

3.320: Lecture 8 (Mar 1 2005)

DENSITY-FUNCTIONAL PRACTICE

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Two panels of a Calvin and Hobbes comic.

Calvin: "Problems often look overwhelming at first...

The secret is to break problems into small manageable chunks.

If you deal with those, you're done before you know it."

Second Hohenberg-Kohn theorem

The variational principle – we have a *new Schrödinger's-like equation*, expressed in terms of the charge density only

$$E_v[n'(\vec{r})] = F[n'(\vec{r})] + \int v_{ext}(\vec{r})n'(\vec{r})d\vec{r} \geq E_0$$

Electronic Total Energy

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

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

The Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \hat{H}_{KS} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2.$$

GGAs, meta-GGA, hybrids

- GGAs: generalized gradient approximations (gradients of the density are introduced, preserving analytical – scaling – features of the unknown exact xc functional. BP88, PW91, PBE...)
- Hybrids: a certain amount of non-local Hartree-Fock exchange is weighed in (B3LYP, PBE0PBE...)

It works !

Material	Expt	Theory	Delta	Type
LaBi	6.57	6.648	1.2%	alloy
CaF ₂	5.4626	5.496	0.6%	halide
Ag	4.086	4.112	0.6%	metal
V	3.028	3.019	-0.3%	metal
ZrN	4.62	4.634	0.3%	misc
NbO	4.2103	4.2344	0.6%	oxide
GaAs	5.653	5.663	0.2%	semiconductor
CoSi ₂	5.36	5.3	-1.1%	silicide

Courtesy of Chris Pickard. Used with permission.

C. J. Pickard 2002

Density-functional theory in practice: the total-energy pseudopotential method

1. Remove tightly bound core electrons: the pseudopotential approach
2. Represent orbitals on a basis (plane waves)
3. Calculate total energy for trial orbitals
 - Kinetic, hartree energy in reciprocal space
 - Exchange-correlation, ext. pot. in real space
 - FFTs !
 - Sum over all states: BZ integrations
4. Iterate or minimize to self-consistency

Pseudopotentials (I)

- Electrons in the inner shells do not contribute to valence bonding – so they are frozen in the state they have in an isolated atom
- Releasing the frozen core does not add any linear term to the energy (von Barth and Gelatt, 1980)

Pseudopotentials (II)

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] Core-states
2s	—	2	-108 eV	
1s	—	2	-1512 eV	

Pseudo-Al
Z = 3

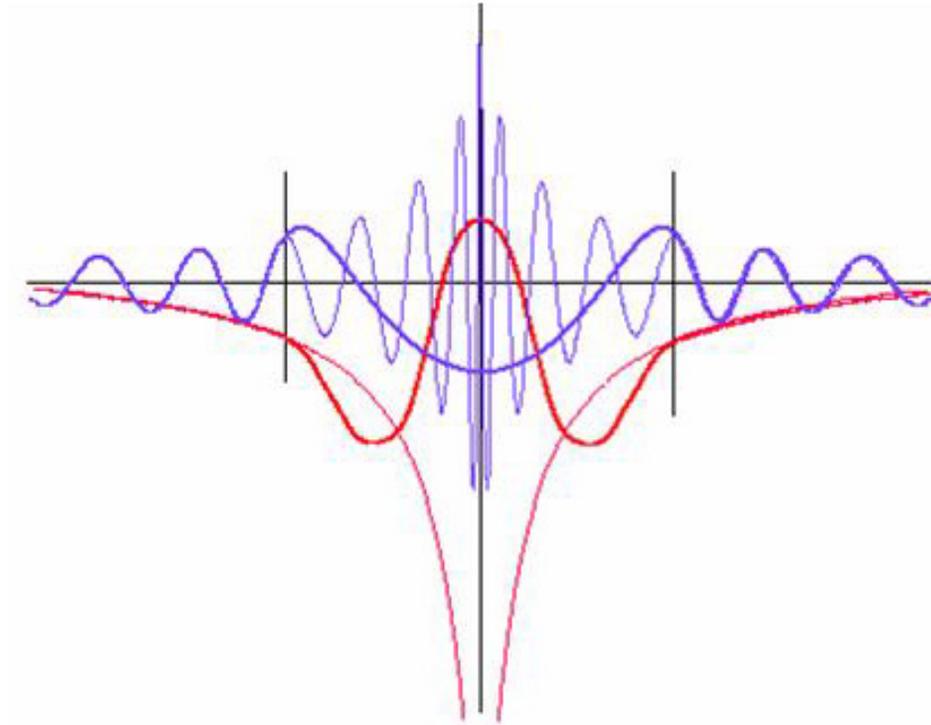
$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}\right) \psi_j = \epsilon_j \psi_j$$

