

Introduction to DFT and the plane-wave pseudopotential method

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A guided tour inside the “black box” of ab-initio simulation.

- The rise of quantum-mechanical simulations.
- Wavefunction-based theory
- Density-functional theory (DFT)
- Quantum theory in periodic boundaries
- Plane-wave and other basis sets
- SCF solvers
- Molecular Dynamics

Recommended Reading and Further Study

- Jorge Kohanoff *Electronic Structure Calculations for Solids and Molecules, Theory and Computational Methods*, Cambridge, ISBN-13: 9780521815918
- Dominik Marx, Jürg Hutter *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods* Cambridge University Press, ISBN: 0521898633
- Richard M. Martin *Electronic Structure: Basic Theory and Practical Methods: Basic Theory and Practical Density Functional Approaches Vol 1* Cambridge University Press, ISBN: 0521782856
- C. Pisani (ed) *Quantum Mechanical Ab-Initio Calculation of the properties of Crystalline Materials*, Springer, Lecture Notes in Chemistry vol.67 ISSN 0342-4901.



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The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble.

P.A.M. Dirac, Proceedings of the Royal Society **A123**, 714 (1929)

Nobody understands quantum mechanics.

R. P. Feynman



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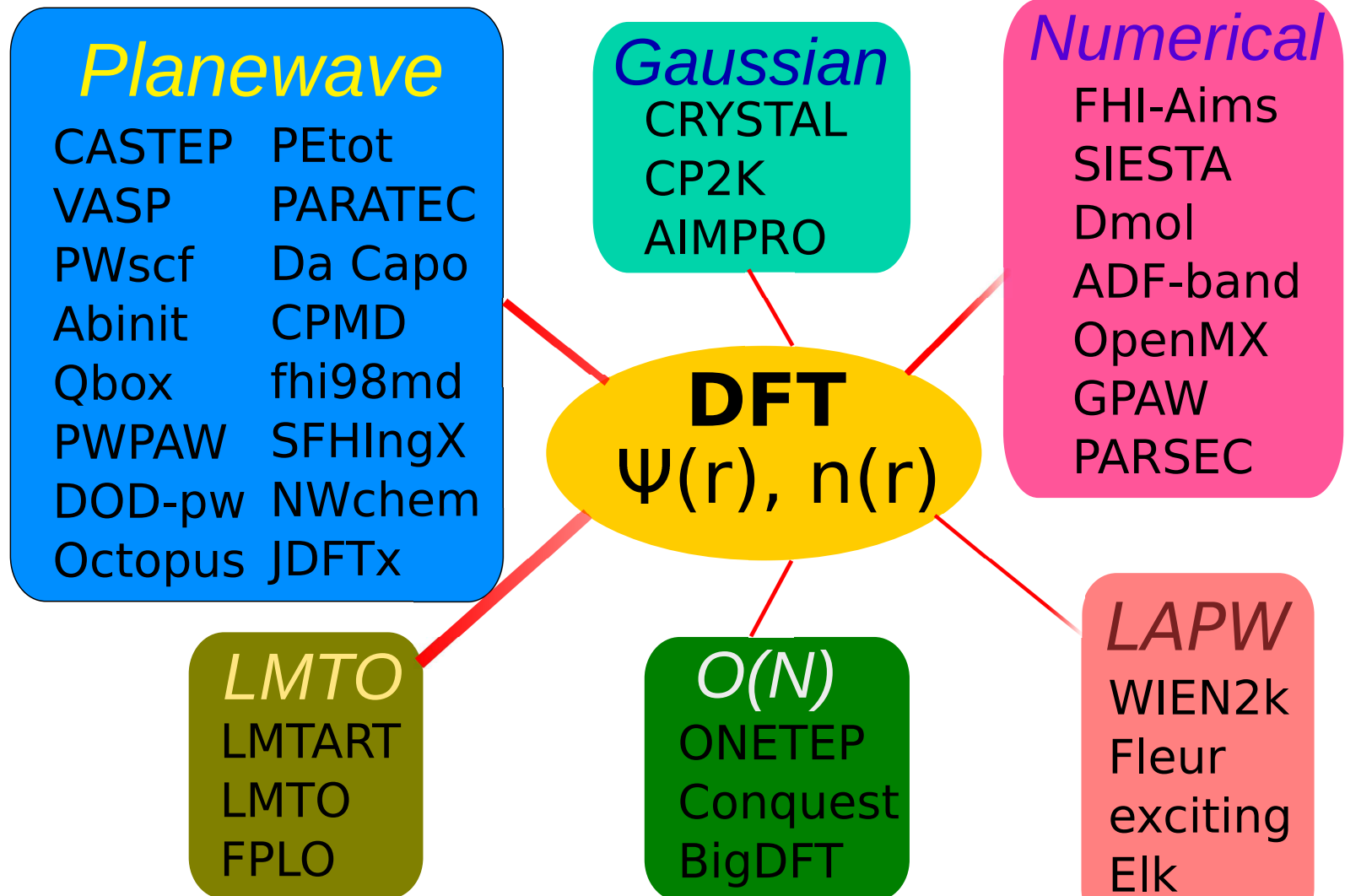
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<http://www.psi-k.org/codes.shtml>



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- Quantum mechanics proper requires full wavefunction of both *electronic* and *nuclear* co-ordinates.
- First approximation is the **Born-Oppenheimer approximation**. Assume that electronic relaxation is much faster than ionic motion ($m_e \ll m_{\text{nuc}}$). Then wavefunction is *separable*

$$\Psi = \Theta(\{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N\})\Phi(\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n\})$$

\mathbf{R}_i are nuclear co-ordinates and \mathbf{r}_i are electron co-ordinates.

- Therefore can treat electronic system as solution of Schrödinger equation in *fixed external potential* of the nuclei, $V_{\text{ext}}\{\mathbf{R}_i\}$.
- **Ground-state energy** of electronic system acts as **potential function** for nuclei.
- Can then apply our tool-box of simulation methods to nuclear system.
- B-O is usually a very good approximation, only fails for coupled electron/nuclear behaviour for example superconductivity, quantum crystals such as He and cases of strong quantum motion such as H in KDP.



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- Ignoring electron spin for the moment and using atomic units ($\hbar = m_e = e = 1$)

$$\left[-\frac{1}{2} \nabla^2 + \hat{V}_{\text{ext}}(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}) + \hat{V}_{\text{e-e}}(\{\mathbf{r}_i\}) \right] \Psi(\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{r}_i\})$$

where $-\frac{1}{2} \nabla^2$ is the **kinetic-energy** operator,

$\hat{V}_{\text{ext}} = -\sum_i \sum_I \frac{Z_i}{|\mathbf{R}_I - \mathbf{r}_i|}$ is the Coulomb potential of the nuclei,

$\hat{V}_{\text{e-e}} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|}$ is the electron-electron Coulomb interaction

and $\Psi(\{\mathbf{r}_i\}) = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is a **3N-dimensional** wavefunction.

- This is a **3N-dimensional** eigenvalue problem.
- E-e term renders even numerical solutions impossible for more than a handful of electrons.
- **Pauli Exclusion principle** $\Psi(\{\mathbf{r}_i\})$ is **antisymmetric** under interchange of any 2 electrons. $\Psi(\dots \mathbf{r}_i, \mathbf{r}_j, \dots) = -\Psi(\dots \mathbf{r}_j, \mathbf{r}_i, \dots)$
- Total **electron density** is $n(\mathbf{r}) = \int \dots \int d\mathbf{r}_2 \dots d\mathbf{r}_n |\Psi(\{\mathbf{r}_i\})|^2$



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- Substituting $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = \phi(\mathbf{r}_1) \dots \phi(\mathbf{r}_n)$ into the Schrödinger equation yields

$$\left[-\frac{1}{2} \nabla^2 + \hat{V}_{\text{ext}}(\{\mathbf{R}_I\}, \mathbf{r}) + \hat{V}_H(\mathbf{r}) \right] \phi_n(\mathbf{r}) = E_n \phi_n(\mathbf{r})$$

where the **Hartree potential**: $\hat{V}_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$ is Coulomb interaction of an electron with average electron density $n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$. Sum is over all **occupied** states.

- $\phi(\mathbf{r}_n)$ is called an **orbital**.
- Now a **3-dimensional** wave equation (or eigenvalue problem) for $\phi(\mathbf{r}_n)$.
- This is an **effective 1-particle wave equation** with an additional term, the **Hartree potential**
- But solution $\phi_i(\mathbf{r})$ depends on electron-density $n(\mathbf{r})$ which in turn depends on $\phi_i(\mathbf{r})$. Requires **self-consistent** solution.
- This is a very poor approximation because $\Psi(\{\mathbf{r}_i\})$ does not have necessary antisymmetry and violates the Pauli principle.



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- Approximate wavefunction by a **slater determinant** which guarantees antisymmetry under electron **exchange**

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \phi_1(\mathbf{r}_2, \sigma_2) & \dots & \phi_1(\mathbf{r}_n, \sigma_n) \\ \phi_2(\mathbf{r}_1, \sigma_1) & \phi_2(\mathbf{r}_2, \sigma_2) & \dots & \phi_2(\mathbf{r}_n, \sigma_n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(\mathbf{r}_1, \sigma_1) & \phi_n(\mathbf{r}_2, \sigma_2) & \dots & \phi_n(\mathbf{r}_n, \sigma_n) \end{vmatrix}$$

- Substitution into the Schrödinger equation yields

$$\left[-\frac{1}{2} \nabla^2 + \hat{V}_{\text{ext}}(\{\mathbf{R}_I\}, \mathbf{r}) + \hat{V}_H(\mathbf{r}) \right] \phi_n(\mathbf{r}) \quad (1)$$

$$- \sum_m \int d\mathbf{r}' \frac{\phi_m^*(\mathbf{r}') \phi_n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \phi_m(\mathbf{r}) = E_n \phi_n(\mathbf{r}) \quad (2)$$

- Also an **effective 1-particle wave equation**. The extra term is called the **exchange** potential and creates repulsion between electrons of like spin.
- Involves orbitals with co-ordinates at 2 different positions. Therefore expensive to solve.



