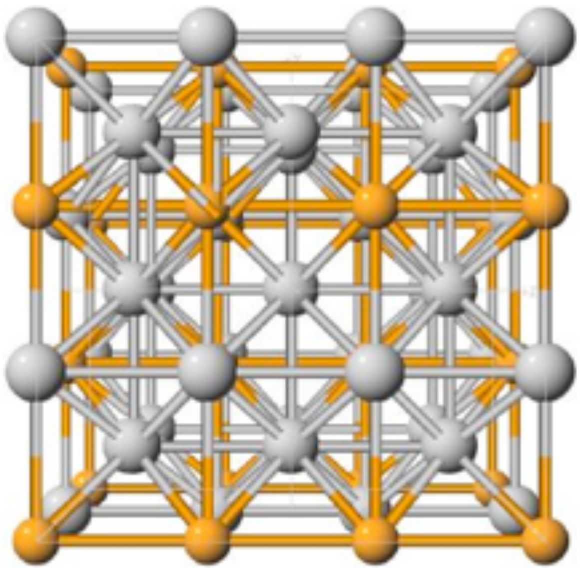
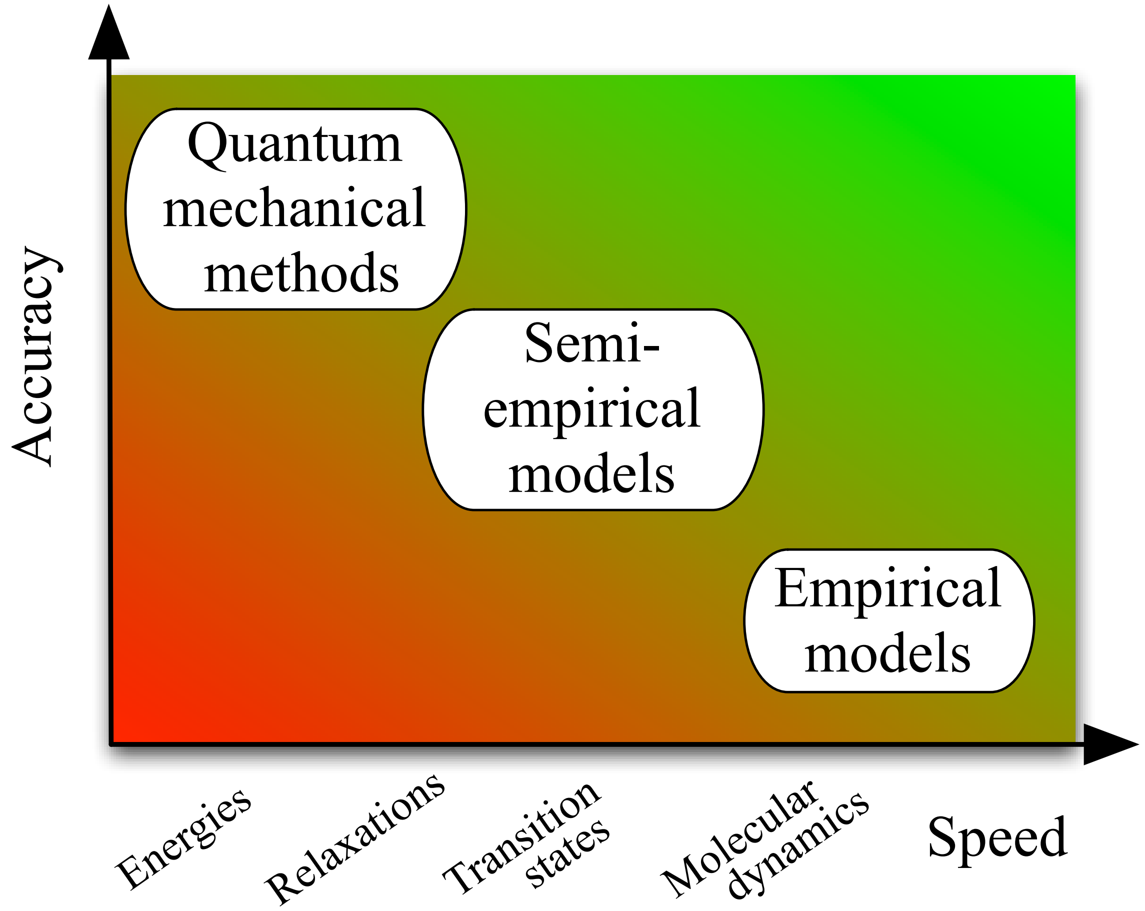
Quantum Mechanics Methods



Energy model

Energy $E(\mathbf{R}_i)$

Hierarchy of energy models



Short Review of Quantum Mechanics

Why do we need quantum mechanics?

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

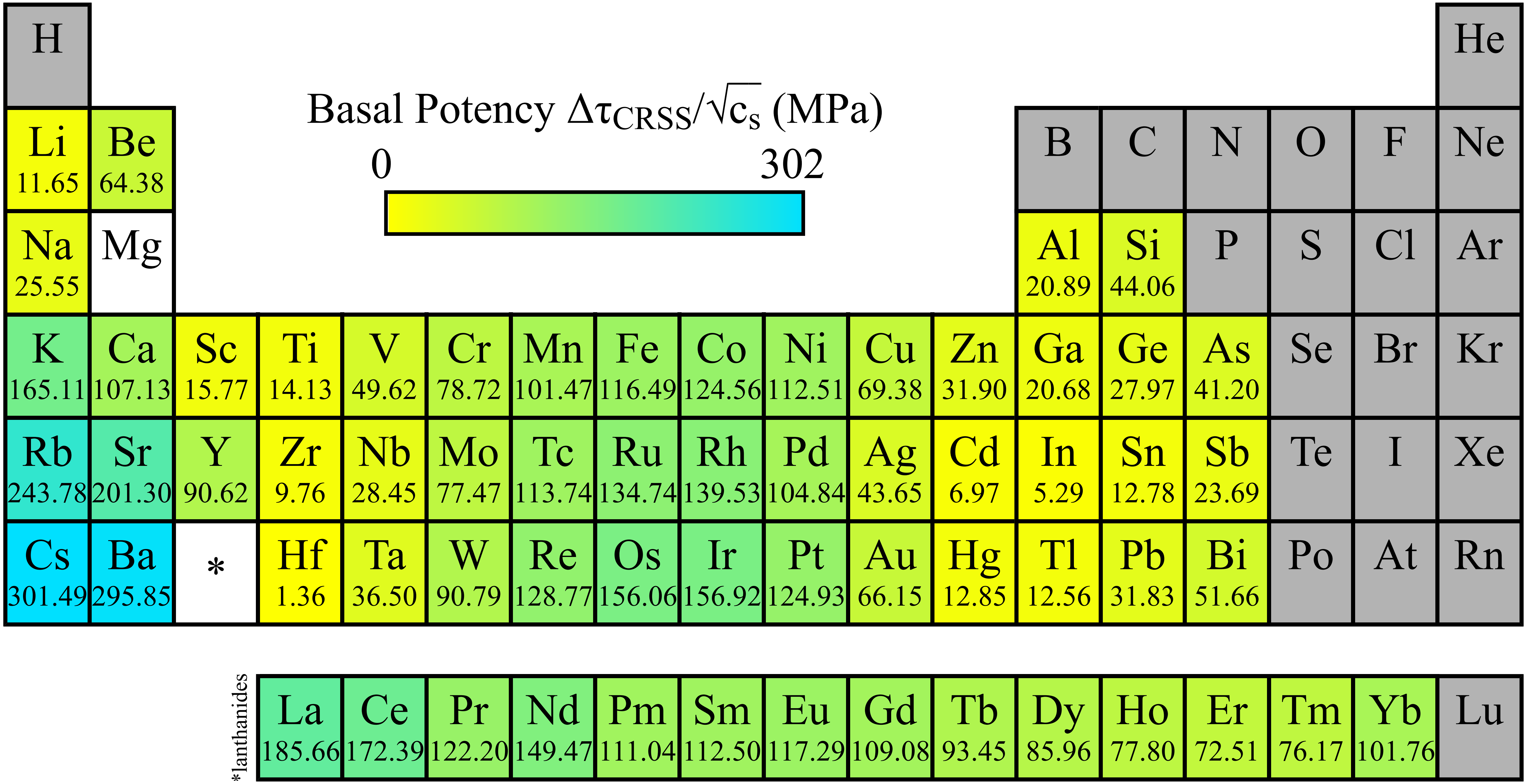
Standard model of matter

- 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

Solute trends in Mg alloys: basal strengthening

Basal potency: increase in basal CRSS with concentration

- correlated with size and basal stacking fault energy change
- derived for dilute limit, zero temperature pinning