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{(\text{ps})}\right) \psi_j^{(\text{ps})} = \epsilon_j \psi_j^{(\text{ps})}$$

Figure by MIT OCW.

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

Pseudopotentials (III)



A schematic representation of the potentials (red lines) and wavefunctions (blue lines) for an atom. The real potential and wavefunction are shown with thin lines, while pseudopotential and wavefunction are shown in thick lines. Outside the cutoff region (vertical black lines) the two are identical.

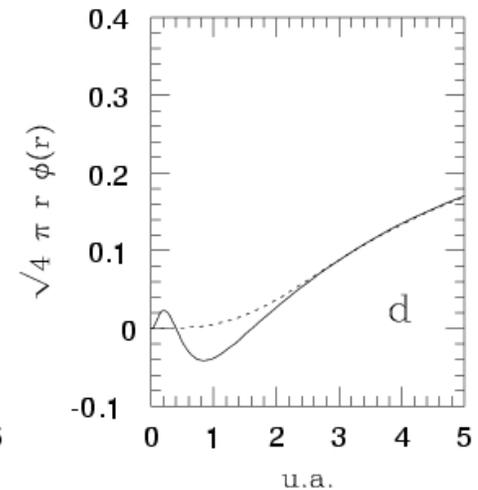
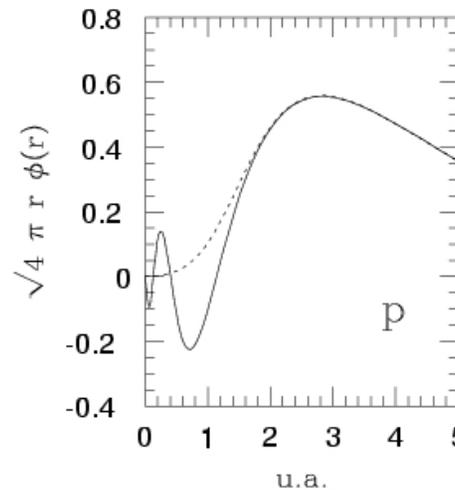
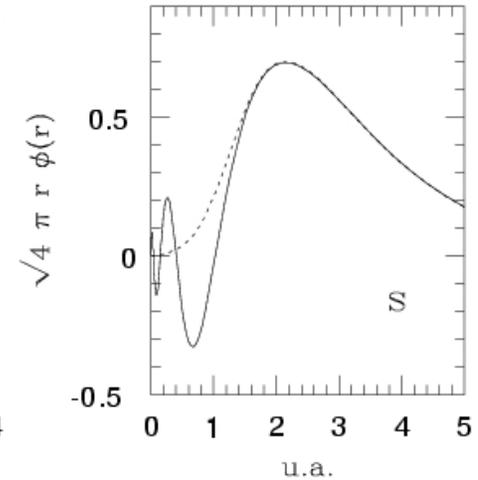
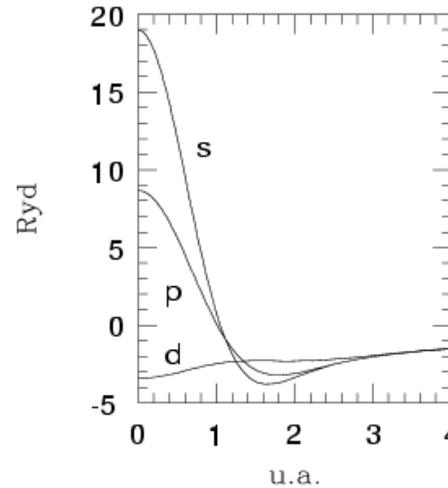
Courtesy of Chris Goringe. Used with permission.

