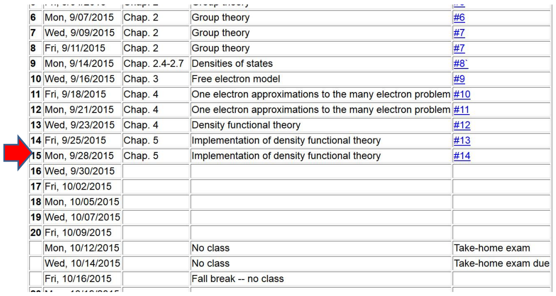
PHY 752 Solid State Physics
11-11:50 AM MWF Olin 1073
Plan for Lecture 15:
Reading: Chapter 5 in GGGPP
Numerical Realizations of Density functional theory

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



6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8`
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015	Chap. 4	One electron approximations to the many electron problem	#10
12	Mon, 9/21/2015	Chap. 4	One electron approximations to the many electron problem	#11
13	Wed, 9/23/2015	Chap. 4	Density functional theory	#12
14	Fri, 9/25/2015	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015	Chap. 5	Implementation of density functional theory	#14
16	Wed, 9/30/2015			
17	Fri, 10/02/2015			
18	Mon, 10/05/2015			
19	Wed, 10/07/2015			
20	Fri, 10/09/2015			
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Take-home exam due
	Fri, 10/16/2015		Fall break -- no class	

Kohn-Sham equations for spherical atom

Equations in Rydberg units

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

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

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

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

Numerical methods for solving the Kohn-Sham equations

Self-consistent solution

$$\text{Iteration } \alpha = 0$$

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

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

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

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

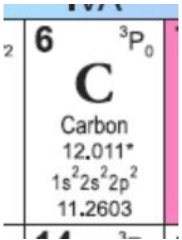
$$n^{\alpha+1}(\mathbf{r}) = x n_{temp}^{\alpha+1}(\mathbf{r}) + (1-x) n^{\backslash\mathrm{alpha}}(\mathbf{r})$$

$$\alpha + 1 \Rightarrow \alpha$$

For spherically symmetric atom:

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

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



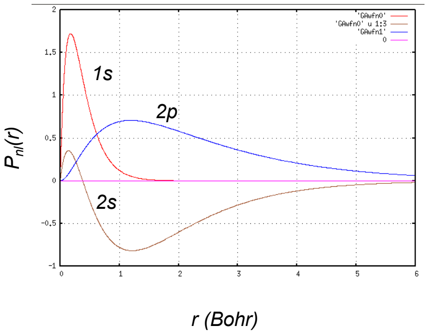
Example for carbon

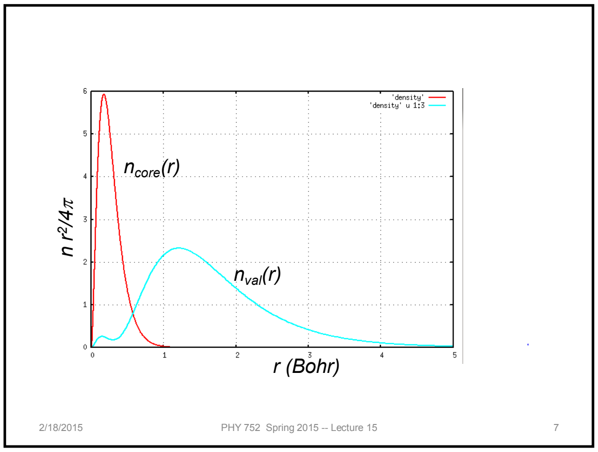
$$n(r) = \sum_i w_{n_i l_i} \left|\phi_{n_i l_i}(r)\right|^2$$

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

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

Results for carbon





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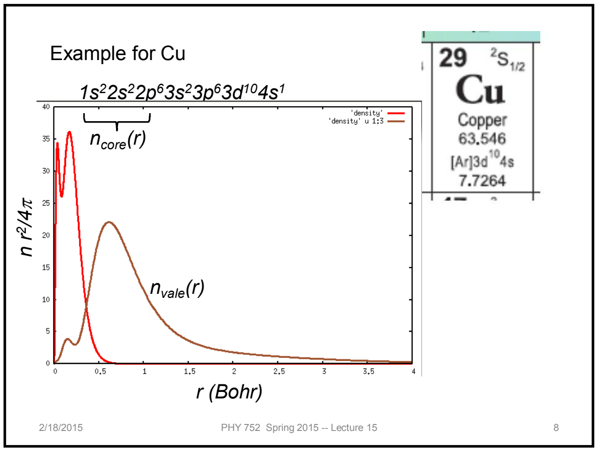

