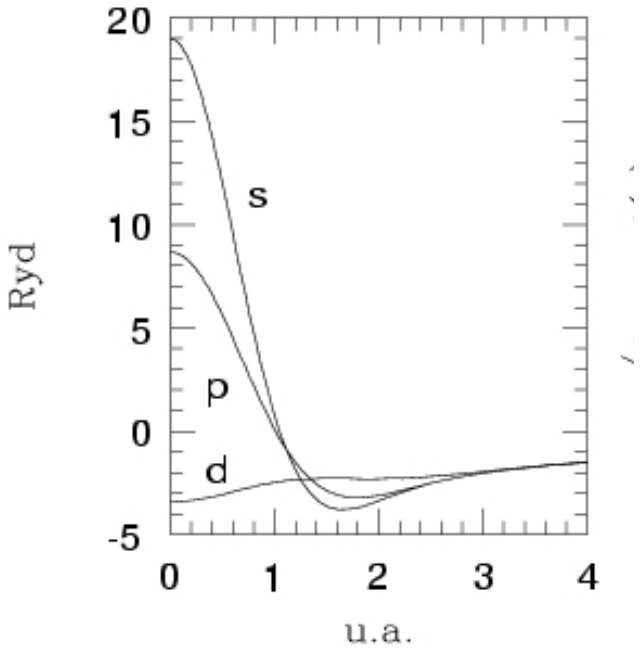
3.320: Lecture 9 (Mar 3 2005)

SUCCESS AND FAILURE

Photos of soccer players removed for copyright reasons.

Pseudopotentials



Occupation, Eigenvalue

3p	1	-2.7 eV	Valence	2p	1	-2.7 eV	
3s	2	-7.8 eV		1s	2	-7.8 eV	

Al
Z =13

2p	6	-69.8 eV
2s	2	-108 eV
1s	2	-1512 eV

Core-states

Pseudo- Al
Z =3

$$\left(-\frac{1}{2}\nabla^2+\upsilon_{eff}\right)\psi_j=\varepsilon_j\psi_j$$

$$\left(-\frac{1}{2}\nabla^2+\upsilon_{eff}^{(ps)}\right)\psi_j^{(ps)}=\varepsilon_j\psi_j^{(ps)}$$

Figure by MIT OCW.

After Pehlke, Eckhard. Lecture on "The Plane-Wave Pseudopotential Method."

Bloch Theorem

$$\psi_{n\vec{k}}(\vec{r}) \quad u_{n\vec{k}}(\vec{r}) \exp\left(i\vec{k}\cdot\vec{r}\right)$$

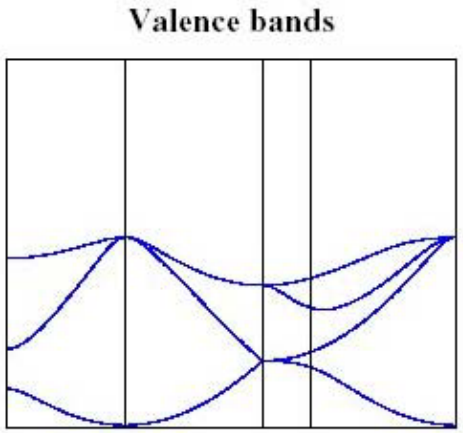
periodic *u* is expanded in planewaves, labeled according to the reciprocal lattice vectors

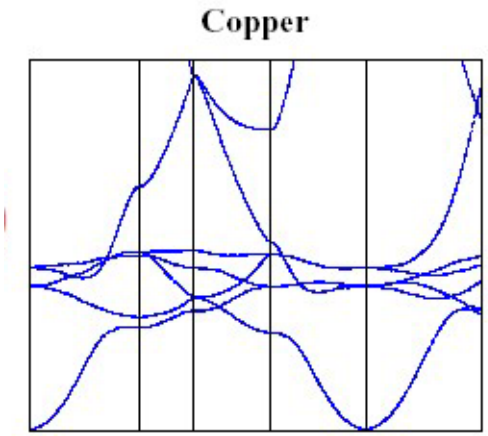
$$u_{n\vec{k}}(\vec{r}) \quad \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$