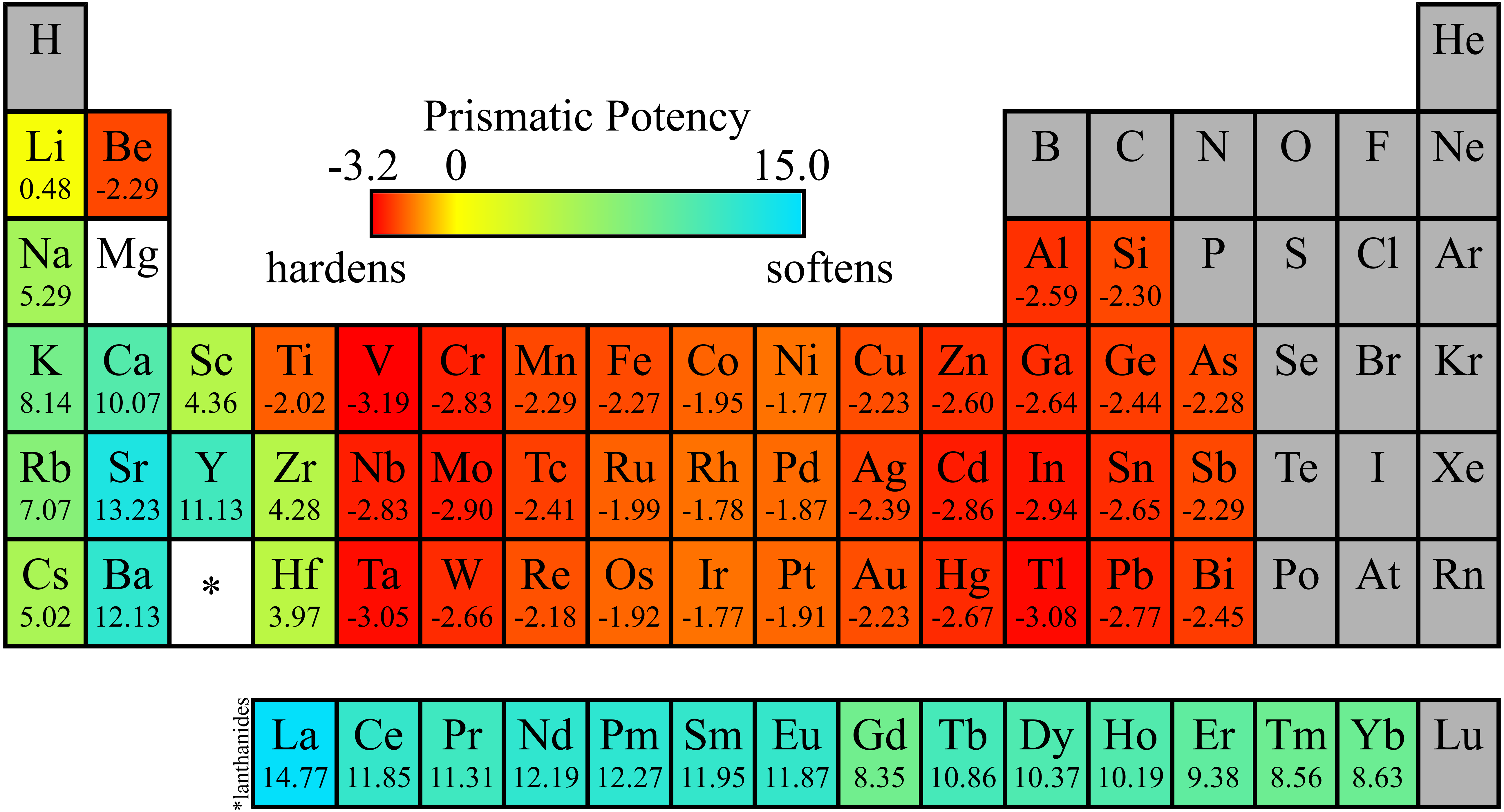
Basal Potency $\Delta\tau_{CRSS}/\sqrt{c_s}$ (MPa)

H																	He
Li 11.65	Be 64.38											B	C	N	O	F	Ne
Na 25.55	Mg											Al 20.89	Si 44.06	P	S	Cl	Ar
K 165.11	Ca 107.13	Sc 15.77	Ti 14.13	V 49.62	Cr 78.72	Mn 101.47	Fe 116.49	Co 124.56	Ni 112.51	Cu 69.38	Zn 31.90	Ga 20.68	Ge 27.97	As 41.20	Se	Br	Kr
Rb 243.78	Sr 201.30	Y 90.62	Zr 9.76	Nb 28.45	Mo 77.47	Tc 113.74	Ru 134.74	Rh 139.53	Pd 104.84	Ag 43.65	Cd 6.97	In 5.29	Sn 12.78	Sb 23.69	Te	I	Xe
Cs 301.49	Ba 295.85	*	Hf 1.36	Ta 36.50	W 90.79	Re 128.77	Os 156.06	Ir 156.92	Pt 124.93	Au 66.15	Hg 12.85	Tl 12.56	Pb 31.83	Bi 51.66	Po	At	Rn
		*lanthanides	La 185.66	Ce 172.39	Pr 122.20	Nd 149.47	Pm 111.04	Sm 112.50	Eu 117.29	Gd 109.08	Tb 93.45	Dy 85.96	Ho 77.80	Er 72.51	Tm 76.17	Yb 101.76	Lu

Solute trends in Mg alloys: prismatic softening

Prismatic potency: maximum possible cross-slip softening

- correlated with prismatic stacking fault energy reduction (except Li)
- strictly for **random binary** solute distribution



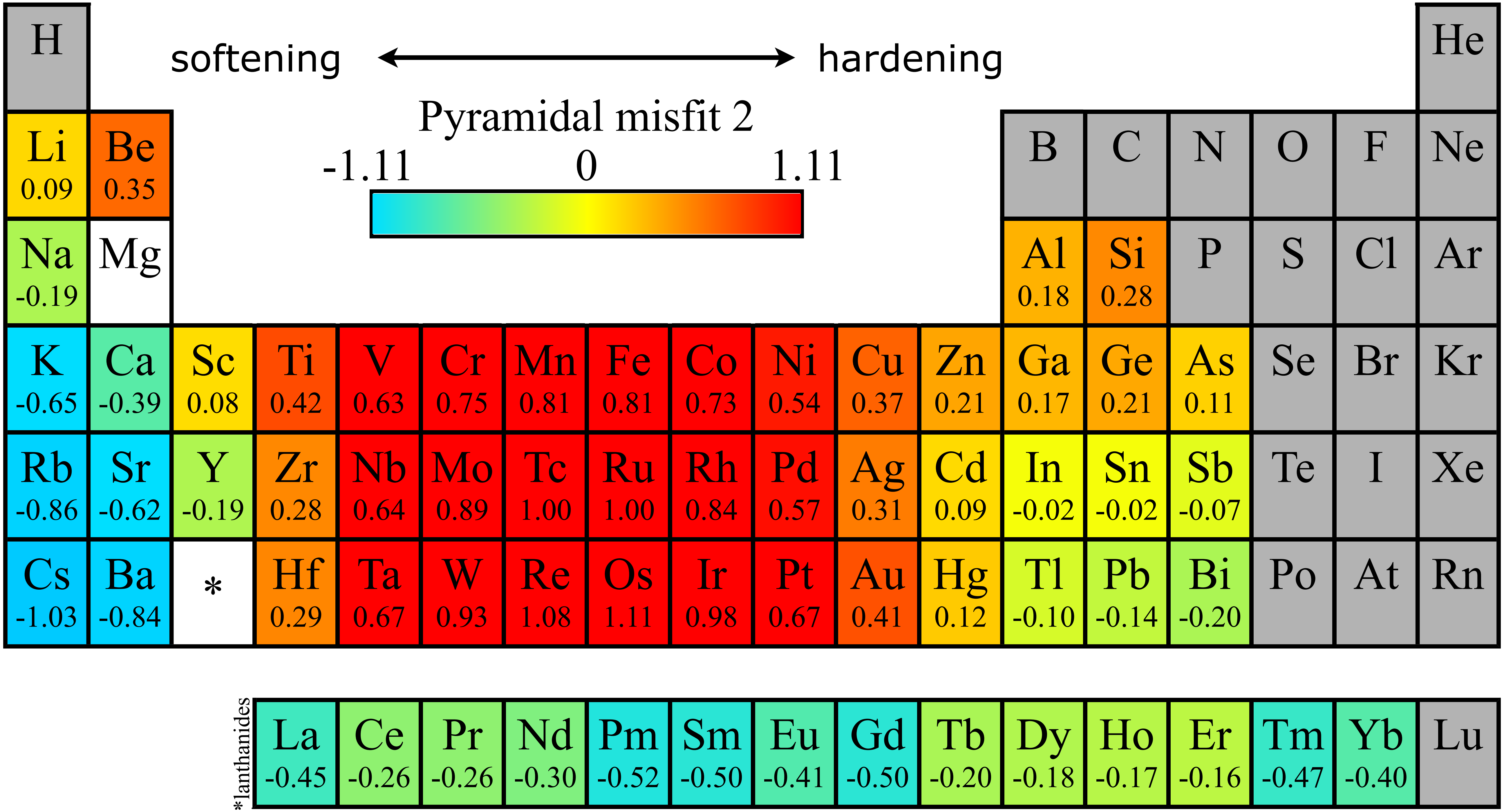
H																	He
Li 0.48	Be -2.29											B	C	N	O	F	Ne
Na 5.29	Mg											Al -2.59	Si -2.30	P	S	Cl	Ar
K 8.14	Ca 10.07	Sc 4.36	Ti -2.02	V -3.19	Cr -2.83	Mn -2.29	Fe -2.27	Co -1.95	Ni -1.77	Cu -2.23	Zn -2.60	Ga -2.64	Ge -2.44	As -2.28	Se	Br	Kr
Rb 7.07	Sr 13.23	Y 11.13	Zr 4.28	Nb -2.83	Mo -2.90	Tc -2.41	Ru -1.99	Rh -1.78	Pd -1.87	Ag -2.39	Cd -2.86	In -2.94	Sn -2.65	Sb -2.29	Te	I	Xe
Cs 5.02	Ba 12.13	*	Hf 3.97	Ta -3.05	W -2.66	Re -2.18	Os -1.92	Ir -1.77	Pt -1.91	Au -2.23	Hg -2.67	Tl -3.08	Pb -2.77	Bi -2.45	Po	At	Rn
		*lanthanides	La 14.77	Ce 11.85	Pr 11.31	Nd 12.19	Pm 12.27	Sm 11.95	Eu 11.87	Gd 8.35	Tb 10.86	Dy 10.37	Ho 10.19	Er 9.38	Tm 8.56	Yb 8.63	Lu