Example for Cu

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

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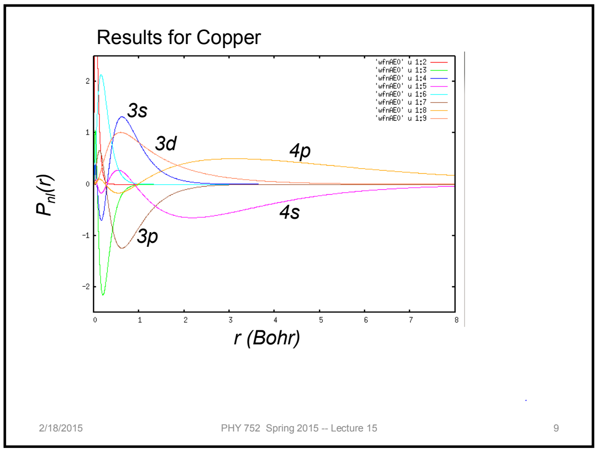

Results for Copper

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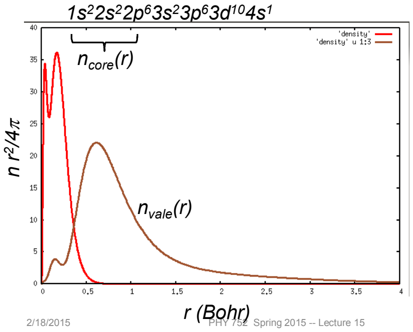
Frozen core approximation

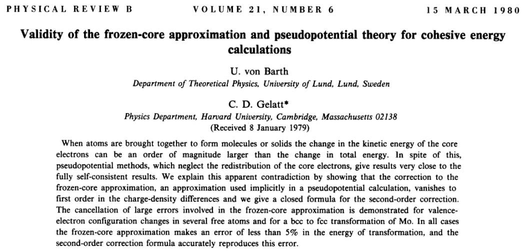
$$n(r) = n_{\text{core}}(r) + n_{\text{vale}}(r)$$

Example for Cu

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



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)

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

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

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

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

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

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

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

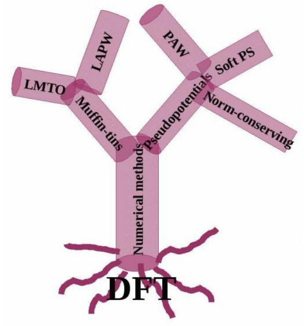
Equations for orbitals $\phi_i(\mathbf{r})$:

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

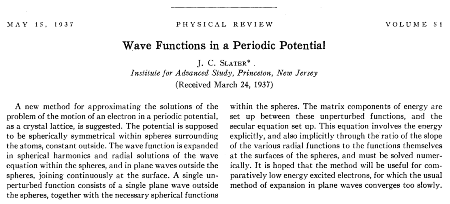
Numerical problem: near each nuclear center --

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

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

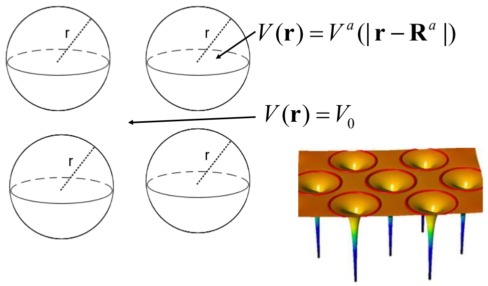
J. C. Slater*
Institute for Advanced Study, Princeton, New Jersey
(Received March 24, 1937)

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



$V(\mathbf{r}) = V^a(|\mathbf{r} - \mathbf{R}^a|)$

$V(\mathbf{r}) = V_0$

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

Muffin tin model continued:

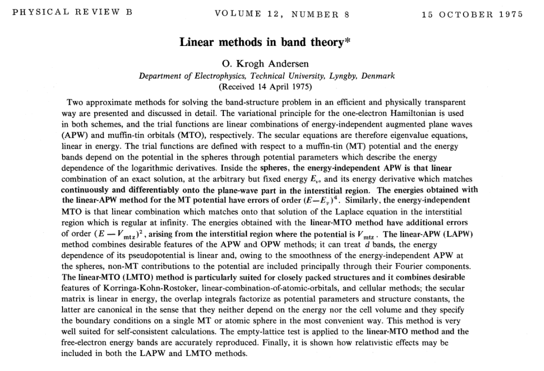
$$V(\mathbf{r}) = \begin{cases} V^a(|\mathbf{r} - \mathbf{R}^a|) & \text{for } |\mathbf{r} - \mathbf{R}^a| \leq \mathscr{R}^a \\ V_0 & \text{otherwise} \end{cases}$$