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- Practical solution of Hartree-Fock developed by John Pople, C. Roothan and others. (Nobel Prize 1998).
- Key is to solve 1-particle effective Hamiltonian in a **self-consistent** loop. Sometimes known as **SCF** methods (Self Consistent Field).
- Hartree-Fock yields reasonable values for total energies of atoms, molecules.
- Basis of all quantum chemistry until 1990s.
- Error in Hartree-Fock energy dubbed **correlation energy**.
- Failures: Excitation energies too large.
- Completely fails to reproduce metallic state. (Predicts logarithmic singularity in DOS at ϵ_F .)
- Various more, accurate (and expensive) methods such as MP2, MP4, Coupled-Cluster, full CI are based on HF methods, and give approximations to the correlation energy.



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- Walter Kohn awarded Nobel Prize for Chemistry for DFT in 1999 with John Pople.
- Many-body wavefunction Ψ contains much irrelevant information. Concentrate instead on **electron density** $n(\mathbf{r})$.
- Hypothesis: $n(\mathbf{r})$ in ground-state contains complete information about system, and all properties can be calculated as an explicit or implicit functional of density. (True for Hartree theory, where $n(\mathbf{r})$ determines effective potential for orbitals.)

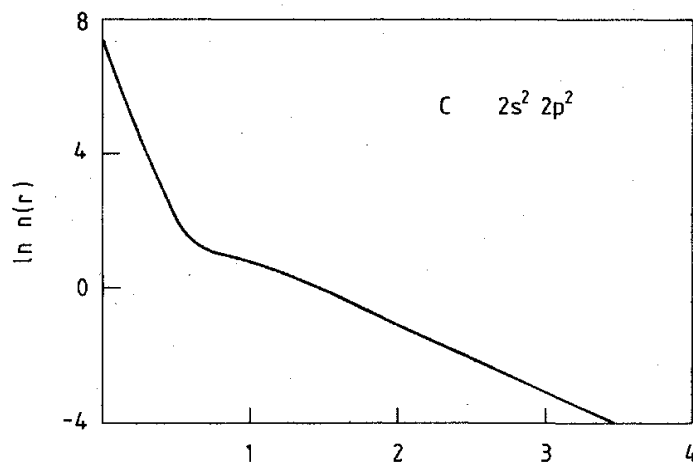


FIG. 1: Spherically averaged density $n(r)$ in ground state of carbon atom as a function of distance r from nucleus.



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- *Ansatz* for total energy

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int d\mathbf{r} \hat{V}_{\text{ext}}(\mathbf{r})n(\mathbf{r}).$$

where $F[n(\mathbf{r})]$ is a **universal** functional of the density.

- In a landmark paper in 1964 Hohenberg and Kohn proved that $n(\mathbf{r})$ is **uniquely specified** by external nuclear potential $\hat{V}_{\text{ext}}(\mathbf{r})$.
- If we knew form of **functional** $F[n(\mathbf{r})]$ we would have a quick and easy alternative to solving the Schrödinger equation. Unfortunately the universe is not so kind!
- Write F as a sum of Kinetic, Hartree and other contributions:

$$F[n(\mathbf{r})] = E_K[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})]$$

- Hartree functional is

$$E_H[n(\mathbf{r})] = \frac{1}{2} \int \int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$$



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- In 1965 Kohn and Sham introduced a method for calculating these terms. Replace our system of **interacting** electrons with a fictitious system of **non-interacting** electrons of the same density. Represent by set of **fictitious** orbitals $\phi_i(\mathbf{r})$ with density given by

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

and introduce **effective Hamiltonian**

$$\left[-\frac{1}{2} \nabla^2 + \hat{V}_{\text{ext}}(\{\mathbf{R}_I\}, \mathbf{r}) + \hat{V}_H(\mathbf{r}) + \hat{v}_{\text{xc}}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = E_n \phi_n(\mathbf{r})$$

- Kinetic energy of **non-interacting** system is given by:

$$E_K[n(\mathbf{r})] = -\frac{1}{2} \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$$

Use this as approximation for kinetic energy functional (defined implicitly via non-interacting effective Hamiltonian).

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- Exchange-correlation potential given by functional derivative.

$$\hat{v}_{xc} = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n}$$

and contains all remaining “uncertainty” about $F[n(\mathbf{r})]$. By comparison with Hartree-Fock effective Hamiltonians, this must include (a) Exchange energy, (b) Correlation energy and (c) the difference between kinetic energies of non-interacting and interacting systems.

- All we have done so far is swept our ignorance of the form of $F[n(\mathbf{r})]$ into one single term. How does this help?

Exchange is small contribution, correlation even smaller. Therefore a reasonable approximation to E_{xc} is a very good approximation to F .

- Although Kohn-Sham DFT uses effective Hamiltonian very reminiscent of Hartree-Fock, **no claim** at all is made about the form of wavefunction.

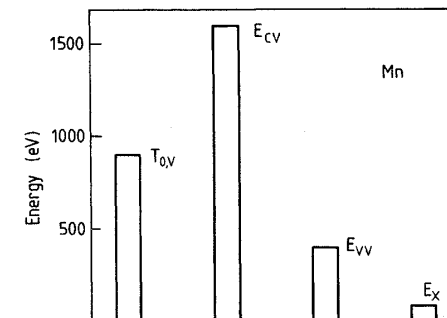


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).



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- DFT would be an exact theory of the ground state if we knew $E_{xc}[n(\mathbf{r})]$.
- Make (approximate) assumption that

$$E_{xc}[n(\mathbf{r})] = \int d\mathbf{r} \quad n(\mathbf{r})\varepsilon_{xc}(n(\mathbf{r}))$$

where $\varepsilon_{xc}(n(\mathbf{r}))$ is the XC energy density at point \mathbf{r} and is a function, not a functional of n .

- This helps because we have available the exact form of $\varepsilon_{xc}(n(\mathbf{r}))$ in the case of a uniform electron gas, from highly accurate quantum monte-carlo calculations. [The exchange part of this $\varepsilon_x(n(\mathbf{r}))$ varies as $n^{1/3}$]
- It's not obvious that the LDA should be any good. The usefulness was not initially appreciated and it was virtually ignored for 10 years!
- Nevertheless DFT with LDA gives a highly satisfactory account of chemical bonding in solids, molecules, surfaces and defects. Less satisfactory for atoms - errors of 2eV or more. Band gaps too low.
- **Generalized Gradient Approximation (GGA):** $V_{xc}(r) = V_{xc}(n, |\nabla n|)$ depends also on local gradient of n .
- See R. O. Jones and O. Gunnarsson *Rev. Mod. Phys.* (1989) **61**(3) 689-745, Ihm, *Rep. Prog. Phys.* (1988) **51** 105-142.



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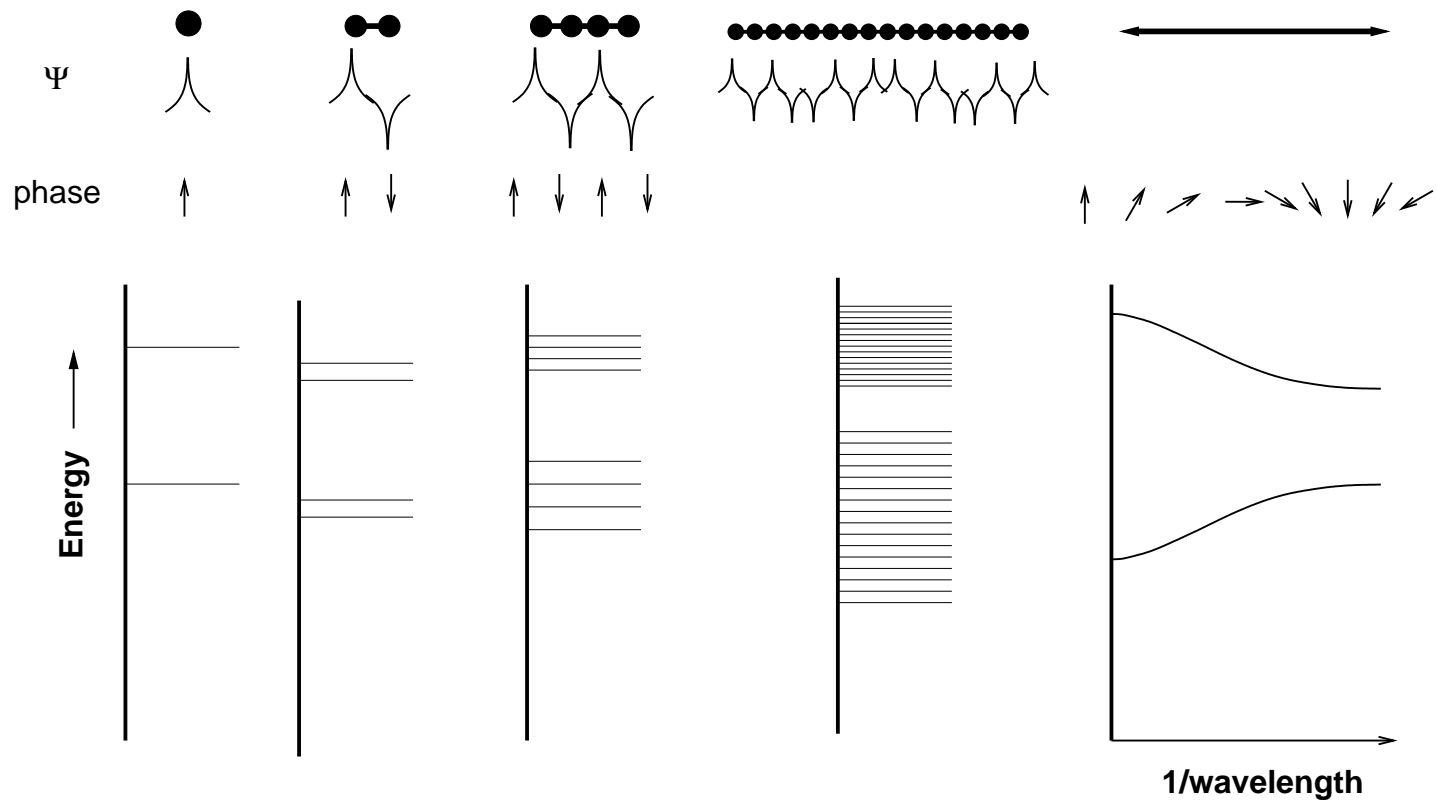
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Atoms Discrete *energy levels*

Diatomic Each atomic level splits into *bonding* and *antibonding* states.