magnesium.matse.illinois.edu

Solute trends in Mg alloys: c+a softening

Change in pyramidal (1$\bar{1}$01) stacking fault with addition of solute

- size, valency change, localization / delocalization of orbitals
- changes to Mg local electronic structure (3s and 2p)



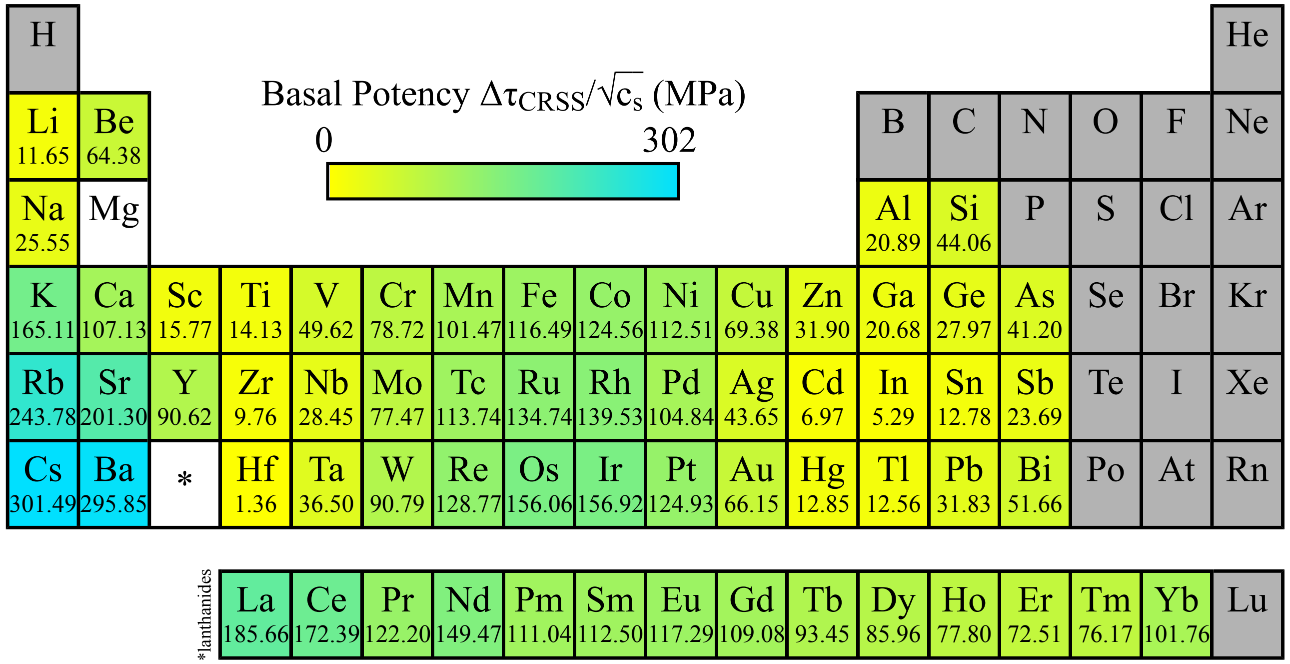
H																	He
Li 0.09	Be 0.35											B	C	N	O	F	Ne
Na -0.19	Mg											Al 0.18	Si 0.28	P	S	Cl	Ar
K -0.65	Ca -0.39	Sc 0.08	Ti 0.42	V 0.63	Cr 0.75	Mn 0.81	Fe 0.81	Co 0.73	Ni 0.54	Cu 0.37	Zn 0.21	Ga 0.17	Ge 0.21	As 0.11	Se	Br	Kr
Rb -0.86	Sr -0.62	Y -0.19	Zr 0.28	Nb 0.64	Mo 0.89	Tc 1.00	Ru 1.00	Rh 0.84	Pd 0.57	Ag 0.31	Cd 0.09	In -0.02	Sn -0.02	Sb -0.07	Te	I	Xe
Cs -1.03	Ba -0.84	*	Hf 0.29	Ta 0.67	W 0.93	Re 1.08	Os 1.11	Ir 0.98	Pt 0.67	Au 0.41	Hg 0.12	Tl -0.10	Pb -0.14	Bi -0.20	Po	At	Rn
		*lanthanides	La -0.45	Ce -0.26	Pr -0.26	Nd -0.30	Pm -0.52	Sm -0.50	Eu -0.41	Gd -0.50	Tb -0.20	Dy -0.18	Ho -0.17	Er -0.16	Tm -0.47	Yb -0.40	Lu

magnesium.matse.illinois.edu

Solute trends in Mg alloys: effect on slip

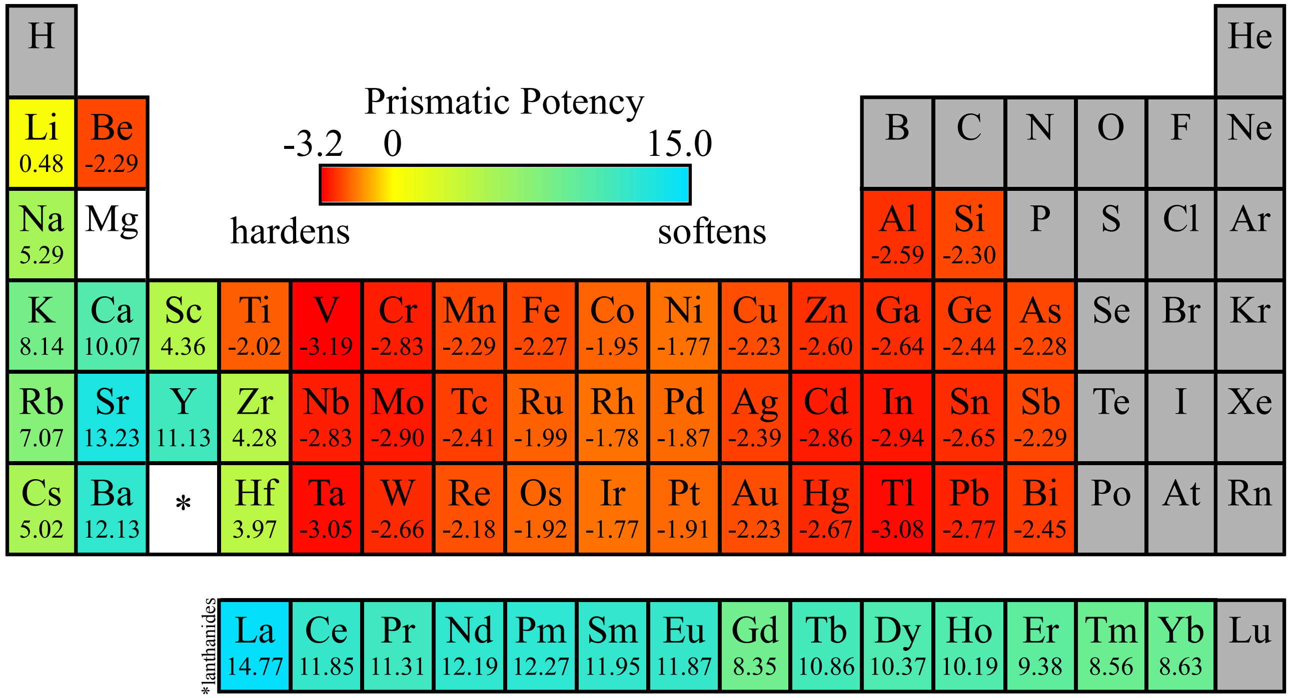
Multiple misfits (changes in SFE) and potencies (changes in slip)