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*

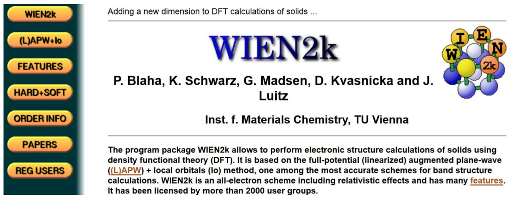
O. Krogh Andersen
Department of Electrophysics, Technical University, Lyngby, Denmark

(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 $(E - V_{\text{mtz}})^2$, **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/



Adding a new dimension to DFT calculations of solids ...

WIEN2k

P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz

Inst. f. Materials Chemistry, TU Vienna

The program package WIEN2k allows to perform electronic structure calculations of solids using density functional theory (DFT). It is based on the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (lo) method, one among the most accurate schemes for band structure calculations. WIEN2k is an all-electron scheme including relativistic effects and has many features. It has been licensed by more than 2000 user groups.

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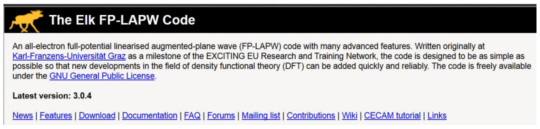
http://elk.sourceforge.net/

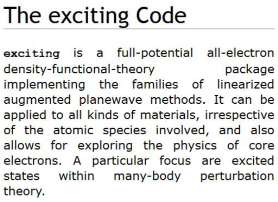


The Elk FP-LAPW Code

An all-electron full-potential linearised augmented-plane wave (FP-LAPW) code with many advanced features. Written originally at Karl-Franzens-Universität Graz as a milestone of the EXCITING EU Research and Training Network, the code is designed to be as simple as possible so that new developments in the field of density functional theory (DFT) can be added quickly and reliably. The code is freely available under the GNU General Public License.

Latest version: 3.0.4

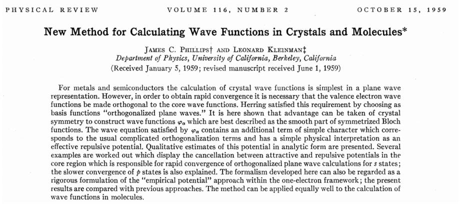
http://exciting-code.org/



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.

Motivation/justification for pseudopotential formalism

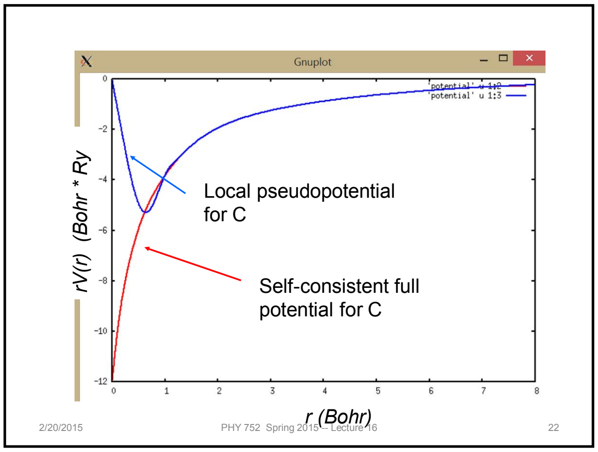


PHYSICAL REVIEW VOLUME 116, NUMBER 2 OCTOBER 15, 1959

New Method for Calculating Wave Functions in Crystals and Molecules*

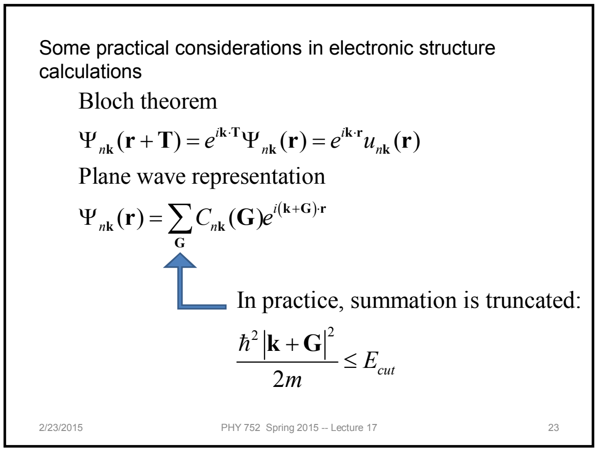
JAMES C. PHILLIPS† AND LEONARD KLEINMAN‡
Department of Physics, University of California, Berkeley, California
(Received January 5, 1959; revised manuscript received June 1, 1959)

