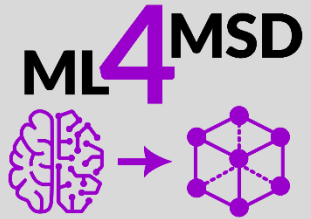# ME 5374-ST

Machine Learning for Materials Science and Discovery

Fall 2025

ML4MSD

Asst. Prof. Peter Schindler

Lecture 14 – Atomistic Modeling 2, Density Functional Theory (DFT)

- Quantum Mechanics and Schrödinger Equation
- Hartree-Fock
- Hohenberg-Kohn Theorems
- Kohn-Sham Equation, DFT, and Local Density Approximation (LDA)
- Band Diagrams and Reciprocal Space
- User Choices: Basis Sets, Atomic Potentials, and Exchange-Correlation Functionals
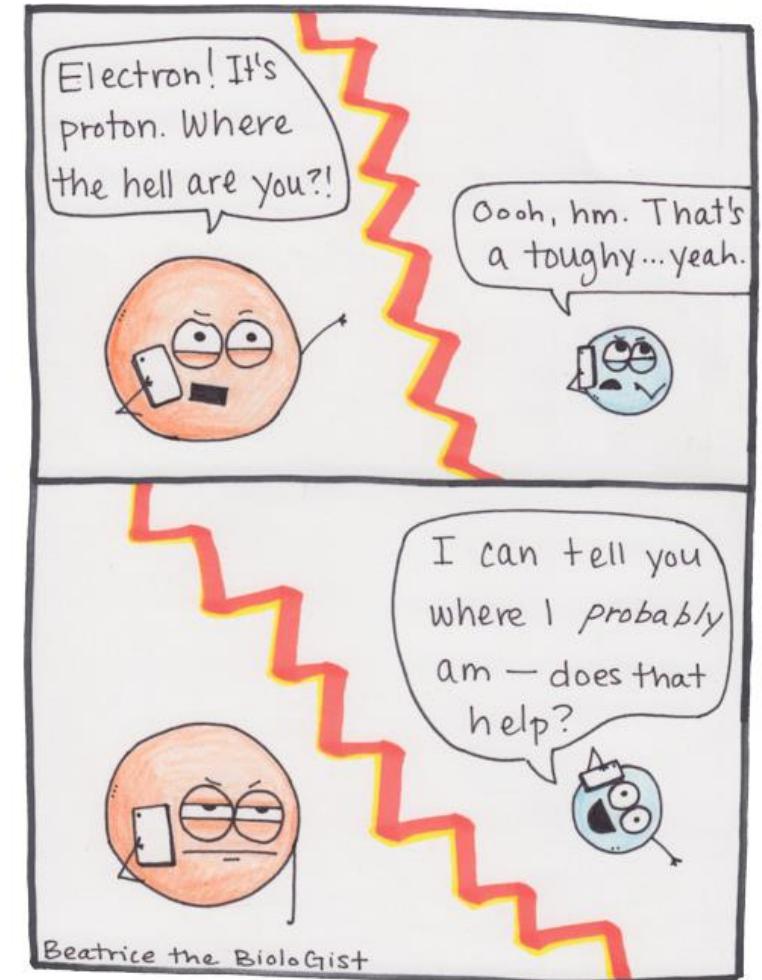- GPAW and ASE Tutorial

Quantum vs. Classical Mechanics

Classical Mechanics

$$\vec{F} = \dot{\vec{p}} \qquad \vec{p} = m \cdot \dot{\vec{r}}$$

$$H = \frac{\vec{p}^2}{2m} + V$$

$$\vec{r}(t), \underbrace{\{\vec{r}(t_0), \dot{\vec{r}}(t_0), \ddot{\vec{r}}(t_0), \ldots\}}_{\text{initial conditions}}$$

Deterministic!

Quantum Mechanics

$$\hat{H}\psi(\vec{r},t) = i\hbar \frac{\partial}{\partial t}\psi(\vec{r},t)$$

$$\vec{p} \rightarrow \hat{\vec{p}} = -i\hbar\vec{\nabla}$$

$$\rho(\vec{r},t) = \left|\psi(\vec{r},t)\right|^2$$

$$\Delta\vec{r} \cdot \Delta\vec{p} \geq \hbar / 2$$

Probabilistic!

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Beatrice the Biologist

Notation: $\dot{\vec{r}} = d\vec{r} / dt$

Applying Quantum Mechanics to Materials

Schrödinger equation can be solved exactly for Hydrogen (*one* e⁻)

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon r}$$

Instead of orbits (Bohr) the solutions represent *electron clouds* (probability distributions) of different shapes → **s,p,d,f orbitals**
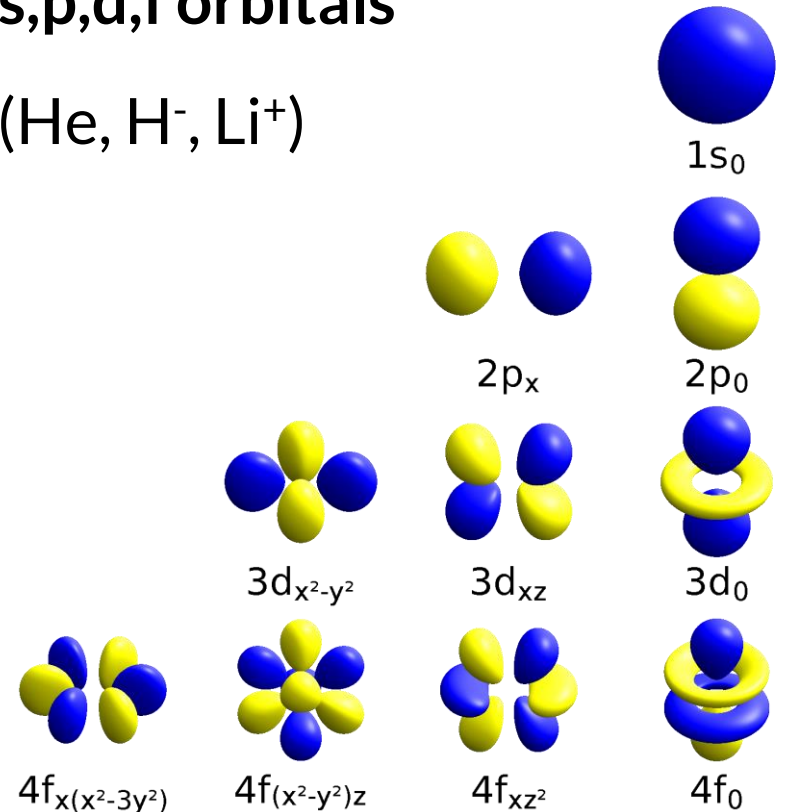
Can also be solved analytically for *two* electrons (He, H⁻, Li⁺)

$$\hat{H} = -\hbar^2\left[\frac{1}{2\mu}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{M}\nabla_1\cdot\nabla_2\right] + \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{|\vec{r}_2 - \vec{r}_1|} - \frac{Z(\vec{r}_1 + \vec{r}_2)}{\vec{r}_1\vec{r}_2}\right]$$

However, *three*-electron system **cannot** be solved analytically

→ *Approximations* necessary

$$\mu = mM/(m+M)$$

$1s_0$

$2p_x$ $2p_0$

$3d_{x^2-y^2}$ $3d_{xz}$ $3d_0$

$4f_{x(x^2-3y^2)}$ $4f_{(x^2-y^2)z}$ $4f_{xz^2}$ $4f_0$

Towards Hartree-Fock: Multi-electron Hamiltonian

Multi electron Hamiltonian (N electrons $\{\vec{r}, m_e\}_N$, M atoms $\{\vec{R}, m_n\}_M$)

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar \nabla_{\vec{R}_i}^2}{2m_n} - \sum_{i=1}^{N} \frac{\hbar \nabla_{\vec{r}_i}^2}{2m_e} + \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z_m}{\left|\vec{r}_i - \vec{R}_j\right|} + \sum_{i=1}^{N}\sum_{j<i}^{N} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{i=1}^{M}\sum_{j<i}^{M} \frac{Z_i Z_j}{\left|\vec{R}_i - \vec{R}_j\right|}$$

$$E_{\text{kin, nucl}} \qquad E_{\text{kin, el}} \qquad \text{nucl – el} \qquad \text{el - el} \qquad \text{nucl – nucl}$$

$$\hat{H}\Phi(\vec{r}_1, \ldots, \vec{r}_N, \vec{R}_1, \ldots \vec{R}_M; t) = i\hbar \frac{\partial}{\partial t} \Phi(\vec{r}_1, \ldots, \vec{r}_N, \vec{R}_1, \ldots \vec{R}_M; t)$$

Mass of nucleus is at least **1800 times** greater than mass of electron

Like: Mass of   to mass of

Towards Hartree-Fock

Multi electron Hamiltonian (N electrons $\{\vec{r}, m_e\}_N$, M atoms $\{\vec{R}, m_n\}_M$)

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar \nabla_{\vec{R}_i}^2}{2m_n} - \sum_{i=1}^{N} \frac{\hbar \nabla_{\vec{r}_i}^2}{2m_e} + \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z_m}{\left|\vec{r}_i - \vec{R}_j\right|} + \sum_{i=1}^{N}\sum_{j<i}^{N} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{i=1}^{M}\sum_{j<i}^{M} \frac{Z_i Z_j}{\left|\vec{R}_i - \vec{R}_j\right|}$$

$E_{\text{kin, nucl}}$ $E_{\text{kin, el}}$ nucl – el   el - el   nucl – nucl

$$\hat{H}\Phi(\vec{r}_1,\ldots,\vec{r}_N,\vec{R}_1,\ldots\vec{R}_M;t) = i\hbar\frac{\partial}{\partial t}\Phi(\vec{r}_1,\ldots,\vec{r}_N,\vec{R}_1,\ldots\vec{R}_M;t)$$