- pyramidal fault energies needed for ⟨c+a⟩ slip
- combined effects even more important



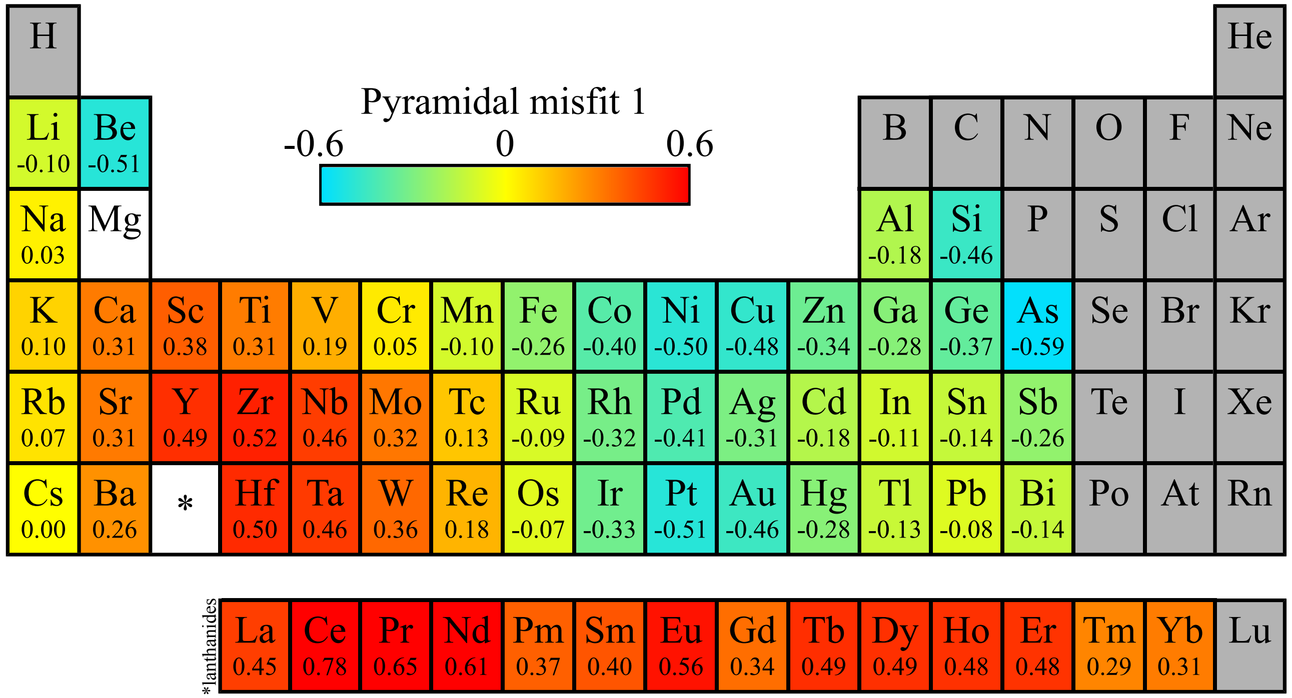
Basal Potency $\Delta\tau_{CRSS}/\sqrt{c_s}$ (MPa)

H																	He
Li 11.65	Be 64.38											B	C	N	O	F	Ne
Na 25.55	Mg											Al 20.89	Si 44.06	P	S	Cl	Ar
K 165.11	Ca 107.13	Sc 15.77	Ti 14.13	V 49.62	Cr 78.72	Mn 101.47	Fe 116.49	Co 124.56	Ni 112.51	Cu 69.38	Zn 31.90	Ga 20.68	Ge 27.97	As 41.20	Se	Br	Kr
Rb 243.78	Sr 201.30	Y 90.62	Zr 9.76	Nb 28.45	Mo 77.47	Tc 113.74	Ru 134.74	Rh 139.53	Pd 104.84	Ag 43.65	Cd 6.97	In 5.29	Sn 12.78	Sb 23.69	Te	I	Xe
Cs 301.49	Ba 295.85	*	Hf 1.36	Ta 36.50	W 90.79	Re 128.77	Os 156.06	Ir 156.92	Pt 124.93	Au 66.15	Hg 12.85	Tl 12.56	Pb 31.83	Bi 51.66	Po	At	Rn
		*lanthanides	La 185.66	Ce 172.39	Pr 122.20	Nd 149.47	Pm 111.04	Sm 112.50	Eu 117.29	Gd 109.08	Tb 93.45	Dy 85.96	Ho 77.80	Er 72.51	Tm 76.17	Yb 101.76	Lu



