

PHY 742 Quantum Mechanics II

1-1:50 AM MWF via video link:

<https://wakeforest-university.zoom.us/my/natalie.holzwarth>

Extra notes for Lecture 33

Some Practical Realizations of Density functional Theory

- 1. Electronic structure of atoms**
- 2. Frozen core approximation**
- 3. Extension of formalism to multi-center analysis**

We will illustrate the practical use of density functional for studying “real” materials.

21	Mon: 03/23/2020	Chap. 17	Quantization of the Electromagnetic Field	#17	03/25/2020
22	Wed: 03/25/2020	Chap. 17	Quantization of the Electromagnetic Field	#18	03/27/2020
23	Fri: 03/27/2020	Chap. 17	Quantization of the Electromagnetic Field	#19	03/30/2020
24	Mon: 03/30/2020	Chap. 18	Photons and atoms		
25	Wed: 04/01/2020	Chap. 10	Multiparticle systems	#20	04/03/2020
26	Fri: 04/03/2020	Chap. 10	Multiparticle systems	#21	04/06/2020
27	Mon: 04/06/2020	Chap. 10	Multielectron atoms	#22	04/08/2020
28	Wed: 04/08/2020	Chap. 10	Multielectron atoms		
	Fri: 04/10/2020	No class	<i>Good Friday</i>		
29	Mon: 04/13/2020	Chap. 10	Multielectron atoms	#23	04/15/2020
30	Wed: 04/15/2020		Hartree-Fock and other formalisms	#24	04/17/2020
31	Fri: 04/17/2020		Density functional theory		
32	Mon: 04/20/2020		Density functional theory for atoms		
33	Wed: 04/22/2020		Practical density functional theory		
34	Fri: 04/24/2020		Brief discussion of BCS theory of superconductivity		
35	Mon: 04/27/2020		Review		
36	Wed: 04/29/2020		Review		

Ongoing schedule

Kohn-Sham equations for spherical atom

Equations in Rydberg units

$$\left(-\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} \right) + v(r) + V_{Hartree}(r) + V_{xc}(r) \right) P_{n,l_i}(r) = \epsilon_{n,l_i} P_{n,l_i}(r)$$

$$v(r) = -\frac{2Z}{r}$$

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

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

Particular equations for atoms.

Numerical methods for solving the Kohn-Sham equations

Self-consistent solution

Iteration $\alpha = 0$

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

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

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

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

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

$\alpha + 1 \Rightarrow \alpha$

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Self consistent procedure

For spherically symmetric atom:

$$\phi_{n,l,m_l}(\mathbf{r}) = \phi_{n,l}(r) Y_{l,m_l}(\hat{\mathbf{r}})$$

$$\phi_{n,l}(r) = \frac{P_{n,l}(r)}{r}$$

Example for carbon

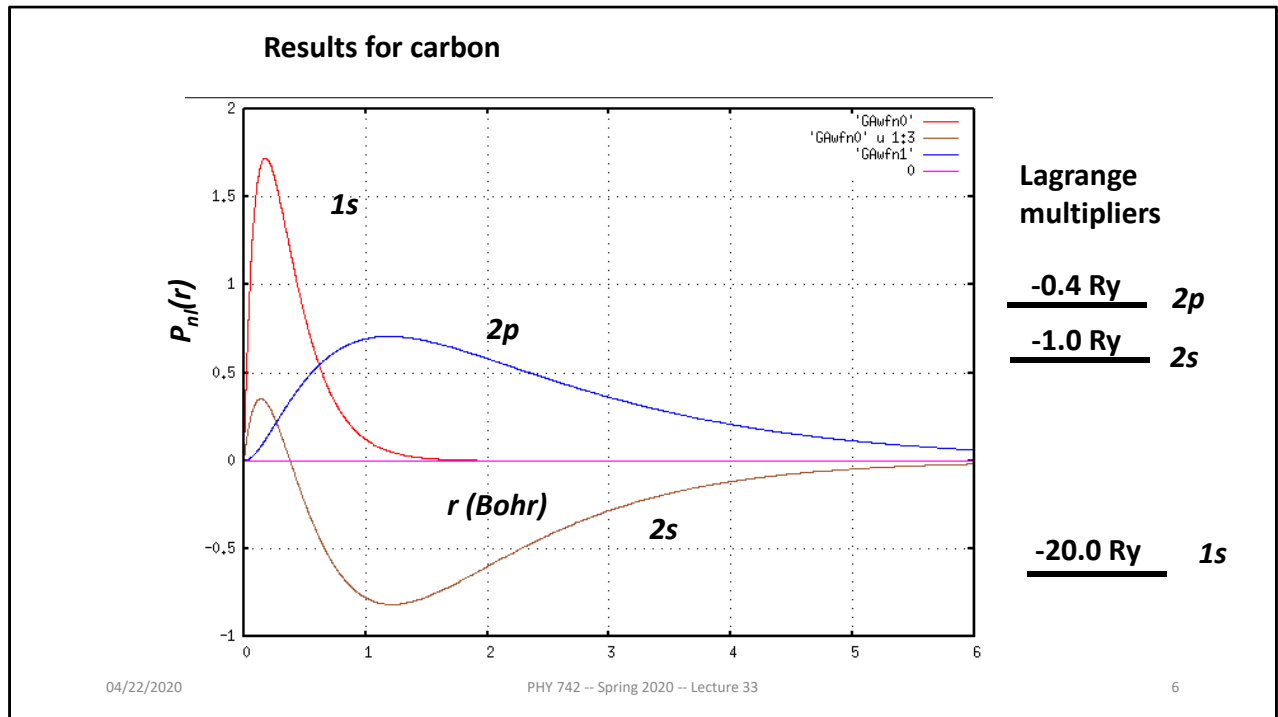
$$n(r) = \sum_i w_{n,l_i} |\phi_{n,l_i}(r)|^2$$

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

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

2	6	³ P ₀
	C	
	Carbon	
	12.011*	
	1s ² 2s ² 2p ²	
	11.2603	

Example for C atom



Plot of self-consistent results for one electron orbitals and their Lagrange multipliers. Is there any physical significance to the Lagrange multipliers?

What is the significance of the Kohn-Sham orbitals and their corresponding Lagrange multipliers?

1. No significance
2. Qualitative significance.
3. Can be interpreted as eigenfunctions/eigenvalues of the one-electron Hamiltonian.
4. With corrections, can be related to physical system.

