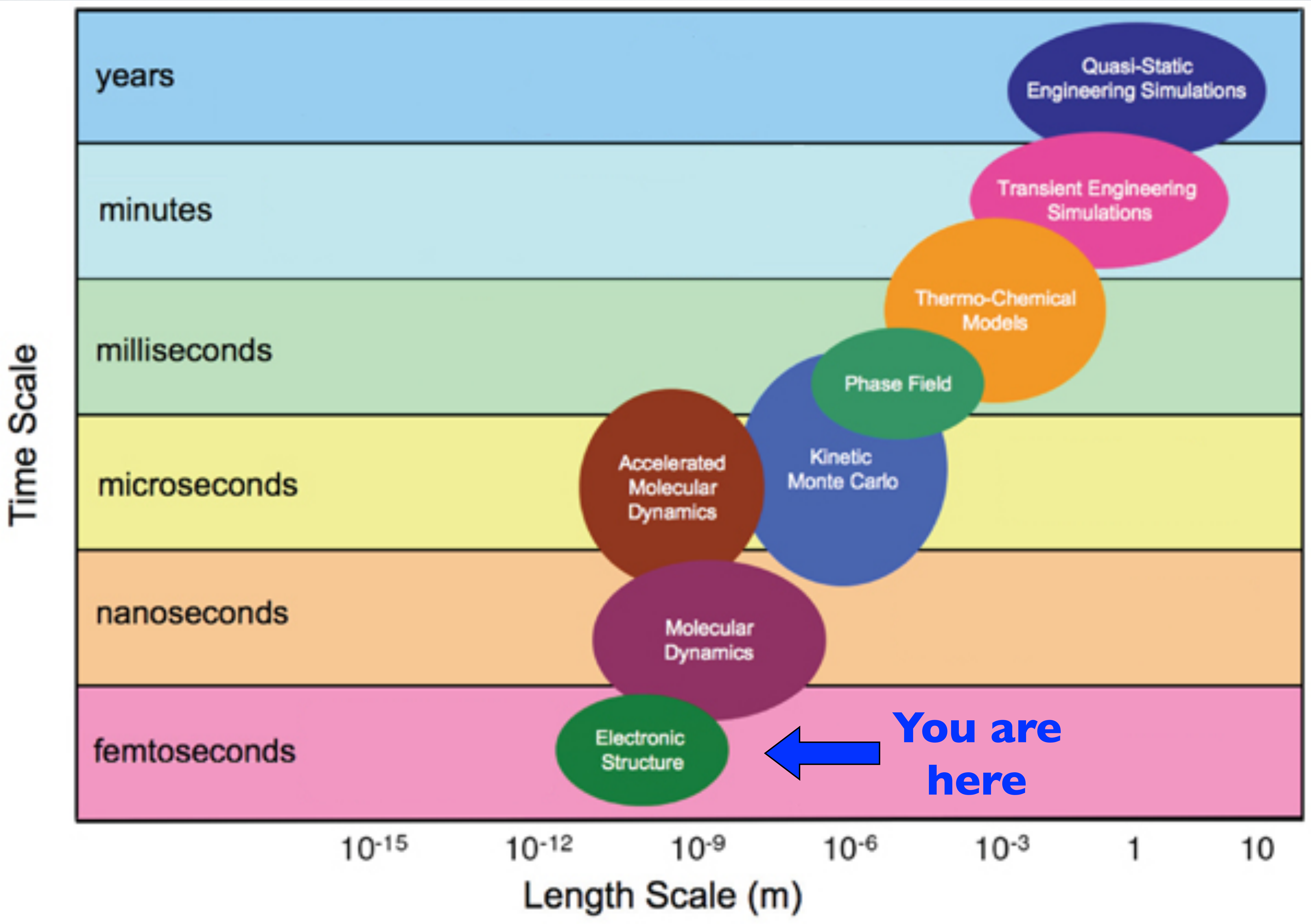
MODULE 2: QUANTUM MECHANICS

Principles and Theory



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http://www.lbl.gov/CS/html/exascale4energy/nuclear.html

Short Review of Quantum Mechanics

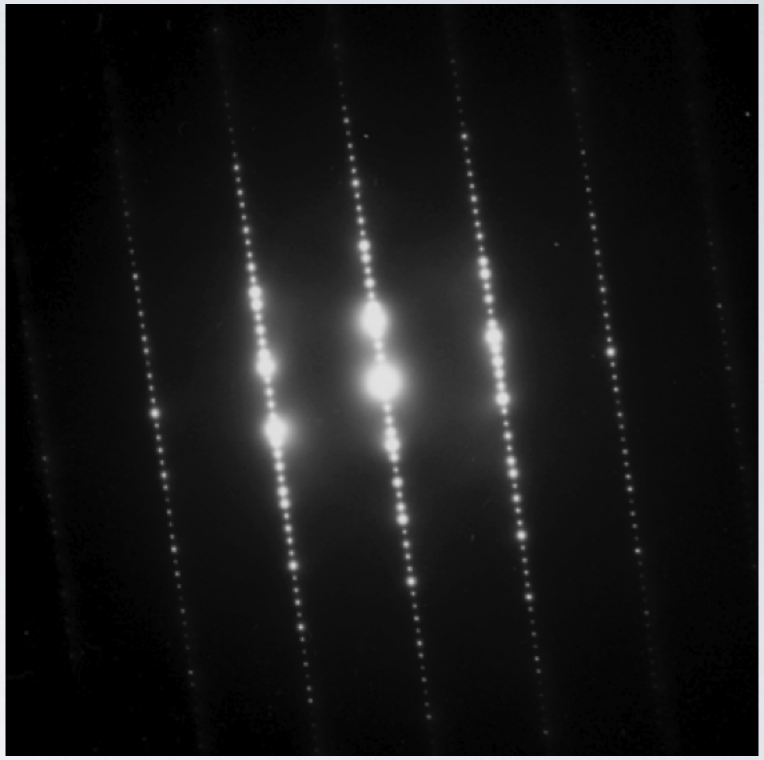
Why do we need quantum mechanics?

- Bonding and structure
- Electronic, magnetic and optical properties of materials
- Chemistry and reactions

Standard model of matter

- Matter consists of atoms
- Atoms consist of
  - Massive, point-like nuclei (protons + neutrons)
  - That are surrounded by tightly bound core electrons
  - And held together in molecules, liquid and solids by the bonds formed by valence electrons

Short Review of Quantum Mechanics



Wave-particle duality

- Planck’s uncertainty relationship

$$\lambda \cdot p = h$$

Schrödinger equation

- Time dependent

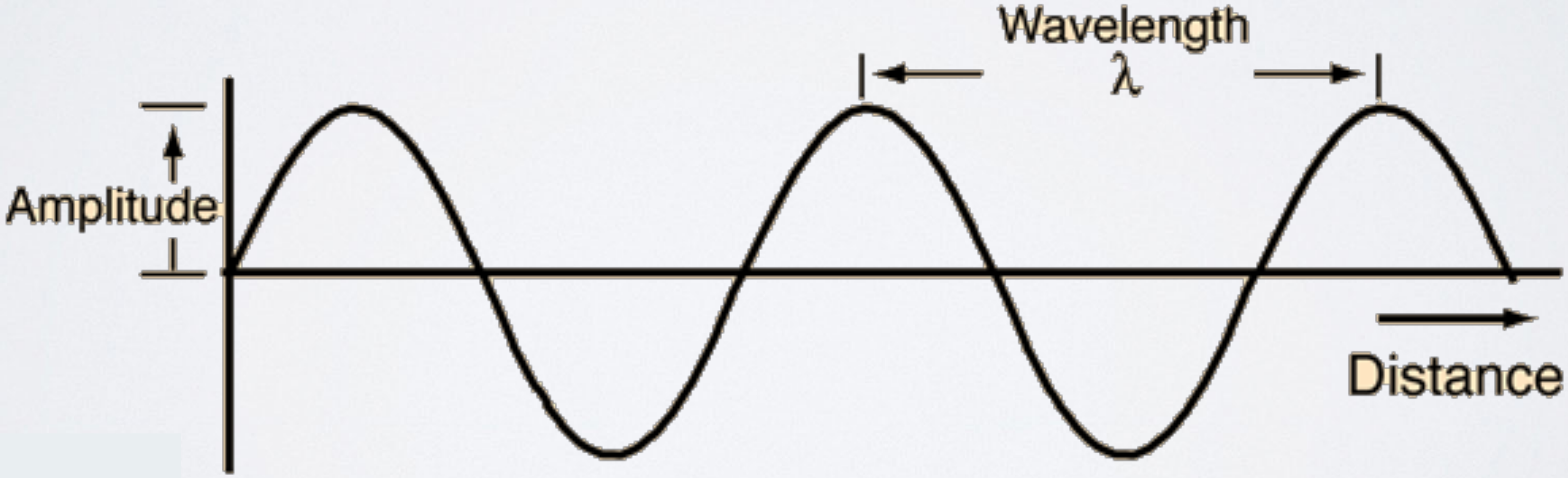
$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\,\Psi(\mathbf{r},t) = i\hbar\,\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

Solutions of the Schrödinger Equation (1)

Free particle

- $V(\mathbf{r}) = 0 \quad \Rightarrow$ Solutions are plane waves

$$\begin{aligned} \Psi_k(\mathbf{r}, t) &= \exp\left(i\,\mathbf{k}\cdot\mathbf{r} - \omega t\right) \\ E_k &= \frac{\hbar^2 k^2}{2m} = \omega\hbar \end{aligned}$$



Solutions of the Schrödinger Equation (2)

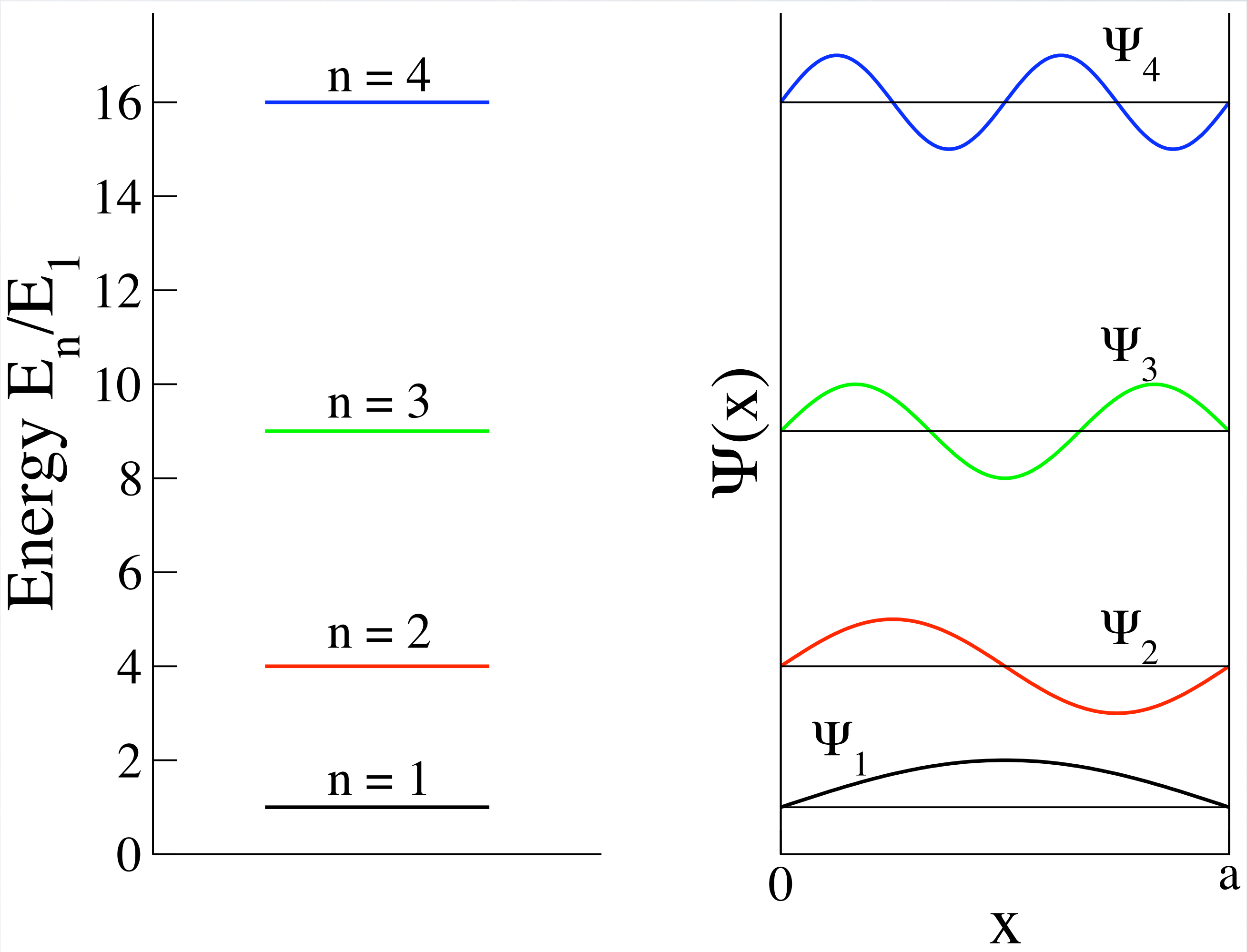
Infinite square well

- Plane waves that vanish at the boundary

$$V(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

$$\varphi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi\, n\, x}{a}\right)$$