For metals and semiconductors the calculation of crystal wave functions is simplest in a plane wave representation. However, in order to obtain rapid convergence it is necessary that the valence electron wave functions be made orthogonal to the core wave functions. Herring satisfied this requirement by choosing as basis functions "orthogonalized plane waves." It is here shown that advantage can be taken of crystal symmetry to construct wave functions φ_α which are best described as the smooth part of symmetrized Bloch functions. The wave equation satisfied by φ_α contains an additional term of simple character which corresponds to the usual complicated orthogonalization terms and has a simple physical interpretation as an effective repulsive potential. Qualitative estimates of this potential in analytic form are presented. Several examples are worked out which display the cancellation between attractive and repulsive potentials in the core region which is responsible for rapid convergence of orthogonalized plane wave calculations for s states; the slower convergence of p states is also explained. The formalism developed here can also be regarded as a rigorous formulation of the "empirical potential" approach within the one-electron framework; the present results are compared with previous approaches. The method can be applied equally well to the calculation of wave functions in molecules.



Local pseudopotential for C

Self-consistent full potential for C



Some practical considerations in electronic structure calculations

Bloch theorem

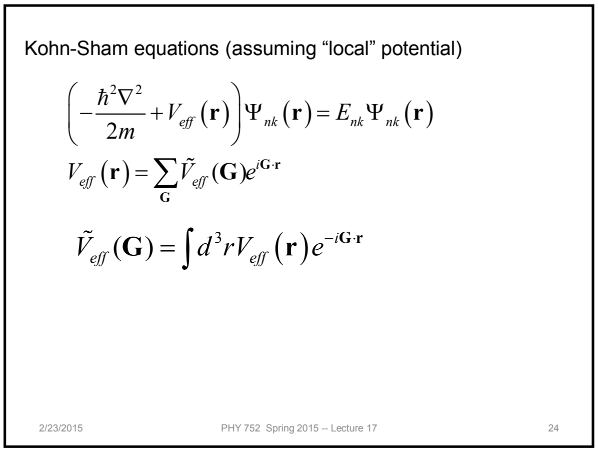
$$\Psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

Plane wave representation

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

In practice, summation is truncated:

$$\frac{\hbar^2|\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut}$$



Kohn-Sham equations (assuming “local” potential)

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{eff}(\mathbf{r})\right)\Psi_{nk}(\mathbf{r}) = E_{nk}\Psi_{nk}(\mathbf{r})$$

$$V_{eff}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{V}_{eff}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$\tilde{V}_{eff}(\mathbf{G}) = \int d^3r V_{eff}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}$$

Digression on evaluation of the Fourier transform of the effective potential

Useful identity:

$$e^{-i\mathbf{G}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^{-l} j_l(Gr) Y_{lm}^{*}(\hat{\mathbf{G}}) Y_{lm}(\hat{\mathbf{r}})$$

Suppose

$$V_{eff}(\mathbf{r}) = \sum_{a\mathbf{T}} V^{a}(\mathbf{r} - \boldsymbol{\tau}^{a} - \mathbf{T})$$

$$\tilde{V}_{eff}(\mathbf{G}) = \int d^3r V_{eff}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}$$

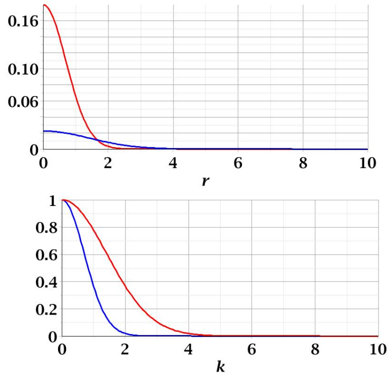
$$= \sum_{a} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}^{a}} \tilde{V}^{a}(\mathbf{G})$$

Digression on evaluation of the Fourier transform of the effective potential

$$\tilde{V}_{eff}(\mathbf{G}) = \sum_{a} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}^{a}} \tilde{V}^{a}(\mathbf{G})$$

$$\tilde{V}^{a}(\mathbf{G}) = 4\pi \sum_{lm} i^{-l} Y_{lm}^{*}(\mathbf{G}) \int d^3r V^{a}(\mathbf{r}) j_l(Gr) Y_{lm}(\hat{\mathbf{r}})$$

Examples of convergence of Fourier transforms:



Convergence of plane wave expansions

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\left(|\mathbf{k}+\mathbf{G}| < \sqrt{2mE_{cut}/\hbar^2}\right)$$