Molecule *Molecular orbitals* at many energy levels

Crystal Continuum of energy levels of same symmetry called *bands*



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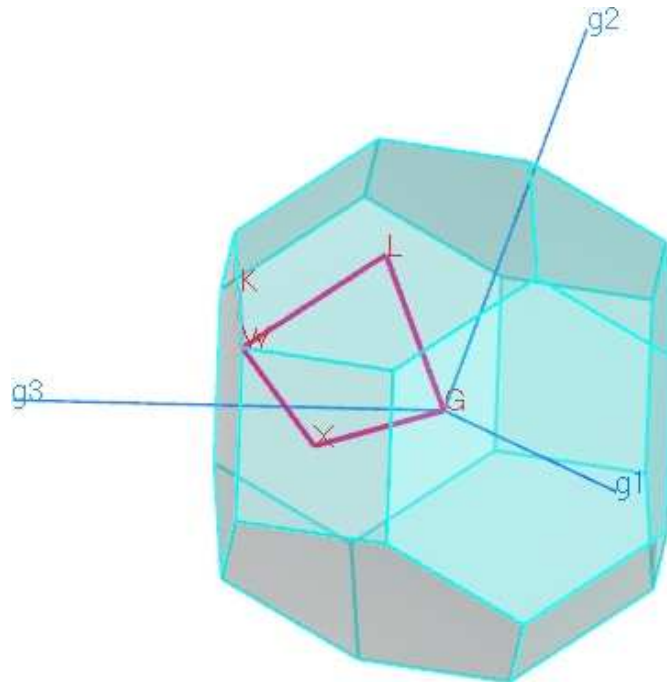
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- 3D vector space of \mathbf{k} called *reciprocal space* ($1/\lambda$).
- “real” and “reciprocal” spaces related by Fourier Transform
- Fourier Transform of crystal lattice is called *reciprocal lattice* and denoted by *reciprocal lattice vectors* $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$,
 $\mathbf{a}^* = \frac{2\pi}{\Omega} \mathbf{b} \times \mathbf{c}$ etc.
- “unit cell” of reciprocal space called *Brillouin Zone* - periodically repeated it fills reciprocal space.
- Electronic states $\phi_{m,\mathbf{k}}$ with \mathbf{k} within BZ form *complete* description of all electronic states in infinite crystal.



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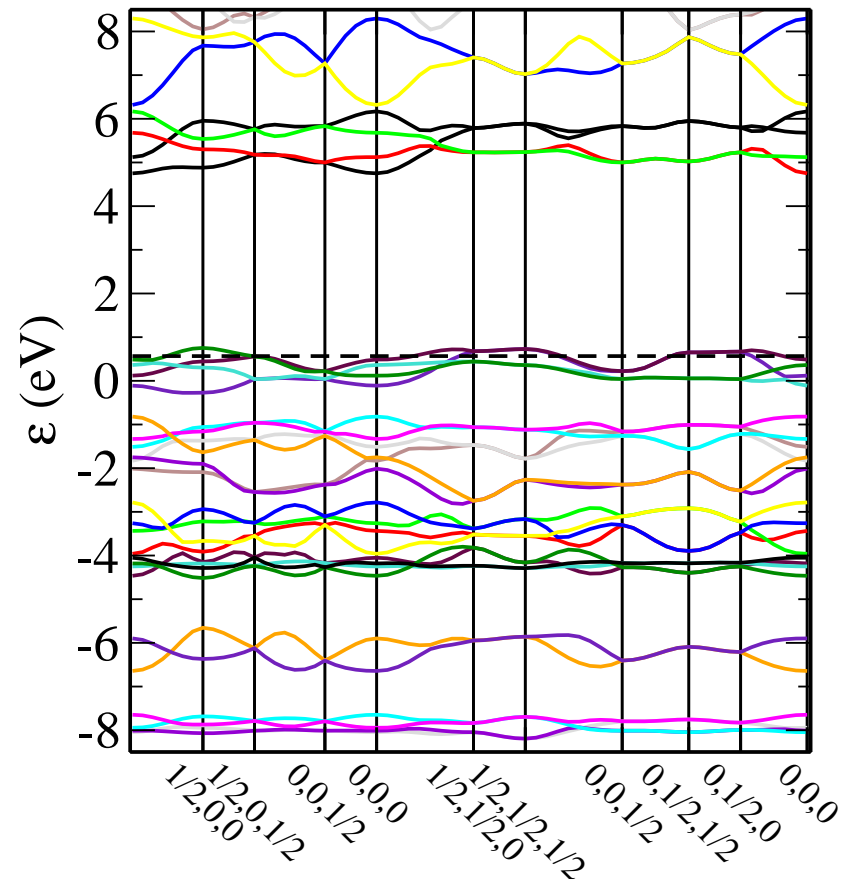
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- KS eigenvalues $\epsilon_{m\mathbf{k}}$ gives rise to **band structure**
- Electrons fill lowest energy states according to *Aufbau* principle.
- Energy bands in molecular solid have low **dispersion** and can be mapped 1-1 onto molecular energy levels.
- Quantum number m in molecular solid corresponds to state label in molecule.

Example: Benzene, Phase III





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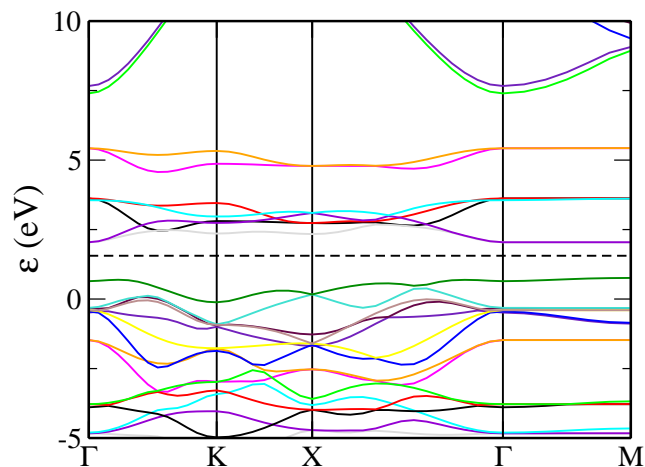
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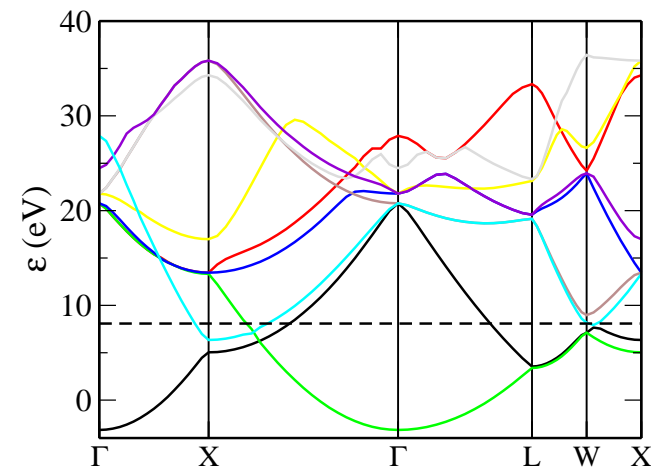
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- Same principles apply as for molecular solids
- Energy above highest occupied state and below lowest unoccupied state called *Fermi energy*



Insulator (MnO_2)

Bands completely occupied or unoccupied.
Fermi energy lies in *band-gap* and divides
(*valence bands*) from (*conduction bands*)



Metal(Al)

Conduction bands partially occupied,
crossed by Fermi level.
In 3D filled states define *Fermi surface*



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- Need to compute ground state energy, not just bandstructure. Given by

$$E = \sum_i^{N_{\text{occ}}} \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \\ + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + E_{\text{xc}}[n(\mathbf{r})] + E_{\text{II}}(\{\mathbf{R}_I\})$$

- The **aufbau** principle is implicit in DFT formalism. Each occupied KS orbital contains 2 “electrons”, so $N_{\text{occ}} = N_e/2$. Density is

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

- KS Orbitals subject to **orthogonality** and **normalization** conditions

$$\int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) = \delta_{ij}$$

- Integrals run over all 3D space, KE term is *not* cell-periodic.



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- Additional term $E_{II}(\{\mathbf{R}_I\})$ is usual electrostatic interaction energy between ions. Computed in usual way, using Ewald Sum for periodic systems.



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- Assuming we have some scheme to generate KS orbitals and energy, we will also need to evaluate **forces** acting on ions. (Numerical derivatives of E inadequate and expensive.)
- Forces given by derivative of total energy

$$F_{I\alpha} = -\frac{dE}{dR_{I\alpha}} = -\frac{\partial E}{\partial R_{I\alpha}} - \sum_i \frac{\delta E}{\delta \phi_i} \frac{\partial \phi_i}{\partial R_{I\alpha}} - \sum_i \frac{\delta E}{\delta \phi_i^*} \frac{\partial \phi_i^*}{\partial R_{I\alpha}}$$

- The **Hellman-Feynman** theorem allows easy calculation of forces. Provided that the ϕ_i are eigenstates of the Hamiltonian the second two terms vanish.
- In plane-wave basis the only terms which depend explicitly on ionic co-ordinates are the external potential and $E_{II}(\{\mathbf{R}_I\})$.

$$\mathbf{F}_I = - \int d\mathbf{r} \frac{dV_{\text{ext}}}{d\mathbf{R}_I} n(\mathbf{r}) - \frac{dV_{II}}{d\mathbf{R}_I}$$

The ions feel only the electrostatic forces due to the electrons and the other ions.

- In *atom-centred* basis (LAPW, GTO, etc) additional terms in force from derivative of orbital basis wrt ionic position - “Pulay forces”.



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- Periodic boundary conditions necessary for same reasons as with parameterized potentials.

$$V_{\text{ext}}(\mathbf{r} + \mathbf{T}) = V_{\text{ext}}(\mathbf{r})$$

where \mathbf{T} is a lattice translation of the simulation cell.