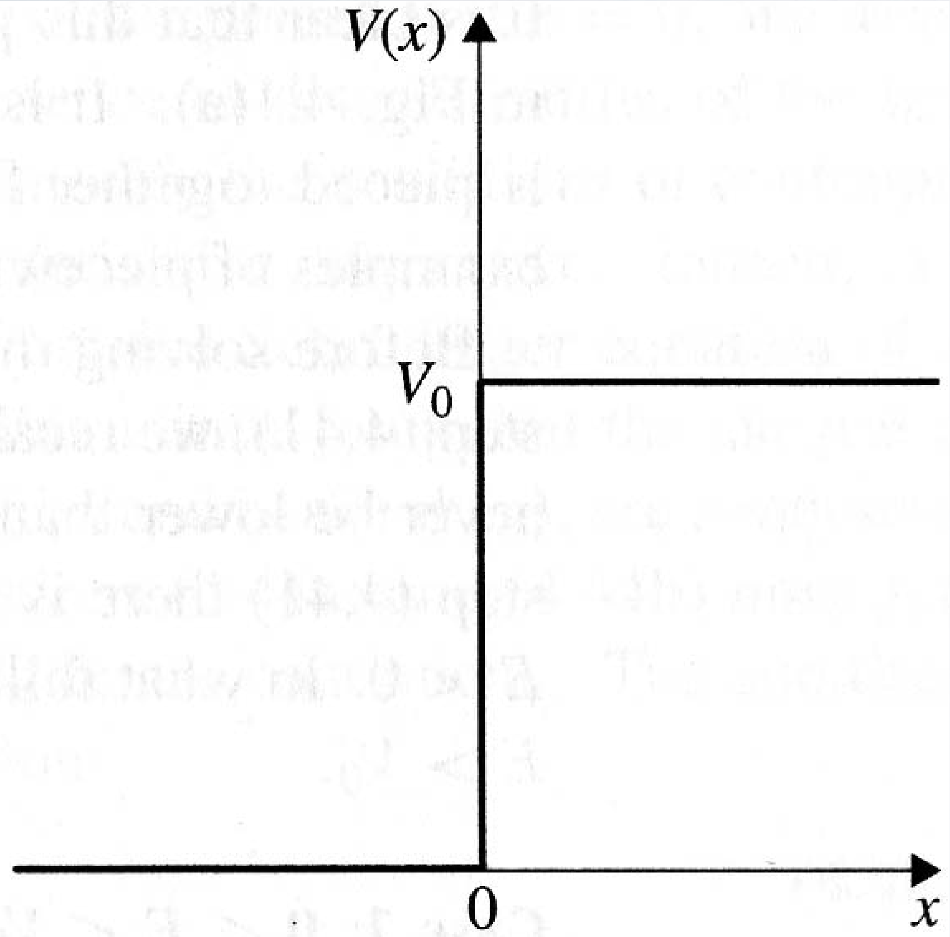
$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

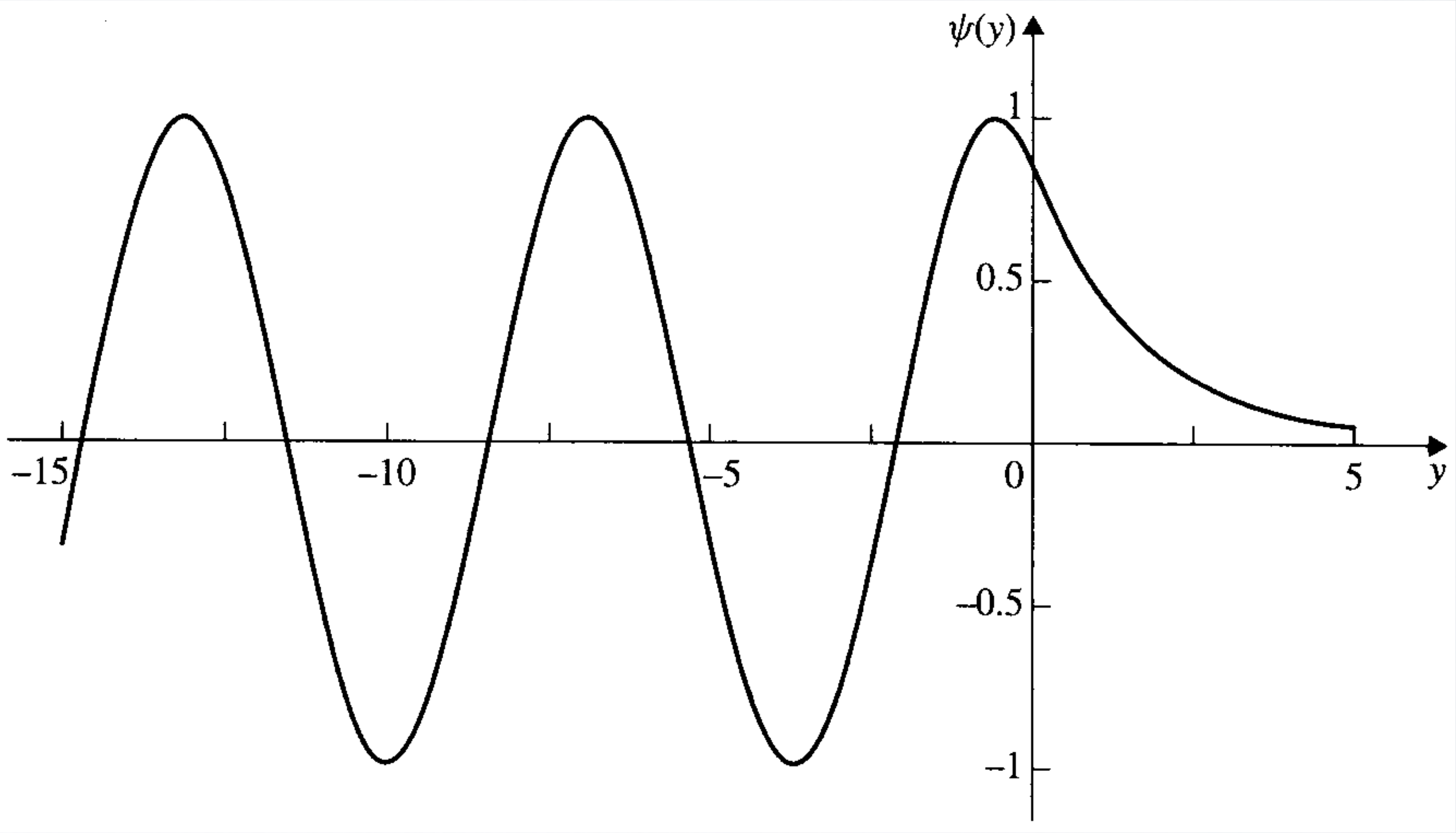


Solutions of the Schrödinger Equation (3)

Metal surface

- Potential step $\Rightarrow$ Plane wave inside metal, exponential decay outside





Solutions for the Coulomb Potential

Spherical Symmetry

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \varphi^2}\end{aligned}$$

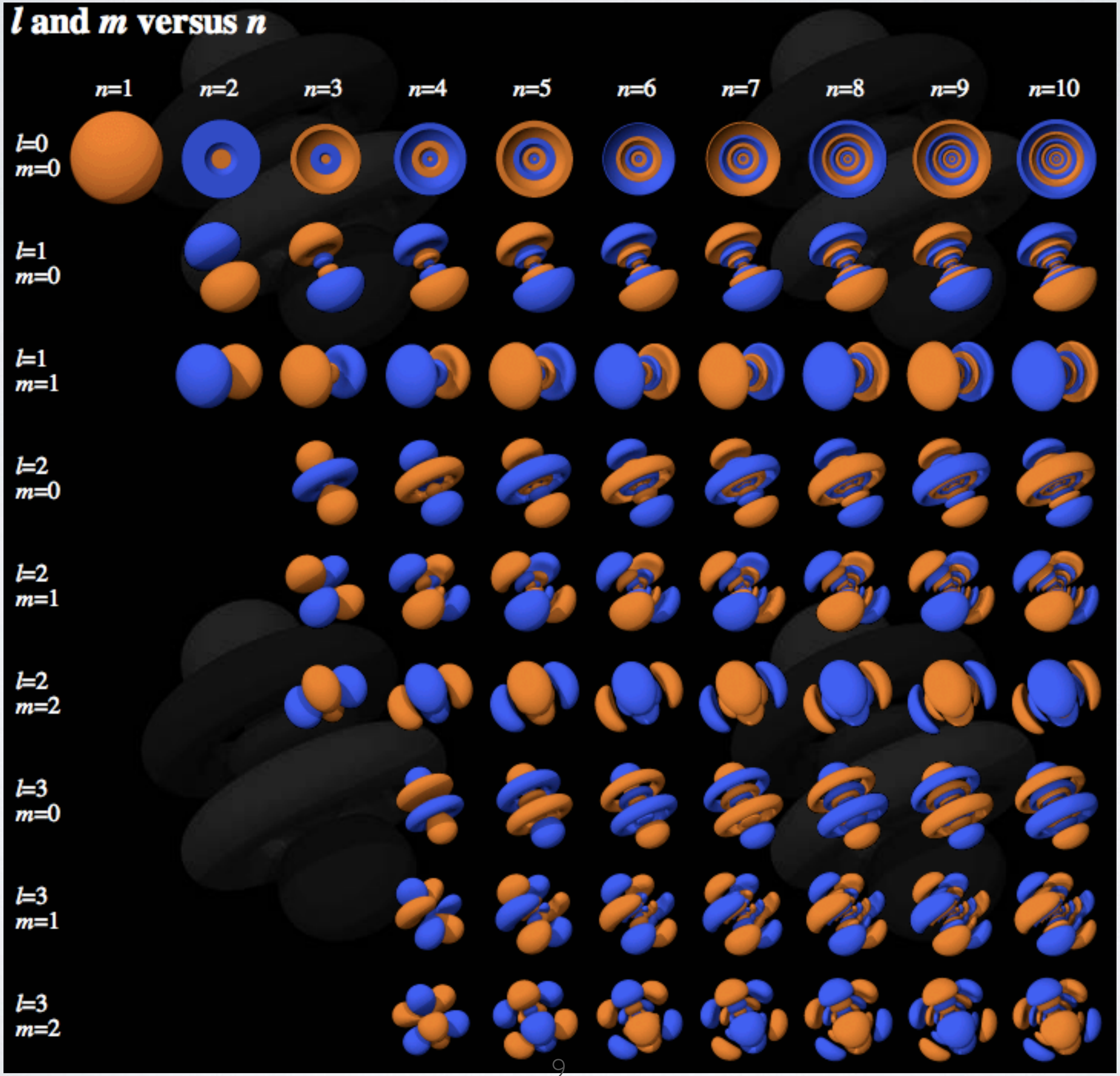
Separation of variables

$$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r) \cdot Y_{lm}(\theta, \varphi)$$