Electron density:

$$n(\mathbf{r}) = 2\sum_{n\mathbf{k}\ (\text{occ})} \left|\Psi_{n\mathbf{k}}(\mathbf{r})\right|^2$$

$$= 2\sum_{n\mathbf{k}\ (\text{occ})} \left|\sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\right|^2$$

$$= \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$|\mathbf{G}| \leq 2\sqrt{2mE_{cut}/\hbar^2}$$

Some practical tricks

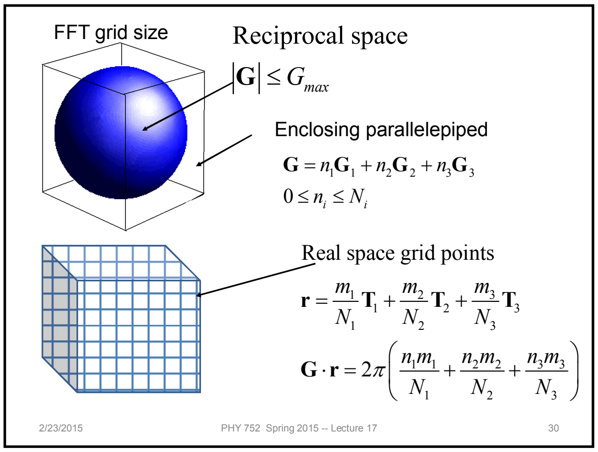
Evaluate periodic portion of wavefunction using FFT

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

Evaluate density on real-space grid

$$n(\mathbf{r}) = 2\sum_{n\mathbf{k}\ (\text{occ})} \left|u_{n\mathbf{k}}(\mathbf{r})\right|^2$$

Fourier space representation of density can be determined by inverse FFT



FFT grid size

Reciprocal space

$$|\mathbf{G}| \leq G_{max}$$

Enclosing parallelepiped

$$\mathbf{G} = n_1\mathbf{G}_1 + n_2\mathbf{G}_2 + n_3\mathbf{G}_3$$

$$0 \leq n_i \leq N_i$$

Real space grid points

$$\mathbf{r} = \frac{m_1}{N_1}\mathbf{T}_1 + \frac{m_2}{N_2}\mathbf{T}_2 + \frac{m_3}{N_3}\mathbf{T}_3$$

$$\mathbf{G}\cdot\mathbf{r} = 2\pi\left(\frac{n_1 m_1}{N_1} + \frac{n_2 m_2}{N_2} + \frac{n_3 m_3}{N_3}\right)$$

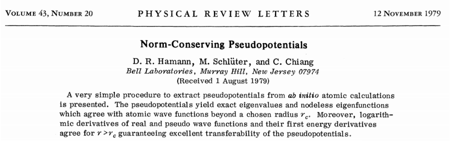
FFT equations http://www.fftw.org/

$$f\left(n_1,n_2,n_3\right)=\sum_{m_1,m_2,m_3}\tilde{f}\left(m_1,m_2,m_3\right)e^{i2\pi\left(\frac{n_1m_1}{N_1}+\frac{n_2m_2}{N_2}+\frac{n_3m_3}{N_3}\right)}$$

$$\tilde{f}\left(m_1,m_2,m_3\right)=\frac{1}{N_1N_2N_3}\sum_{n_1,n_2,n_3}f\left(n_1,n_2,n_3\right)e^{-i2\pi\left(\frac{n_1m_1}{N_1}+\frac{n_2m_2}{N_2}+\frac{n_3m_3}{N_3}\right)}$$

How can we construct a pseudopotential?

Norm-conserving pseudopotentials

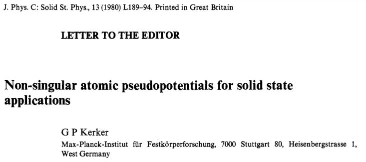


VOLUME 43, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1979

Norm-Conserving Pseudopotentials

D. R. Hamann, M. Schlüter, and C. Chiang
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 1 August 1979)

A very simple procedure to extract pseudopotentials from *ab initio* atomic calculations is presented. The pseudopotentials yield exact eigenvalues and nodeless eigenfunctions which agree with atomic wave functions beyond a chosen radius r_c. Moreover, logarithmic derivatives of real and pseudo wave functions and their first energy derivatives agree for $r > r_c$ guaranteeing excellent transferability of the pseudopotentials.



J. Phys. C: Solid St. Phys., 13 (1980) L189–94. Printed in Great Britain

LETTER TO THE EDITOR

Non-singular atomic pseudopotentials for solid state applications

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