- **observables** must also be periodic in simulation cell, so $n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$
- wavefunctions are NOT observable so $\phi(\mathbf{r})$ are NOT cell-periodic.
- can multiply ϕ by arbitrary complex function $c(\mathbf{r})$ with $|c| = 1$.
- **Bloch's Theorem** gives form of wavefunctions in periodic potential (see any solid state physics text for proof).

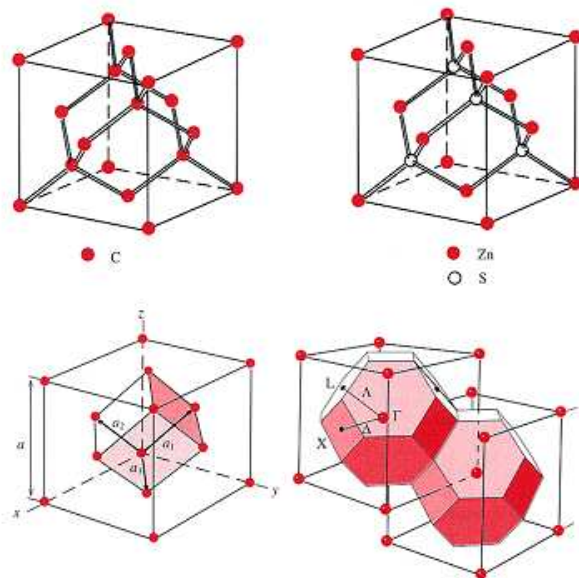
$$\phi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = \exp(i\mathbf{k} \cdot \mathbf{T})\phi_{\mathbf{k}}(\mathbf{r})$$

$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{\mathbf{k}}(\mathbf{r})$$

where $u_{\mathbf{k}}(\mathbf{r})$ is a **periodic** function $u(\mathbf{r} + \mathbf{T}) = u(\mathbf{r})$

- The **Bloch functions** $u(\mathbf{r})$ are easily representable on a computer program, unlike $\phi(\mathbf{r})$.
- Bloch states have 2 labels, eigenstate m and wavevector \mathbf{k} .

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- Smallest geometric volume with full space-group symmetry and which can be periodically repeated to fill wavevector space *reciprocal-space* known as *Brillouin Zone*.
- Kinetic energy term in total energy rewritten in terms of Bloch functions

$$T = \int_{\text{BZ}} d\mathbf{k} \int_{\Omega} d\mathbf{r} u_{\mathbf{k}}^*(\mathbf{r}) (-i\nabla + \mathbf{k})^2 u_{\mathbf{k}}(\mathbf{r})$$

\int_{Ω} is over one cell rather than all space.

- Charge density can also be expressed in terms of $u_{\mathbf{k}}(\mathbf{r})$.

$$n(\mathbf{r}) = \sum_m \int_{\text{BZ}} d\mathbf{k} u_{m\mathbf{k}}^*(\mathbf{r}) u_{m\mathbf{k}}(\mathbf{r})$$

- All terms in Hamiltonian now expressed in terms of *cell-periodic* quantities. Need only store values of $u_{m\mathbf{k}}(\mathbf{r})$ for a single simulation cell in computer representation.

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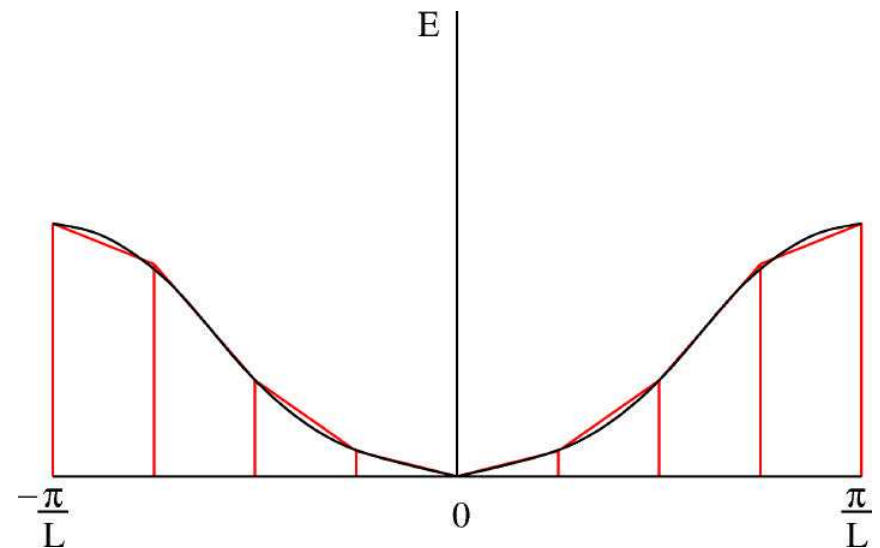
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- In a real calculation replace integral $\int_{\text{bz}} d\mathbf{k}$ with sum over discrete set of wavevectors \sum_k^{BZ} (“k-points”).
- In practice, use points on a regular grid for 3d integration (Monkhorst and Pack, *Phys. Rev. B* 13,5188 (1976))

Example Integration



Nuts and Bolts 2001

Lecture 6: Plane waves etc.

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- Fineness of grid is a **convergence parameter**. Number needed for convergence varies **inversely** with simulation cell volume.
- In metals, where bands are **partially** filled, need much **finer** k-point grid spacing to represent *fermi surface*.



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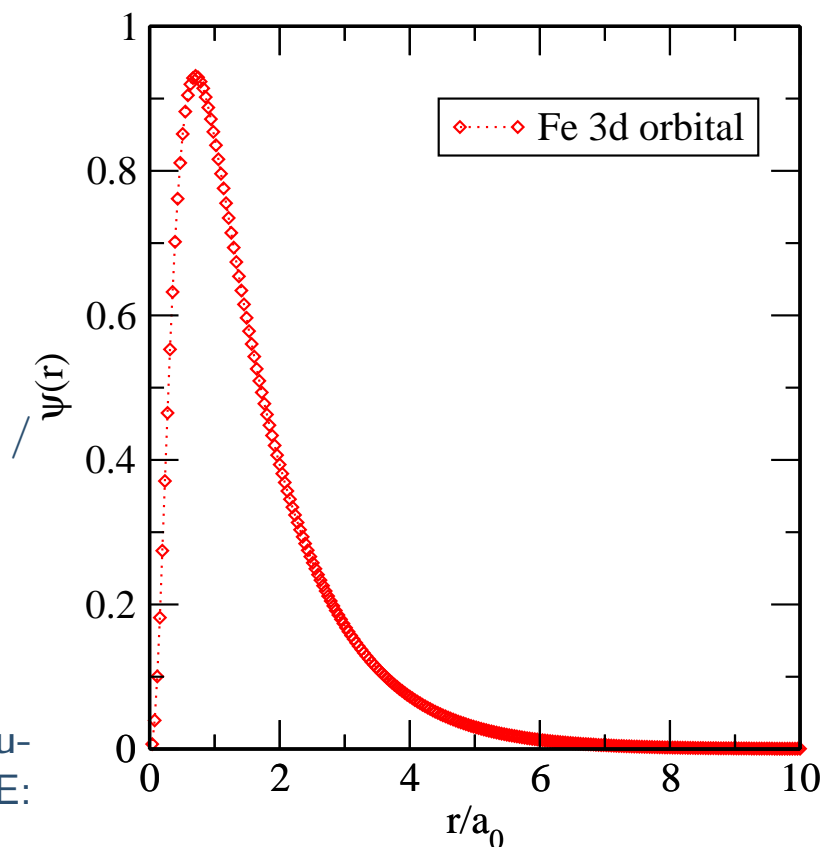
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Numerical representation of orbitals
wavefunctions on computer should be

- compact
- efficient
- accurate

Simple discretization insufficiently accurate derivatives needed to compute K.E:

$$-\nabla^2 \phi$$





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How to solve the
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- Need way of representing KS orbitals (in fact the Bloch functions $u_{m\mathbf{k}}(\mathbf{r})$) in the computer.
- Usually represent as sum of selected **basis functions**

$$u_{m\mathbf{k}}(\mathbf{r}) = \sum_{i=1}^{N_f} c_{m\mathbf{k},i} f_i(\mathbf{r})$$

- $f_i(\mathbf{r})$ chosen for convenience in evaluating integrals, which are rewritten entirely in terms of coefficients $c_{m\mathbf{k},i}$.
- Basis functions form a **finite set** (N_f), so number of coefficients $c_{m\mathbf{k},i}$ is finite and can be stored in computer.
- **Truncation** of basis set to N_f members constitutes an **approximation** to Bloch functions. N_f is another **convergence parameter**.
- K-S or H-F Hamiltonians take form of *matrix* of basis coefficients and equations become *matrix-eigenvalue* equations

$$H_{\mathbf{k},ij} c_{m\mathbf{k},j} = \epsilon_{m\mathbf{k}} c_{m\mathbf{k},i}$$

and possible computer algorithms to solve them are suggested.