Are you local ?

Different **angular momenta** scatter differently from the core (states that have shell below them with same angular momentum are repelled more)



Non-local PP



Back to the one-electron problem

- How do we solve the set of one-particle differential equations that come from Hartree, Hartree-Fock, or Density-Functional theory ?

$$\left[-\frac{1}{2} \nabla^2 + \sum_I V(\vec{R}_I - \vec{r}) + \text{Mean Field Term} \right] \varphi(\vec{r}) = \varepsilon \varphi(\vec{r})$$

Solution: expansion in a basis

$$\varphi(\vec{r}) = \sum_{n=1,k} c_n f_n(\vec{r})$$

Two graphs removed for copyright reasons.

What choice for a basis ?

- For molecules: often atomic orbitals, or localized functions as Gaussians
- For solids, periodic functions such as sines and cosines (plane waves)

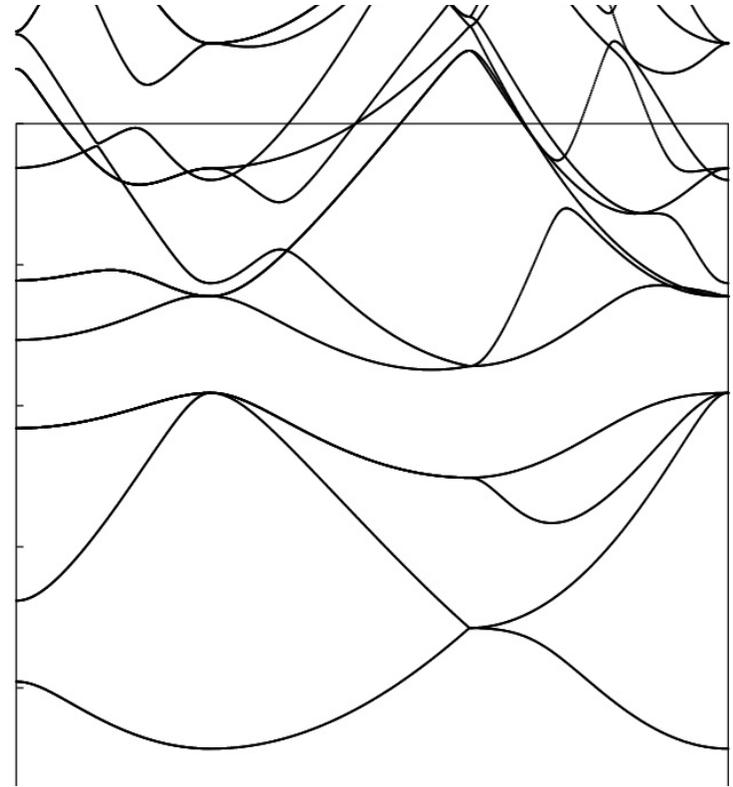
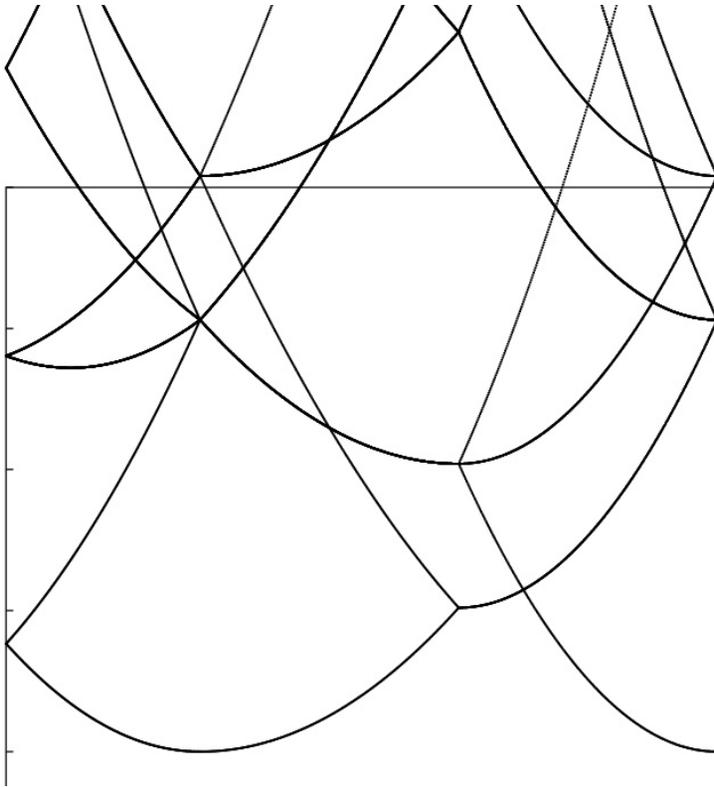
Bloch Theorem