Born-Oppenheimer approximation

classically

$$\Phi\left(\{\vec{r}\}_N,\{\vec{R}\}_M;t\right) = \chi\left(\{\vec{R}\}_N;t\right)\cdot\Psi\left(\{\vec{r}\}_N,\{\vec{R}\}_M\right)$$

fixed $\{\vec{R}\}_M$

$$\left[-\sum_{i=1}^{N}\frac{\hbar\nabla_i^2}{2m} + \sum_{i=1}^{N}V_{\text{nuc}}(\vec{r}_i) + \sum_{i=1}^{N}\sum_{j<i}^{N}\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|}\right]\Psi(\vec{r}_1,\ldots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\ldots,\vec{r}_N)$$

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Notation: $\{\vec{R}\}_M = \vec{R}_1,\vec{R}_2,\ldots,\vec{R}_M$

Hartree-Fock

Hartree approximation: Electrons are **uncorrelated**

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2) \cdot \ldots \cdot \psi_N(\vec{r}_N)$$

N single electron equations (Hartree equ.) – **Mean field** approx.

$$\left[-\frac{\hbar\nabla^2}{2m} + V_{nuc}(\vec{r}) + \sum_{j \neq i}^{N} \int d\vec{r}' \frac{\left|\psi_j(\vec{r}')\right|^2}{|\vec{r} - \vec{r}'|} \right] \psi_i(\vec{r}) = E_i \cdot \psi_i(\vec{r})$$

Missing: Electron correlation and Fermion **exchange interaction**

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2) = \psi_2(\vec{r}_2) \cdot \psi_1(\vec{r}_1) \neq -\Psi(\vec{r}_2, \vec{r}_1)$$

$$\Psi(\vec{r}_1, \vec{r}_2 = \vec{r}_1) = \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_1) \neq 0 \quad \text{Violates Pauli exclusion}$$

Slater determinant adds exchange **exactly**
(but not correlation)

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) \end{vmatrix}$$

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Performance of Hartree-Fock

- **Binding energies** for materials generally *underestimated* by 10-50%
  → due to *neglected correlation effects*
- Despite that, **geometries** for molecules/solids are pretty ok (few % deviations)
- **Bandgaps** typically off by factor of order unity

- The exact exchange of HF calculations make a good starting point for **perturbative methods** to include correlation effects
- Since HF calculations are usually *less accurate* than DFT and require equal or greater computational effort
  → Materials calculations typically employ DFT

Hohenberg-Kohn Theorems

$$V_{\text{nuc}} \rightarrow \hat{H} \rightarrow \psi \rightarrow E_{\text{total}}$$
$$\rho$$
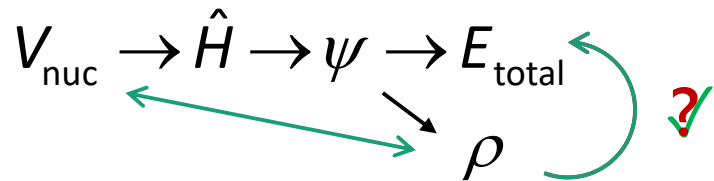
1. Electron density *uniquely* defines multi-electron system:

$$E_{\text{total}} = E[\rho(\vec{r})]$$

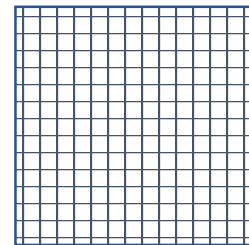2. $\min\left[E[\rho(\vec{r})]\right] = E[\rho_0(\vec{r})]$ where $\rho_0 =$ ground state density

Profound feature: *Calculation of wavefunction not required*

Number of parameters needed for

p^{3N} N-electron wavefunction

p^3 electron density

Np^3 N single-electron wavefunctions

Grid with *p* points
in each dimension

Northeastern
University

Overcoming the Exponential Wall

For example, look at **Oxygen** atom (8 electrons)

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5,\vec{r}_6,\vec{r}_7,\vec{r}_8) \quad \text{depends on 24 coordinates in 3D}$$

Let's do a rough sampling of the *multi-electron wavefunction*

10 entries / coordinate $\longrightarrow$ 10^{24} entries

1 Byte / entry $\longrightarrow$ 10^{24} Bytes

1 TB = 10^{12} Bytes / HDD $\longrightarrow$ 10^{12} Hard disk drives

0.5 kg / HDD $\longrightarrow$ $5 \cdot 10^8$ tons of HDDs
(500 million tons ~10 x Great Wall)

Equivalent sampling for *KS single-electron wavefunctions*:

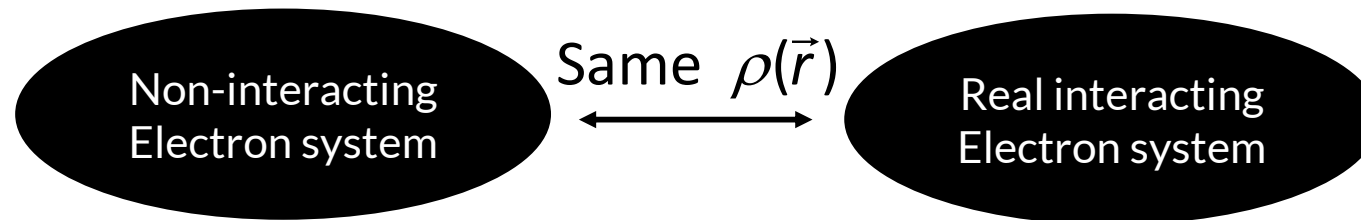8 independent coordinates in 3D $\rightarrow$ $8 \cdot 10^3$ Bytes = **8 kB**

Density Functional Theory (DFT) & Kohn-Sham Equations

But the kinetic energy (as a functional of density)
→ requires *exact multi-electron* wavefunction

Instead
introduce fictitious, *single-electron*, uncorrelated electron states (like in HF)
that give the **same total electron density** as the exact multi-electron state.

Non-interacting
Electron system

Same $\rho(\vec{r})$

Real interacting
Electron system

$$\left[-\frac{\hbar \nabla^2}{2m} + V_{\text{nuc}}(\vec{r}) + \sum_j \int d\vec{r}' \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} + \underbrace{\frac{\delta E_{\text{XC}}[\rho(\vec{r})]}{\delta \rho(\vec{r})}}_{V_{XC}[\rho(\vec{r})]} \right] \psi_i(\vec{r}) = E_i \cdot \psi_i(\vec{r})$$

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LDA: The True Success of DFT

In principle, KS equations are *exact.* However, form of XC in terms of density remains *unknown* → necessary to use **approximations**

Simplest approach for exchange-correlation functional:
Consider a **uniform electron gas** of density ρ

$$E_{XC}^{LDA}[\rho(\vec{r})] = \int d\vec{r}\ \rho(\vec{r})\,\epsilon_{XC}[\rho(\vec{r})]$$
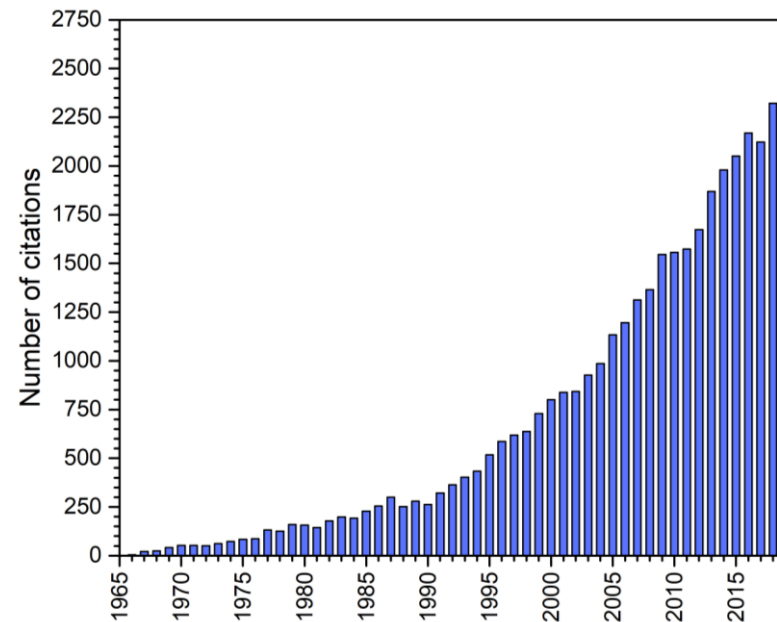
"Self-consistent equations including Exchange and Correlation Effects"
W. Kohn and L. J. Sham,
Phys. Rev. 140 (1965)

LDA: Trends and Limitations

- Favors homogeneous density: *Overestimates* binding energies (unlike HF)
- *Bond lengths, bond angles, vibration frequencies* **agree** with experiment to within a few percent. Bond lengths generally too small (overbound)
- *More accurate* than Hartree-Fock!
- Lack of **long-range correlations**: Unable to describe *London* or *dispersive interactions* (van der Waals)
- **Self-interaction** of electrons problematic:

  - **Localized states** (d,f -states) are not described very well

  - **Band gaps** *too small* (factor ~2) $\rightarrow$ optical abs. spectra wrong & dielectric constant too large.