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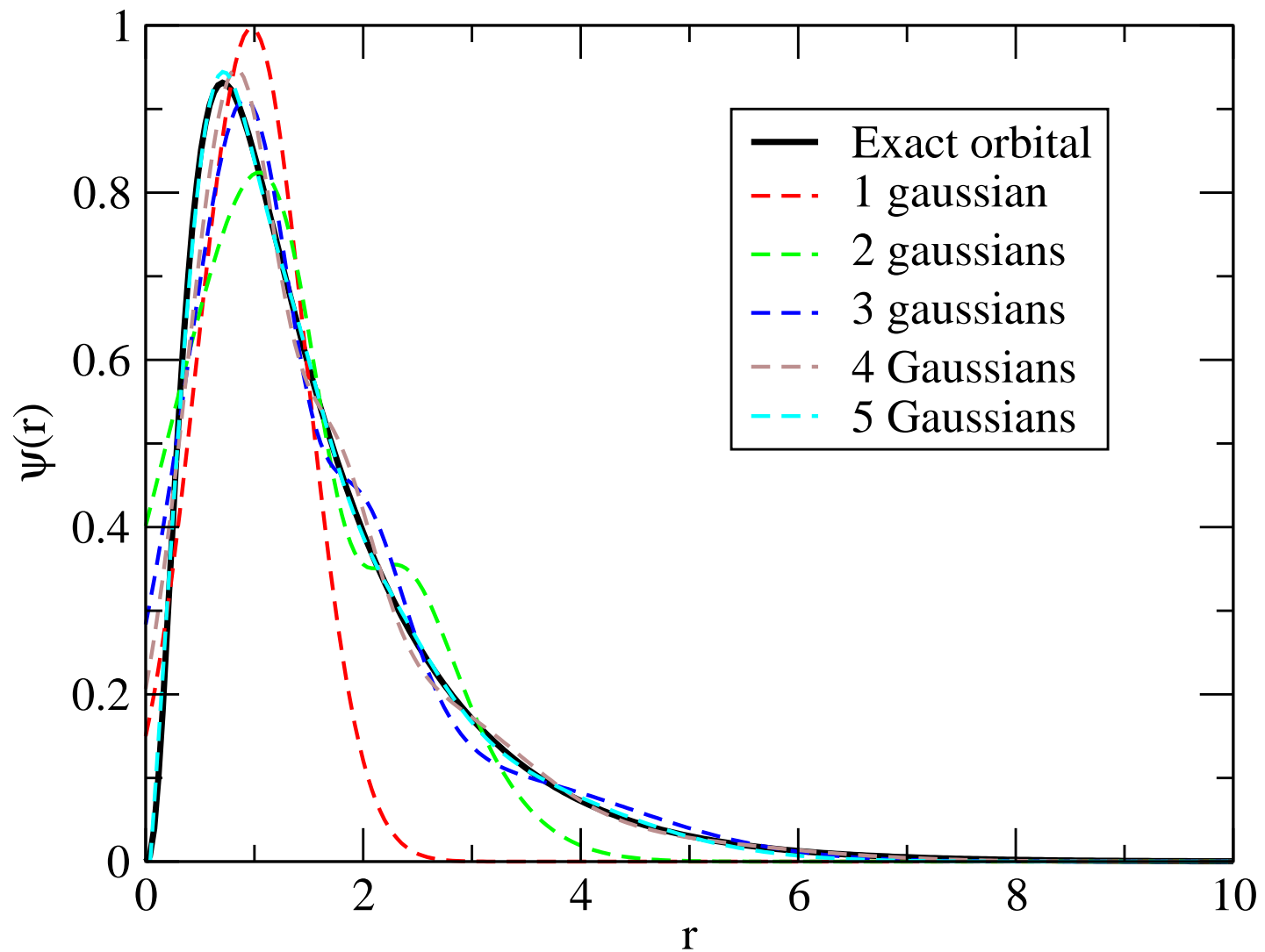
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$$\psi_i(\mathbf{r}) = \sum_{jlm} C_{ij,lm} e^{-\alpha_i r^2} Y_{lm}(\hat{\mathbf{r}})$$

Pros

- Compact: only small number of $C_{ij,lm}$ needed
- Integrals (needed to evaluate Hamiltonian) are *analytic*
- Huge literature describing sets of diverse quality.

Cons

- Over complete: risk of *linear dependence*
- Non-orthogonal: overlap gives risk of *Basis Set Superposition Error*
- Awkward to systematically improve - somewhat of a dark art - experience needed.
- Need to master arcane terminology, 3-21G, 6-21G**, "double-zeta+polarization", "diffuse"
- Atom-centred \Rightarrow difficult "Pulay" terms in forces, stresses and force-constants.



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$$\psi_i(\mathbf{r}) = \sum_{lm} f_{lm}(r) Y_{lm}(\hat{\mathbf{r}})$$

where f_{lm} is stored on a radial numerical grid. e.g. DMOL, FHI-Aims, SIESTA

Pros

- Better completeness than with Gaussians.

Cons

- Integrals must be evaluated numerically
- Harder to control integration accuracy
- Harder to evaluate kinetic energy accurately.



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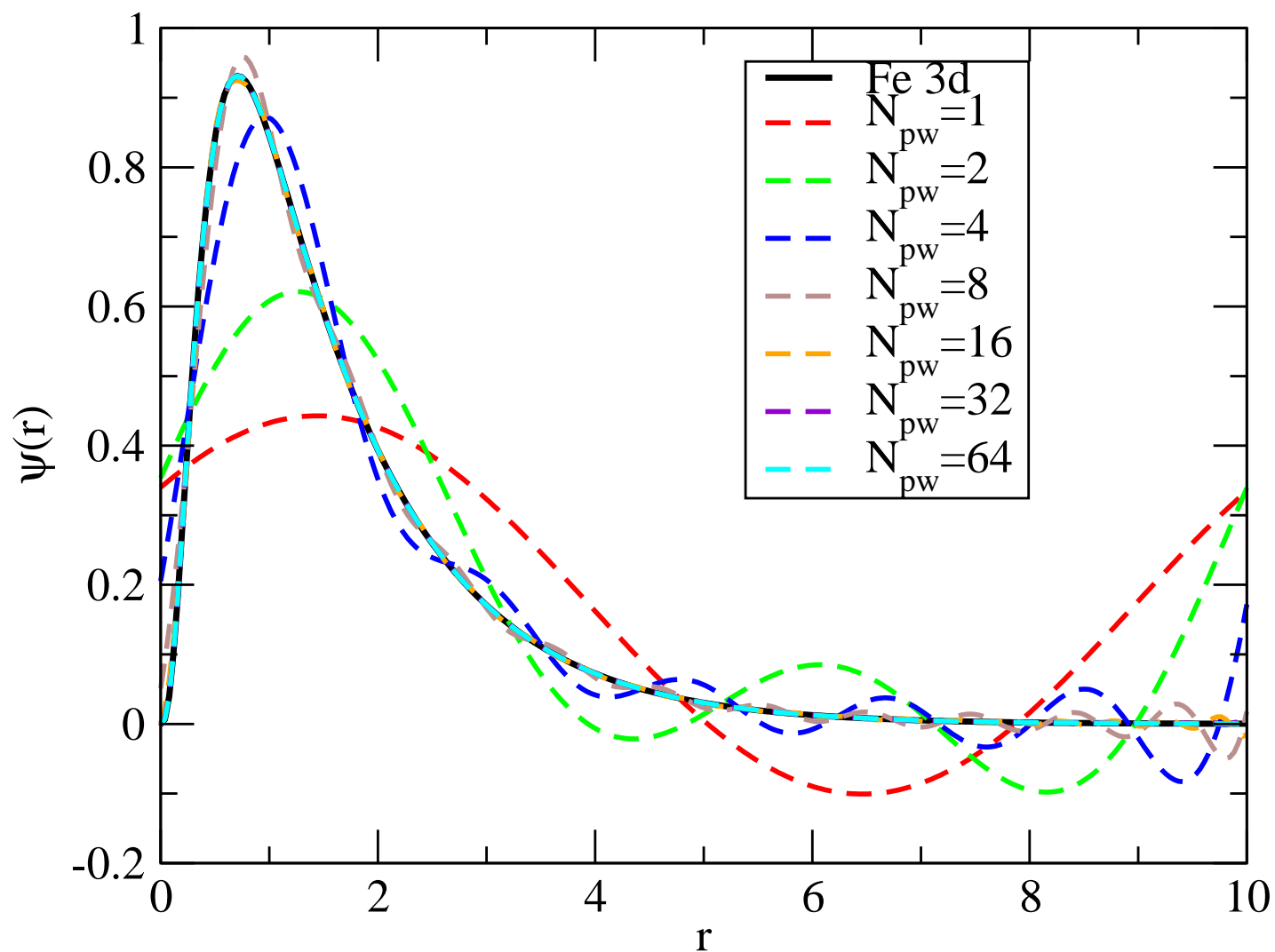
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$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}}^{|\mathbf{G}| < G_{\max}} c_{i\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

Pros

- *Fourier Series* expansion of $\psi(\mathbf{r})$: Fourier coefficients $c_{i\mathbf{k},\mathbf{G}}$ stored on regular grid of \mathbf{G} .
- Can use highly efficient FFT algorithms to transform between \mathbf{r} -space and \mathbf{G} -space representations.
- $O(N^2)$ scaling of CPU time and memory allows for 100s of atoms.
- Complete and Orthonormal. No BSSE or linear dependence.
- Simple to evaluate forces, stresses and force-constants.
- Not atom-centred \Rightarrow unbiased
- Systematically improvable to convergence with single parameter G_{\max} .

Cons

- Very large number of basis coefficients needed (10000 upwards). Impossible to store Hamiltonian matrix.
- Sharp features and nodes of $\psi(\mathbf{r})$ of core electron prohibitively expensive to represent \Rightarrow need *pseudopotentials*
- Vacuum as expensive as atoms.



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GTOs “Gaussian-type orbitals” Very widely used in molecular calculations, also periodic because integrals are analytic and can be tabulated. **Atom-centering** can be a disadvantage, giving rise to additional terms in forces and biasing the calculation. Only small numbers of basis functions needed per atom.

STOs: “Slater-type orbitals” atom-centered but uses eigenfunctions of atomic orbitals.

MTOs: “Muffin-Tin orbitals”. Atom centred using eigenfunctions in spherically-symmetric, truncated potential (muffin-tin).

Plane Waves: Very widely used in solid-state calculations.

Formally equivalent to a **Fourier series**. Can use powerful Fourier methods including FFTs to perform integrals. Ideally suited to periodic system. Unbiased by atom position. Systematically improvable convergence by increasing G_{\max} .

APW “Augmented Plane Waves” a mixed basis set of spherical harmonics centred on atoms and plane-waves in interstitial region. LAPW methods highly accurate but restricted to small systems.



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How to solve the
equations

- See M. Payne *et al Rev. Mod. Phys.* **64**, (1045) 1992
- Expressed in terms of plane-wave coefficients $c_{m\mathbf{k}}(\mathbf{G})$ the total KS energy is

$$E_{\text{KS}} = \sum_{\mathbf{k}} \sum_m \sum_{\mathbf{G}} |\mathbf{G} + \mathbf{k}|^2 |c_{m\mathbf{k}}(\mathbf{G})|^2 + \sum_{\mathbf{G} \neq 0} V_{\text{ext}}(\mathbf{G}) n(\mathbf{G})$$

$$+ \sum_{\mathbf{G} \neq 0} \frac{|n(\mathbf{G})|^2}{|\mathbf{G}|^2} + \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n(\mathbf{r})) + E_{\text{II}}(\{\mathbf{R}_I\})$$

There are only **single** sums over \mathbf{G} or \mathbf{r} which can therefore be evaluated in $O(N_G)$ operations.