Equation for radial wave functions

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right] R_{nl}(r) = E\, R_{nl}(r)$$

The Periodic System of Elements



http://www.orbitals.com/orb/orbtable.htm

Basis Set Expansion (Matrix Formulation)

Expand wave function in set of *n* orthogonal functions $$|\psi\rangle = \sum_{n=1}^{k} c_n |\varphi_n\rangle$$

Plugging this solution into the Schrödinger equation yields and multiplying with function φ_m yields

$$\begin{aligned}
\langle\varphi_m|\mathcal{H}|\psi\rangle &= E\langle\varphi_m|\psi\rangle \\
\sum_{n=1}^{k} c_n \langle\varphi_m|\mathcal{H}|\varphi_n\rangle &= E\, c_m \\
\sum_{n=1}^{k} H_{mn} c_n &= E\, c_m
\end{aligned}$$

$$\begin{pmatrix} H_{11} & \cdots & H_{1k} \\ \vdots & & \vdots \\ H_{k1} & \cdots & H_{kk} \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix}$$

Variational Principle

$$E[\Phi] = \frac{\langle \Phi | \mathcal{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0$$

$$E[\Phi] = E_0 \quad \Leftrightarrow \quad \text{If } \Phi \text{ is the groundstate}$$

Example: The hydrogen atom

$$\begin{aligned} \Psi_\alpha &= c \cdot \exp(-\alpha\, r) \\ E[\Phi_\alpha] &= \frac{\langle \Phi_\alpha | \mathcal{H} | \Phi_\alpha \rangle}{\langle \Phi_\alpha | \Phi_\alpha \rangle} \end{aligned}$$

The Hydrogen Atom

Ansatz:

$$\begin{aligned}\Psi_\alpha &= c \cdot \exp(-\alpha\, r) \\ E[\Phi_\alpha] &= \frac{\langle \Phi_\alpha | \mathcal{H} | \Phi_\alpha \rangle}{\langle \Phi_\alpha | \Phi_\alpha \rangle}\end{aligned}$$

Calculate:

$$\langle \Phi_\alpha | \Phi_\alpha \rangle \qquad \langle \Phi_\alpha | -\frac{1}{2}\nabla^2 | \Phi_\alpha \rangle \qquad \langle \Phi_\alpha | -\frac{1}{r} | \Phi_\alpha \rangle$$

Use:

$$\langle \ldots | \ldots \rangle = \int_0^\infty 4\pi r^2 \ldots d^3 r \qquad \int_0^\infty r^n \exp(-ar) = \frac{n!}{a^{n+1}}$$

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \varphi^2}\end{aligned}$$

The Hydrogen Atom

Result:

$$\langle \Phi_\alpha | \Phi_\alpha \rangle = \pi \frac{c^2}{\alpha^3}, \quad \langle \Phi_\alpha | -\frac{1}{2}\nabla^2 | \Phi_\alpha \rangle = \pi \frac{c^2}{2\alpha}, \quad \langle \Phi_\alpha | -\frac{1}{r} | \Phi_\alpha \rangle = \pi \frac{c^2}{\alpha^2}$$

Write out the energy as a function of *α* and minimize with respect to *α*:

$$E(\alpha) = \frac{\pi \frac{c^2}{2\alpha} - \pi \frac{c^2}{\alpha^2}}{\pi \frac{c^2}{\alpha^3}} = \frac{1}{2}\alpha^2 - \alpha$$

$$\frac{d}{d\alpha} E(\alpha) = \alpha - 1 = 0$$

Atomic Units

Quantity	Name	Symbol	SI value
Energy	Hartree energy	Ha	$4.359\,744\,17(75)\times10^{-18}$ J
Length	Bohr radius	a_0	$5.291\,772\,108(18)\times10^{-11}$ m
Mass	Electron rest mass	m_e	$9.109\,3826(16)\times10^{-31}$ kg
Electric charge	Elementary charge	e	$1.602\,176\,53(14)\times10^{-19}$ C
Electrostatic force constant	Coulombs constant	$1/4\pi\varepsilon_0$	8.9875516×10^{9} $C^{-2}Nm^{2}$

http://www.orbitals.com/orb/orbtable.htm

The Many-Electron Problem

$$\left[-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2-\sum_{i=1}^{n}\frac{Z}{r_i}+\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)=E\,\psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)$$

Example: Fe atom

- Fe has 26 electrons ⇒ wave function has 3×26 = 78 variables
- Store wave function on a grid
- Use a coarse grid of only 10 points along each direction
- To store wave function would require storage of **10^{78} numbers**
- Single precision 1 number = 4 Bytes

- Compare that to all the data stored worldwide **1 zettabyte = 10^{21} Bytes**

The Hartree Method

Independent electron method

- Assume that electrons move independently of each other
- Each electron moves in an effective potential that consists of
  - Attraction of nuclei
  - Average repulsive interaction of other electrons

- Many-body wave function as product of single-particle orbitals

$$\boxed{\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \varphi_1(\mathbf{r}_1)\,\varphi_2(\mathbf{r}_2)\,\ldots\,\varphi_n(\mathbf{r}_n)}$$

The Hartree Method

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\mathbf{R}_I-\mathbf{r}_i)+\underbrace{\sum_{j\neq i}\int|\varphi_j(\mathbf{r}_j)|^2\,\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}d^3r_j}_{\text{Hartree potential}}\right]\varphi_i(\mathbf{r}_i)=\epsilon\,\varphi_i(\mathbf{r}_i)$$

Douglas Hartree and Arthur Porter's Meccano differential analyzer built in 1934 at a cost of £20. It achieved an accuracy of about 2%.

Illustration of Electron Correlations

Uncorrelated
Cars are smeared out

Uncorrelated
Electrons described by their independent density, electrons can get arbitrary close

http://www.digital-photography-school.com/how-to-shoot-light-trails

Correlated
Cars avoid each other

Correlated
Electrons avoid each other to due to the Coulomb interaction between them

http://www.flickr.com/photos/88943727@N00/101166668/

The Hartree-Fock Method

What is missing in the Hartree approximation

- Wave function is not **antisymmetric**
- Does not include electron **correlation**

Antisymmetry for Fermions

- Exchanging two identical (indistinguishable) fermions changes the sign of the wave function

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_k, \ldots, \mathbf{r}_n) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_n)$$

Pauli Exclusion Principle

- Two electrons cannot be in the same quantum state
- Consequence of the antisymmetry

Slater Determinants

Slater determinant

- Antisymmetric product of single particle orbitals

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \left\| \begin{matrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_n(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_n(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \varphi_1(\mathbf{r}_n) & \varphi_2(\mathbf{r}_n) & \cdots & \varphi_n(\mathbf{r}_n) \end{matrix} \right\|$$

- Swapping rows in a determinant changes the sign

The Hartree-Fock Method

Hartree-Fock equation for orbitals φλ

- Use of variational principle leads to set of equations for φλ

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_I V(\mathbf{R}_I - \mathbf{r}_i)\right] \varphi_\lambda(\mathbf{r}_i) +$$

$$\left[\sum_\mu \int \varphi_\mu^*(\mathbf{r}_j)\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\varphi_\mu(\mathbf{r}_j)d^3r_j\right] \varphi_\lambda(\mathbf{r}_i) -$$

$$\sum_\mu \left[\int \varphi_\mu^*(\mathbf{r}_j)\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\varphi_\lambda(\mathbf{r}_j)d^3r_j\right] \varphi_\mu(\mathbf{r}_i) = \epsilon\varphi_\lambda(\mathbf{r}_i)$$

The Exchange Term

$$\sum_{\mu}\left[\int \varphi_{\mu}^{*}(\mathbf{r}_j)\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\varphi_{\lambda}(\mathbf{r}_j)d^3r_j\right]\varphi_{\mu}(\mathbf{r}_i)$$

- Describes effect of exchange of electrons
- *Cannot* be written in the form

$$V_{\lambda}^{\mathrm{x}}(\mathbf{r}_i)\varphi_{\lambda}(\mathbf{r}_i)$$

- Instead it is of the form

$$\int V_{\lambda}^{\mathrm{x}}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\lambda}(\mathbf{r}_j)d^3r_j$$

- This is called a *non-local potential*

Successes and Limitations of Hartree-Fock

Successes

- Good for atomic properties
- Self-interaction free
- Good starting point for correlated-electron methods

Limitations

- Schrödinger equation: $H\,\Psi = E\,\Psi \;\Rightarrow\; E_{\text{exact}}$
- Hartree-Fock equations: $F\,\phi_i = \varepsilon_i\,\phi_i \;\Rightarrow\; E_{\text{HF}}$
- Any effect beyond HF is called correlation $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$
- Size of correlation energy $E_{\text{corr}} < 1\%$ of E_{exact}

  Example: N_2 molecule: $E_{\text{corr}} = 14.9$ eV $< 1\%$ of E_{exact}
- **However**: binding energy $N_2 \rightarrow N + N$ is

  D_e(Hartree-Fock) = 5.1 eV, D_e(exp) = 9.9 eV

Thus, there are large contribution from the correlation energy to relative energies, *i.e.* chemical reaction energies.

Beyond Hartree-Fock

Hartree Fock configuration

- HF Slater determinant is built from lowest energy 1-e orbitals

$$\Psi^0_{\mathrm{HF}} = \left|\varphi_1\,\varphi_2\,\ldots\varphi_K\right|$$

- Slater determinant is also called a configuration since it refers to certain filled orbitals

Configuration interaction method

- Add additional configurations to the wave functions that mix in “excited” states
- Excite electron from orbital *i* to orbital *K*+1

$$\Psi^1_{\mathrm{HF}} = \left|\varphi_1\,\varphi_2\ldots\varphi_{K+1}\ldots\varphi_K\right|$$