- Works *well* for **covalent, ionic bonds** but *not well* for weak bonds (Hydrogen)
- **Wrong asymptotic behavior** of the effective potential: decays exponentially rather than $1/r \rightarrow$ no Rydberg series in atoms/molecules and negatively charged ions unstable
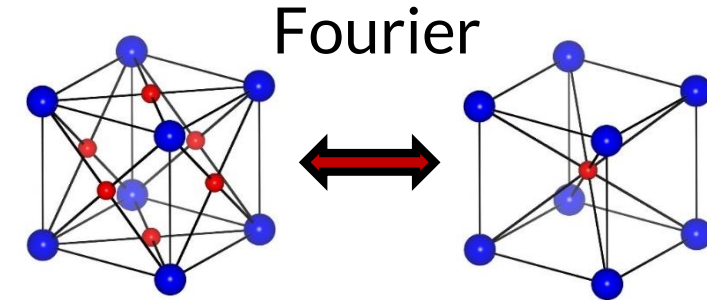- Cohesive energies, elastic properties, bulk modulus up to ~20% error

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Reciprocal Space and Brillouin Zone

Lattice basis vectors: $\vec{a}, \vec{b}, \vec{c}$

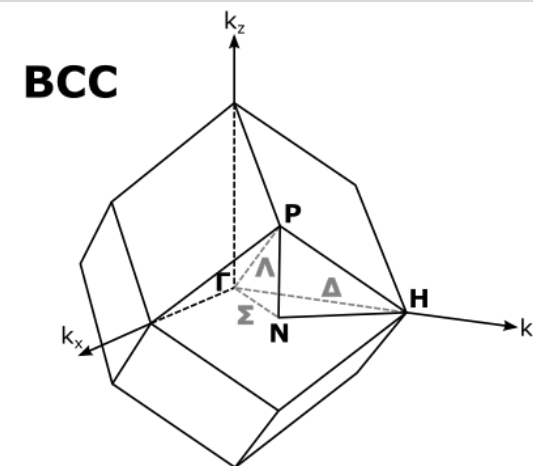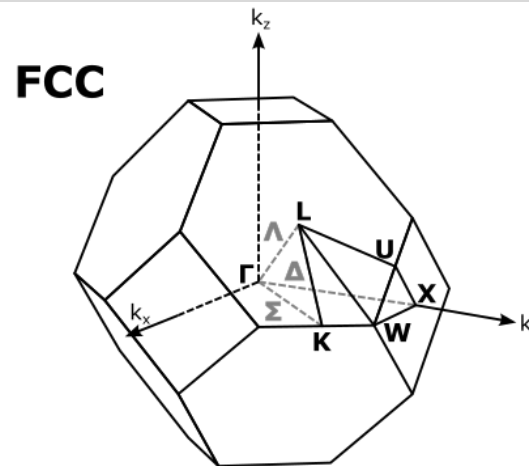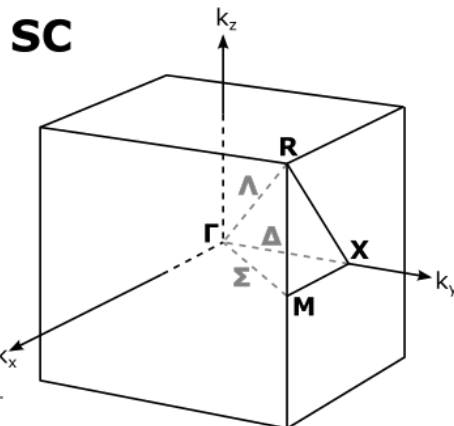**Reciprocal lattice** (*k*-space) basis vectors are given by

$$\vec{a}^* = \frac{2\pi}{V}\left(\vec{b} \times \vec{c}\right) \quad \vec{b}^* = \frac{2\pi}{V}\left(\vec{a} \times \vec{c}\right) \quad \vec{c}^* = \frac{2\pi}{V}\left(\vec{a} \times \vec{b}\right)$$
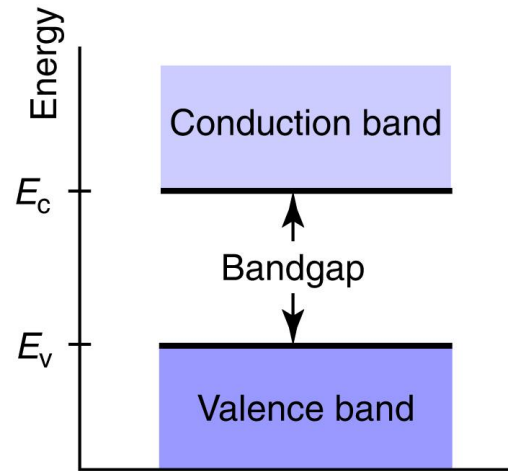
where $V = \vec{a} \cdot \left(\vec{b} \times \vec{c}\right)$

Fourier

Analogy in signal processing
→time *vs.* frequency domain

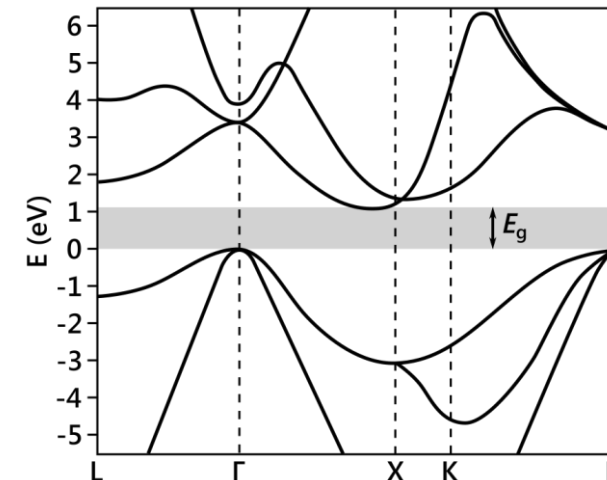**1st Brillouin Zone = Wigner-Seitz cell in reciprocal space**