Other possibilities - many

- Gaussian basis sets (Hartree-Fock codes)
- Real space representations
- LCAO (Linear combination of atomic orbitals)
- LMTO (Linear muffin-tin orbitals), LAPW (Linearized augmented plane waves), PAW (Projector-augmented wave)

Brillouin Zone integrations





- Sampling at one point (the best – Baldereschi point, or the simplest – Gamma point)
- Sampling at regular meshes (Monkhorst-Pack grids)
- For metallic systems, integration of the discontinuity is improved introducing a fictitious electronic temperature

Iterations to Selfconsistency

- Construct the external potential (array of non-local psp)
- Choose the plane-wave basis set cutoff, k-point sampling

- Pick a trial electronic density
- Construct the Hamiltonian operator: Hartree and exchange-correlation
- Solve Kohn-Sham equations for the given Hamiltonian (e.g. by diagonalization)
- Calculate the new charge density
- Iterate

Self-consistent ground state

- Iterative diagonalizations (Davidson, Lancsoz, non-scf conjugate gradients + mixing strategy)

$$\hat{H}^{\left[n(\vec{r})\right]}\psi(\vec{r}) \quad E\psi(\vec{r})$$

- Direct minimization (Car-Parrinello, conjugate gradients)

Matrix Diagonalization

$$\hat{H}^{\left[n(\vec{r})\right]}\psi(\vec{r}) \quad E\psi(\vec{r}) \qquad |\psi\rangle \quad \sum_{n\ 1,k} c_n |\varphi_n\rangle$$

$$\sum_{n\ 1,k} c_n \langle \varphi_m | \hat{H} | \varphi_n \rangle \quad Ec_m$$

$$\begin{pmatrix} H_{11} & \cdots\cdots & H_{1k} \\ \vdots & & \vdots \\ H_{k1} & \cdots\cdots & H_{kk} \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix}$$

Constrained non-linear minimization

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^{\star}(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\, d\mathbf{r} + E_H[n(\mathbf{r})] + \\ + E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})\, d\mathbf{r}$$

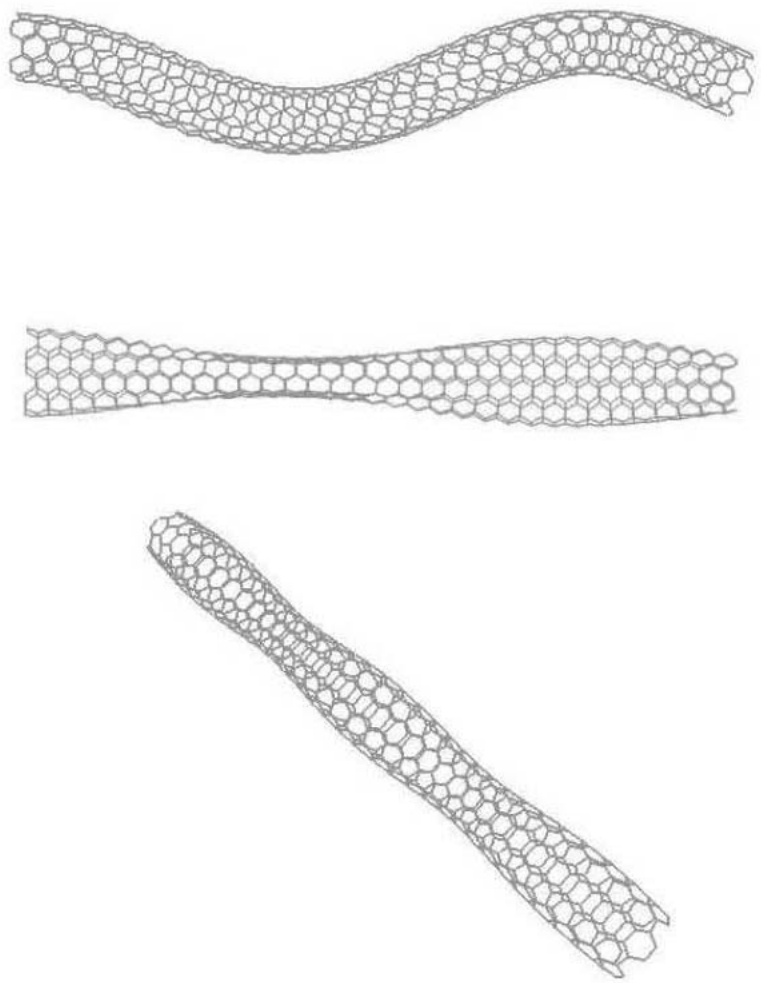
$$E_H[n(\vec{r})] \quad \frac{1}{2}\iint \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1\, d\vec{r}_2$$