$$\Psi_{\mathrm{CI}} = c_0\,\Psi_0 + c_1\,\Psi_1 + c_2\,\Psi_2 + \ldots$$

Density Functional Theory

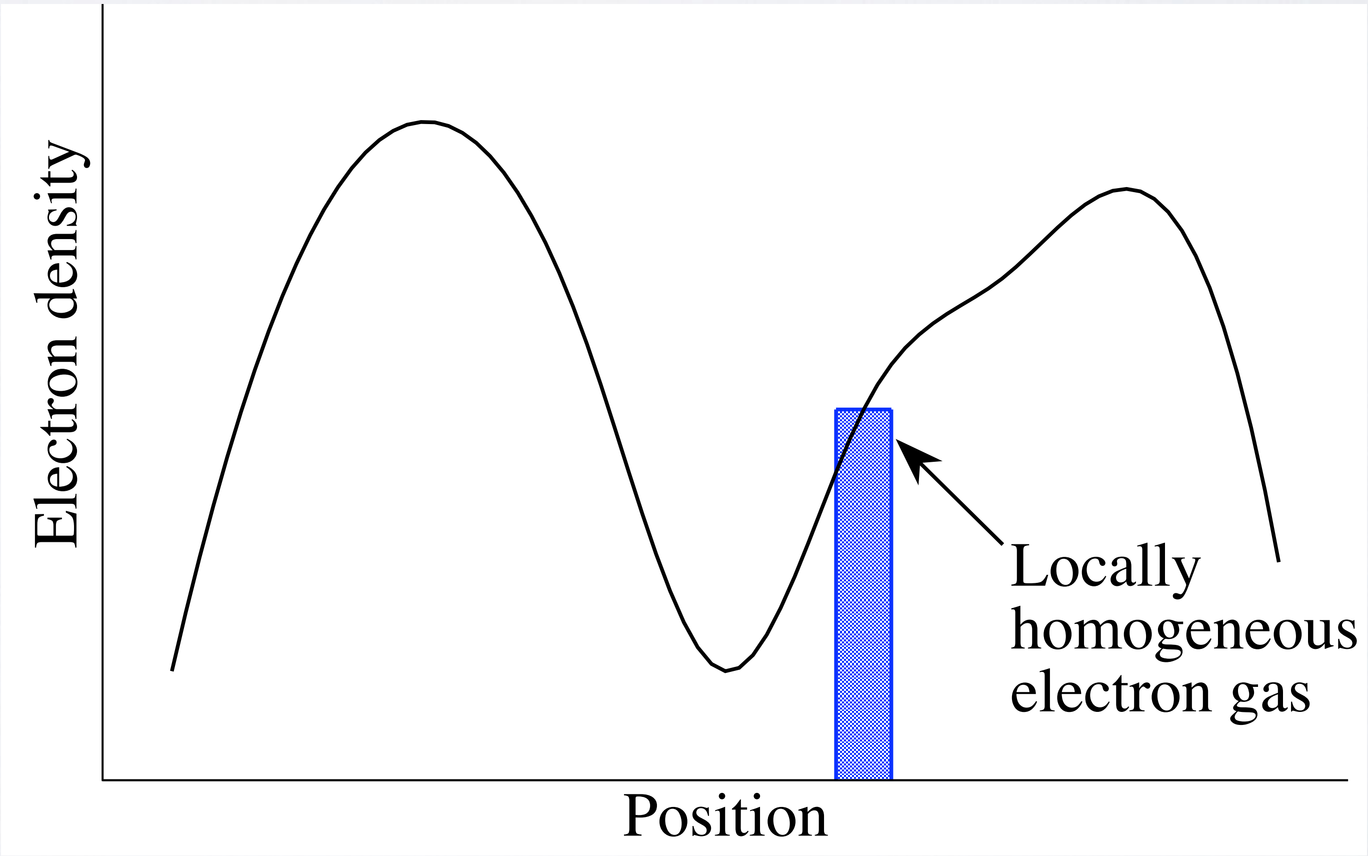
- Theory for the ground state energy of a system as a function of the *electron density* **instead** of the *wave function*

- Walter Kohn received the Nobel prize in 1998 for his development of density functional theory

Motivation

$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ Function of **3N** variables

$\rho(\mathbf{r})$ Function of **3** variables



The Hohenberg-Kohn Theorems

- The external potential and the number of electrons define the problem
- Schrödinger's equation in principle uniquely determines the wave functions
- All system properties follow from the wave functions

⇒ HK Thm I: The energy and everything else (incl. the density) is a determined by V_{ext} and N_{el}

$$\begin{tikzcd}
V_{\mathrm{ext}}(\mathbf{r}) \arrow[d, Rightarrow, "\text{Schrödinger equation}"'] & \varrho_0(\mathbf{r}) \arrow[l, Rightarrow, "\text{Hohenberg-Kohn Theorem}"'] \\
\Psi_i(\mathbf{r}_1, \ldots \mathbf{r}_N) \arrow[r, Rightarrow] & \Psi_0(\mathbf{r}_1, \ldots \mathbf{r}_N) \arrow[u, Rightarrow, "\text{Integration of } |\Psi_0|^2 \text{ over N-1 electron coordinates}"']
\end{tikzcd}$$

The Universal Functional

- Since the ground state density determines all properties, the ground state energy and its components are a functional of the density

$$E^0_{\mathrm{tot}} = E_{\mathrm{kin}}[\rho^0] + V_{\mathrm{ext}}[\rho^0] + V_{\mathrm{el-el}}[\rho^0]$$

- V_{ext} is known

$$V_{\mathrm{ext}}[\rho^0] = \int V_{ext}(\mathbf{r})\,\rho(\mathbf{r}) d^3r$$

- For the kinetic energy and the e-e interaction

$$F[\rho^0] = E_{\mathrm{kin}}[\rho^0] + V_{\mathrm{el-el}}[\rho^0]$$

- Form of this functional is the same for any molecule or solid

⇒ HK Thm II: A universal energy functional can be defined in terms of the density, *F*[*ρ*], and the exact ground state is the functional minimum

(But, the functional form is unknown!)

2nd Hohenberg-Kohn Theorem

- The groundstate energy can be obtained variationally.
- The density that minimizes the total energy is the exact groundstate density.

$$E[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r \geq E_0$$

The Kohn-Sham Equations

Mapping to a non-interacting system

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

- Why? The kinetic energy of the non-interacting system is well defined.

$$T_S[\rho(\mathbf{r})] = -\frac{1}{2}\sum_{i=1}^{N}\int \varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})$$

- Universal functional now takes the form

$$F[\rho(\mathbf{r})] = T_S[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{\mathrm{xc}}[\rho(\mathbf{r})]$$

- Electron-electron interaction is separated into two terms, the Hartree term (Coulomb interaction) and the unknown(!) exchange-correlation energy term

$$E_H[\rho(\mathbf{r})] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3r\,d^3r' \qquad E_{\mathrm{xc}}[\rho(\mathbf{r})] = ?$$

Euler-Lagrange Equations

Minimize energy with respect to variations of the density

$$\frac{\delta}{\delta\rho}\left\{F[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r - \mu\left(\int \rho(\mathbf{r})d^3r - N\right)\right\} = 0$$

$$\frac{\delta F[\rho(\mathbf{r})}{\delta\rho(\mathbf{r})} + V_{\text{ext}} = \mu$$

- Resulting equations have a similar form as the Schrödinger equation and are known as the Kohn-Sham equations

$$\underbrace{\left[-\frac{1}{2}\nabla^2 + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\right]}_{\mathcal{H}_{\text{KS}}} \varphi_i(\mathbf{r}) = \epsilon_i\, \varphi_i(\mathbf{r})$$

Summary

Hohenberg-Kohn theorem

$$\begin{tikzcd}
V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] & \varrho_0(\mathbf{r}) \arrow[l, Rightarrow] \\
\Psi_{\text{i}}(\mathbf{r}_1, \ldots \mathbf{r}_{\text{N}}) \arrow[r, Rightarrow] & \Psi_0(\mathbf{r}_1, \ldots \mathbf{r}_{\text{N}}) \arrow[u, Rightarrow]
\end{tikzcd}$$

Kohn-Sham
⇔

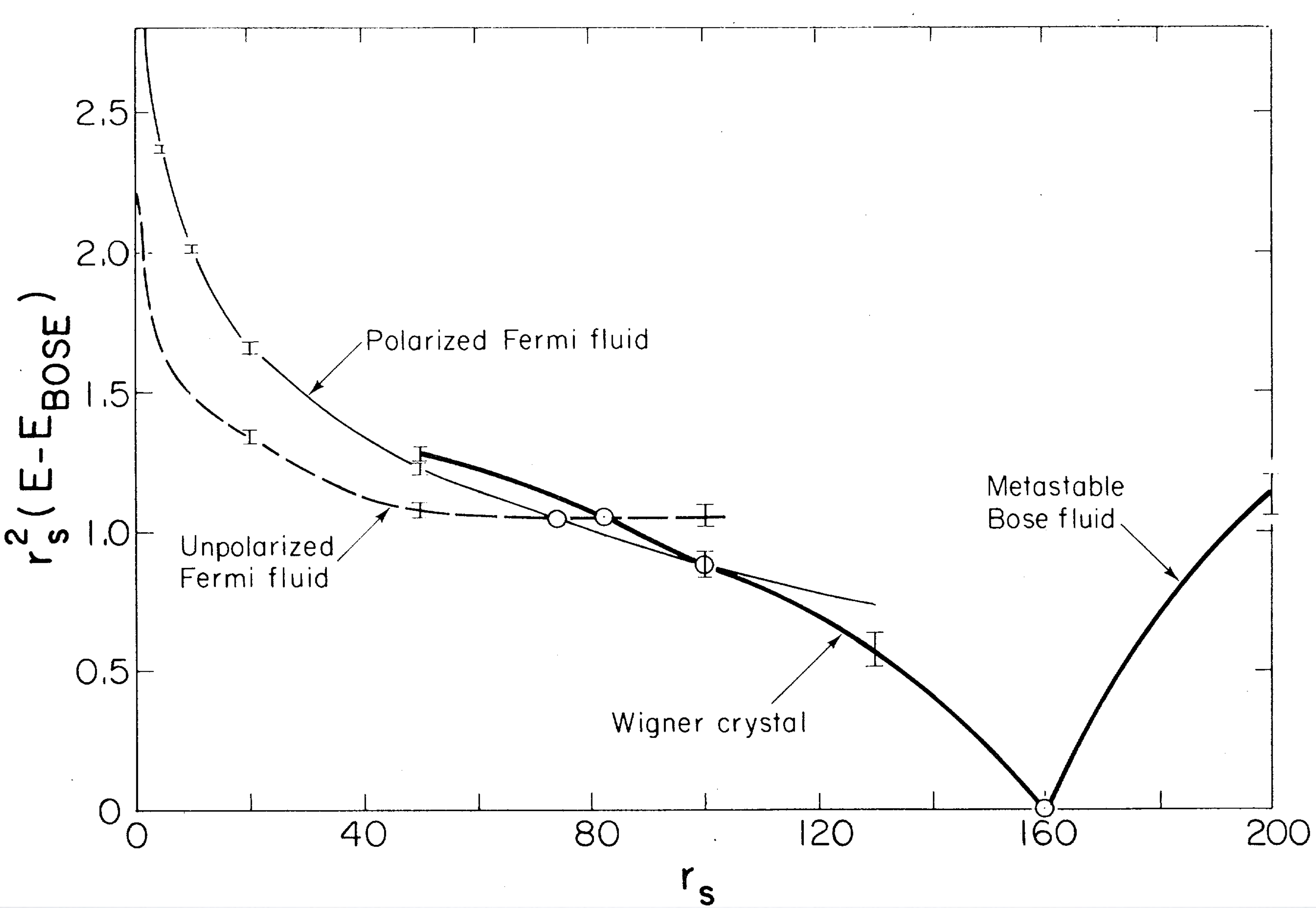
Hohenberg-Kohn theorem applied to non-interacting electrons

$$\begin{tikzcd}
\varrho_0(\mathbf{r}) \arrow[r, Rightarrow] & V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] \\
\varphi_{\text{i=1,N}}(\mathbf{r}) \arrow[u, Rightarrow] & \varphi_{\text{i}}(\mathbf{r}) \arrow[l, Rightarrow]
\end{tikzcd}$$

$$E[\{\varphi_i(\mathbf{r})\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})d^3r + E_{\text{H}}[\rho(\mathbf{r})] + \underset{\uparrow}{E_{\text{xc}}[\rho(\mathbf{r})]} + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r$$

But exchange-correlation functional is still not known!