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Band Diagrams

Semiconductor Devices

DFT / Optoelectronics

Space coordinate

Sufficient for understanding most electronic devices

k-space coordinate

Detailed band diagram, essential to understand opto-electronic devices

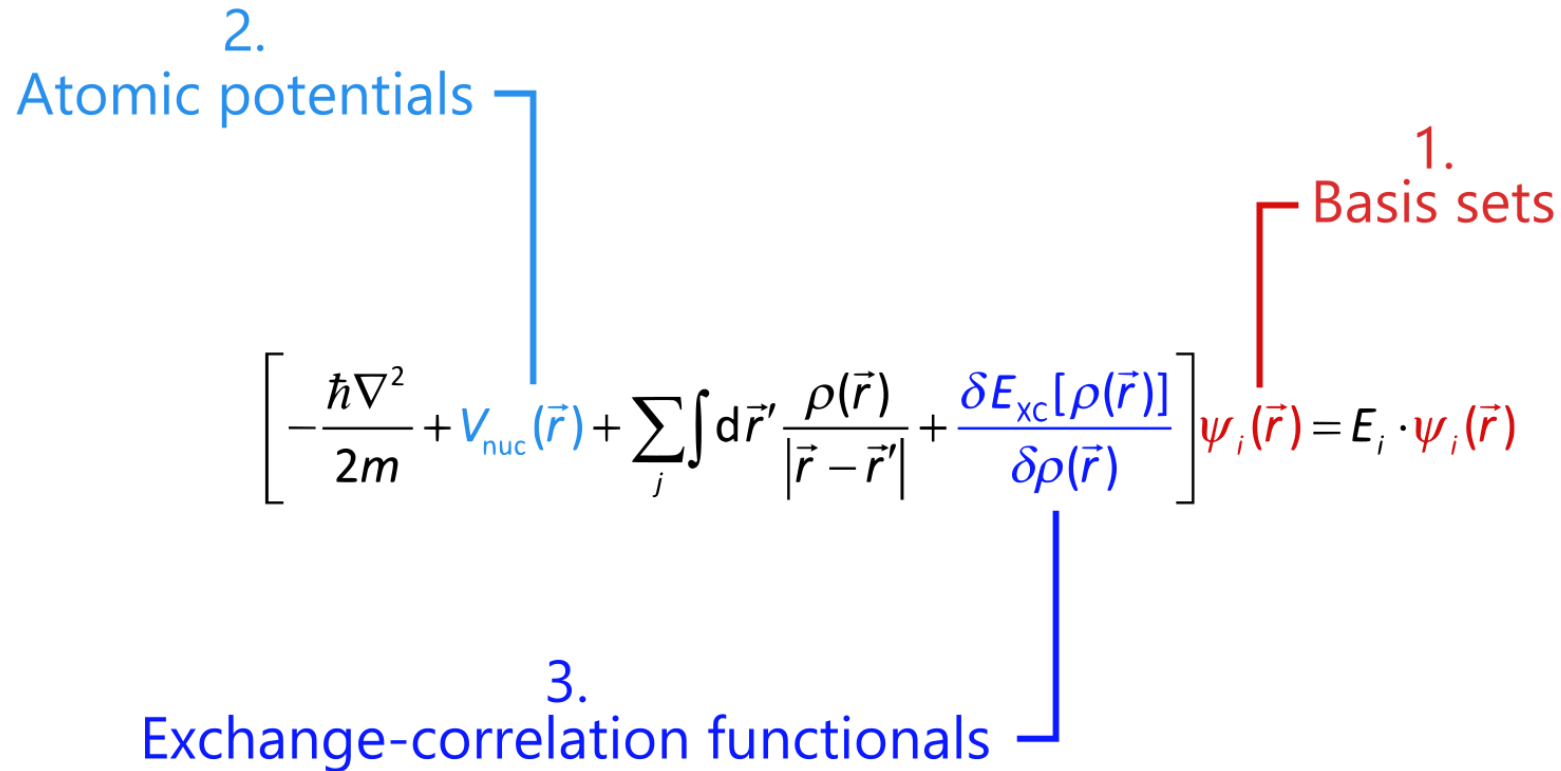Asst. Prof. Peter Schindler

Overview of DFT Knobs to Turn

2.
Atomic potentials

1.
Basis sets

3.
Exchange-correlation functionals

$$\left[-\frac{\hbar \nabla^2}{2m} + V_{\text{nuc}}(\vec{r}) + \sum_j \int d\vec{r}' \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{\text{xc}}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \right] \psi_i(\vec{r}) = E_i \cdot \psi_i(\vec{r})$$
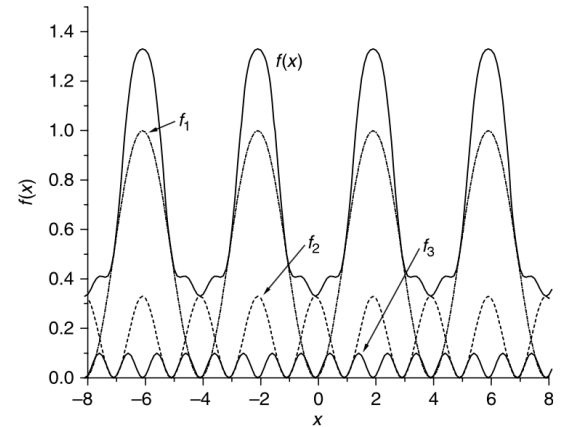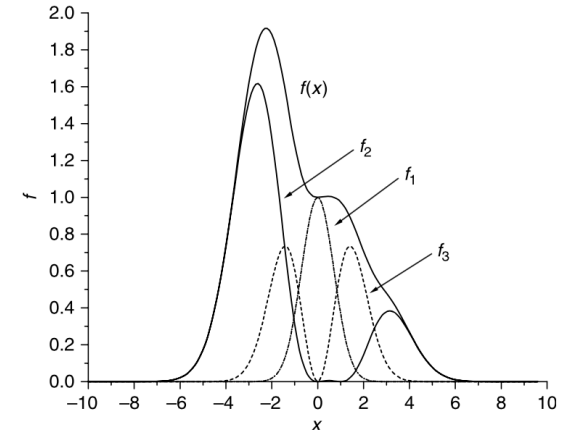
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1. Basis Sets

Localized (centered around atoms)
• Resemble atomic orbitals
(e.g., Gaussians, Slater)
• Describes *molecules* well/efficiently
→ mainly used by chemists

Extended (plane waves)
• Complete basis set
• Periodic boundary conditions (PBC)
• Describes bulk *crystal* structures well/efficiently
→ mainly used by physicists & material scientists

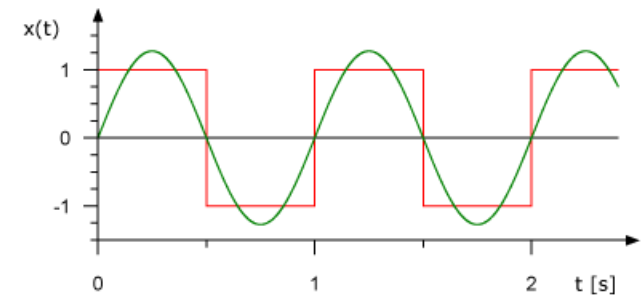# Plane Waves: Pros & Cons

+

- E_{cutoff} only parameter to *systematically improve* basis set
- Same basis set for molecules and solids
- No finite-basis set errors on forces ("*Pulay forces*")
- Established, highly optimized algorithms (FFTs, efficient charge-density mixing, etc.)

–

- Pseudopotentials needed ($\rightarrow$ not all-electron)
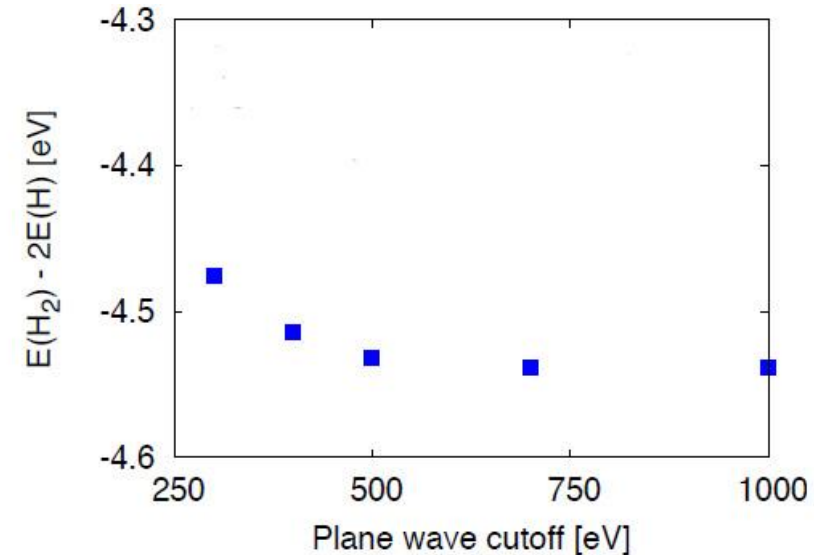- Large basis sets required (especially for vacuum)
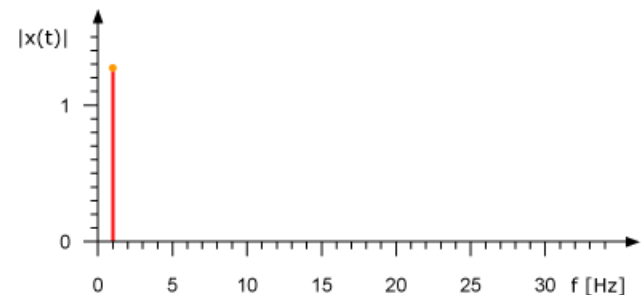
Convergence (w.r.t. E_{cutoff})

Calculation of **energy differences** using the same calculation parameters (XC functional, *k*-point mesh, PW cutoff, PPs) typically *converge faster*

This is due to *systematic cancellation of errors* associated with lack of total convergence of BZ integration, PW cutoff, etc.
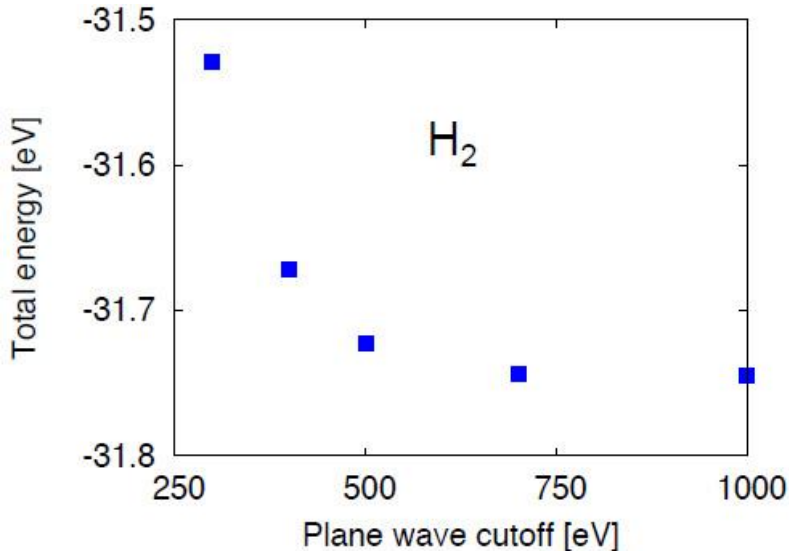
Convergence (w.r.t. *k*-points)

Convergence is not necessarily monotonous

Convergence of magnetic moment or forces may require denser *k*-point sampling than energy

k-point test for hexagonal Co with 30Ry cutoff and a=2.49Å

Magnetic moment vs. k=point sampling for hex Co with a=2.49Å
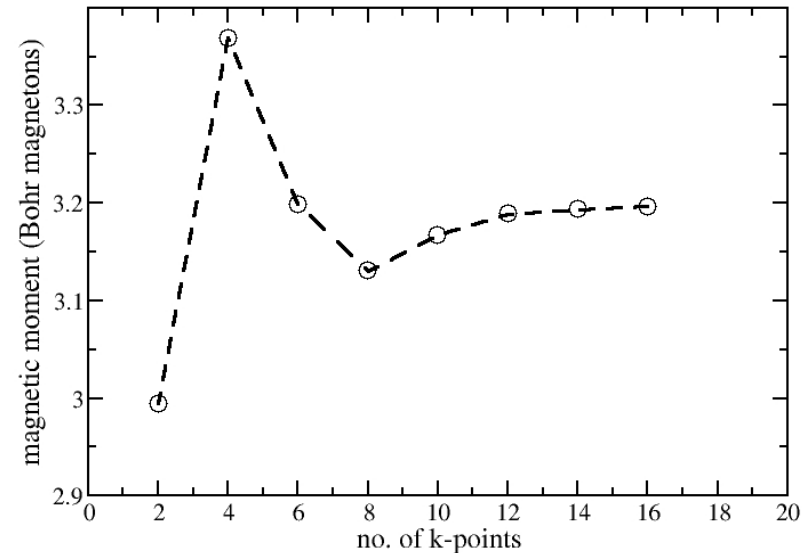
2. Pseudopotentials
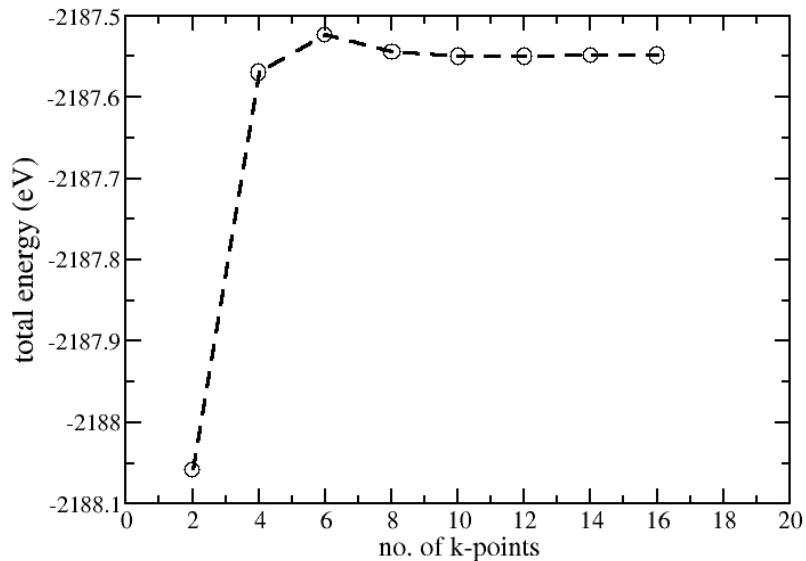
Electrons divided into
- *Core electrons* – chemically **inactive**; ignore explicit description
- *Valence electrons* – chemically **active**; include screening of nucleus

Valence states also require high energy cutoffs near the core region

>10,000 plane waves required versus 10s of Gaussians per atom

"Ab initio" potentials determined from an all electron calculation for a single atom.