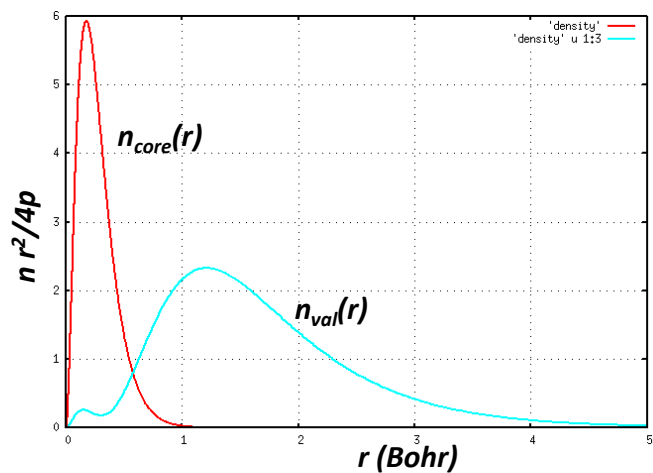
Lagrange
multipliers

-0.4 Ry 2p

-1.0 Ry 2s

-20.0 Ry 1s

Electron density



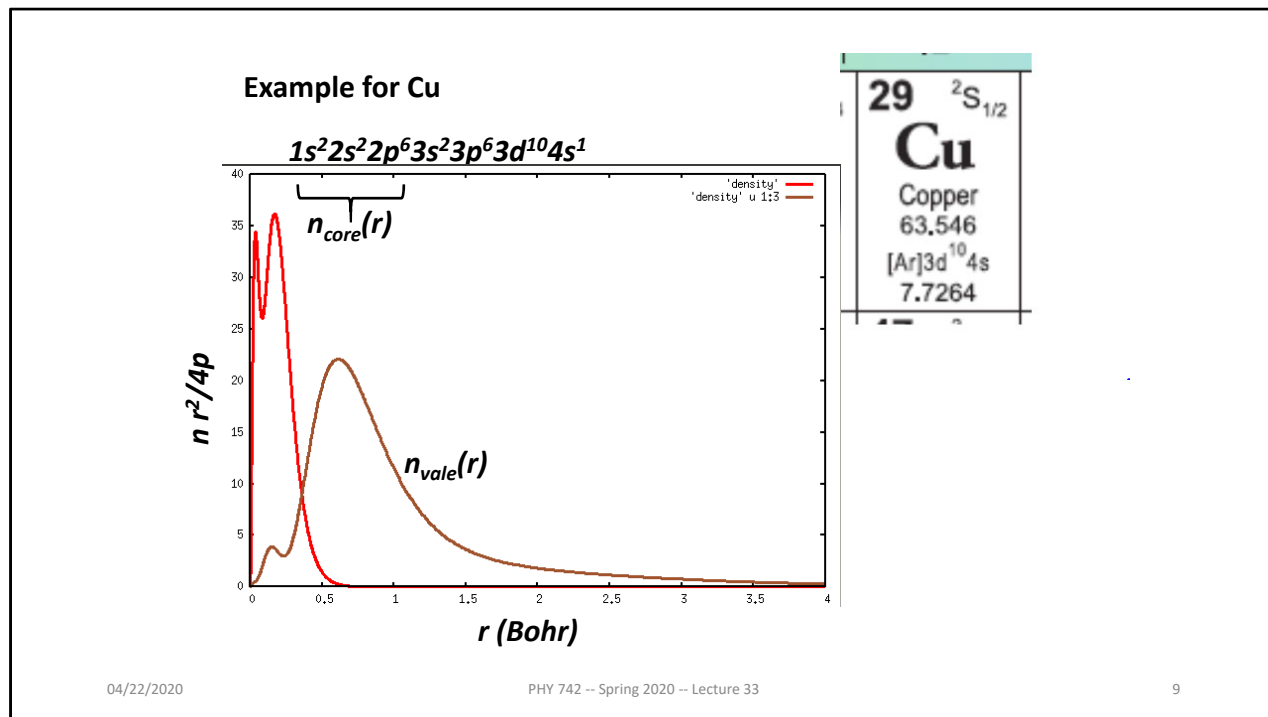
Electron density has been determined variationally.

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Here is a plot of the electron density, separating the core and valence contributions.



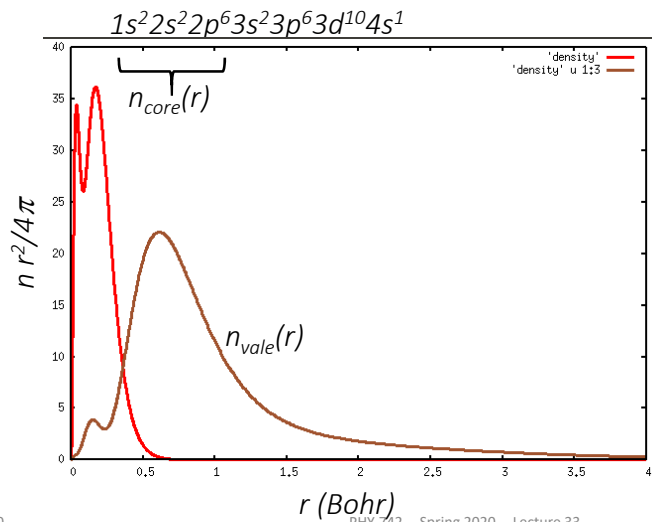
The separation of core and valence density contributions is more obvious/important for Cu

Frozen core approximation

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

Example for Cu

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



Modified variational problem

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It is convenient to make the so-called “frozen” core approximation

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.

Early paper on the frozen core approximation.

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

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This paper studied the numerical properties of the frozen core approximation.

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

$$E_v[n] = T + E_v[n] + E_{Hartree}[n] + E_{xc}[n]$$

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

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

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

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

Partitioning of the Hamiltonian terms.