What about E_{xc}? The Local Density Approximation



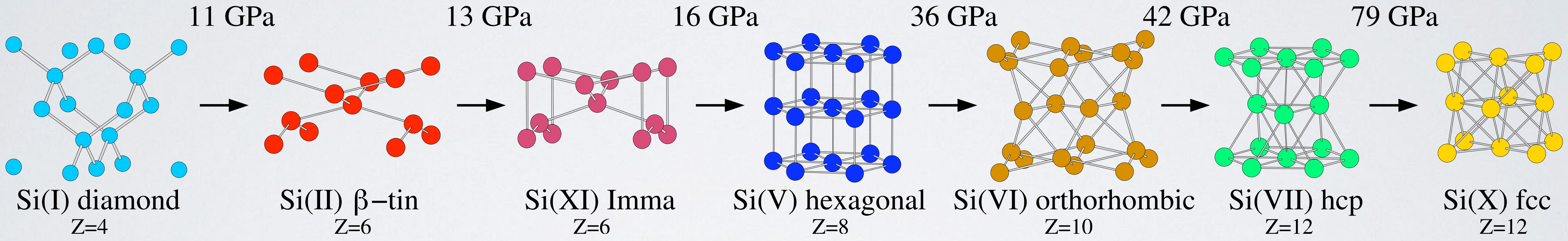
D. M. Ceperley and B. J. Alder, "Ground State of the Electron Gas by a Stochastic Method" Phys. Rev. Lett. 45, 566 (1980). http://link.aps.org/abstract/PRL/v45/p566

The Phases of Silicon

Under pressure Si displays 11 crystal phases

- LDA correctly predicts the energetic order of all these phases

Compression



11 GPa → 13 GPa → 16 GPa → 36 GPa → 42 GPa → 79 GPa

Si(I) diamond
Z=4

Si(II) β−tin
Z=6

Si(XI) Imma
Z=6

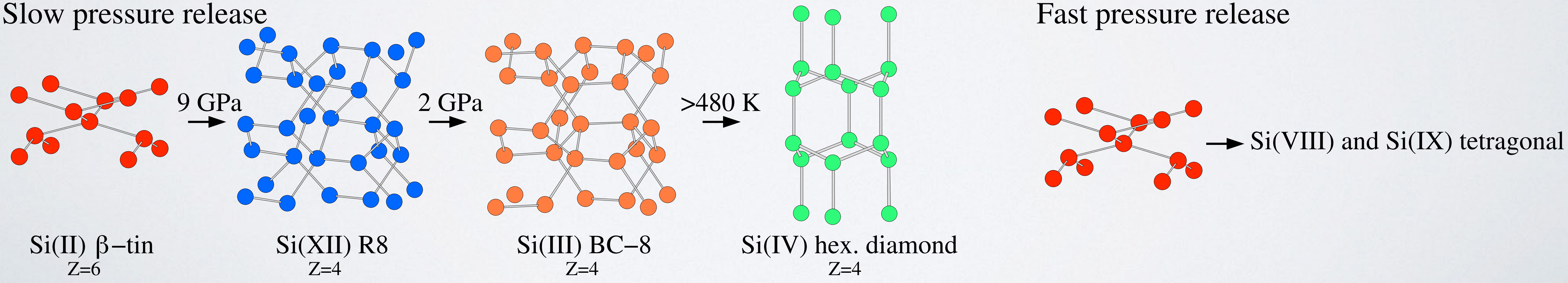
Si(V) hexagonal
Z=8

Si(VI) orthorhombic
Z=10

Si(VII) hcp
Z=12

Si(X) fcc
Z=12

Decompression



Slow pressure release

9 GPa → 2 GPa → >480 K

Si(II) β−tin
Z=6

Si(XII) R8
Z=4

Si(III) BC−8
Z=4

Si(IV) hex. diamond
Z=4

Fast pressure release

→ Si(VIII) and Si(IX) tetragonal

Phys. Rev. B 24, 7210 (1981), ibid. 49, 5329 (1994), ibid. 69, 134112 (2004)

Exchange-Correlation Functionals

Local density approximation (LDA)

- Based on Ceperley & Alder’s calculations for the uniform electron gas by quantum Monte Carlo (a stochastic method for quantum particles)

Generalized gradient approximations (GGA: PW91, PBE)

- Gradients of the density are introduced
- Preserve analytic scaling features of the unknown exact functional

Meta-GGA (TPSS)

- Include information about curvature of the density

Hybrid density functionals (B3LYP, HSE)

- Based on GGA or meta-GGA approximations
- Add some non-local Hartree-Fock exchange to the functional

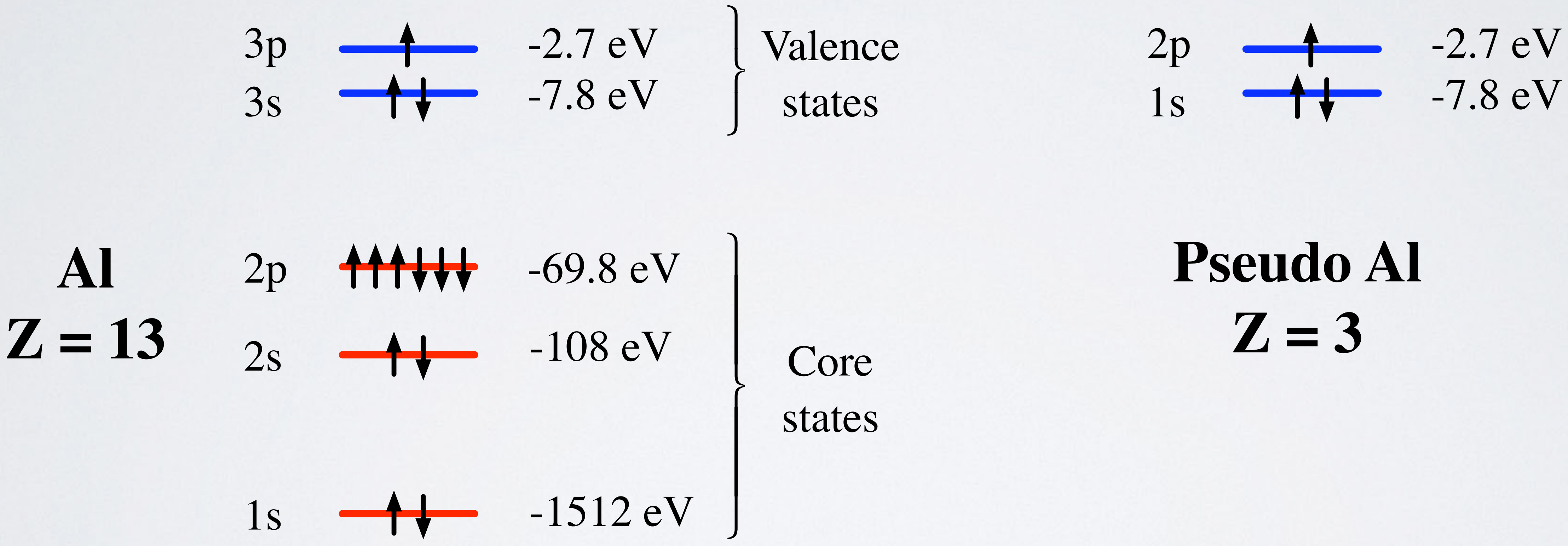
Density Functional Theory in Practice

1. Remove tightly bound core electrons: the pseudopotential approach
2. Represent orbitals with a basis (plane waves or Gaussians)
3. Calculate total energy for trial orbitals
    - Kinetic and Hartree energy in reciprocal space
    - Exchange-correlation energy and external potential in real space
    - Method can take advantage of Fast Fourier Transformations
    - Sum over all states: BZ integrations
4. Minimize energy and iterate charge density to self-consistency

Pseudopotentials

Electrons in the inner shells do not contribute to bonding

- Core electrons are effectively frozen
- Replace Coulomb potential between electrons and nuclei with effective potential, the pseudopotential



$$\boxed{\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}\right]\varphi_i = \epsilon_i\,\varphi_i}$$

$$\boxed{\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\text{pseudo}}\right]\varphi_i^{\text{pseudo}} = \epsilon_i\,\varphi_i^{\text{pseudo}}}$$