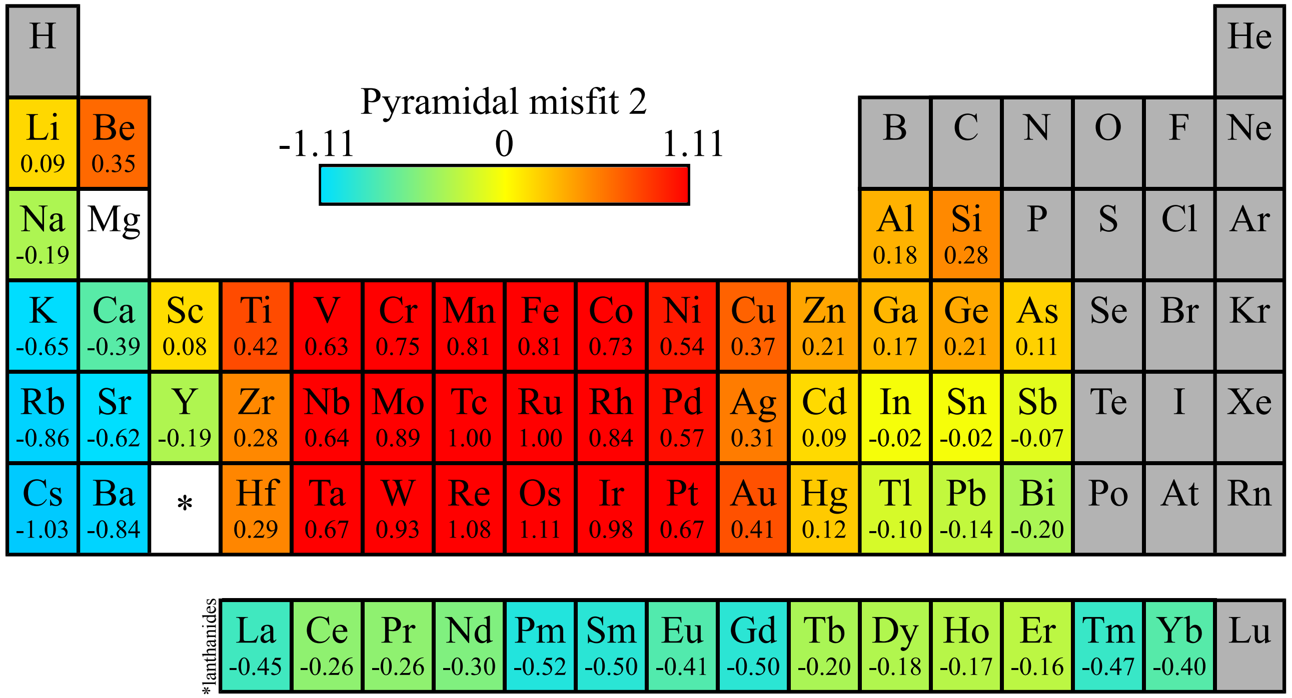
Prismatic Potency

H																	He
Li 0.48	Be -2.29											B	C	N	O	F	Ne
Na 5.29	Mg											Al -2.59	Si -2.30	P	S	Cl	Ar
K 8.14	Ca 10.07	Sc 4.36	Ti -2.02	V -3.19	Cr -2.83	Mn -2.29	Fe -2.27	Co -1.95	Ni -1.77	Cu -2.23	Zn -2.60	Ga -2.64	Ge -2.44	As -2.28	Se	Br	Kr
Rb 7.07	Sr 13.23	Y 11.13	Zr 4.28	Nb -2.83	Mo -2.90	Tc -2.41	Ru -1.99	Rh -1.78	Pd -1.87	Ag -2.39	Cd -2.86	In -2.94	Sn -2.65	Sb -2.29	Te	I	Xe
Cs 5.02	Ba 12.13	*	Hf 3.97	Ta -3.05	W -2.66	Re -2.18	Os -1.92	Ir -1.77	Pt -1.91	Au -2.23	Hg -2.67	Tl -3.08	Pb -2.77	Bi -2.45	Po	At	Rn
		*lanthanides	La 14.77	Ce 11.85	Pr 11.31	Nd 12.19	Pm 12.27	Sm 11.95	Eu 11.87	Gd 8.35	Tb 10.86	Dy 10.37	Ho 10.19	Er 9.38	Tm 8.56	Yb 8.63	Lu



Pyramidal misfit 1

H																	He
Li -0.10	Be -0.51											B	C	N	O	F	Ne
Na 0.03	Mg											Al -0.18	Si -0.46	P	S	Cl	Ar
K 0.10	Ca 0.31	Sc 0.38	Ti 0.31	V 0.19	Cr 0.05	Mn -0.10	Fe -0.26	Co -0.40	Ni -0.50	Cu -0.48	Zn -0.34	Ga -0.28	Ge -0.37	As -0.59	Se	Br	Kr
Rb 0.07	Sr 0.31	Y 0.49	Zr 0.52	Nb 0.46	Mo 0.32	Tc 0.13	Ru -0.09	Rh -0.32	Pd -0.41	Ag -0.31	Cd -0.18	In -0.11	Sn -0.14	Sb -0.26	Te	I	Xe
Cs 0.00	Ba 0.26	*	Hf 0.50	Ta 0.46	W 0.36	Re 0.18	Os -0.07	Ir -0.33	Pt -0.51	Au -0.46	Hg -0.28	Tl -0.13	Pb -0.08	Bi -0.14	Po	At	Rn
		*lanthanides	La 0.45	Ce 0.78	Pr 0.65	Nd 0.61	Pm 0.37	Sm 0.40	Eu 0.56	Gd 0.34	Tb 0.49	Dy 0.49	Ho 0.48	Er 0.48	Tm 0.29	Yb 0.31	Lu

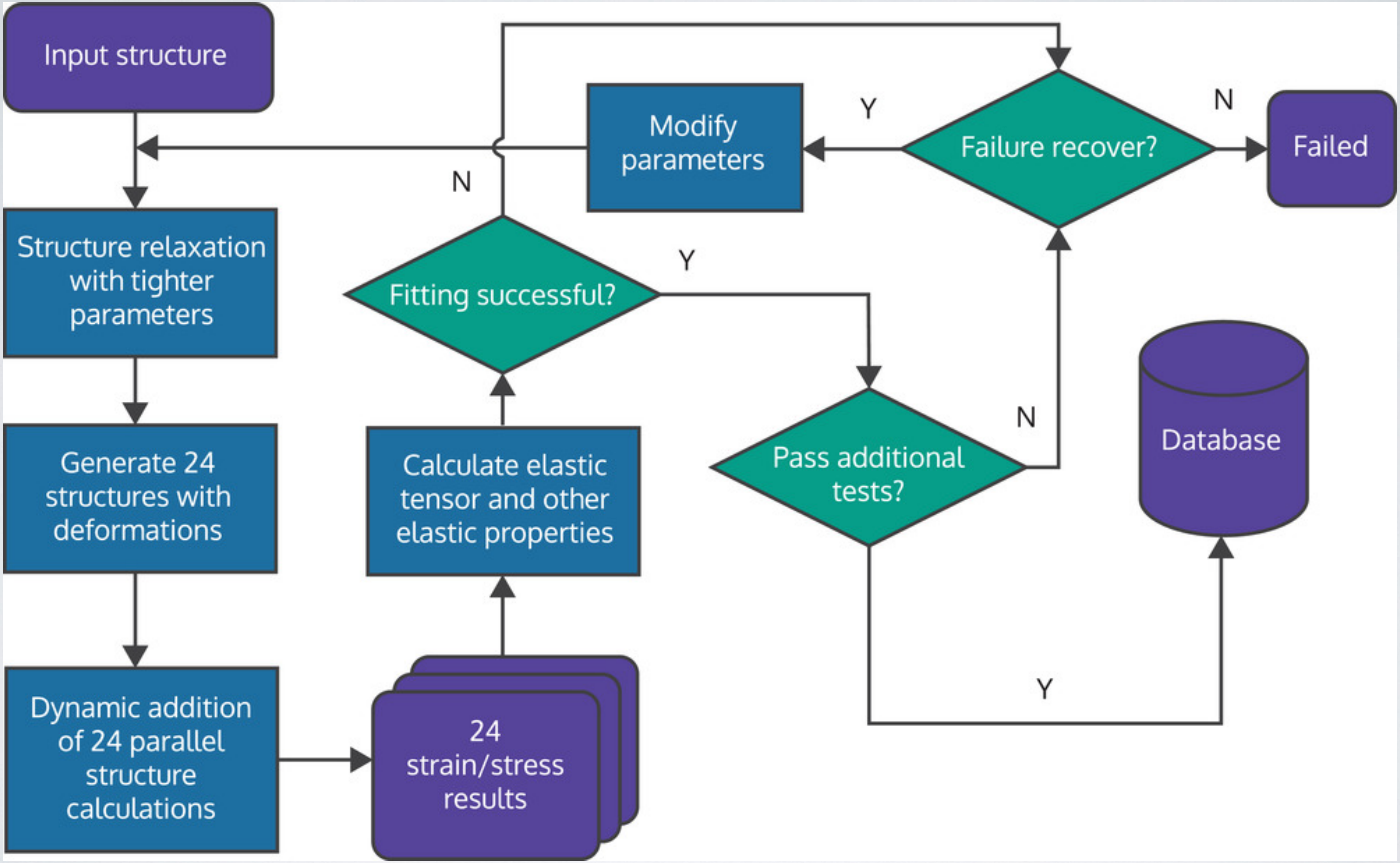


Pyramidal misfit 2

H																	He
Li 0.09	Be 0.35											B	C	N	O	F	Ne
Na -0.19	Mg											Al 0.18	Si 0.28	P	S	Cl	Ar
K -0.65	Ca -0.39	Sc 0.08	Ti 0.42	V 0.63	Cr 0.75	Mn 0.81	Fe 0.81	Co 0.73	Ni 0.54	Cu 0.37	Zn 0.21	Ga 0.17	Ge 0.21	As 0.11	Se	Br	Kr
Rb -0.86	Sr -0.62	Y -0.19	Zr 0.28	Nb 0.64	Mo 0.89	Tc 1.00	Ru 1.00	Rh 0.84	Pd 0.57	Ag 0.31	Cd 0.09	In -0.02	Sn -0.02	Sb -0.07	Te	I	Xe
Cs -1.03	Ba -0.84	*	Hf 0.29	Ta 0.67	W 0.93	Re 1.08	Os 1.11	Ir 0.98	Pt 0.67	Au 0.41	Hg 0.12	Tl -0.10	Pb -0.14	Bi -0.20	Po	At	Rn
		*lanthanides	La -0.45	Ce -0.26	Pr -0.26	Nd -0.30	Pm -0.52	Sm -0.50	Eu -0.41	Gd -0.50	Tb -0.20	Dy -0.18	Ho -0.17	Er -0.16	Tm -0.47	Yb -0.40	Lu