- $\sum_{\mathbf{G}}$ runs over all $|\mathbf{G} + \mathbf{k}| < G_{\text{max}}$. Assuming that $c_{m\mathbf{k}}(\mathbf{G})$ decreases rapidly with G , accuracy can be *systematically improved* by increasing G_{max} .
- It is common to quote plane-wave *cutoff energy*

$$E_c = \frac{\hbar^2 G_{\text{max}}^2}{2m_e}$$

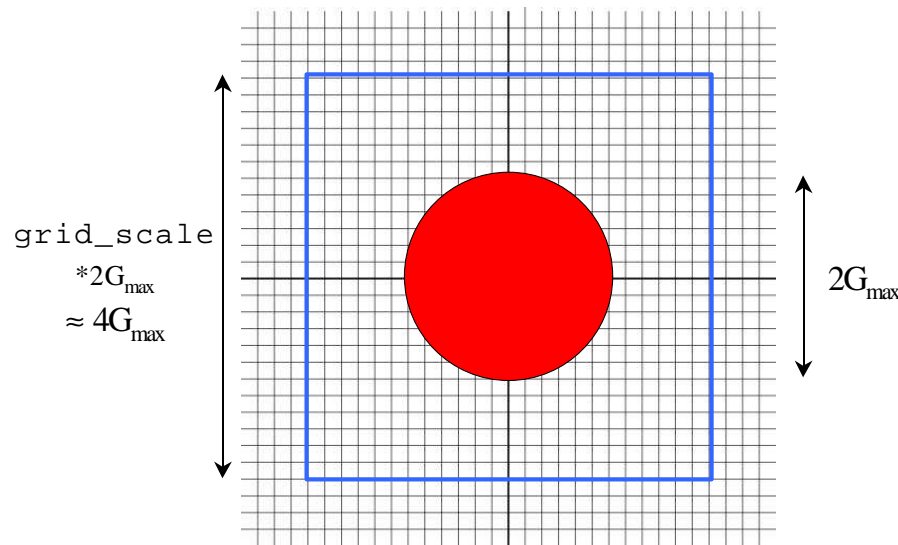
instead of G_{max} .



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- Store $c_{m\mathbf{k}}(\mathbf{G})$ and $n(\mathbf{r})$ on 3-dimensional **grid**, and can use FFTs to map between real and reciprocal-space. Example, density $n(\mathbf{r})$ constructed as $n(\mathbf{r}) = \sum_{\mathbf{k}} \sum_m^{\text{occ}} |u_{m\mathbf{k}}(\mathbf{r})|^2$ where $u_{m\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{m\mathbf{k}}(\mathbf{G}) \exp(i\mathbf{G}\cdot\mathbf{r})$ which requires 1 FFT for each band and k-point to transform $u_{m\mathbf{k}}(\mathbf{G})$ into real-space. To compute Hartree and local, potential terms, we need $n(\mathbf{G}) = \sum_{\mathbf{r}} n(\mathbf{r}) \exp(-i\mathbf{G}\cdot\mathbf{r})$
- Need twice maximum grid dimension to store charge density as orbitals.

The FFT Grid



Nuts and Bolts 2001

Lecture 6: Plane waves etc.

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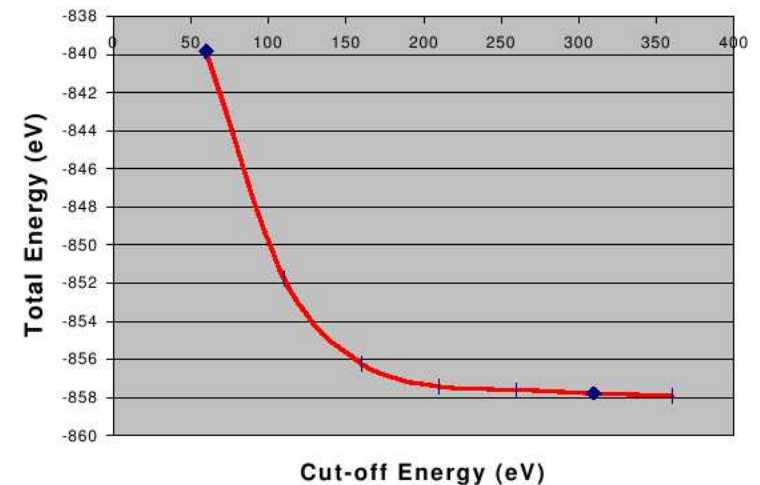
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- Can *systematically improve* basis set to full or desired level of convergence.
- Unbiased basis set, independent of nature of bonding.
- Highly efficient Fourier methods available for implementation.
- $O(N^2)$ scaling of CPU time and memory allows for 100s of atoms.
- Many plane-waves needed to model rapid variations in electron density.
- Vacuum as expensive as atoms.

Convergence with E_{cut} (Si8)





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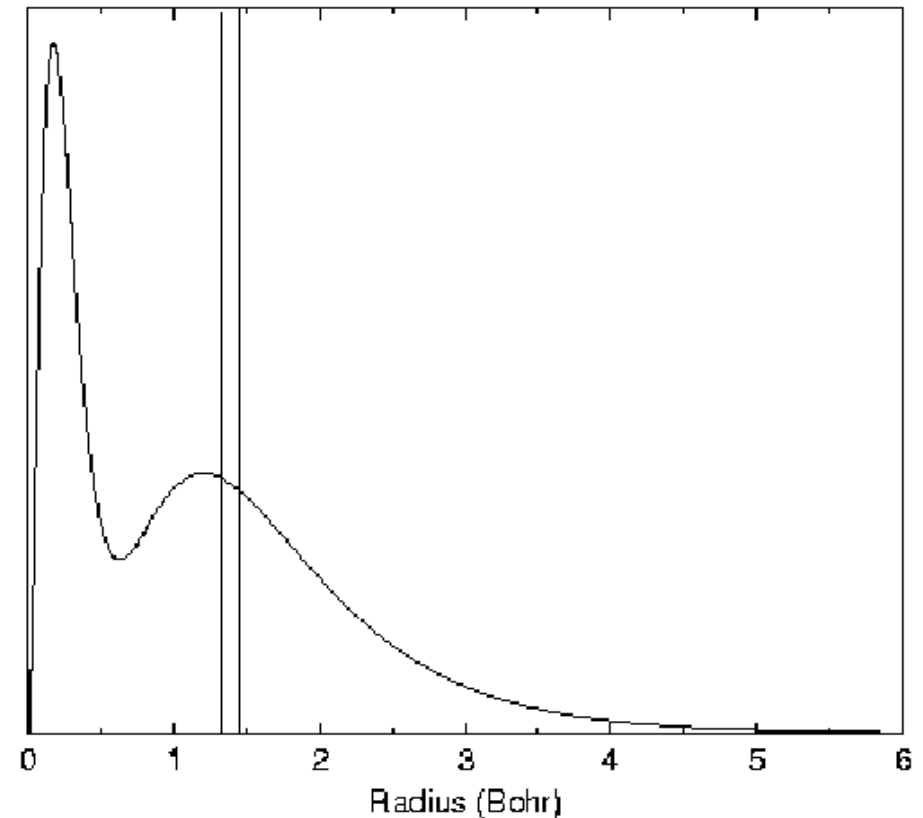
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How to solve the
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- Steep ionic potential $V(r) = -\frac{Ze}{r}$ near ion causes rapid oscillations of $\phi(r)$.
- High-frequency Fourier components need very high energy plane-wave cutoff.
- Filled shells of core electrons are **unperturbed** by crystalline environment. All chemical bonding involves **valence electrons** only.

Carbon Atom

All-electron Charge Density





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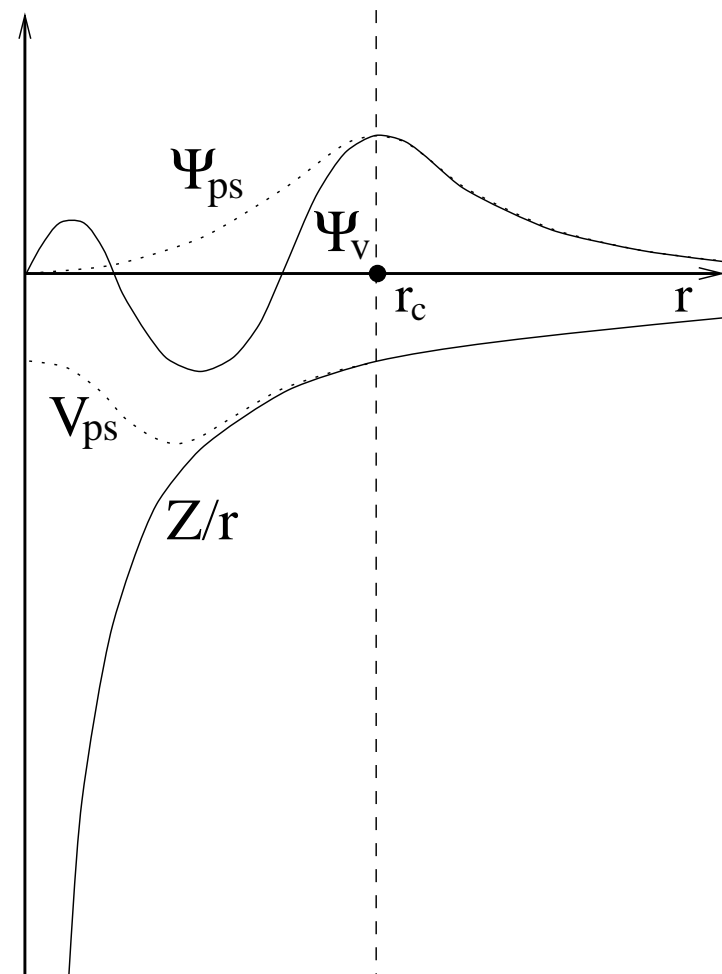
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How to solve the
equations

- Replace strong ionic potential with weaker **pseudopotential** which gives **identical** valence electron wavefunctions outside core region, $r > r_c$. This gives identical scattering properties.
- Pseudo-wavefunction has **no nodes** for $r < r_c$ unlike true wavefunction.
- Smooth ϕ_{pseudo} can be represented with few plane waves.
- Pseudopotentials imply the **Frozen Core approximation**
- **Ab-initio** pseudopotentials are calculated from **all-electron** DFT calculations on a single atom.
- Can be calculated using **relativistic** Dirac equation incorporating relativity of core electrons into PSP. Valence electrons usually non-relativistic.