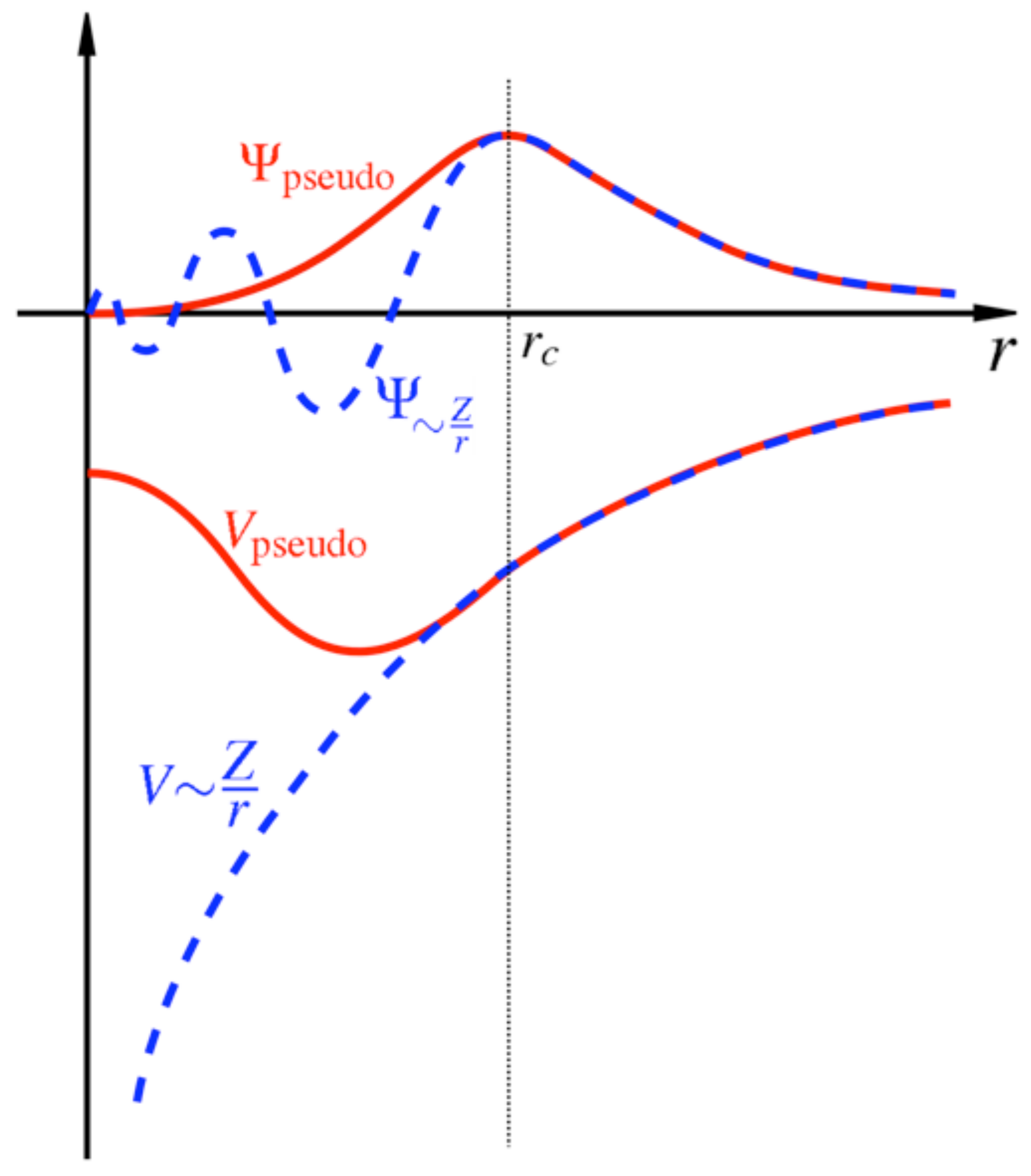
Pseudopotentials

The pseudopotential and the wave function

- Real potential and wave function are shown in blue

- Pseudopotential and pseudo wave function in red

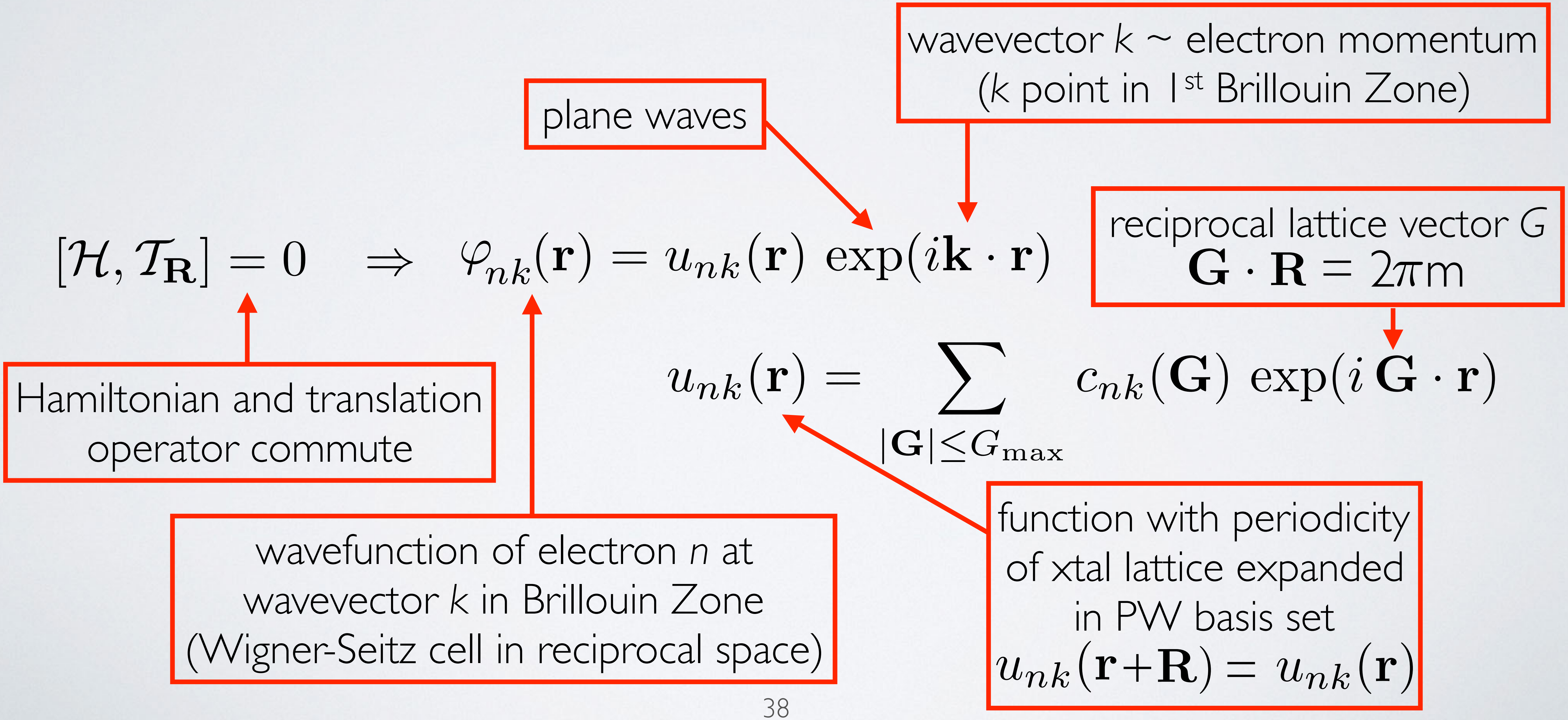
- Outside the cutoff region (vertical black line)
  the two are identical



Bloch Theorem — G’s and k’s

Basis set choices

- For molecules: use atomic orbitals, or localized functions like Gaussians
- For solids, periodic functions such as sines and cosines (i.e., plane waves)
- Use **Bloch Theorem** for periodic solids:



wavevector *k* ~ electron momentum (*k* point in 1st Brillouin Zone)

plane waves

$$[\mathcal{H}, \mathcal{T}_{\mathbf{R}}] = 0 \quad \Rightarrow \quad \varphi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r})\ \exp(i\mathbf{k}\cdot\mathbf{r})$$

reciprocal lattice vector *G*
$\mathbf{G}\cdot\mathbf{R} = 2\pi m$

$$u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}|\leq G_{\max}} c_{nk}(\mathbf{G})\ \exp(i\,\mathbf{G}\cdot\mathbf{r})$$

Hamiltonian and translation operator commute

wavefunction of electron *n* at wavevector *k* in Brillouin Zone (Wigner-Seitz cell in reciprocal space)

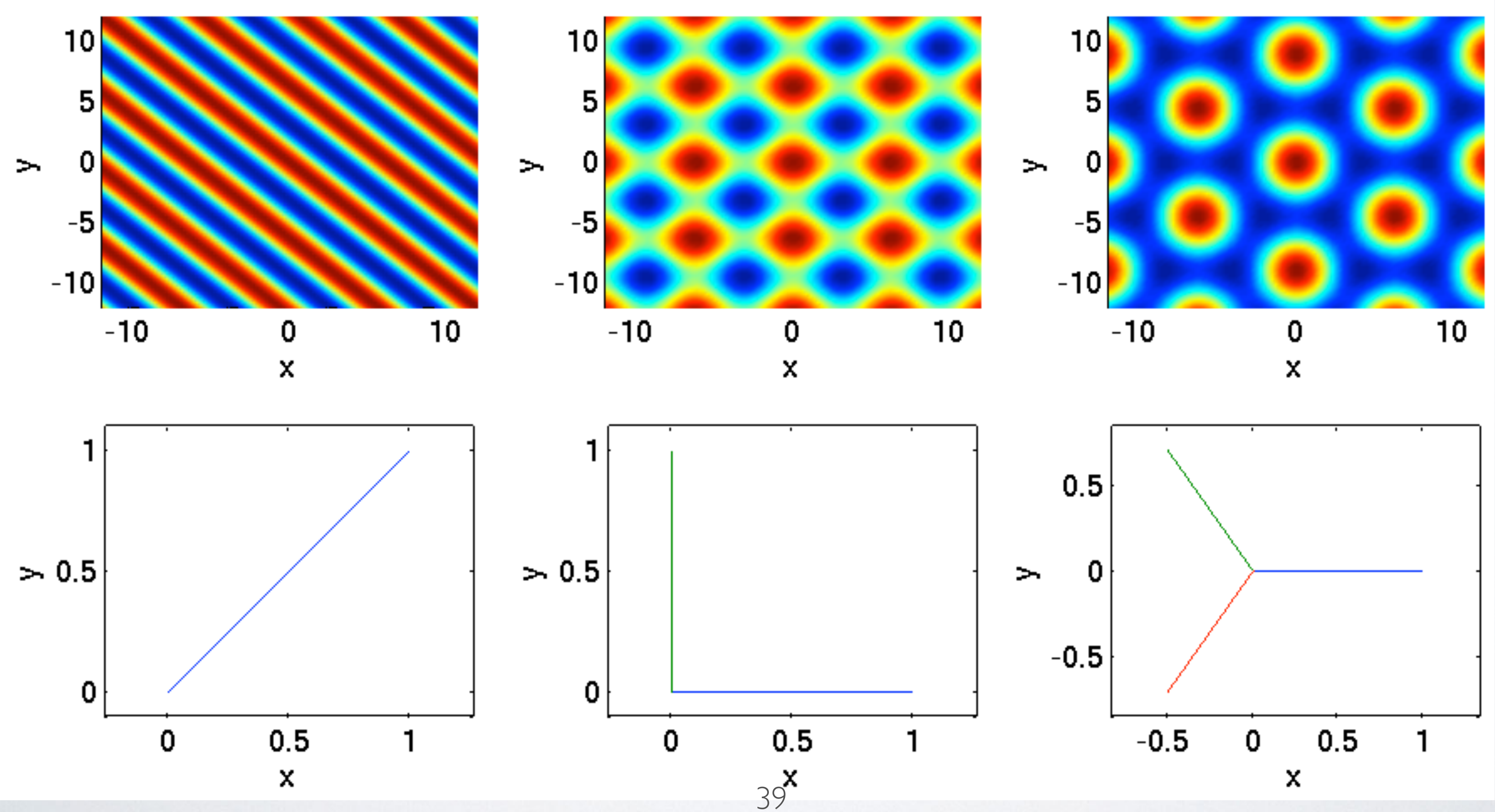
function with periodicity of xtal lattice expanded in PW basis set
$u_{nk}(\mathbf{r}+\mathbf{R}) = u_{nk}(\mathbf{r})$

G’s: Plane Wave Basis Set

- Superposition of plane waves to represent orbitals with xtal lattice periodicity

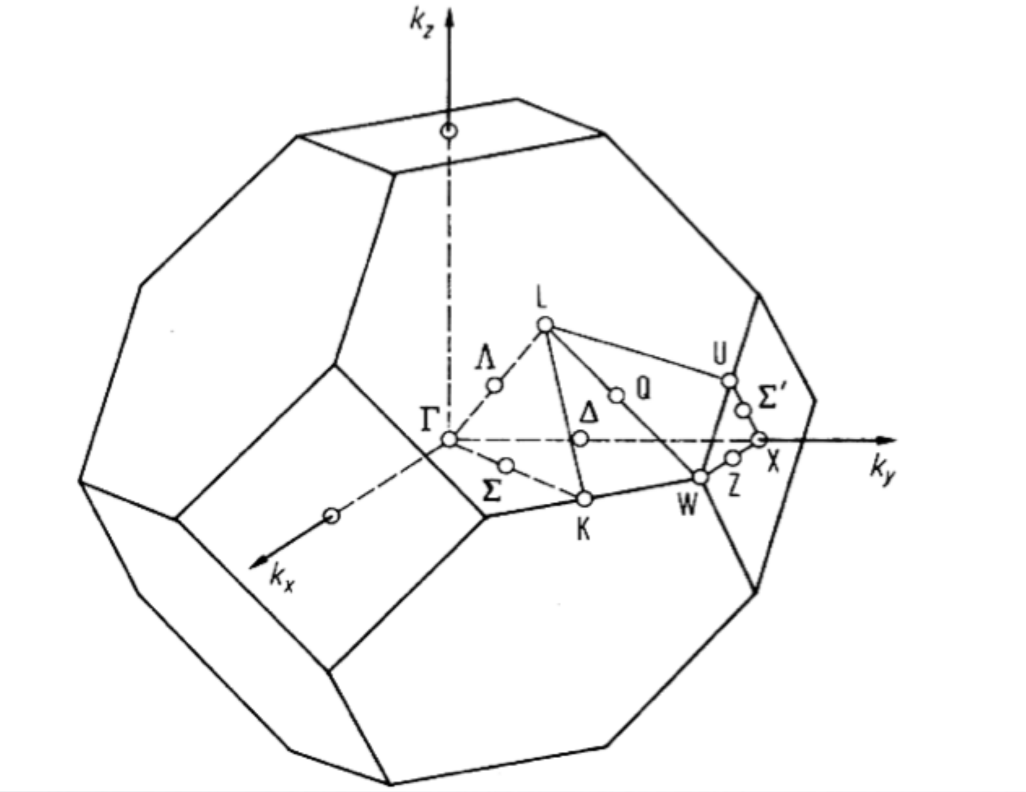
$$u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}|\leq G_{\max}} c_{nk}(\mathbf{G})\,\exp(i\,\mathbf{G}\cdot\mathbf{r})$$

