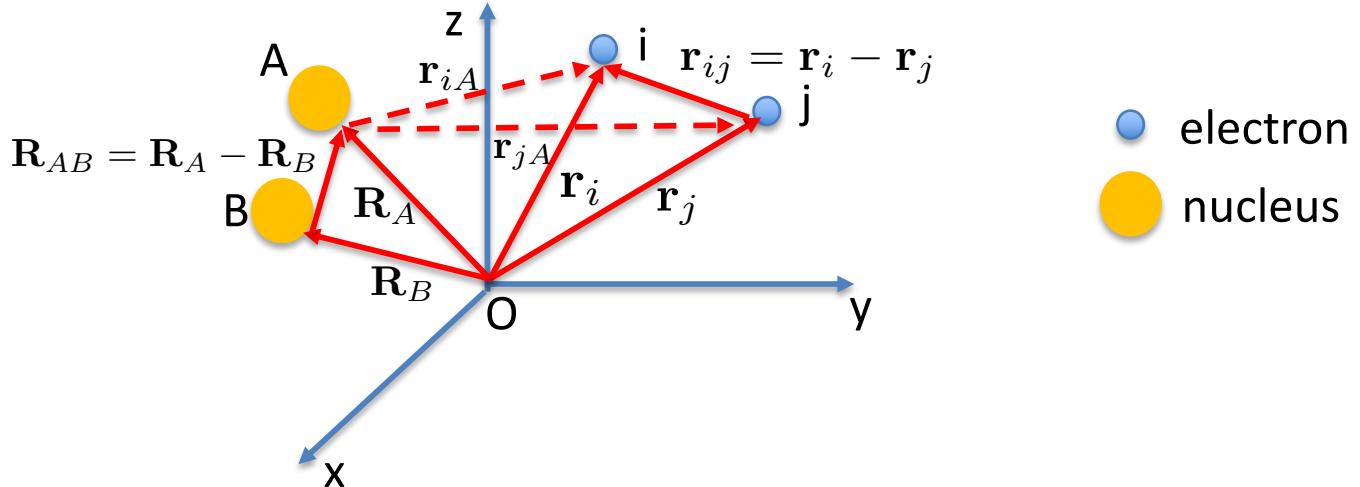
Graphene band structures (experiment & theory)



Valence band photoemission spectroscopy (VB-PES)

PRB **58**, 9817 (1998)
 BIS: Bremsstrahlung isochromat spectroscopy





Hamiltonian for a many particle system reads

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_A^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_{iA}|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\mathbf{r}_{ij}|} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_{AB}|}$$

K.E. of electrons K.E. of nuclei Electron-electron repulsion
 Electron-nucleus attraction nucleus-nucleus repulsion

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

Schroedinger equation for a many particle (N electrons, M nuclei) system reads

$$H\psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) = E_i \psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$$

Born-Oppenheimer approximation

Decouple electronic and nuclear degrees of freedom

Hamiltonian for electron system only

$$H_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_{iA}|} + \sum_i^N \sum_{j>i}^N \frac{1}{|\mathbf{r}_{ij}|}$$

Schroedinger equation for electron system only

$$H_{el} \phi_{el} = E_{el} \phi_{el}$$

The electronic wave function reads

$$\phi_{el} = \phi_{el}(\{\mathbf{r}_i\}; \{\mathbf{R}_A\})$$

The total energy becomes

$$E_{tot} = E_{el} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_{AB}|}$$

Solve the nuclear problem. As the electrons move faster, consider their average energy

$$\begin{aligned} H_{nu} &= -\frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 + \langle E_{el} \rangle + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_{AB}|} \\ &= -\frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 + E_{el}(\{\mathbf{R}_A\}) + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_{AB}|} \\ &= -\frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 + E_{tot}(\{\mathbf{R}_A\}) \end{aligned}$$

↑
Provides potential energy surface
for nuclear motion

Nuclear Schroedinger equation

$$H_{nu} \phi_{nu} = E_{nu} \phi_{nu}$$

The total wavefunction

$$\psi(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) = \phi_{el}(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) \phi_{nu}(\{\mathbf{R}_A\})$$

Linear variational problem

Expand the wavefunction by linear combination of basis functions

$$|\tilde{\psi}\rangle = \sum_{i=1}^N c_i |\phi_i\rangle$$

Basis functions are real and orthonormal

$$\langle \phi_i | \phi_j \rangle = \langle \phi_j | \phi_i \rangle = \delta_{ij}$$

Overlap matrix element

$$\begin{aligned} \langle \tilde{\psi} | \tilde{\psi} \rangle &= \sum_{ij} c_i c_j \langle \phi_i | \phi_j \rangle \\ &= \sum_{ij} c_i c_j \delta_{ij} \\ &= \sum_i c_i^2 = 1 \end{aligned}$$

Hamiltonian matrix element

$$\langle \tilde{\psi} | H | \tilde{\psi} \rangle = \sum_{ij} c_i \langle \phi_i | H | \phi_j \rangle c_j = \sum_{ij} c_i c_j H_{ij}$$

Goal: Find the set of parameters for which $\langle \tilde{\psi} | H | \tilde{\psi} \rangle$ has a minimum value

$$\frac{\partial}{\partial c_k} \langle \tilde{\psi} | H | \tilde{\psi} \rangle = 0 \quad k = 1, 2, \dots, N$$

Lagrange's method of undetermined parameters

Define a Lagrangian with a multiplier E

$$\begin{aligned}\Lambda(c_1, \dots, c_N, E) &= \langle \tilde{\psi} | H | \tilde{\psi} \rangle - E(\langle \tilde{\psi} | \tilde{\psi} \rangle - 1) \\ &= \sum_{ij} c_i c_j H_{ij} - E \left(\sum_i c_i^2 - 1 \right)\end{aligned}$$

The minimum of both Λ and $\langle \tilde{\psi} | H | \tilde{\psi} \rangle$ occurs for the same values of the coefficients

$$\frac{\partial \Lambda}{\partial c_k} = 0 \quad \text{for } k = 1, 2, \dots, N$$

Evaluate above and get

$$\sum_j c_j H_{kj} + \sum_i c_i H_{ik} - 2E c_k = 0$$

$$\text{As } H_{ij} = H_{ji}$$

$$\sum_j H_{ij} c_j - E c_i = 0$$

In matrix notation,

$$\underline{Hc} = E\underline{c}$$

Solve to obtain eigenvalues and eigenvectors