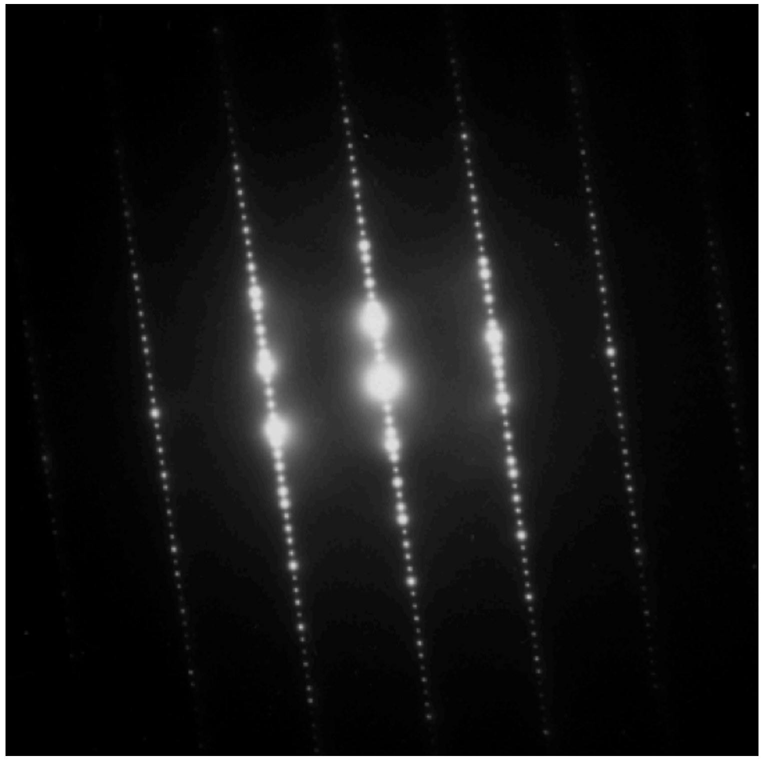
magnesium.matse.illinois.edu

Example of high-throughput



Advanced Science, Volume: 6, Issue: 21, First published: 01 September 2019, DOI: (10.1002/advs.201900808)

Short Review of Quantum Mechanics



Wave-particle duality

- Planck's uncertainty relationship

$$\lambda \cdot p = h$$

Schrödinger equation

- Time dependent

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

Exercise for Schrödinger equation

1) List as many mathematical characteristics of the Schrödinger equation as you can think of.
   - Think: Quadratic?, Homogeneous? etc.

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

Exercise for Schrödinger equation

2) Solve the Schrödinger equation by separation of variables

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

$$\Psi(\mathbf{r},t)=\varphi(\mathbf{r})\cdot f(t)$$

Solutions of the Schrödinger Equation (1)

Free particle

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

$$\Psi_k(\mathbf{r}, t) \quad = \quad \exp\left(i\,\mathbf{k}\cdot\mathbf{r} - \omega t\right)$$

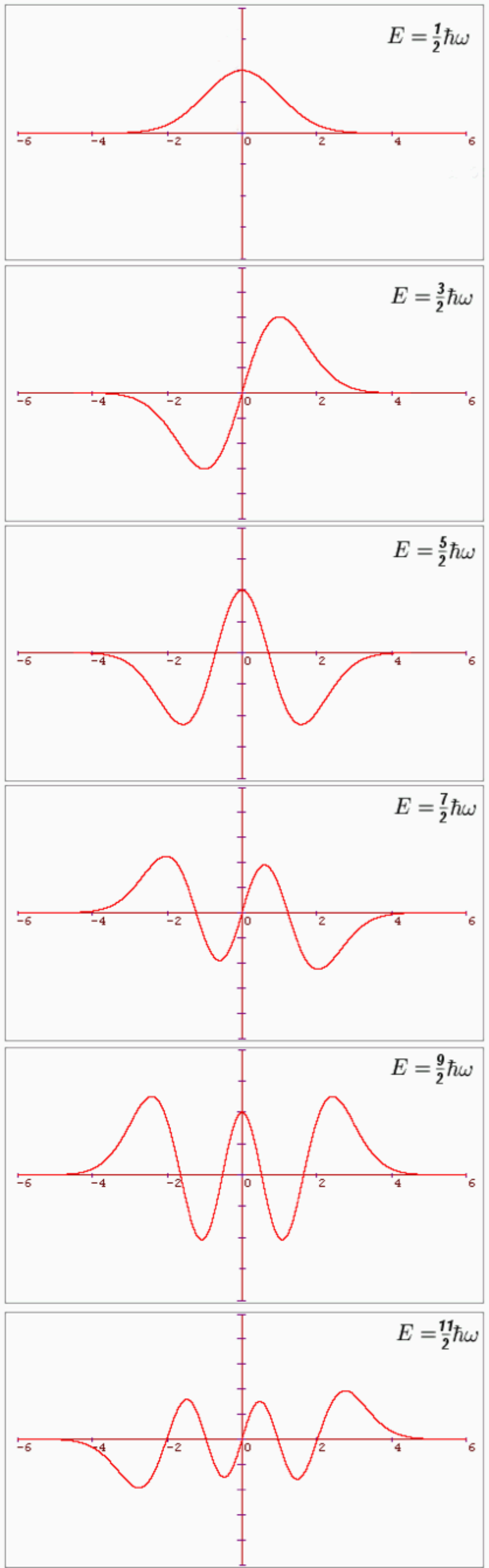
$$E_k \quad = \quad \frac{\hbar^2 k^2}{2m} = \omega\hbar$$

Harmonic oscillator

$$V(x) \quad = \quad \frac{1}{2} k\, x^2$$

$$\varphi_n(x) \quad = \quad c_n \cdot \exp\left(-\frac{m\omega^2 x^2}{2\hbar}\right) \cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}}\,x\right)$$

$$E_n \quad = \quad \left(n + \frac{1}{2}\right)\hbar\,\omega$$

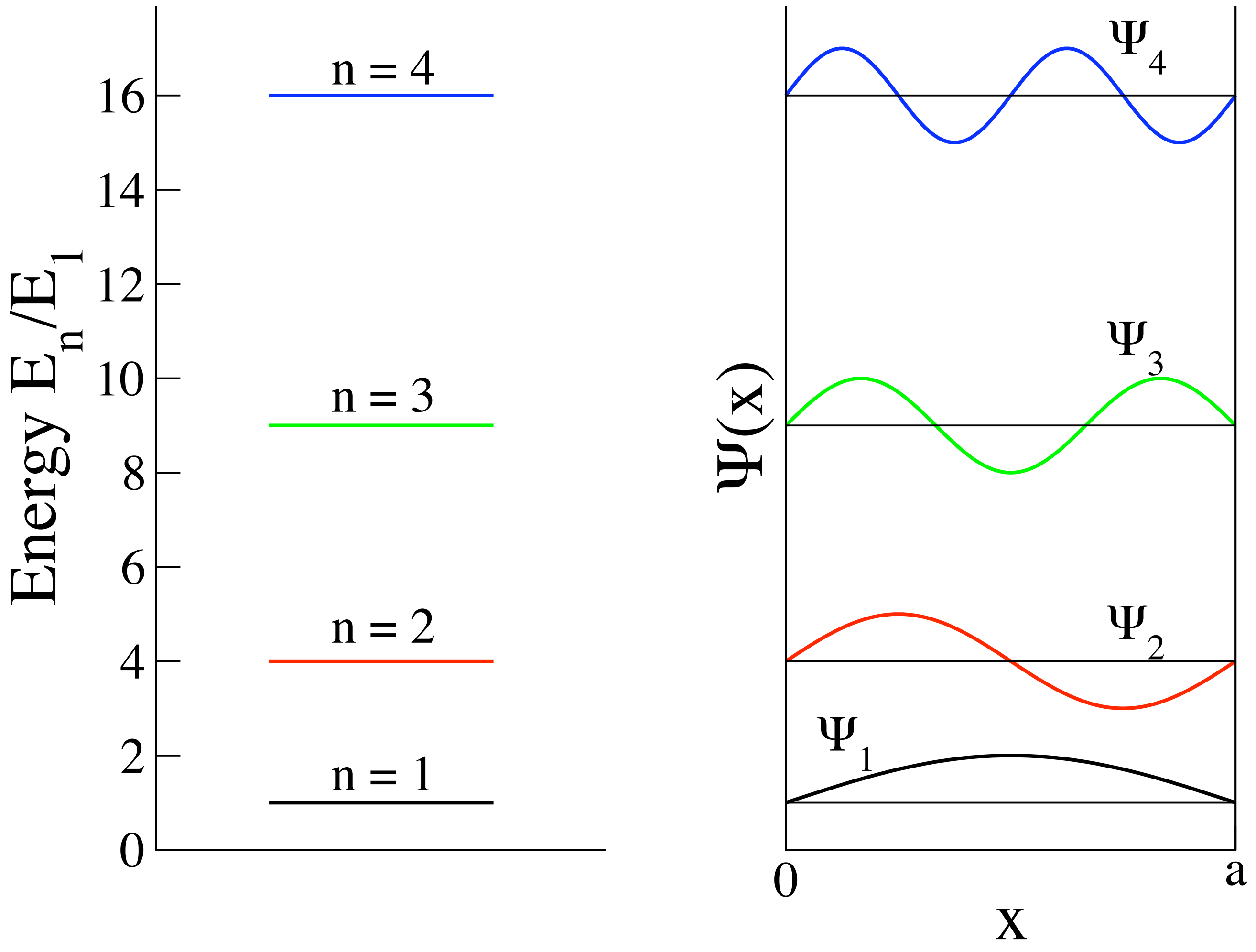


Solutions of the Schrödinger Equation (2)