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

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

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 --

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

On top of the approximations made so far, we need to be able to solve the equations numerically.

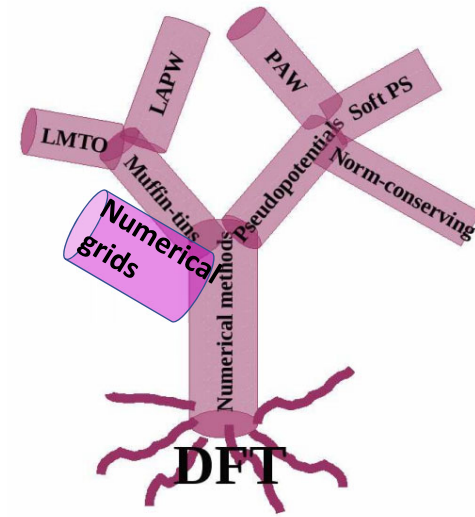
Why did we not worry about the divergent electron-nucleus interaction for an atom?

1. We should have, but ignored it.
2. We should have, but it is not a problem for atoms.
3. Other...

How does the divergent electron-nucleus interaction affect multi atom systems?

1. It is not worse than the problem for atoms.
2. It is worse than the problem for atoms.

Practical solution of Kohn-Sham equations in solids



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Many methods have evolved to solve the numerical problems. Here are illustrated two main branches.

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

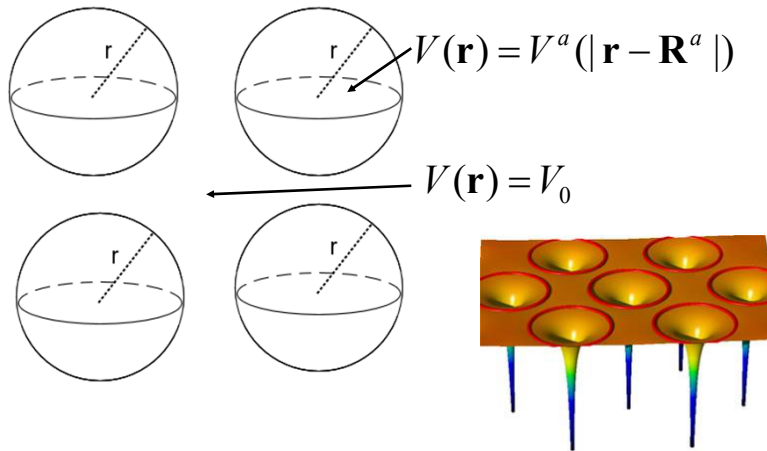
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The muffin tin approach was developed by John Slater in the 1930's.

Muffin tin potential construction



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

Some visualizations of the muffin tins.

Muffin tin model continued:

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

Problems with APW and KKR Green's function schemes

- 1. Difficult numerically to find Kohn-Sham energies e_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>

Some details

Linear methods in band theory*

O. Krogh Andersen

Department of Electrophysics, Technical University, Lyngby, Denmark

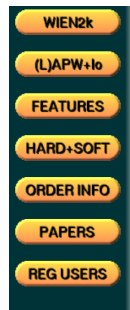
(Received 14 April 1975)

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_0 , and its energy derivative which matches continuously and differentially 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 $(E - E_0)^4$. 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.

The original method of Slater was not very efficient. O. K. Andersen showed how to make the numerical work more efficient by linearizing the equations. Later authors improved the physics as well (relaxed the restrictions) of the muffin tin.

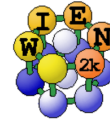
Modern software based on LAPW method --

<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.

A modern code package using this method.

<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

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<http://exciting-code.org/>

The exciting Code

`exciting` is a full-potential all-electron density-functional-theory package implementing the families of linearized augmented plane wave 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.

More LAPW codes.