Valence eigenvalues and wave function properties at boundary **reproduced by pseudopotential.**

ψ_{pseudo}

$\psi_{Z/r}$

r_{cutoff}

r

V_{pseudo}

$V \sim Z/r$
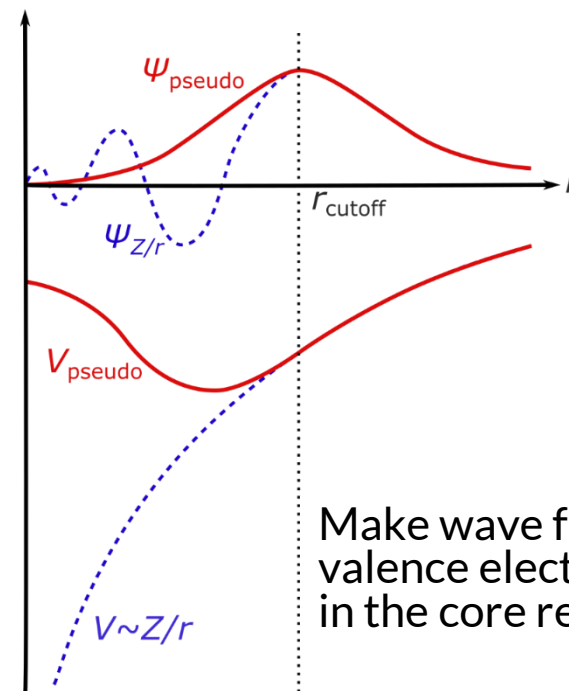
Make wave functions of valence electrons **soft** in the core region

3. XC Functionals – Jacob's Ladder

Constraint satisfaction *"non-empirical"*	"Heaven of chemical accuracy" (1 kcal/mol)		Property satisfaction *"empirical"*
RPA	EXX + partial exact correlation	$\{\psi_i\}^{\text{unocc.}}$	B2PLYP
PBE0, HSE	Hybrid/Meta-GGA	$E_{\text{EXX}}^{\text{HF}}, \{\psi_i\}^{\text{occ.}}$	**B3LYP**, M06
TPSS	Meta-GGA	$\vec{\nabla}^2 \rho(\vec{r}), \tau(\vec{r})$	mPWB95
PBE, PW91	GGA	$\left|\vec{\nabla}\rho(\vec{r})\right|$	BLYP, BP86
Truly "*ab-initio*"?	**LDA**	$\rho(\vec{r})$	

"Hartree Earth"

Accuracy / Computational Cost
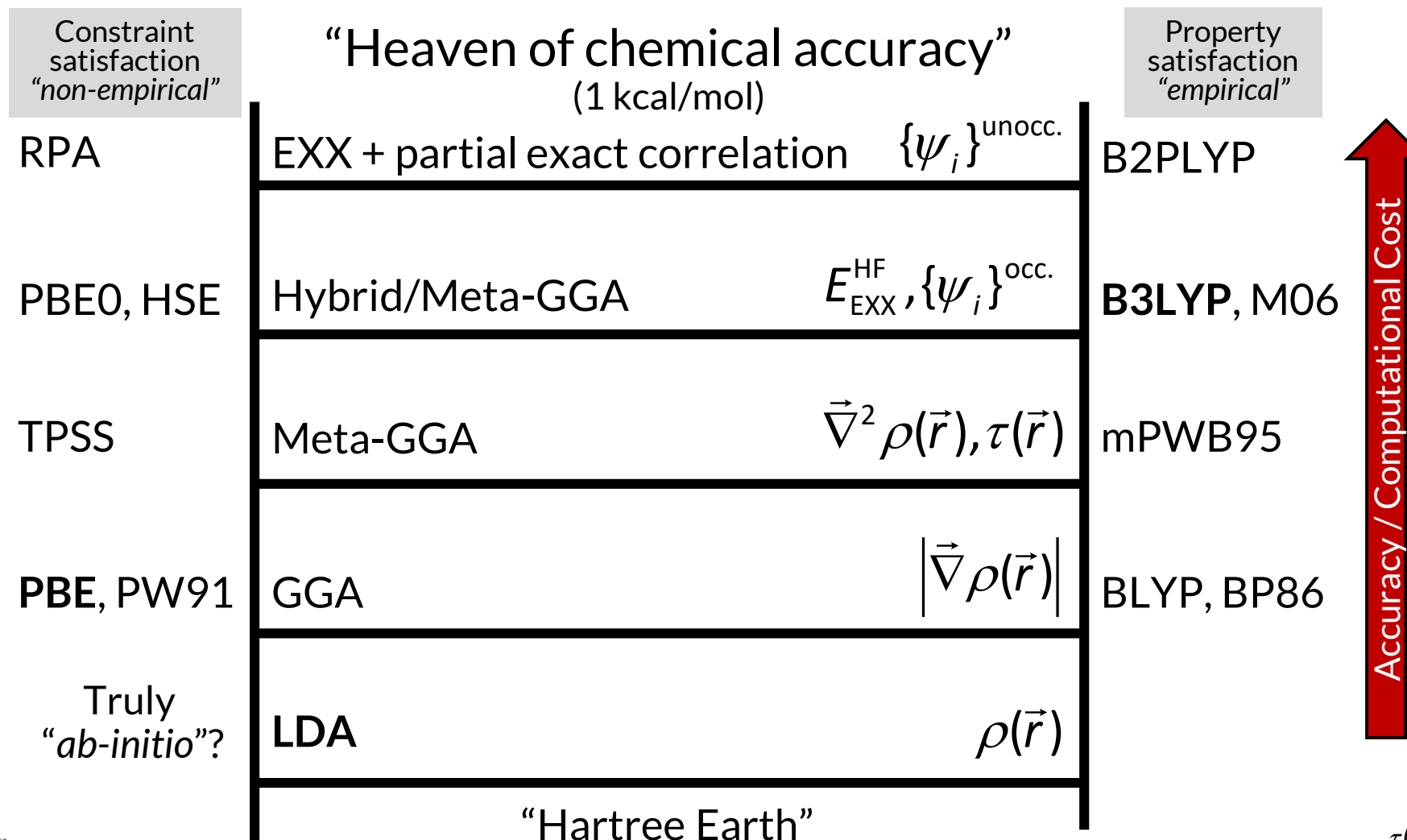
$$\tau(\vec{r}) = \sum_i^N \left|\vec{\nabla}\psi_i(\vec{r})\right|^2$$

Accuracy of Common XC Functionals

Mol.	Exp.	UHF	LSDA	PBE	MGGA	B3LYP	MP2
H_2	174.5	133.9	180.3	166.7	182.5	—	165.7
Li_2	39.3	4.8	37.9	31.7	35.9	33.5	25.5
Be_2	4.8	11.2	20.6	15.6	7.2	—	−1.6
N_2	364.0	183.3	427.1	387.6	365.2	365.6	368.1
F_2	62.1	−15.9	124.6	85.1	68.8	57.7	111.6
LiH	92.4	52.6	96.9	85.2	93.1	92.9	86.1
OH	169.6	108.4	197.9	175.0	171.8	172.3	165.7
HF	225.7	154.6	259.1	226.3	221.0	222.1	227.9
H_2O	370.0	245.4	424.9	373.2	366.7	368.1	366.5
NH_3	473.9	318.7	537.5	480.8	476.2	478.4	462.1
CH_4	668.2	522.7	737.2	669.0	671.1	670.4	661.3
CO	413.2	277.3	476.3	428.4	408.0	408.3	423.9
NO	243.7	84.5	316.2	273.9	252.6	248.0	242.2
Cl_2	92.4	—	132.1	103.7	94.7	87.8	—
Mean average error:		-93.8	41.1	7.7	1.5	0.8	0.3
RMS error:		109.8	48.4	14.0	4.6	0.7	15.6
Computational cost:		N^4	N^3	N^3 -N^4	N^3 -N^4	N^4	N^5

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Source: ChemEng 444, Prof. Norskov

Limitations of DFT

- Choosing best **XC functional** depends on property/application
- Typically, computational costs *limit unit cells* to (few) 100 atoms
- Does not directly describe electronic *excitations*
- Tends to **underestimate bandgaps** due to self-interaction error and over-delocalized wavefunctions
- Does not reproduce *non-adiabatic* effects (Born-Oppenheimer)
- Problems arise when *accurate* xc-effects are *crucial* like in strongly correlated systems
- Incorrectly describes (or not at all) *relativistic* effects

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Ab initio Molecular Dynamics (AIMD)

Hellmann-Feynman theorem

$$\frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda} = \left\langle \psi_\lambda \left| \frac{\mathrm{d}H_\lambda}{\mathrm{d}\lambda} \right| \psi_\lambda \right\rangle$$
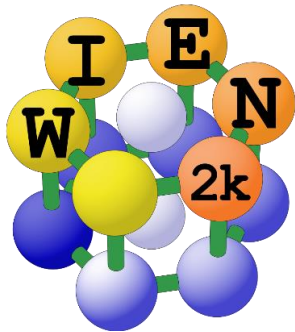
Gives us forces directly from the electron density:

$$F_{x,i} = -\frac{\partial E}{\partial X_i} = -\left\langle \psi \left| \frac{\mathrm{d}H}{\mathrm{d}X_i} \right| \psi \right\rangle = Z_i \left(\int \mathrm{d}\vec{r}\, \rho(\vec{r}) \frac{x - X_i}{\left| \vec{r} - \vec{R}_i \right|^3} - \sum_{\alpha \neq i}^{M} Z_\alpha \frac{X_\alpha - X_i}{\left| \vec{R}_\alpha - \vec{R}_i \right|^3} \right)$$

These forces do **not** require parametrization like classical molecular dynamics!