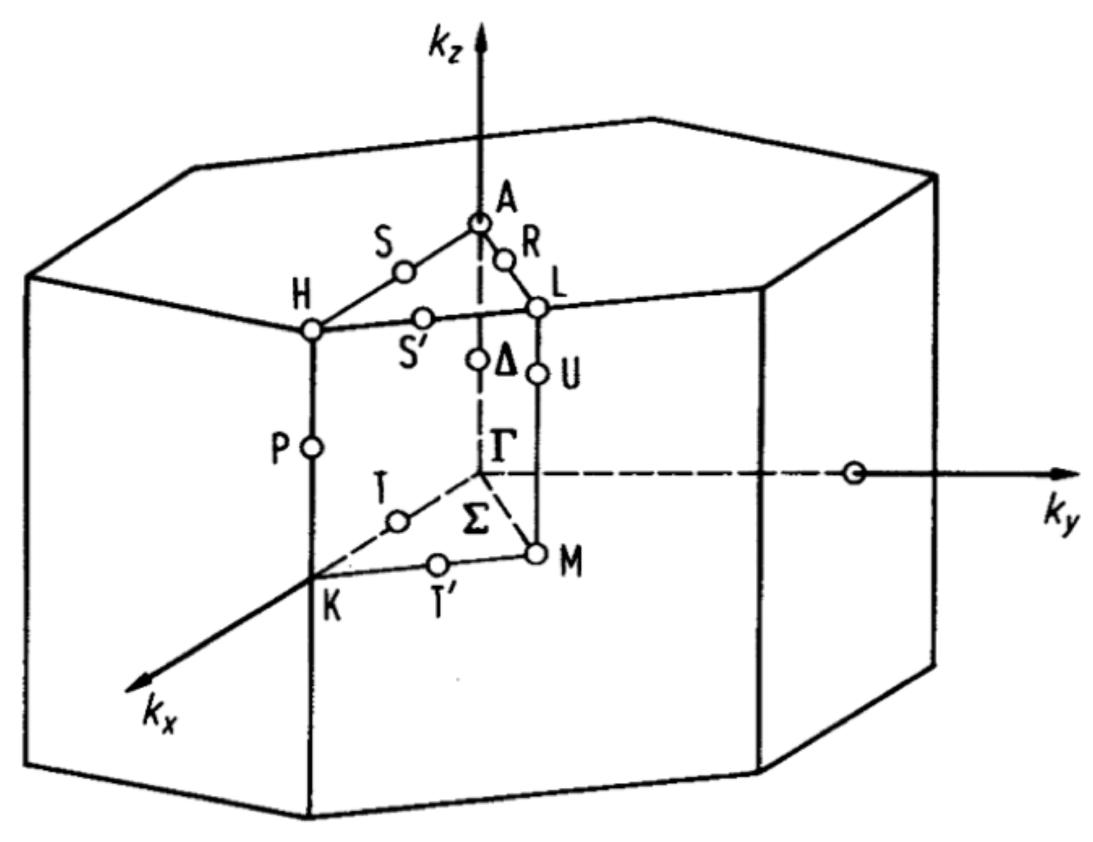
- Increase size of basis set to approach completeness (i.e., convergence)



k's: 1$^{\text{st}}$ Brillouin Zone (1BZ)

- Crystal structures defined by Bravais lattice $\{\mathbf{a}_i\}$ and basis
- *Reciprocal lattice* $$\mathbf{b}_k = 2\pi \cdot \frac{\mathbf{a}_l \times \mathbf{a}_m}{\mathbf{a}_k \cdot (\mathbf{a}_l \times \mathbf{a}_m)}$$
- *Brillouin zone* is the ***Wigner-Seitz cell of the reciprocal lattice***





k’s: 1^{st} Brillouin Zone (1BZ)

- The wavefunction (and energy) of each electron depends on both its quantum number *n* and its position *k* (i.e., its momentum) within the 1BZ

- We must solve a different Kohn-Sham equation for each *n* and *k*

$$\hat{h}_{\mathbf{k}}\, \psi_{n,\mathbf{k}}(\mathbf{r}) = \varepsilon_{n,\mathbf{k}}\, \psi_{n,\mathbf{k}}(\mathbf{r})$$

- Bloch Thm has allowed us to replace analysis of ~infinite number of electrons in the xtal with only those in BZ but at an infinite number of k points!

- Payoff is that wavefunctions change smoothly in *k* so in practice consider finite number of *k*-points — sampling over a *k*-space grid, refine grid until convergence

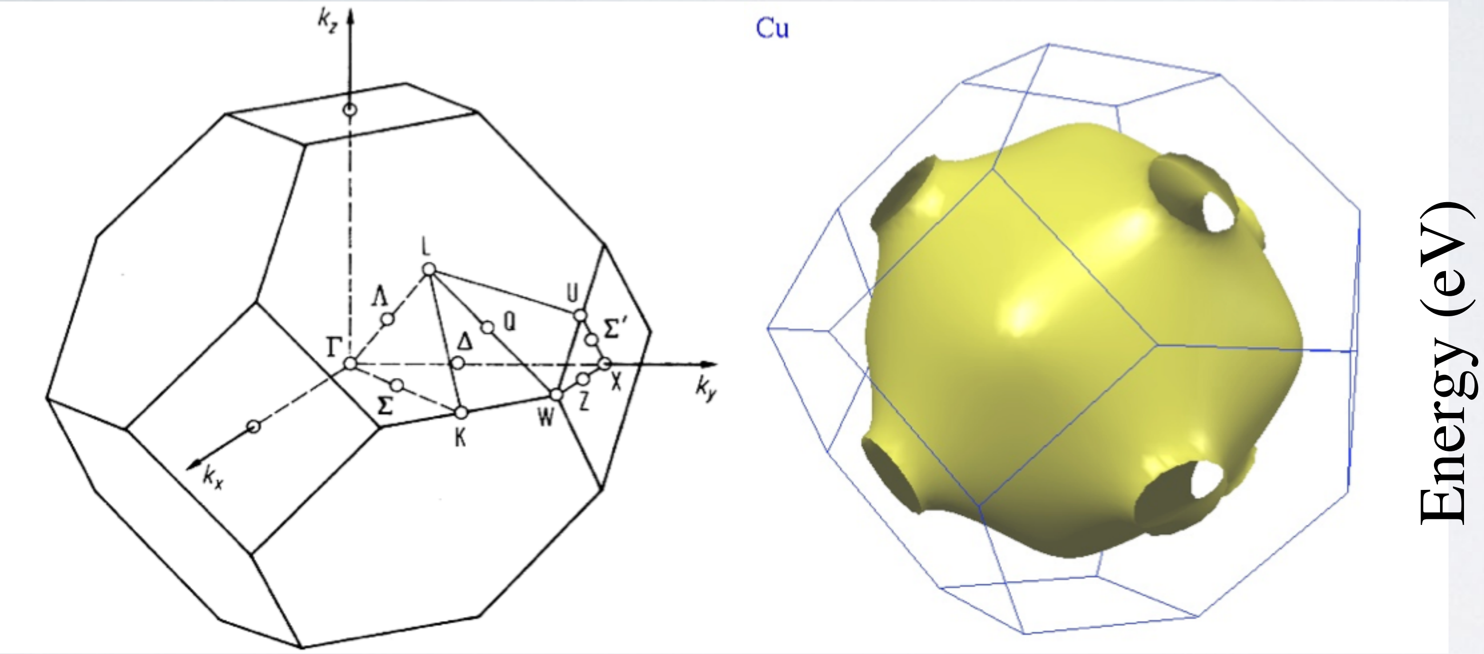
- Real-space quantities are computed by a **discrete sum over *n*** and **integration over *k* within the Brillouin Zone (approximated over a grid at finite k-points)**

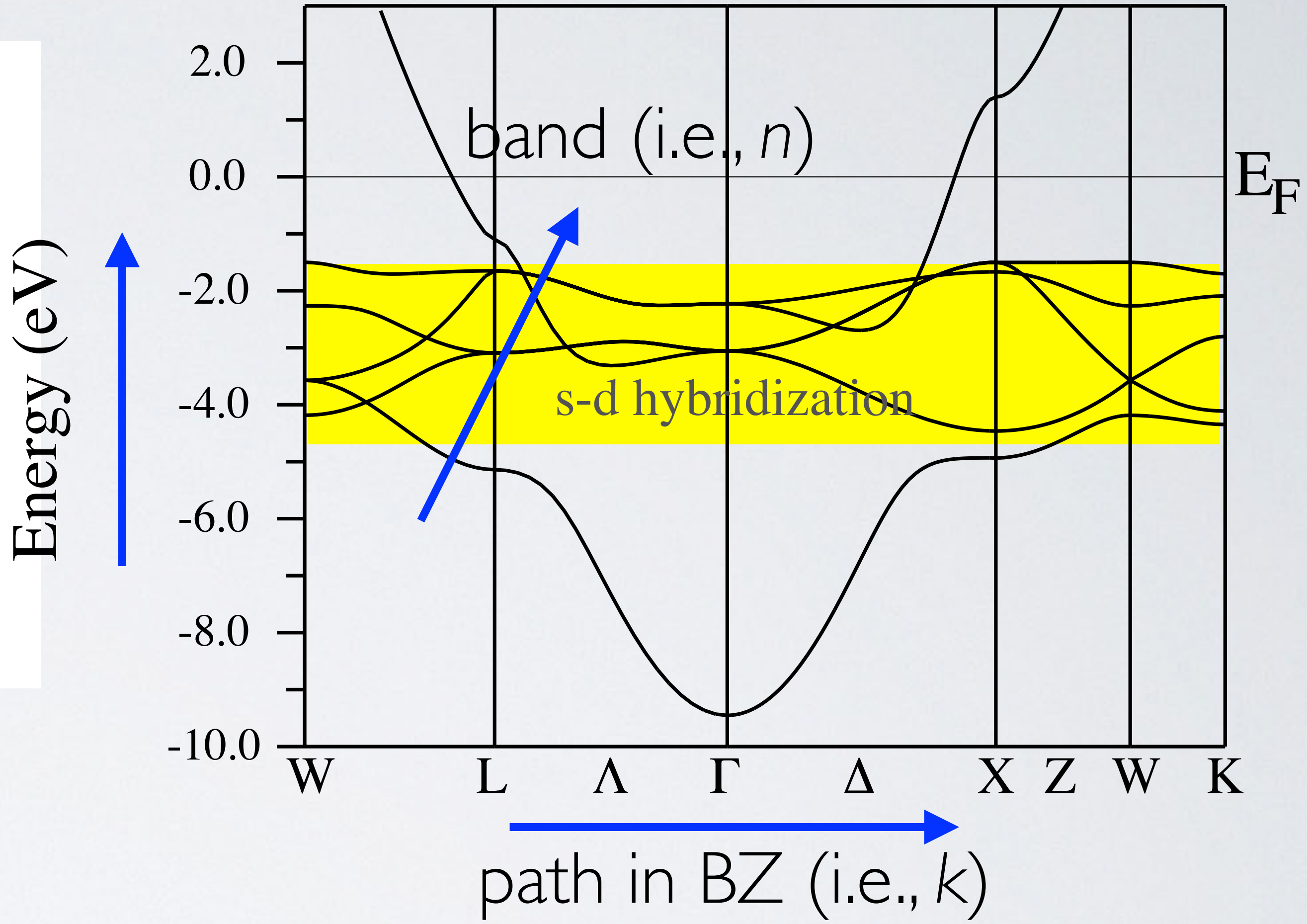
- e.g. density, n(**r**)

$$n(\mathbf{r}) = \frac{V_{\mathrm{cell}}}{(2\pi)^3} \int_{1\mathrm{BZ}} \left(\sum_{n=1}^{N_{\mathrm{el}}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2 \right) d\mathbf{k}$$

k's: Band Structure Plot — $\varepsilon_{n,k}$

- Copper: Band structure calculated with Wien2k





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

$$\hat{h}_{\mathbf{k}}\,\psi_{n,\mathbf{k}}(\mathbf{r}) = \varepsilon_{n,\mathbf{k}}\,\psi_{n,\mathbf{k}}(\mathbf{r})$$

- *Nearly free electron s*-band dominates at low and high energies
- *Hybridization* of *nearly-free s* and *atomic-like d* orbitals at intermediate energies