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)

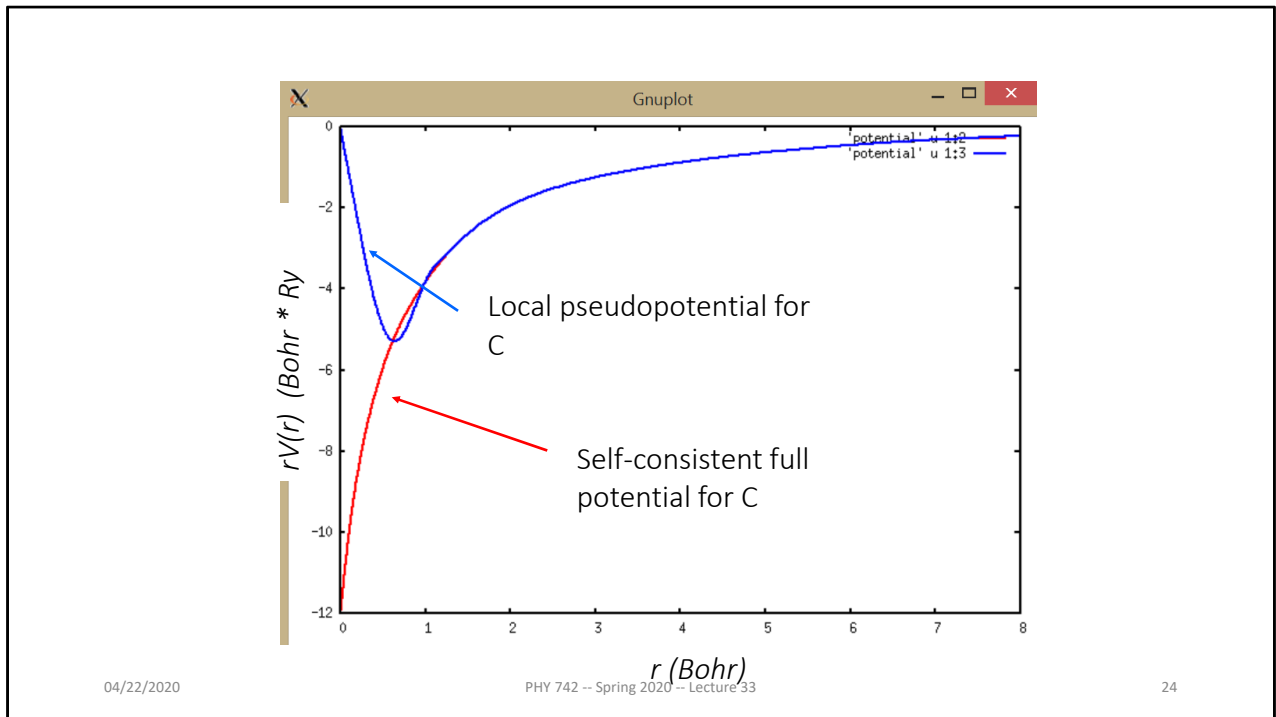
For metals and semiconductors the calculation of crystal wave functions is simplest in a plane wave representation. However, in order to obtain rapid convergence it is necessary that the valence electron wave functions be made orthogonal to the core wave functions. Herring satisfied this requirement 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_n which are best described as the smooth part of symmetrized Bloch functions. The wave equation satisfied by ϕ_n 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.

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Another approach was the pseudopotential approach initiated by Phillips and Kleinman.



The pseudopotential replaces the all-electron potential with a specially smoother one while maintaining the correct physics in the mathematics.

Kohn-Sham equations (assuming “local” pseudo potential)

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

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

$$\tilde{V}_{eff}(\mathbf{G}) = \int d^3r V_{eff}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} \quad \text{Convergent representation for pseudopotentials}$$

Ideally, the pseudopotential will represent the same physics as the “real” potential

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

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With the pseudopotential, the Kohn-Sham equations can be solved with plane wave expansions over all space.

Outlook for density functional methods for modeling real materials

- 1. Workhorse method for simulations of materials**
- 2. Important to know its range of validity**
- 3. Extensions of density functional theory**
 - a. Corrections for modeling excited states**
 - b. Corrections for treating systems with many configurations in the ground state; perhaps can be treated using model Hamiltonians**
 - c. First-principles many electron treatments – quantum Monte Carlo, quantum chemistry methods**

Do you imagine density functional theory begin part of your life?

- 1. Yes**
- 2. No**