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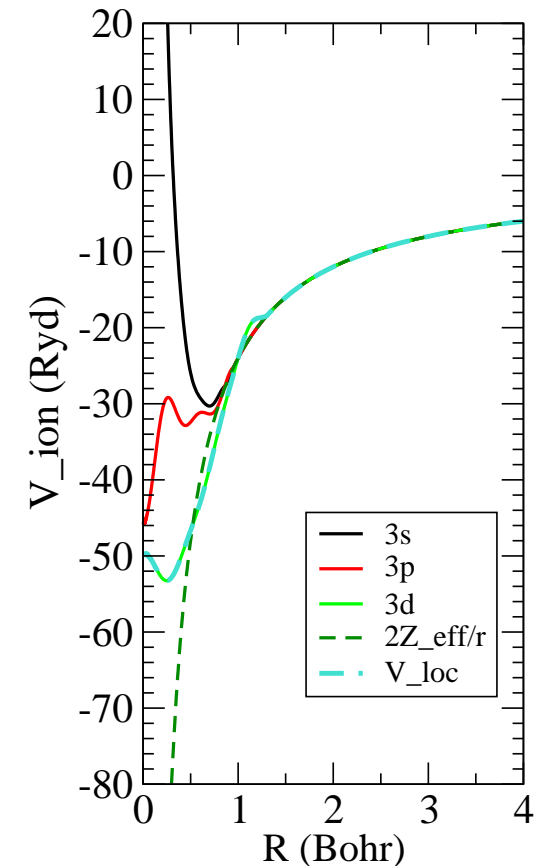
- Simple “local” potential $V_{PS}(r)$ insufficient for accurate description of most elements.
- Almost always use **nonlocal** pseudopotential operator

$$V_{PS} = \sum_{l,m} |Y_{lm} \rangle V_l(r) \langle Y_{lm}|$$

where $|Y_{lm} \rangle$ are spherical harmonics of angular momentum l .

- Several prescriptions to generate pseudopotentials; *Hamman-Schluter, Chang, Kerker, Trouiller-Martins, Optimised (Rappe), Vanderbilt*.
- Additional technicalities lead to **norm-conserving vs ultrasoft**.
- Goal has been to get “smoothest” pseudo-wavefunctions to reduce plane-wave cutoff energy. Vanderbilt ultrasoft pseudopotentials give lowest cutoff energies and high accuracy.

Ionic pseudopotential: Ti





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How to solve the
equations

- Norm conservation \Rightarrow nodeless 2p, 3d, 4f states inevitably hard
- Vanderbilt [PRB **41**,7892(1990)] relax norm-conservation.

$$\hat{V}_I^{\text{NL}} = \sum_{jk} D_{jk} |\beta_j\rangle \langle \beta_k|$$

with

$$D_{jk} = B_{jk} + \epsilon_j q_{jk}$$

and

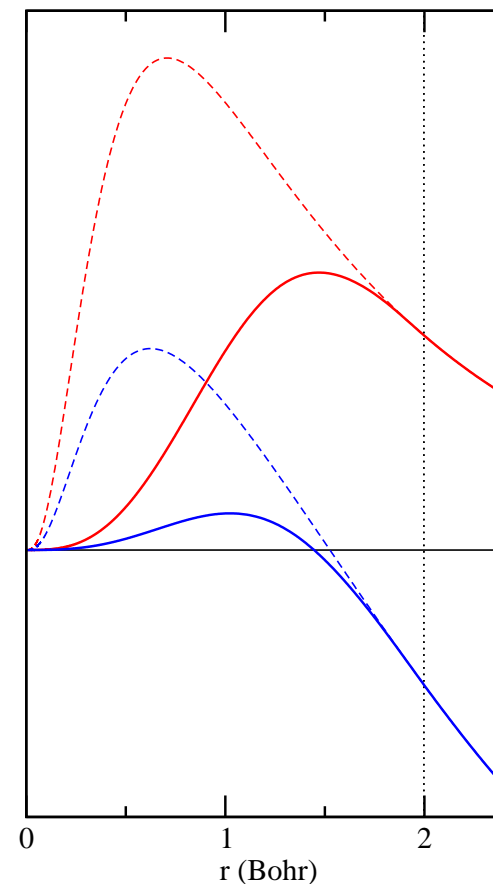
$$Q_{jk}(r) = \psi_j^{*,\text{AE}}(r) \psi_k^{\text{AE}}(r) - \phi_j^{*,\text{PS}}(r) \phi_k^{\text{PS}}(r)$$

$$q_{jk} = \langle \psi_j^{\text{AE}} | \psi_k^{\text{AE}} \rangle - \langle \phi_j^{\text{PS}} | \phi_k^{\text{PS}} \rangle$$

$$= \int_0^{r_c} Q_{jk}(r) dr$$

- $Q_{jk}(r)$ are *augmentation functions*

Fe 3d USP





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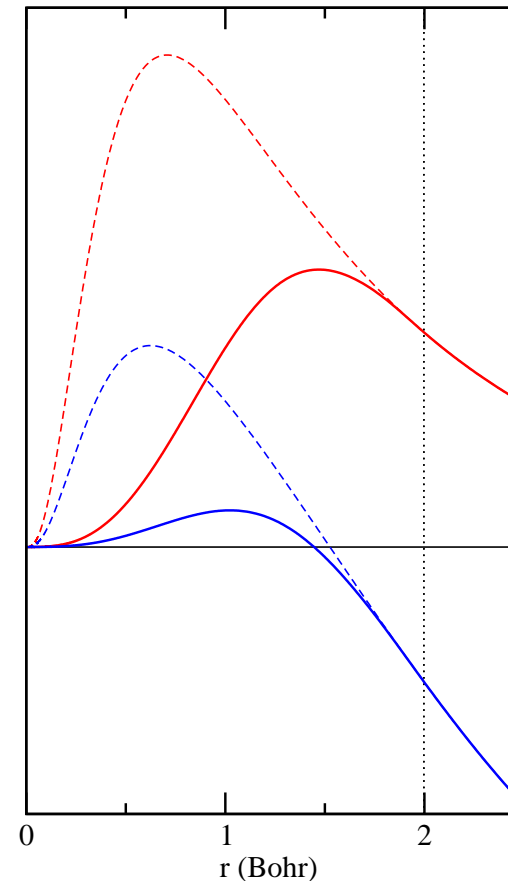
$$Q_{jk}(r) = \psi_j^{*,\text{AE}}(r) \psi_k^{\text{AE}}(r) - \phi_j^{*,\text{PS}}(r) \phi_k^{\text{PS}}(r)$$

$$q_{jk} = \langle \psi_j^{\text{AE}} | \psi_k^{\text{AE}} \rangle - \langle \phi_j^{\text{PS}} | \phi_k^{\text{PS}} \rangle$$

$$= \int_0^{r_c} Q_{jk}(r) dr$$

- $Q_{jk}(r)$ are *augmentation functions*

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With **overlap operator** \hat{S} defined as

$$\hat{S} = \hat{1} + \sum_{jk} q_{jk} |\beta_j\rangle \langle \beta_k|$$



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orthonormality of $\psi^{\text{AE}} \Rightarrow$ **S-orthonormality** of ψ^{PS}

$$\langle \psi_j^{\text{AE}} | \psi_k^{\text{AE}} \rangle = \langle \phi_j^{\text{PS}} | S | \phi_k^{\text{PS}} \rangle = \delta_{jk}$$



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$$n(r) = \sum_i |\phi_i(\mathbf{r})|^2 + \sum_{jk} \rho_{jk} Q_{jk}(r); \quad \rho_{jk} = \sum_i \langle \phi_i | \beta_j \rangle \langle \beta_k | \phi_i \rangle$$



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The K-S equations are transformed into **generalised eigenvalue** equations

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What gain does this additional complexity give?



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How to solve the
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- ϕ^{PS} can be made much smoother by dropping norm-conservation.
- Charge density restored by augmentation.
- Transferrability restored by use of 2 or 3 projectors for each l
- Quantities q_{jk} , B_{jk} are just numbers and $|\beta_j(r)\rangle$ required to construct \hat{S} are similar to norm-conserving projectors.
- Only functions $Q_{jk}(r)$ have fine r-dependence, and they only appear when constructing augmented charge density.
- Everything except $Q_{jk}(r)$ easily transferred from atomic to grid-based plane wave code.