The one-particle effective Hamiltonian \hat{H} in a periodic lattice commutes with the lattice-translation operator $\hat{T}_{\mathbf{R}}$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

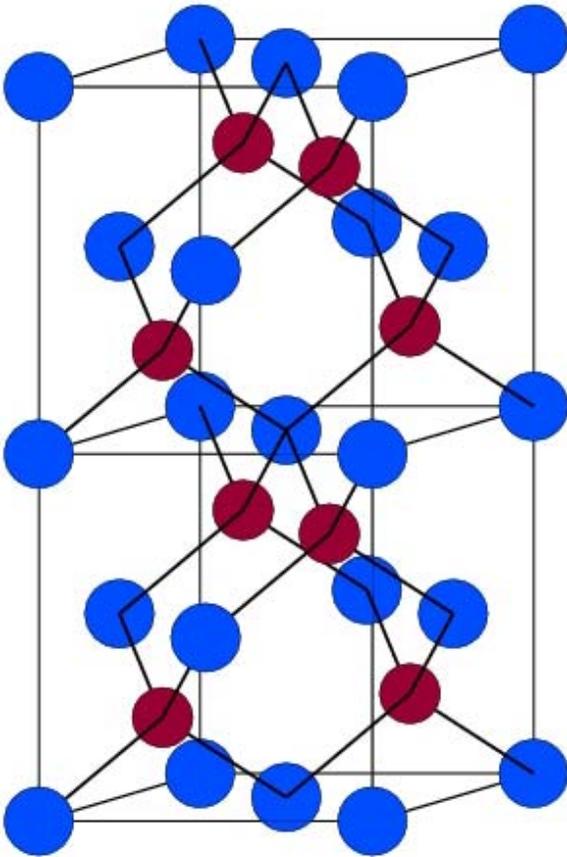
$$[\hat{H}, \hat{T}_{\mathbf{R}}] = 0 \Rightarrow \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

- n, k are the quantum numbers (band index and crystal momentum), u is periodic
- From two requirements: a translation can't change the charge density, and two translations must be equivalent to one that is the sum of the two

Band Structures: Free Electron Gas, Silicon



Direct (Real) and Reciprocal Space



$$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

Plane wave expansion

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

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

The plane waves basis set

- Systematic improvement of completeness/resolution
- Huge number of basis elements – only possible because of pseudopotentials
- Allows for easy evaluation of gradients and Laplacian
- Kinetic energy in reciprocal space, potential in real space
- Basis set does not depend on atomic positions: there are no Pulay terms in the forces

Examples: Poisson equation

Other possibilities - many

- Gaussian basis sets (Hartree-Fock codes)
- Real space representations
- LCAO
- LMTO, LAPW, PAW

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/FHIImd2001/program.html> ,
(L3 Pehlke, L2 Kratzer, L4 Fuchs)
- Hartree-Fock for solids, Dovesi *et al.*, *Physica Status Solidi (b)* **217**, 63 (2000).

References (practice)

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