→ *"Ab initio Molecular Dynamics"*

Overview of (some) DFT Codes

	Periodic		Molecular
Plane waves	**All-electron (augmented)**	**Local orbitals**	

Remark: Rough classification; most codes fall into several categories

Overview of DFT Variants (and Zoo of Acronyms)

Atomic orbitals
  Gaussians
  Slater type
  Numerical

All-electron full potential
All-electron muffin-tin potential
All-electron PAW
Pseudopotential
  Norm-conserving
  Ultra-soft

Plane waves

Augmentation
  FPLAPW, LMTO, ASW

Fully numerical (real space)

$$\left[-\frac{\hbar\nabla^2}{2m} + V_{\text{nuc}}(\vec{r}) + \sum_j \int \mathrm{d}\vec{r}' \frac{\rho(\vec{r})}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{\text{XC}}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right]\psi_i(\vec{r}) = E_i \cdot \psi_i(\vec{r})$$

Fully relativistic
Semi-relativistic
Non-relativistic

LDA
GGA
Meta-GGA
Hyrbid/Meta-GGA
Range-seperated XC functionals
DFT+U
Partial exact correlation, RPA

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DFT Property Predictions

$$\left[-\frac{\hbar\nabla^2}{2m} + V_{\text{nuc}}(\vec{r}) + \sum_j \int d\vec{r}' \frac{\rho(\vec{r})}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{\text{XC}}[\rho(\vec{r})]}{\delta\rho(\vec{r})} \right] \psi_i(\vec{r}) = E_i \cdot \psi_i(\vec{r})$$

"ab-inito"

Structural
Lattice constants
Bond length
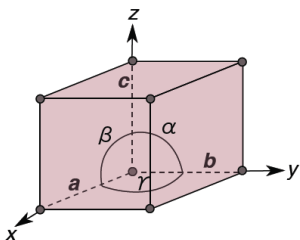
Mechanical
Bulk modulus
Stress tensor σ_{ij}

Optical / Electrical
Dielectric constant
Absorption spectra
Density of states
Band structure
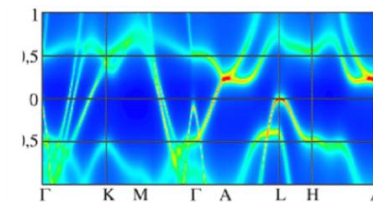
Surface
Work function
Surface/cleavage energy
Adsorption energy
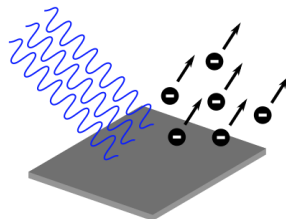
Magnetic
Magnetic ordering
Magnetic moment
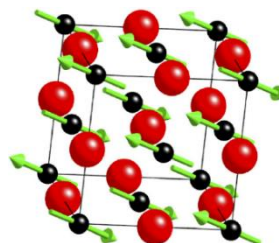
Thermodynamic
Vibrational entropy
Phase stability (Hull diagram)

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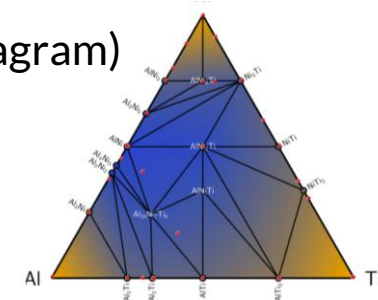
Practical and High-throughput DFT

Writing DFT input files by hand

Using Python

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Tutorial: GPAW and ASE

Atomic Simulation Environment (ASE) is a *Python package* for
- Building **atomic structures**
- Structure optimization and molecular dynamics
- **Analysis** and visualization

ASE relies on *external calculator* which provides total energies, forces, etc.
- **GPAW**, VASP, QE, Castep, Abinit, etc.
- Input files are *Python scripts* (simple format, yet powerful!)

Has simple graphical user interface (**ase gui**)

ASE
Atoms Objects, Analysis

Atoms, positions, cell,...

Energies, forces, densities,...

Calculator
(GPAW, VASP, QE,...)
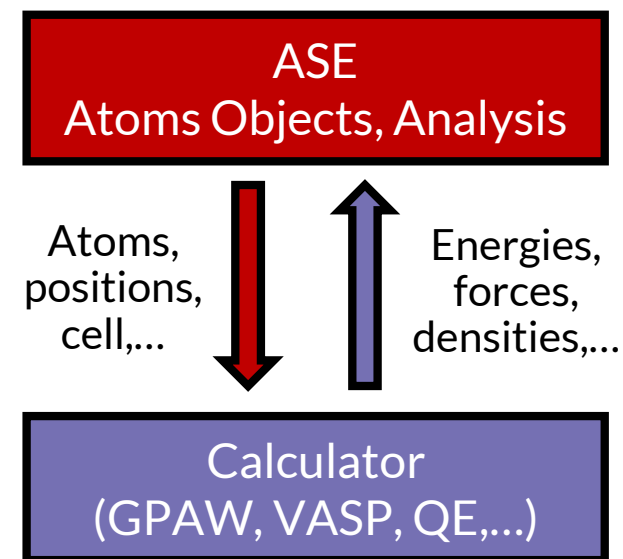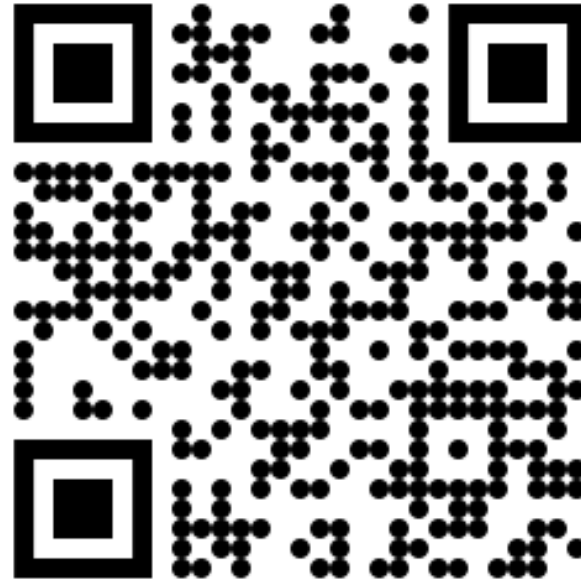
Lecture Feedback

Please, scan the QR code and take a minute to let me know how the lecture was and mention any **feedback/questions**

This form is **anonymous!**

Supplementary Slides

But why Does it Work so well?

Works surprisingly well, because **valence electrons**
(which accounts for bonding) often have *slowly varying densities*

$$\left[-\frac{\hbar\nabla^2}{2m} + V_{\text{nuc}}(\vec{r}) + \sum_j \int d\vec{r}' \frac{\rho(\vec{r})}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{\text{xc}}[\rho(\vec{r})]}{\delta\rho(\vec{r})} \right] \psi_i(\vec{r}) = E_i \cdot \psi_i(\vec{r})$$

Total energy contributions for Mn atom

Small contribution!
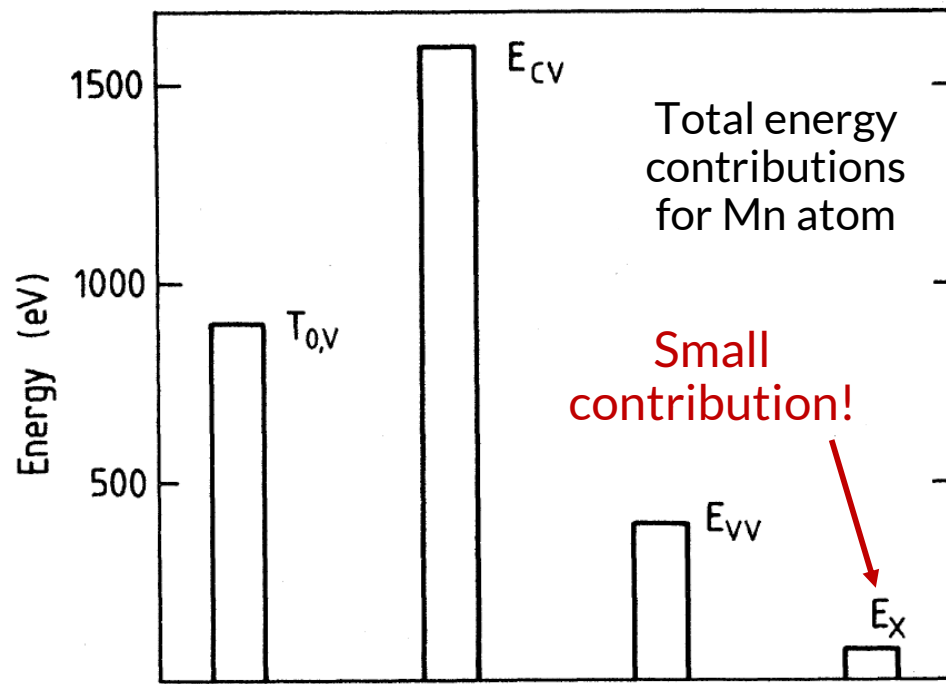
But, kinetic part!
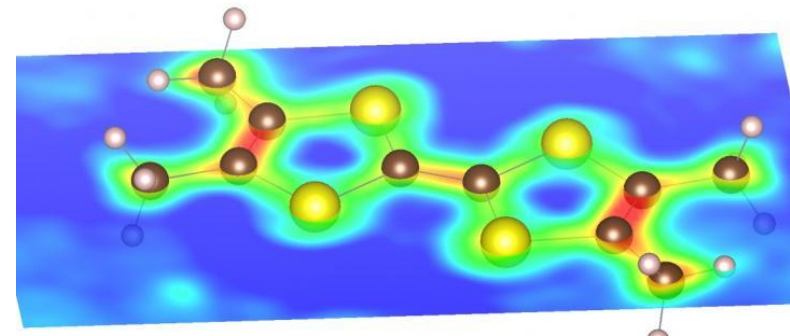
Jones, Gunnasson, Rev. Mod. Phys. 61 (1989)