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- Vanderbilt USP \Rightarrow *pseudize* $Q_{jk}(r)$ at some $r_{\text{inner}} \approx r_c/2$, preserving norm and higher moments of charge density.
- Blöchl PAW \Rightarrow add radial grids around each atom to represent $Q_{jk}(r)$ and $n_{\text{aug}}(\mathbf{r})$
- In PW code add 2nd, denser FFT grid for $n_{\text{aug}}(\mathbf{r})$ (and $V_{\text{H}}(\mathbf{r})$ - specified by parameter `fine_grid_scale`).
- Set `fine_grid_scale`= 2..4 depending on r_c and r_{inner} ; good guess is r_c/r_{inner}



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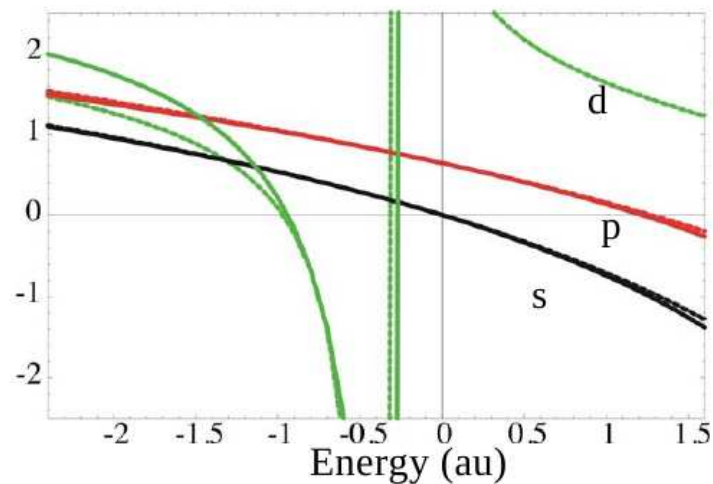
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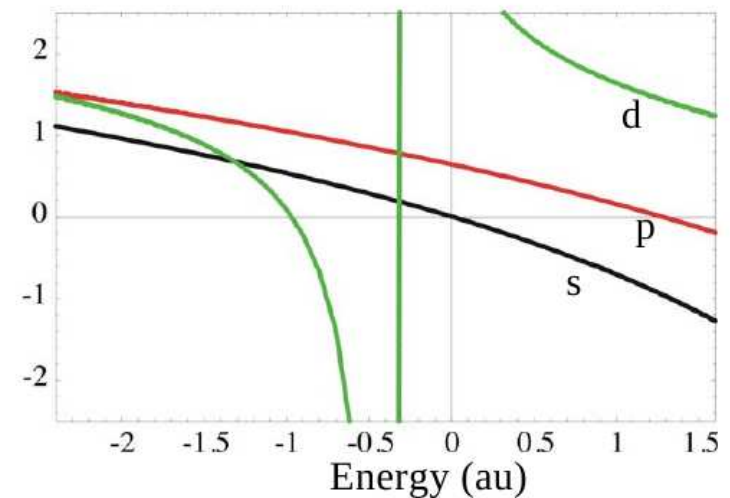
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How to solve the
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Zinc:
One Beta per angular momentum channel



Zinc:
Two Betas per angular momentum channel



- logarithmic derivative ($\frac{d}{dr} \log \phi(r)$) vs energy plots are guide to transferrability.
- 2 projectors \Rightarrow superior transferrability.



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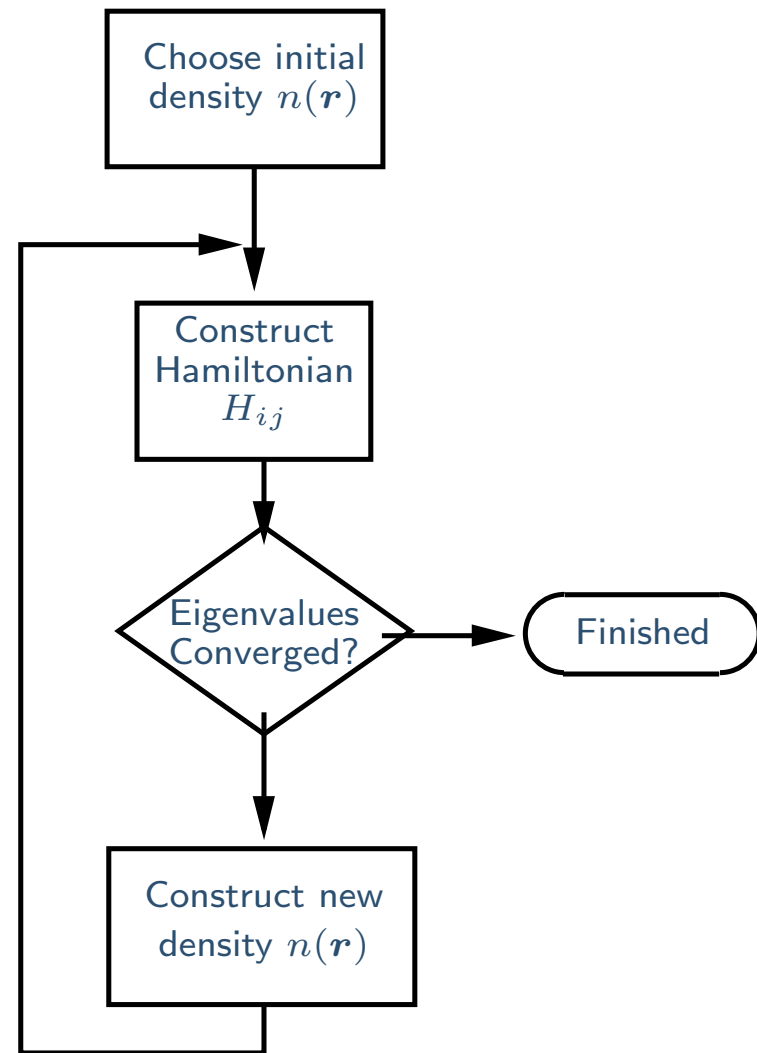
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Summary of important
concepts

- K-S Hamiltonian is *effective* Hamiltonian as Hartree term depends on electron density $n(\mathbf{r})$. But density depends on orbitals, which in turn are eigenvectors of Hamiltonian.
- Need to find *self-consistent* solution where $c_{m\mathbf{k},i}$ are eigenvalues of Hamiltonian matrix whose electron density is constructed from $c_{m\mathbf{k},i}$.
- In practice never converges.





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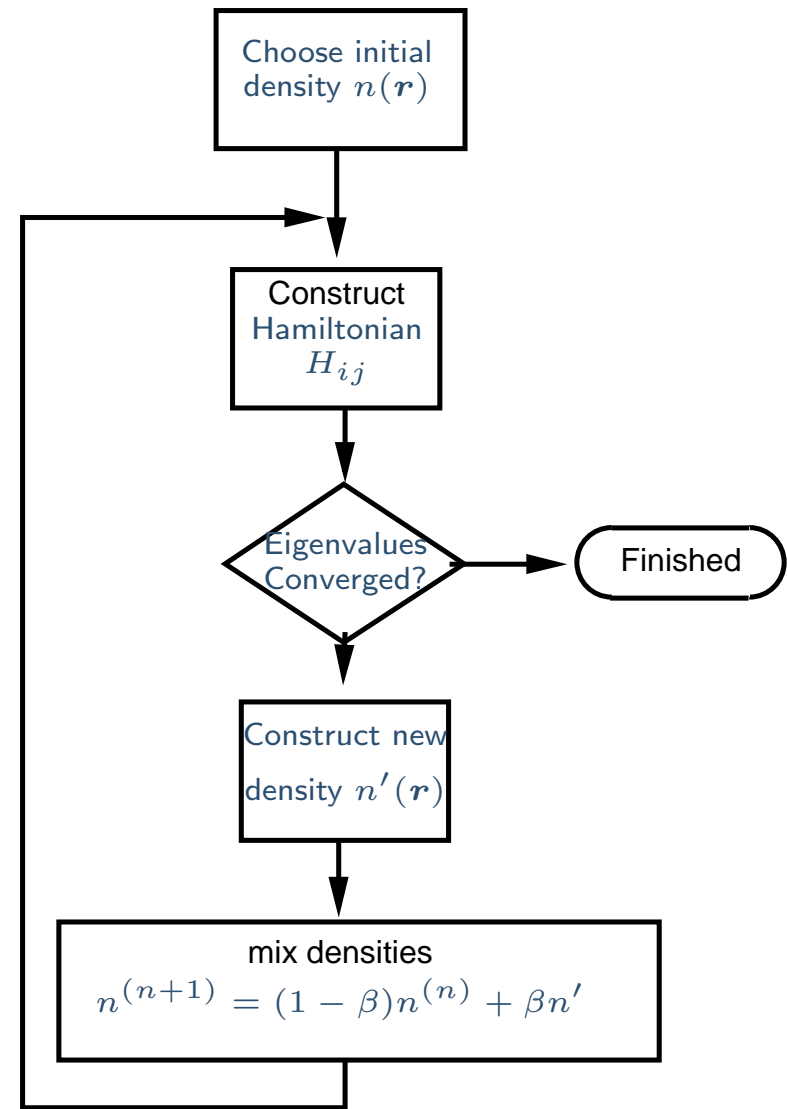
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Summary of important
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- Convergence may be stabilised by mixing fraction of “new” density with density from previous iteration.
- Variety of more sophisticated mixing algorithms available, due to Pulay, Kerker, Broyden.
- Commonly used in Quantum Chemistry, LAPW, LMTO, LCAO-GTO codes with small basis set.
- A plane-wave basis set contains 10,000+ coefficients $\Rightarrow H_{ij}$ is far too large to store.
- Don't actually construct H_{ij} ; use iterative solver to find only lowest-lying eigenvalues of occupied states(plus a few extra).





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- Instead of solving matrix eigenvalue problem, exploit variational character of total energy.
- Ground-state energy is *function* of plane-wave coefficients $c_{m\mathbf{k}}(\mathbf{G})$ the total energy KS is

$$E = \sum_{\mathbf{k}} \sum_m \sum_{\mathbf{G}} |\mathbf{G} + \mathbf{k}|^2 |c_{m\mathbf{k}}(\mathbf{G})|^2 + \sum_{\mathbf{G} \neq 0} V_{\text{ext}}(\mathbf{G}) n(\mathbf{G}) \\ + \sum_{\mathbf{G} \neq 0} \frac{|n(\mathbf{G})|^2}{|\mathbf{G}|^2} + \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n(\mathbf{r})) + E_{\text{II}}(\{\mathbf{R}_I\})$$

- Vary coefficients to minimize energy using *conjugate-gradient* or other optimization methods subject to constraint that orbitals are *orthogonal*

$$\sum_{\mathbf{G}} c_{m\mathbf{k}}^*(\mathbf{G}) c_{n\mathbf{k}}(\mathbf{G}) = \delta_{mn}$$

- Can vary one band at a time, or all coefficients simultaneously, giving a *all-bands* method. See M. Payne *et al Rev. Mod. Phys.* **64**, 1045 (1992); M. Gillan *J. Phys Condens. Matt.* **1** 689-711 (1989)



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Summary of important
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- Hartree-Fock approximation to many-body QM. Exchange.
- Density Functional Theory: Kohn-Sham methods,.
- LDA and GGA approximations to exchange-correlation energy.
- Electrons in periodic boundary conditions; reciprocal space and Brillouin-Zones.
- Band-structure in solids
- Basis sets – atomic and plane-wave
- Pseudopotentials
- SCF methods.