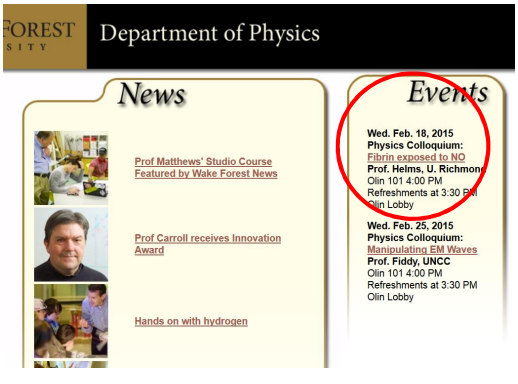
PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 15:
Reading: Chapter 10 in MPM
Numerical Realizations of Density functional theory

1. **Electronic structure of atoms**
2. **Integration of the radial equations**
3. **Frozen core approximation**
4. **Extension of formalism to multi-center analysis**

	Lecture date	MPM Reading	Topic	Assign.	Due date
1	Mon: 01/12/2015	Chap. 1 & 2	Crystal structures	#1	01/23/2015
2	Wed: 01/14/2015	Chap. 1 & 2	Some group theory	#2	01/23/2015
	Fri: 01/16/2015	No class	NAWH out of town		
	Mon: 01/19/2015	No class	MLK Holiday		
3	Wed: 01/21/2015	Chap. 1 & 2	Some group theory	#3	01/23/2015
4	Fri: 01/23/2015	Chap. 1 & 2	Some more group theory	#4	01/26/2015
5	Mon: 01/26/2015	Chap. 7.3	Some more group theory	#5	01/28/2015
6	Wed: 01/28/2015	Chap. 6	Electronic structure; Free electron gas	#6	01/30/2015
7	Fri: 01/30/2015	Chap. 7	Electronic structure; Model potentials	#7	02/02/2015
8	Mon: 02/02/2015	Chap. 8	Electronic structure; LCAO	#8	02/04/2015
9	Wed: 02/04/2015	Chap. 8	Electronic structure; LCAO and tight binding	#9	02/06/2015
10	Fri: 02/06/2015	Chap. 8	Band structure examples	#10	02/09/2015
11	Mon: 02/09/2015	Chap. 9	Electron-electron interactions	#11	02/11/2015
12	Wed: 02/11/2015	Chap. 9	Electron-electron interactions	#12	02/13/2015
13	Fri: 02/13/2015	Chap. 9	Electron-electron interactions	#13	02/16/2015
14	Mon: 02/16/2015	Chap. 10	Electronic structure calculation methods	#14	02/18/2015
15	Wed: 02/18/2015	Chap. 10	Electronic structure calculation methods	#15	02/20/2015
16	Fri: 02/20/2015	Chap. 10	Electronic structure calculation methods	#16	02/23/2015

Note: Take-home exam scheduled for the week of March 2nd.



WFU Physics Colloquium

TITLE: Structural and Mechanical Properties of Fibrin Exposed to Nitric Oxide

SPEAKER: Dr. Christine Helms,

Department of Physics
University of Richmond

TIME: Wednesday February 18, 2015 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

Fibrin fibers are a major component of blood clots, which perform the mechanical and structural task of stemming the flow of blood. Therefore mechanical and structural properties of clots and their constituent fibrin fibers are important for understanding and

Kohn-Sham equations for spherical atom

Equations in Rydberg units

$$\left(-\left(\frac{d^2}{dr^2}-\frac{l_i(l_i+1)}{r^2}\right)+V_{ee}(r)+V_{exc}(r)+v(r)\right)P_{n_i l_i}(r)=\epsilon_{n_i l_i}P_{n_i l_i}(r)$$

$$V_{ee}(r)=\frac{\delta E_{ee}[n]}{\delta n}=2\left(\frac{1}{r}\int_0^r r'^2\,dr'n(r')+\int_r^\infty r'\,dr'n(r')\right)$$

$$V_{exc}(r)=\frac{\delta E_{exc}[n]}{\delta n}=-\frac{2}{\pi}\left(3\pi^2\right)^{1/3}n(r)^{1/3}+V_c(r)$$