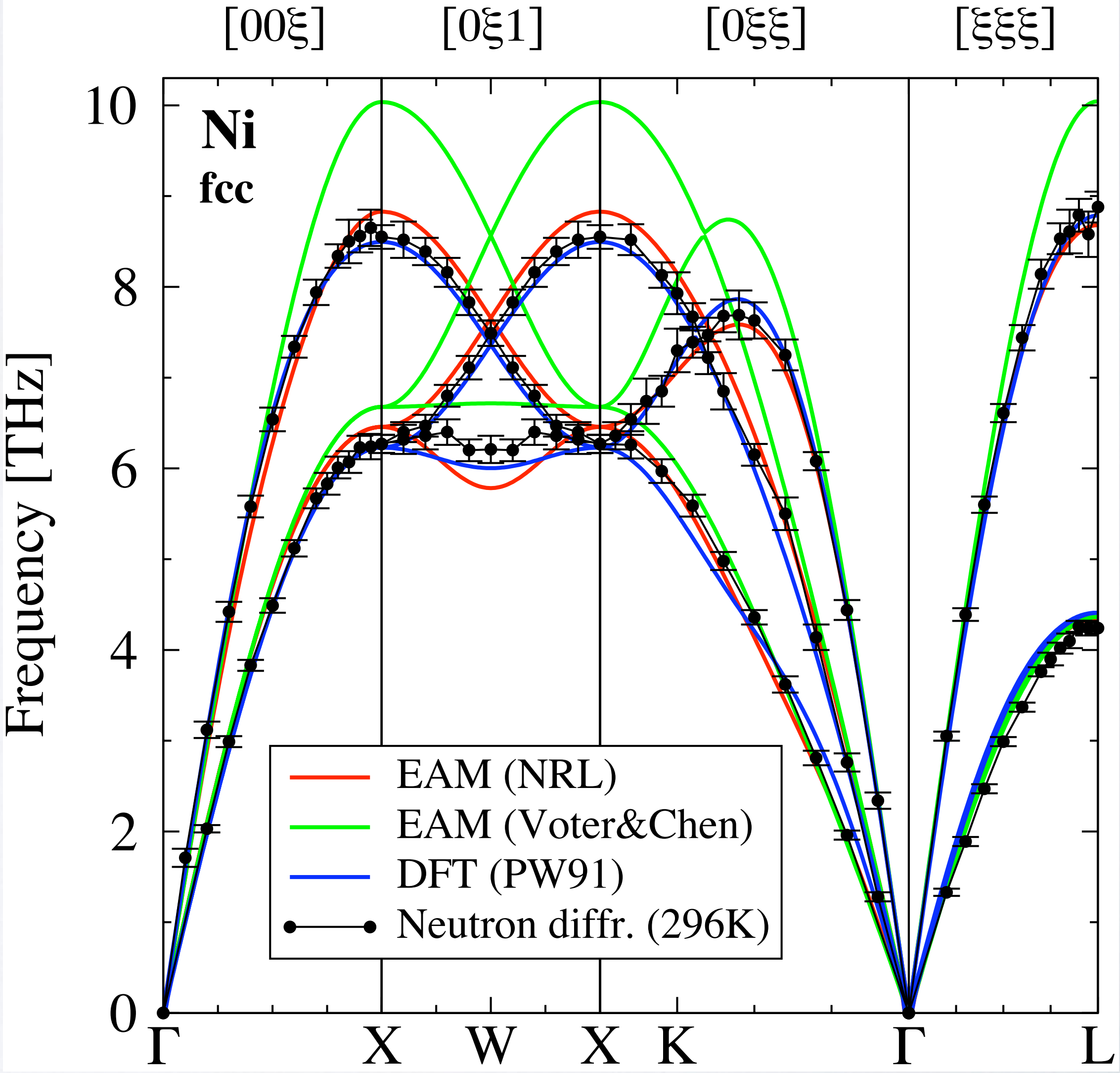
Successes and Failures of DFT

Structural and elastic properties

- Lattice parameters are typically within a few percent of experimental values and often accurate to better than 1%
- The bulk modulus and other elastic constants are usually within 10%

Vibrational Properties

- Forces = 1st derivative of energy with respect to atomic displacement
- Forces are accurate to better than 10% (similar to elastic constants)
- Vibrational frequencies are the 2nd derivatives
- Their accuracy is about 1/2 the accuracy of the forces or about 5%



Successes and Failures of DFT

Defect energies

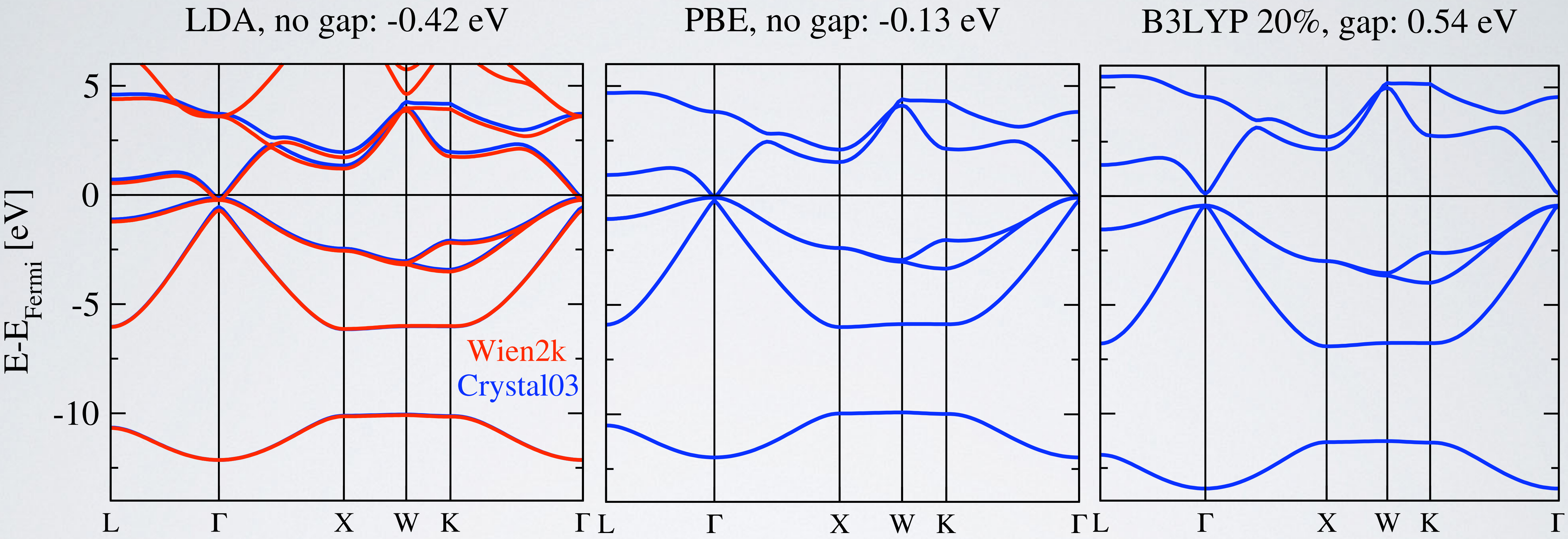
- In many cases such as for metals, vacancy and interstitial energies are highly accurate (within 0.1 eV)
- In some cases such as interstitial defects in silicon, DFT is too low by about 1 eV predicting a 3–3.5 eV formation energy instead of the 4.5 eV of experiments and QMC [Phys. Rev. B 74, 121102(R) (2006)]

Excited states and gaps

- Local density approximation fails for excited states
- Bandgaps in LDA and GGA are usually underestimated by 20–50%
- In some cases such as Ge, LDA predicts a metallic instead of semiconducting state
- Hybrid functionals (e.g. B3LYP and HSE) improve the accuracy to about 10%

The bandgap problem of DFT

Example: Bandstructure of InAs



LDA, no gap: -0.42 eV

PBE, no gap: -0.13 eV

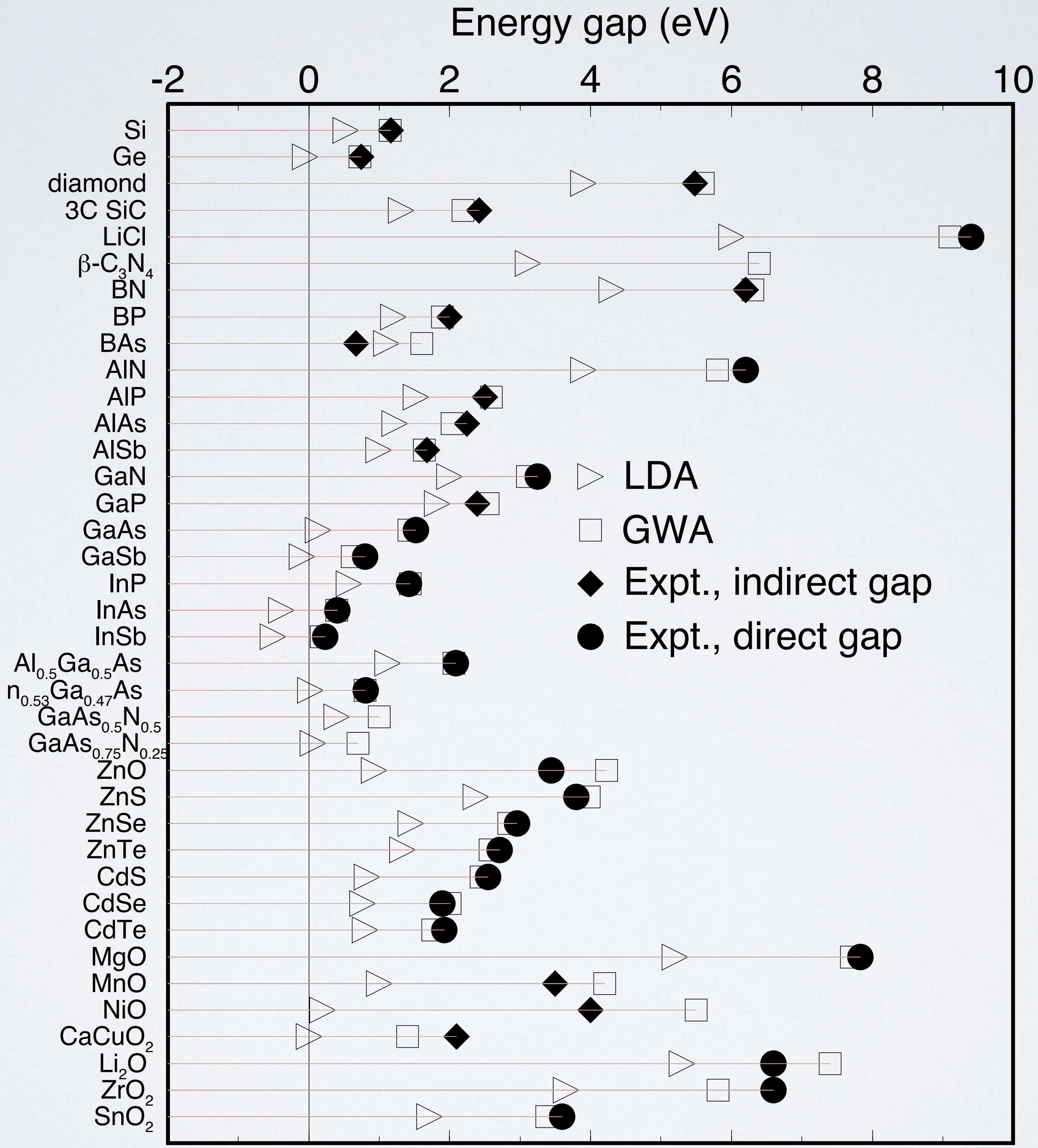
B3LYP 20%, gap: 0.54 eV

- Experimental bandgap: 0.41 eV

Band gap problem: LDA and GGA yield a metallic ground state!

- Practical solution: **Hybrid functionals** B3LYP & HSE (0.39 eV)
- Better solution: **GW approximation or QMC methods**

Beyond DFT – The GW approximation



Summary of Density Functional Theory

LDA

- Lattice constants: 1-3% too small
- Cohesive Energies: 5-20% too strongly bound
- Bulk Modulus: 5-20% (largest errors for late TM)
- Bandgaps: too small

GGA

- Improves cohesive energies
- Often but not always better for lattice parameters
- Important for magnetic systems

Hybrid functionals

- Improved band gaps, often very accurate

Always check the accuracy of the computational method by benchmarking against experimental data or more accurate theory.