Constrained non-linear minimization

Practice and Outlook

- Techniques and applications (from k-points to DNA and superconductivity)
- Beyond GGA: WDA, TDDFT, QMC
- Connection to approximate methods

Phonons



Phonon Dispersions (Linear Response Theory)

• Exp. neutron scattering data (J.L. Warren et al, Phys. Rev. 158, 805 - 1967)

— Our GGA results

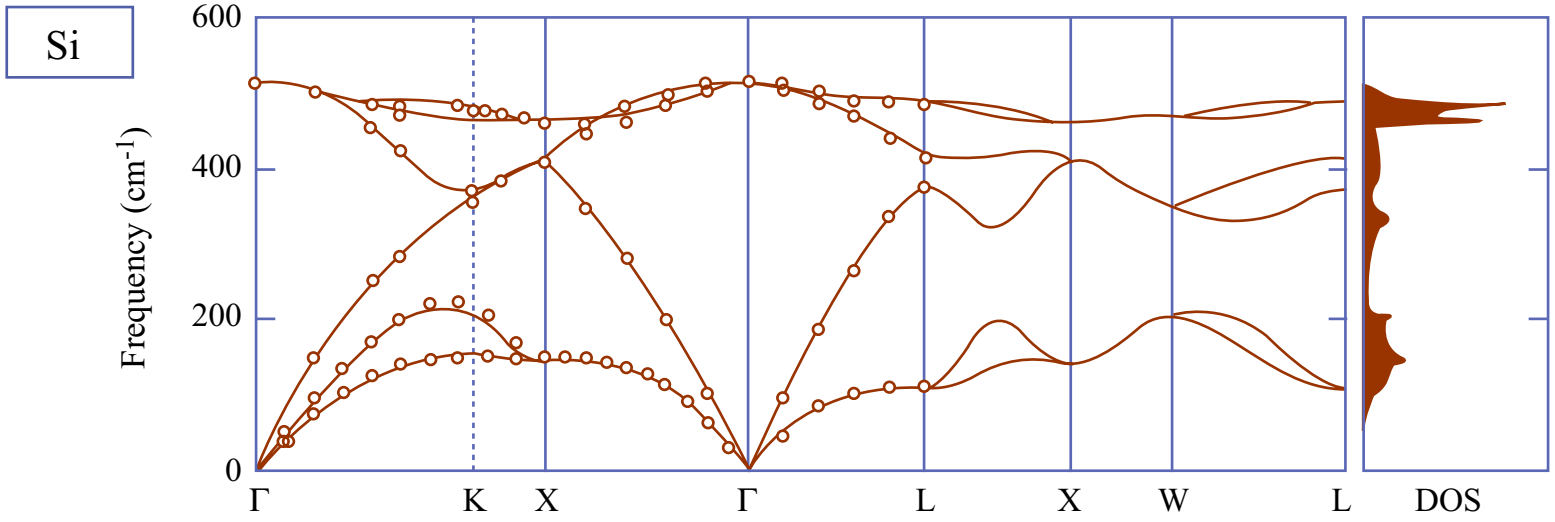


Figure by MIT OCW.