$$V_{ext}(r)=\frac{\delta E_{ext}[n]}{\delta n}=v(r)=-\frac{2Z}{r}$$

Numerical methods for solving the Kohn-Sham equations

Self-consistent solution

Iteration $\alpha=0$

$$\left\{\phi_i^\alpha(\mathbf{r})\right\}$$

$$n^\alpha(\mathbf{r})=\sum_i\left|\phi_i^\alpha(\mathbf{r})\right|^2$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V^\alpha{}_{ee}(\mathbf{r})+V^\alpha{}_{ex}(\mathbf{r})+v(\mathbf{r})\right)\phi_i^{\alpha+1}(\mathbf{r})=\epsilon_i\phi_i^{\alpha+1}(\mathbf{r})$$

$$n_{temp}^{\alpha+1}(\mathbf{r})=\sum_i\left|\phi_i^{\alpha+1}(\mathbf{r})\right|^2$$

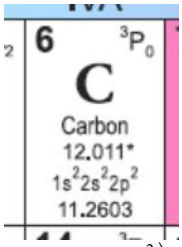
$$n^{\alpha+1}(\mathbf{r})=xn_{temp}^{\alpha+1}(\mathbf{r})+(1-x)n^{\backslash\text{alpha}}(\mathbf{r})$$

$\alpha+1\Rightarrow\alpha$

For spherically symmetric atom:

$$\phi_{n_i l_i m_i}(\mathbf{r}) = \phi_{n_i l_i}(r) Y_{l_i m_i}(\hat{\mathbf{r}})$$

$$\phi_{n_i l_i}(r) = \frac{P_{n_i l_i}(r)}{r}$$



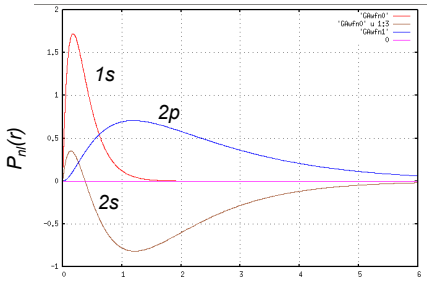
Example for carbon

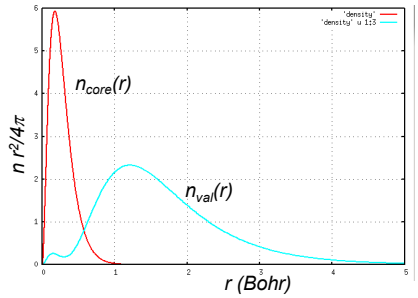
$$n(r) = \sum_i w_{n_i l_i} \left|\phi_{n_i l_i}(r)\right|^2$$

$$= 4\pi\left(2\left|\phi_{1s}(r)\right|^2 + 2\left|\phi_{2s}(r)\right|^2 + 2\left|\phi_{2p}(r)\right|^2\right)$$

$$= \frac{4\pi}{r^2}\left(2\left|P_{1s}(r)\right|^2 + 2\left|P_{2s}(r)\right|^2 + 2\left|P_{2p}(r)\right|^2\right)$$

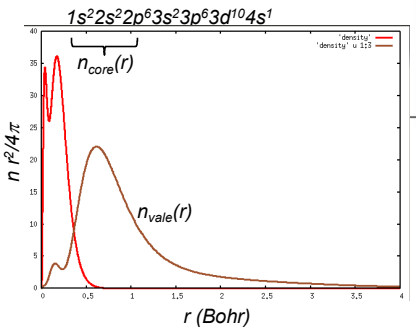
Results for carbon

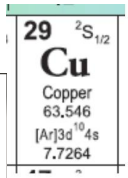




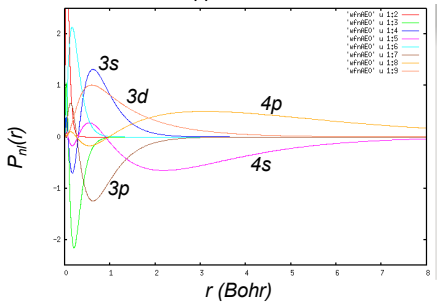
Example for Cu

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$





Results for Copper



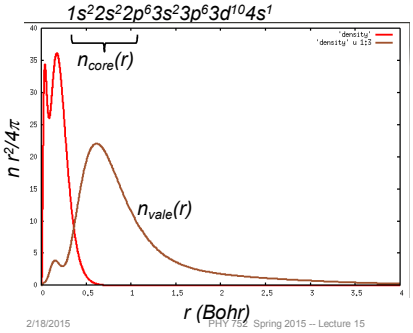
Frozen core approximation

$$n(r) = n_{\text{core}}(r) + n_{\text{vale}}(r)$$

Example for Cu

Variationally optimize energy wrt $n_{\text{vale}}(r)$

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$



Systematic study of frozen core approximation in DFT

PHYSICAL REVIEW B VOLUME 21, NUMBER 6 15 MARCH 1980

Validity of the frozen-core approximation and pseudopotential theory for cohesive energy calculations