Infinite square well

- Plane waves that vanish at the boundary

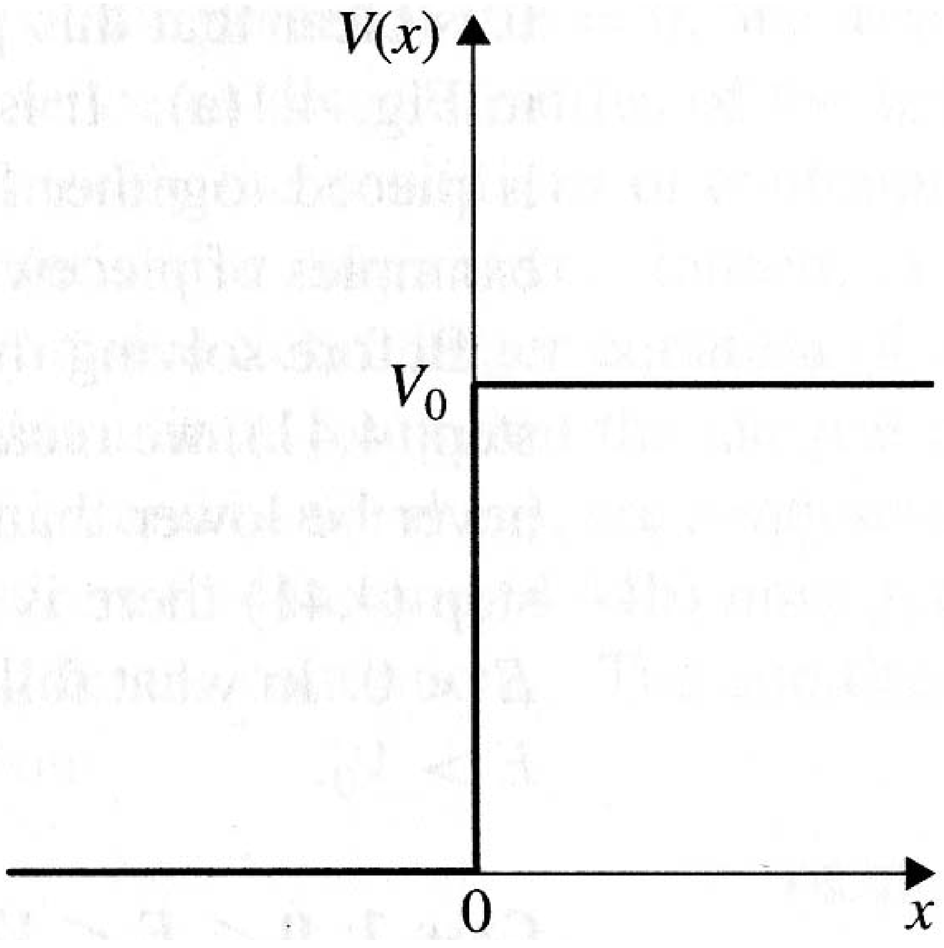
$$
\begin{aligned}
V(x) &= \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{otherwise} \end{cases} \\
\varphi_n(x) &= \sqrt{\frac{2}{a}}\,\sin\left(\frac{\pi\, n\, x}{a}\right) \\
E_n &= \frac{\hbar^2 \pi^2 n^2}{2ma^2}
\end{aligned}
$$

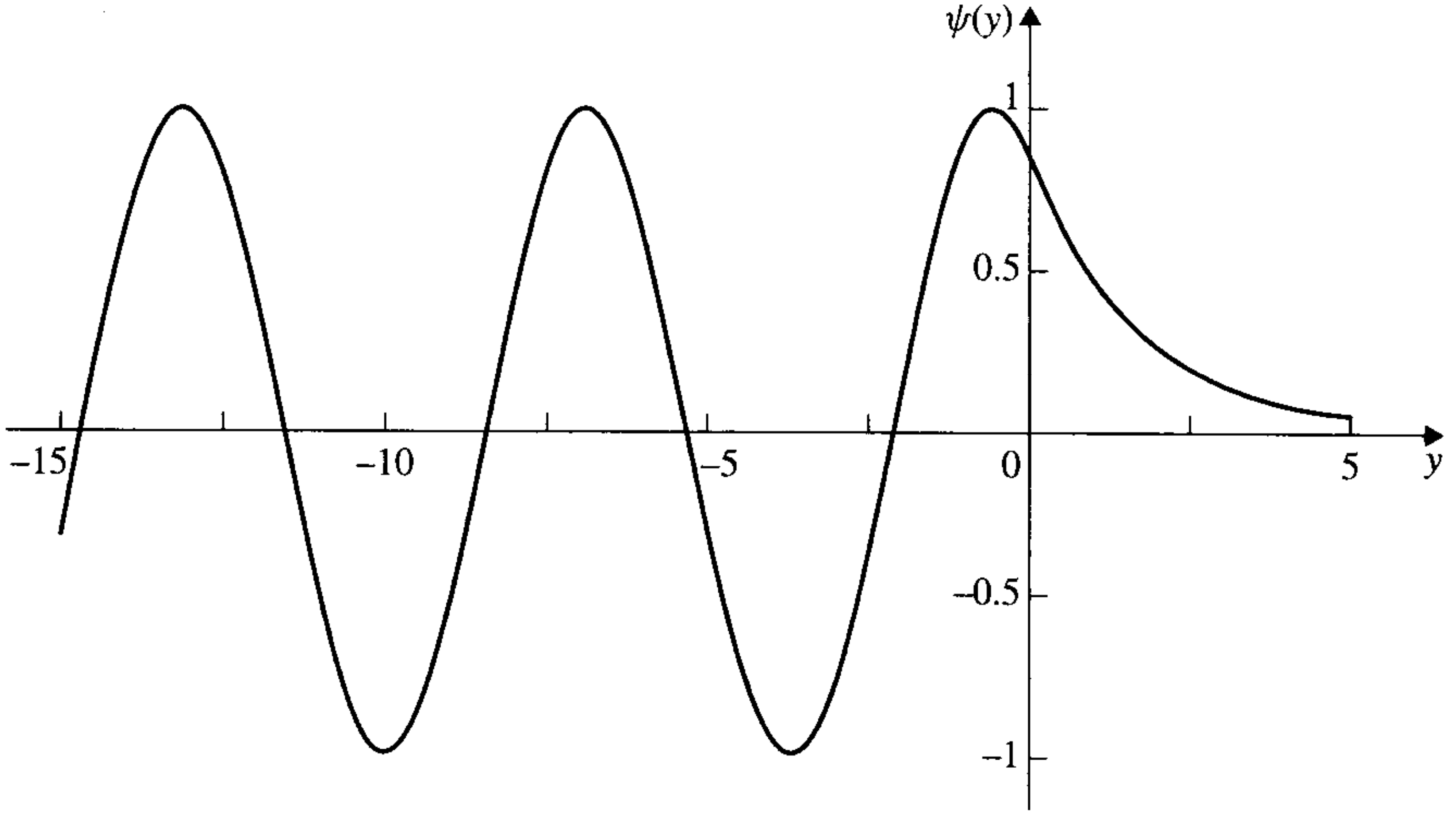


Solutions of the Schrödinger Equation (3)