Credit: Shunsuke Kitou

Energy Band Diagrams – Qualitative

Probability distr. 1-atom
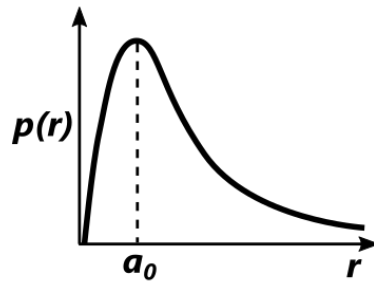
Overlap of 2 atoms
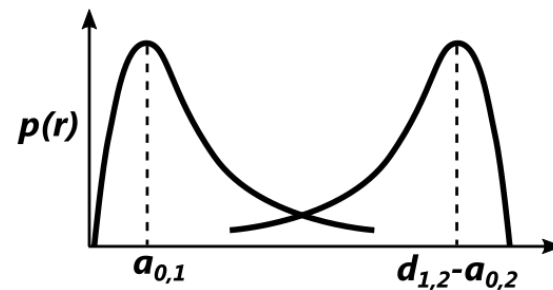
Overlap causes energy level split
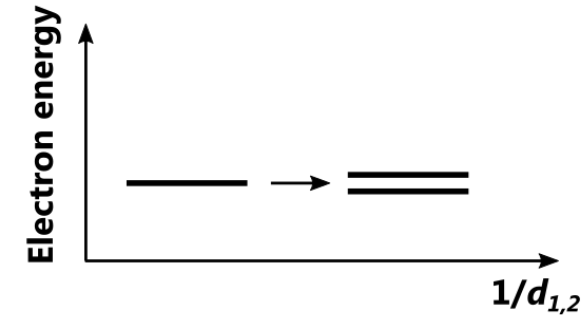
Pauli's exclusion principle – One electron (Fermion) per quantum state.
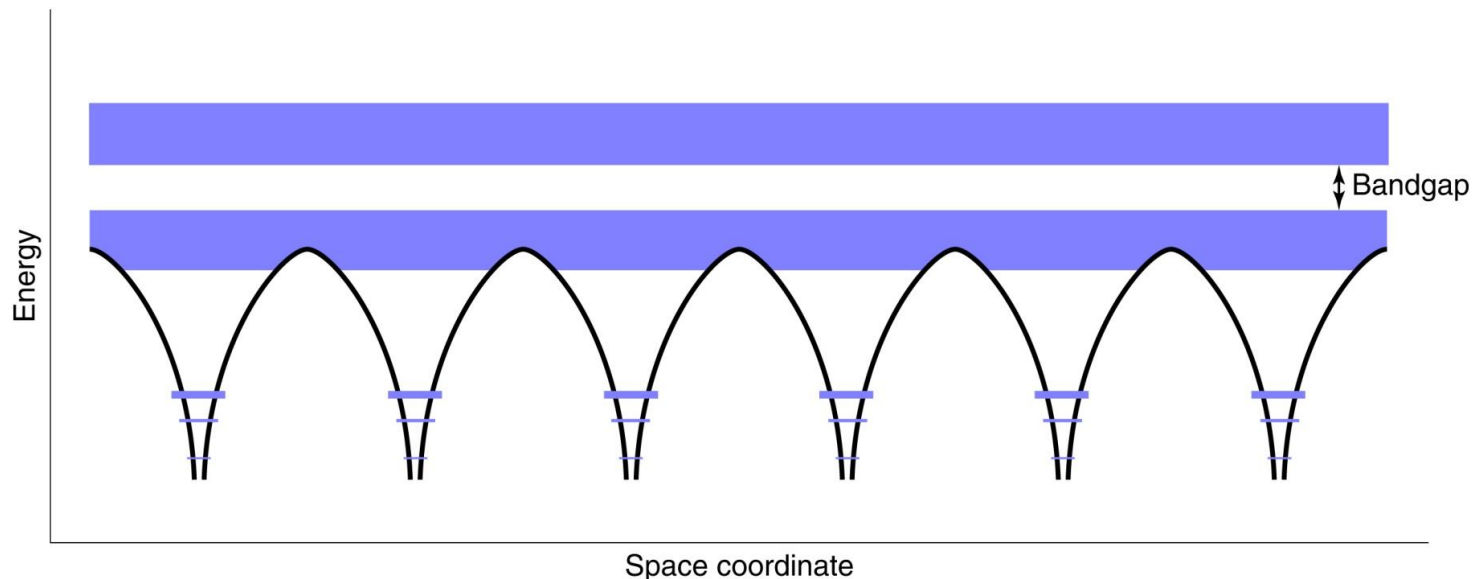
Bloch Waves
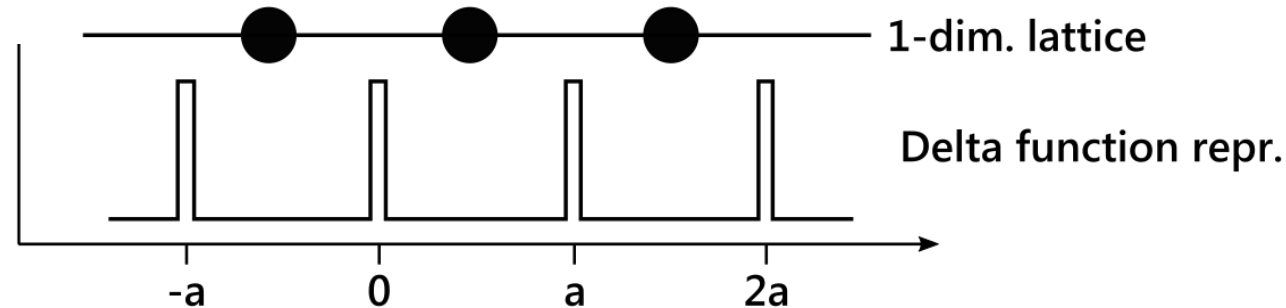
$$-\frac{\hbar^2}{2m_0}\frac{d^2\,\psi(x)}{d\,x^2}+U(x)\psi(x)=E\psi(x)$$

Potential has lattice symmetry $\quad U(x+a)=U(x)$

Bloch theorem (Felix Bloch, 1928):

Periodicity of lattice potential $\quad U(\vec{r}+\vec{G})=U(\vec{r})$

$$\psi_{n\vec{k}}=\exp(i\vec{k}\vec{r})\cdot u_{n\vec{k}}(\vec{r}),\qquad u_{n\vec{k}}(\vec{r}+\vec{G})=u_{n\vec{k}}(\vec{r})$$

Plane wave envelope

Bloch waves with lattice periodicity
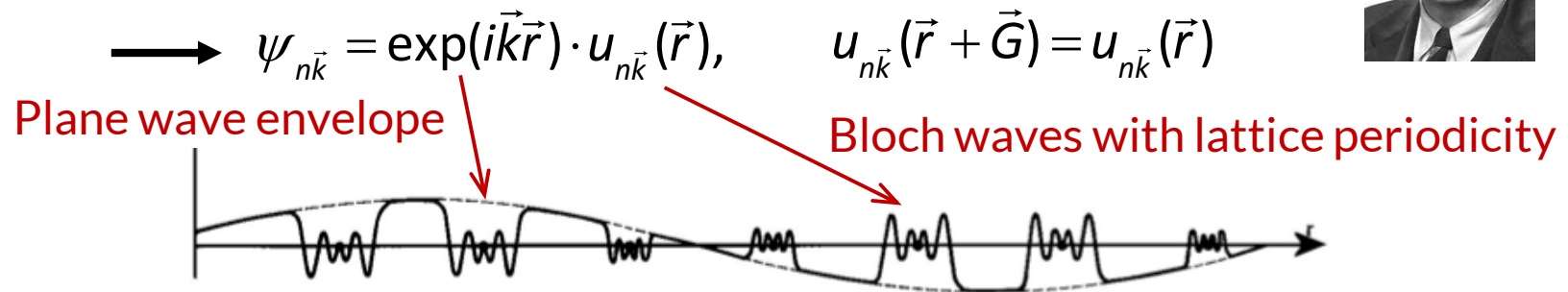
Band Diagrams – Quantitative

Solving Schrödinger equation gives dispersion relationship: *E* vs. wave vector *k*