U. von Barth
Department of Theoretical Physics, University of Lund, Lund, Sweden

C. D. Gelatt*
Physics Department, Harvard University, Cambridge, Massachusetts 02138
(Received 8 January 1979)

When atoms are brought together to form molecules or solids the change in the kinetic energy of the core electrons can be an order of magnitude larger than the change in total energy. In spite of this, pseudopotential methods, which neglect the redistribution of the core electrons, give results very close to the fully self-consistent results. We explain this apparent contradiction by showing that the correction to the frozen-core approximation, an approximation used implicitly in a pseudopotential calculation, vanishes to first order in the charge-density differences and we give a closed formula for the second-order correction. The cancellation of large errors involved in the frozen-core approximation is demonstrated for valence-electron configuration changes in several free atoms and for a bcc to fcc transformation of Mo. In all cases the frozen-core approximation makes an error of less than 5% in the energy of transformation, and the second-order correction formula accurately reproduces this error.

http://journals.aps.org/prb/abstract/10.1103/PhysRevB.21.2222

Variational relations for DFT in frozencore approximation (Kohn-Sham formulation)

$$E_v[n] = T + E_{ext}[n] + E_{ee}[n] + E_{exc}[n]$$

$$T = T^{\text{core}} + T^{\text{vale}}$$

$$E_{ext}[n] \equiv \int d^3r\ v(\mathbf{r})\Big(\ n^{\text{core}}(\mathbf{r}) + n^{\text{vale}}(\mathbf{r})\Big)$$

$$E_{ee} = \frac{e^2}{2}\int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = E_{ee}^{\text{core-core}} + E_{ee}^{\text{core-vale}} + E_{ee}^{\text{vale-vale}}$$

$$E_{exc}[n] = E_{exc}[n^{\text{core}} + {}^{\text{vale}}]$$

Practical solution to Kohn-Sham equations for single particle orbitals:

For $n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$

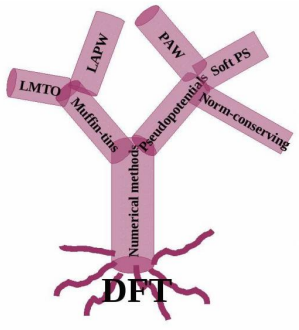
Equations for orbitals $\phi_i(\mathbf{r})$:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Numerical problem: near each nuclear center --

$$V(\mathbf{r}) \approx -\frac{Z^a e^2}{|\mathbf{r}-\mathbf{R}^a|}$$

Practical solution of Kohn-Sham equations in solids



Muffin tin potential construction

MAY 15, 1937 PHYSICAL REVIEW VOLUME 51

Wave Functions in a Periodic Potential

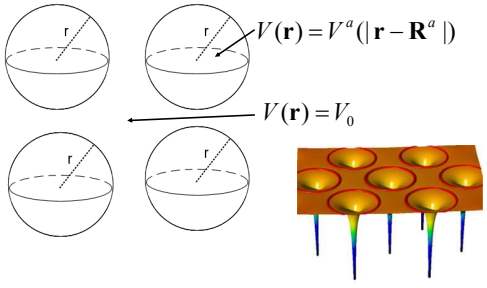
J. C. Slater*
Institute for Advanced Study, Princeton, New Jersey
(Received March 24, 1937)

A new method for approximating the solutions of the problem of the motion of an electron in a periodic potential, as a crystal lattice, is suggested. The potential is supposed to be spherically symmetrical within spheres surrounding the atoms, constant outside. The wave function is expanded in spherical harmonics and radial solutions of the wave equation within the spheres, and in plane waves outside the spheres, joining continuously at the surface. A single unperturbed function consists of a single plane wave outside the spheres, together with the necessary spherical functions within the spheres. The matrix components of energy are set up between these unperturbed functions, and the secular equation set up. This equation involves the energy explicitly, and also implicitly through the ratio of the slope of the various radial functions to the functions themselves at the surfaces of the spheres, and must be solved numerically. It is hoped that the method will be useful for comparatively low energy excited electrons, for which the usual method of expansion in plane waves converges too slowly.