Thermodynamical Properties (Vibrational Free Energy)

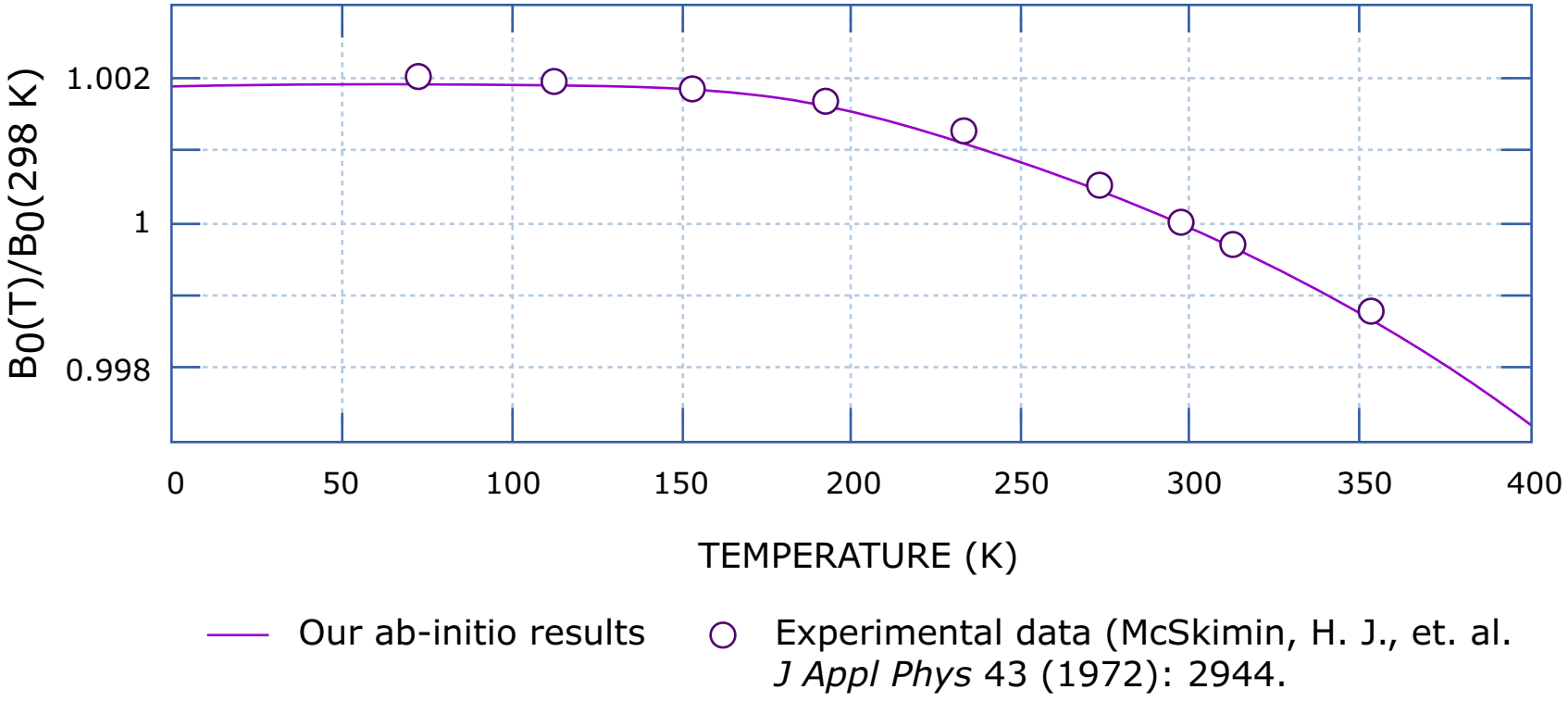
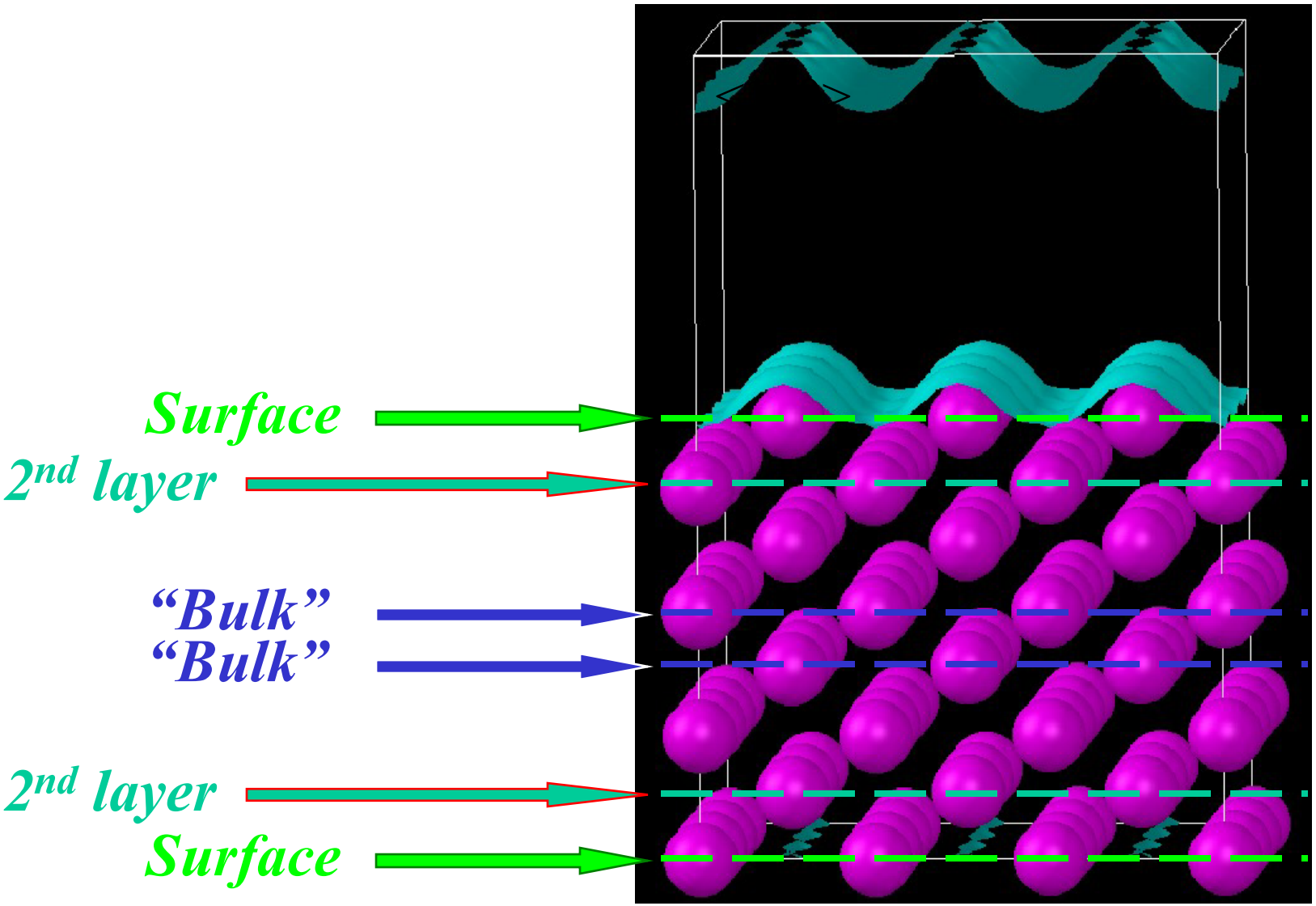