For free electron: $E(k) = \dfrac{\hbar k^2}{2m}$

Dispersion relationship E(k) for 1-dim. lattice

$E(k) = \dfrac{\hbar k^2}{2m}$
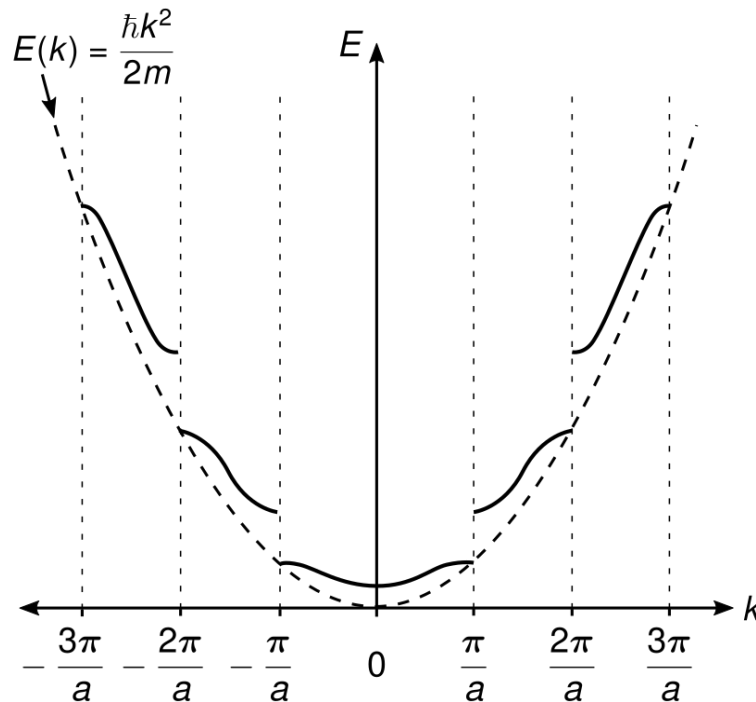
Reduced zone scheme
(1st Brillouin zone)

Band diagram

Gap

Band

Gap

Band

Gap

Band

Γ - point
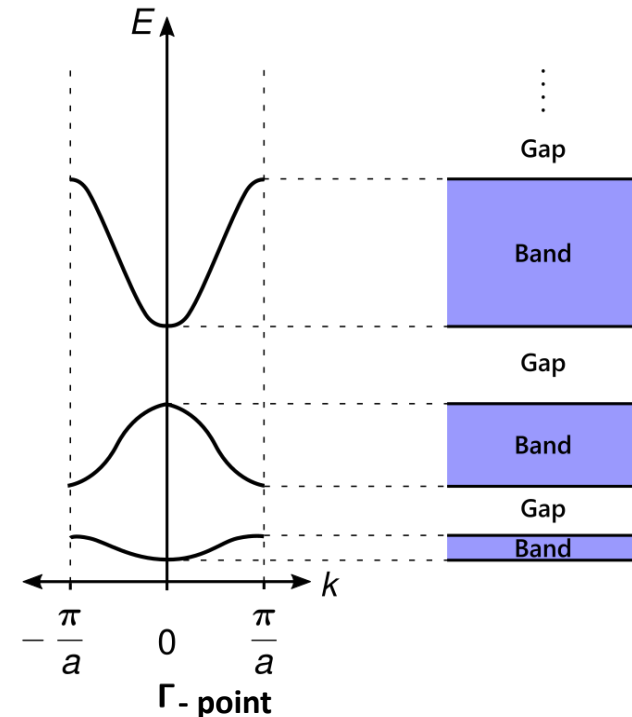
DFT Calculation Procedure – Self-Consistent Field (SCF)

Pick atomic geometry

Guess density (in practice PW components) $\rho(\vec{r}); \; c_{i,\vec{k}+\vec{G}}$

User input

Convergence

Calculate effective potential $\qquad V_{\text{eff}}(\vec{r}) = V_{\text{nuc}}(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{\text{xc}}[\rho(\vec{r})]$

Pseudopotential $\qquad\qquad\qquad\qquad$ XC functional

For k in irreducible Brillouin zone: $\qquad \left[-\frac{\hbar \nabla^2}{2m} + V_{\text{eff}}(\vec{r}) \right] \psi_{i,\vec{k}}(\vec{r}) = E_{i,\vec{k}} \cdot \psi_{i,\vec{k}}(\vec{r})$

Plane wave approach

$\psi_{i,k}(\vec{r}) = e^{i\vec{k}\vec{r}} u_{i,\vec{k}}(\vec{r}) \qquad u_{i,\vec{k}}(\vec{r}) = \sum_{\vec{G}}^{\vec{G}_{\text{max}}} c_{i,\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G})\vec{r}} \qquad \frac{\hbar^2}{2m} \left(\vec{k} + \vec{G}_{\text{max}} \right)^2 \leq E_{\text{kin}}^{\text{cutoff}}$

Cutoff energy

$\sum_{\vec{G}'} \left[\hat{H}_{\vec{k}+\vec{G},\vec{k}+\vec{G}'} - E_{i,\vec{k}} \delta_{\vec{G},\vec{G}'} \right] c_{i,\vec{k}+\vec{G}'} = 0 \quad \xrightarrow{\text{Solve}} \quad \rho_{\text{new}}(\vec{r}) = \sum_{i,\vec{k}}^{occ.} \left| \psi_{i,\vec{k}}(\vec{r}) \right|^2$

Yes $\qquad\qquad\qquad\qquad |\rho_{\text{new}}(\vec{r}) - \rho(\vec{r})| < \delta \qquad\qquad\qquad\qquad$ No

$\rho_{\text{next-iteration}} = (1-\alpha)\rho + \alpha\rho_{\text{new}}$

Calculate energy (equation below) and forces (Hellmann-Feynman-Theorem)

$E_{\text{total}}[\rho(\vec{r})] = \sum_{i,\vec{k}}^{occ.} E_{i,\vec{k}} - \int d\vec{r} \, V_{\text{eff}}(\vec{r})\rho(\vec{r}) + \int d\vec{r} \, V_{\text{nuc}}(\vec{r})\rho(\vec{r}) + \frac{1}{2} \int d\vec{r} \, d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + E_{\text{xc}}[\rho(\vec{r})]$

Relativistic Effects

Electrons deep in the core region can exhibit kinetic energies sufficient to produce relativistic effects.
These effects are generally not important for **Z<14 (silicon)**

Scalar relativistic effects
Can be incorporated into pseudopotentials from relativistic all electron calculation

Spin-orbit interactions
These occur when valence electron spins interact with magnetic fields generated by relativistic core states
These can be incorporated within a spin-density functional theory approach

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Types of Pseudopotentials

Pseudopotentials are
- not unique (e.g., optimizable smoothness)
- generally energy- and *l*-dependent (non-local)

Norm-conserving [Hamann, Schluter, Chiang, 1979]
- Generally most *accurate* (transferrable) but most *expensive* (high # of PWs required)

Ultra-soft [Vanderbilt, 1990]
- Requires *lower cutoffs* for first shell atoms
- No norm conservation – the missing *core charge density* must be specified along with the PP

Projector Augmented Wave (PAW) [Blochl, 1994]
- Includes core states as "frozen-core" for all electron calculations
- Similar to ultrasoft: *Linearized version* of PAW

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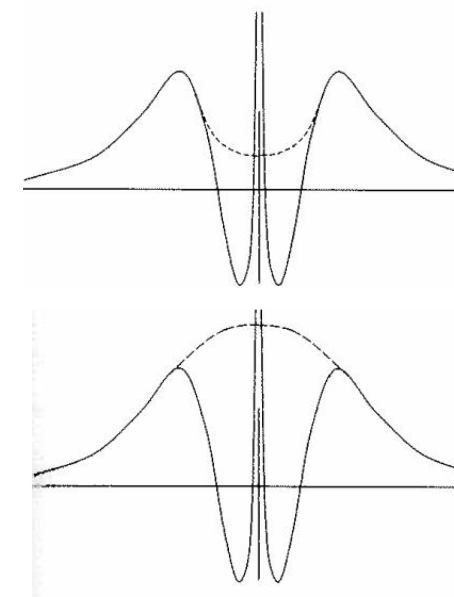
A Look at a Pseudopotential File

Not important for
Z<14 (silicon)

l dependency

```
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Generated using Vanderbilt code, version    7   3   6
Author: kfg          Generation date:    1     4    15
Automatically converted from original format
     1           The Pseudo was generated with a Scalar-Relativistic Calculation
     1.60000000000E+00    Local Potential cutoff radius
 nl  pn  l    occ                Rcut              Rcut US              E pseu
 4S   4   0   2.00     0.00000000000        1.50000000000        -7.27487498300
 4P   4   1   6.00     0.00000000000        1.50000000000        -4.59453496500
 4D   4   2  10.00     0.00000000000        1.70000000000        -0.83552577500
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 5P   5   1   0.00     0.00000000000        1.50000000000        -0.24577891300
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     0                      Version Number
    Ag                      Element
    US                      Ultrasoft pseudopotential         PP-type
     T                      Nonlinear Core Correction
 SLA  PW   PBX  PBC    PBE  Exchange-Correlation functional    XC functional used
   19.00000000000        Z valence
 -295.21248450600        Total energy
    0.00000      0.00000 Suggested cutoff for wfc and rho
     2                    Max angular momentum component
   887                    Number of points in mesh
     5       6            Number of Wavefunctions, Number of Projectors
 Wavefunctions           nl  l    occ
                         4S   0   2.00
                         4P   1   6.00
                         4D   2  10.00
                         5S   0   0.50
                         5P   1   0.00
</PP_HEADER>
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Practical Pseudopotential Tips

- Norm conserving PPs with small core radii (requiring high PW cutoffs) are generally the *most accurate* PPs

- Use the **same type** of PP for all atoms in your system

- PPs are created for use with a specific **exchange-correlation functional** – ensure all PPs in your system were created with the *same functional*

- Compute property of interest twice *using different types* of PPs to (roughly) assess variation

- The PW cutoff for a set of atoms will be determined by **hardest PP** of the set

Generate or Download Pseudopotentials:
opium.sourceforge.net/ (Opium PP Generation Project)

th.fhi-berlin.mpg.de/th/fhi98md/fhi98PP/ (fhi98PP PP program)

physics.rutgers.edu/gbrv/ (**Vanderbilt Ultra-soft PPs**)