http://journals.aps.org/pr/abstract/10.1103/PhysRev.51.846

Augmented Plane Wave (APW) approximation

Muffin tin potential construction



http://www.jara.org/de/research/jara-hpc/forschung/details/simlab-ai/performance-modeling-for-linear-algebra-in-fleur/

Muffin tin model continued:

$$V(\mathbf{r}) = \begin{cases} V^a(|\mathbf{r}-\mathbf{R}^a|) & \text{for } |\mathbf{r}-\mathbf{R}^a| \le \mathscr{R}^a \\ V_0 & \text{otherwise} \end{cases}$$

Problems with APW and KKR Green's function schemes

1. Difficult numerically to find Kohn-Sham energies ε_i
2. Potential form unrealistic especially for covalent materials

➔Linearized equations – O. K. Andersen

http://journals.aps.org/prb/abstract/10.1103/PhysRevB.12.3060

PHYSICAL REVIEW B VOLUME 12, NUMBER 8 15 OCTOBER 1975

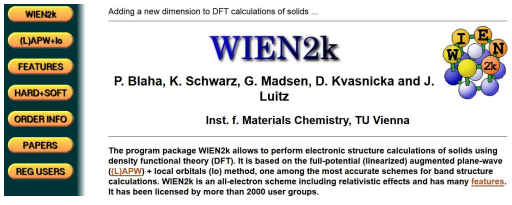
Linear methods in band theory*

O. Krogh Andersen
Department of Electrophysics, Technical University, Lyngby, Denmark
(Received 14 April 1975)

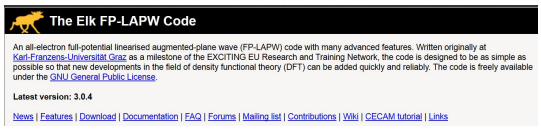
Two approximate methods for solving the band-structure problem in an efficient and physically transparent way are presented and discussed in detail. The variational principle for the one-electron Hamiltonian is used in both schemes, and the trial functions are linear combinations of energy-independent augmented plane waves (APW) and muffin-tin orbitals (MTO), respectively. The secular equations are therefore eigenvalue equations, linear in energy. The trial functions are defined with respect to a muffin-tin (MT) potential and the energy bands depend on the potential in the spheres through potential parameters which describe the energy dependence of the logarithmic derivatives. Inside the spheres, the energy-independent APW is that linear combination of an exact solution, at the arbitrary but fixed energy E_ν, and its energy derivative which matches continuously and differentiably onto the plane-wave part in the interstitial region. The energies obtained with the linear-APW method for the MT potential have errors of order $(E-E_\nu)^4$. Similarly, the energy-independent MTO is that linear combination which matches onto that solution of the Laplace equation in the interstitial region which is regular at infinity. The energies obtained with the linear-MTO method have additional errors of order $(E-V_{\mathrm{mtz}})^2$, arising from the interstitial region where the potential is V_{mtz}. The linear-APW (LAPW) method combines desirable features of the APW and OPW methods; it can treat d bands, the energy dependence of its pseudopotential is linear and, owing to the smoothness of the energy-independent APW at the spheres, non-MT contributions to the potential are included principally through their Fourier components. The linear-MTO (LMTO) method is particularly suited for closely packed structures and it combines desirable features of Korringa-Kohn-Rostoker, linear-combination-of-atomic-orbitals, and cellular methods; the secular matrix is linear in energy, the overlap integrals factorize as potential parameters and structure constants, the latter are canonical in the sense that they neither depend on the energy nor the cell volume and they specify the boundary conditions on a single MT or atomic sphere in the most convenient way. This method is very well suited for self-consistent calculations. The empty-lattice test is applied to the linear-MTO method and the free-electron energy bands are accurately reproduced. Finally, it is shown how relativistic effects may be included in both the LAPW and LMTO methods.

Modern software based on LAPW method --

http://www.wien2k.at/



http://elk.sourceforge.net/



http://exciting-code.org/

The exciting Code

exciting is a full-potential all-electron density-functional-theory package implementing the families of linearized augmented planewave methods. It can be applied to all kinds of materials, irrespective of the atomic species involved, and also allows for exploring the physics of core electrons. A particular focus are excited states within many-body perturbation theory.