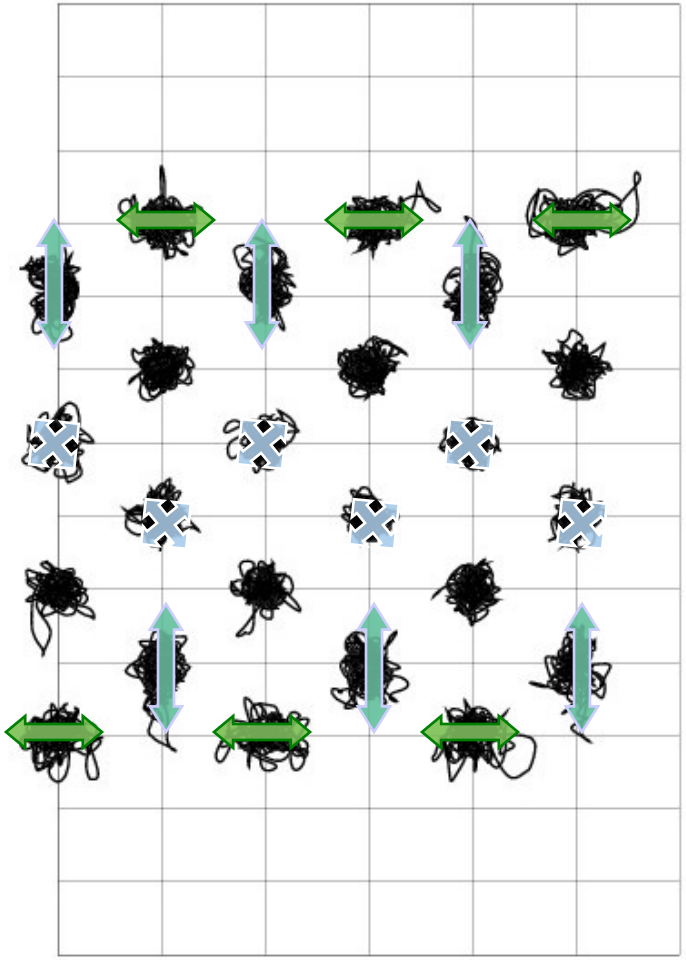
Figure by MIT OCW.

Ab-initio results compared to experimental data of H.J. McSkimin et al., J. Appl. Phys. 43, 2944 -1972.

Dynamics in Al(110)



Al(110) Mean Square Displacements



Computational LEED

Graph removed for copyright reasons.
Interlayer relaxation vs. Temperature (K).
Source: Marzari, N., et al. "Thermal contraction and disordering of the Al(110) surface." *Physical Review Letters* 82, no.16 (1999): pp.3296-9.

References (theory)

- W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*
- R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*
- W. Kohn, *Nobel lecture*
- F. Jensen, *Introduction to Computational Chemistry*
- J. M. Thijssen, *Computational Physics*
- B. H. Bransden and C. J. Joachim, *Physics of Atoms and Molecules*
- K. Burke: *The ABC of DFT,* http://dft.rutgers.edu/kieron/beta/

References (practice)

- Payne, Teter, Allan, Arias, Joannopoulos, *Review of Modern Physics* **64**, 1045 (1992).
- Lecture notes from

  http://www.FHI-Berlin.MPG.DE/th/Meetings/FHImd2001/program.html ,

  (L3 Pehlke, L2 Kratzer, L4 Fuchs)
- Hartree-Fock for solids, Dovesi *et al.*, *Physica Status Solidi (b)* **217**, 63 (2000).

Software

- Gaussian (http://www.gaussian.com) ($$) (chemistry, Hartree-Fock, DFT, correlated approaches)
- Gamess-UK (http://www.cse.clrc.ac.uk/qcg/gamess-uk/) ($) (chemistry, Hartree-Fock, DFT, correlated approaches)

- Materials Studio/Cerius (http://www.accelrys.com) ($$) (DFT, planewave, ultrasoft)
- Crystal (http://www.chimifm.unito.it/teorica/crystal) ($) (Hartree-Fock)
- VASP (http://cms.mpi.univie.ac.at/vasp) ($) (DFT, planewave, ultrasoft, PAW)

- ESPRESSO (http://www.pwscf.org) (free) (DFT, planewave, ultrasoft, linear-response theory, Car-Parrinello)
- ABINIT (http://www.abinit.org) (free) (DFT, planewave, linear-response theory, GW)
- CPMD (http://www.cpmd.org) (free) (DFT, planewave, Car-Parrinello, time-dependent DFT)

- CASINO (http://www.tcm.phy.cam.ac.uk/~mdt26/cqmc.html) (free) (Quantum Monte Carlo)