Metal surface

- Potential step ⇒ Plane wave inside metal, exponential decay outside





Solutions for the Coulomb Potential

Spherical Symmetry

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

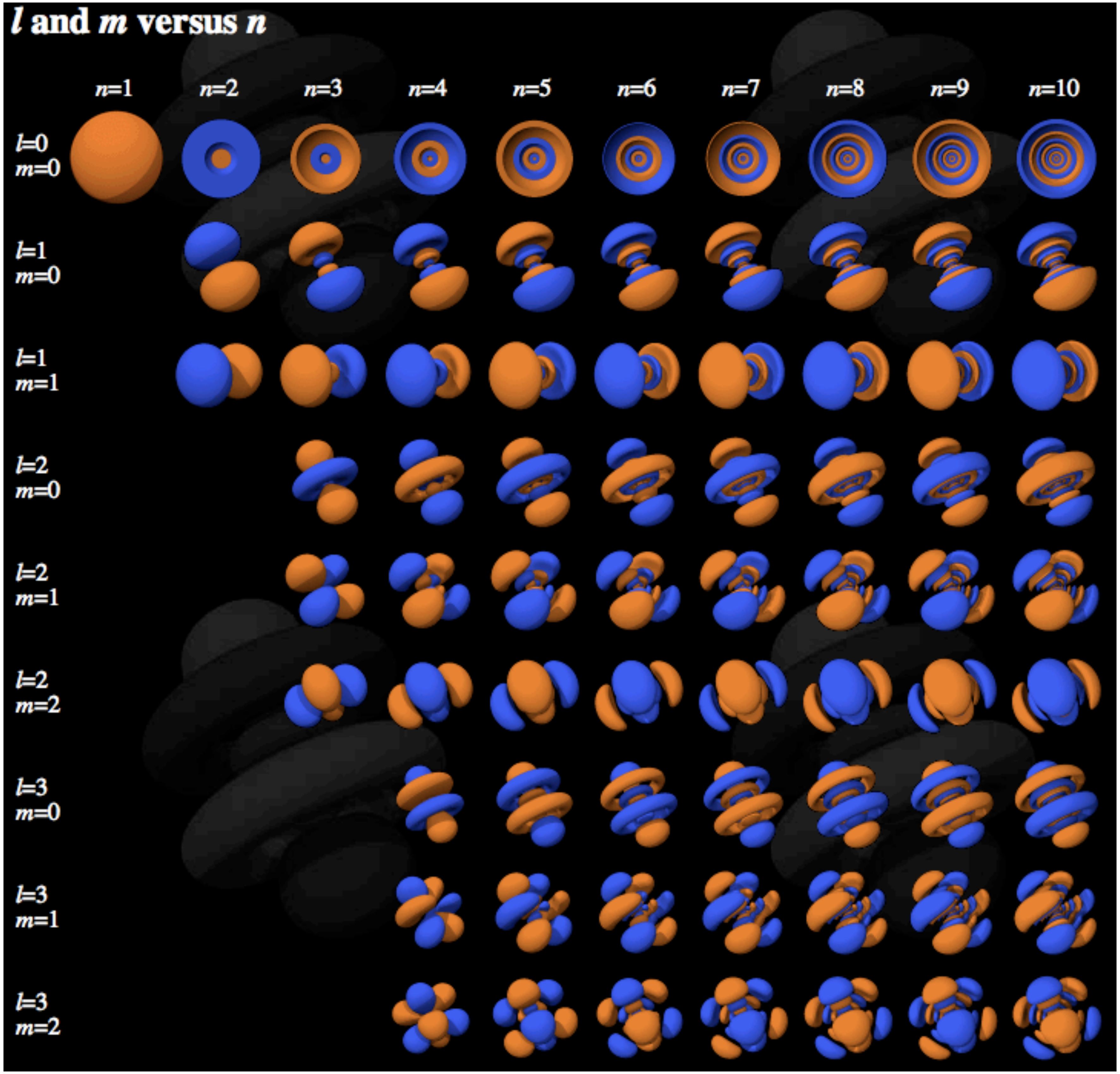
Separation of variables

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

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

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

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

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

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

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

Douglas Rayner Hartree and Porter 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

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

- Swapping rows in a determinant changes the sign

The Hartree-Fock Method

Hartree-Fock equation for orbitals φ_λ

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

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

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

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

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

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

- Instead it is of the form

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

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

  Example: N_2 molecule: $E_{corr} = 14.9$ 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

$$\Psi^0_{\text{HF}} = \left|\varphi_1\,\varphi_2\;\cdots\varphi_K\right|$$

- 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

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

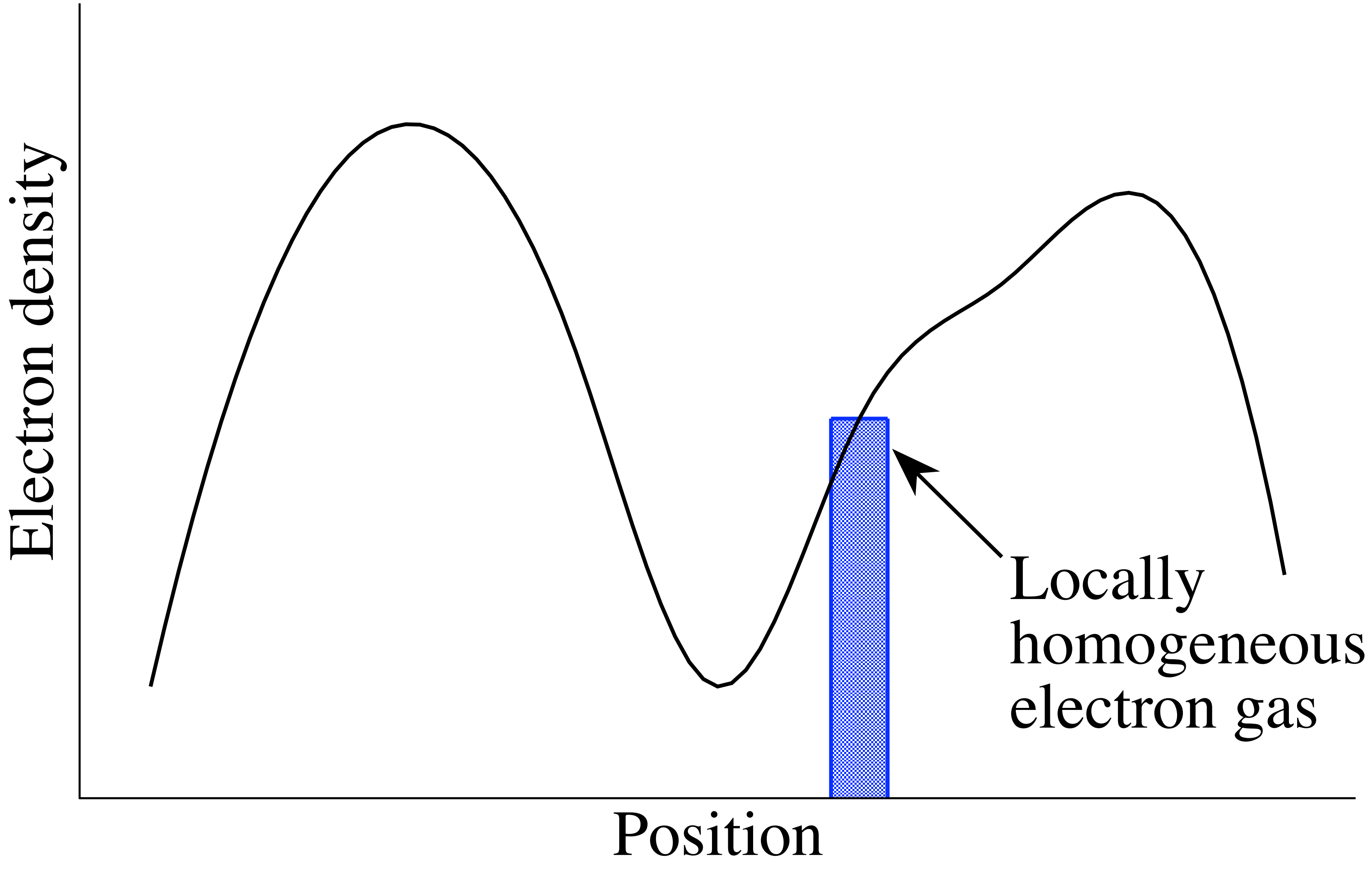
$$\Psi_{\text{CI}} = c_0\,\Psi_0 + c_1\,\Psi_1 + c_2\,\Psi_2 + \ldots$$

Thomas-Fermi Approach

Motivation

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

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



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

⇒ Hence the energy and everything else
is a functional of 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

⇒ Universal functional $F[\varrho]$

Functional form unknown

2nd Hohenberg-Kohn Theorem

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

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

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

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

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

$$E_H = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3r\,d^3r'$$

Euler-Lagrange Equations

Minimize energy with respect to variations of the density

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

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

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

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

Summary

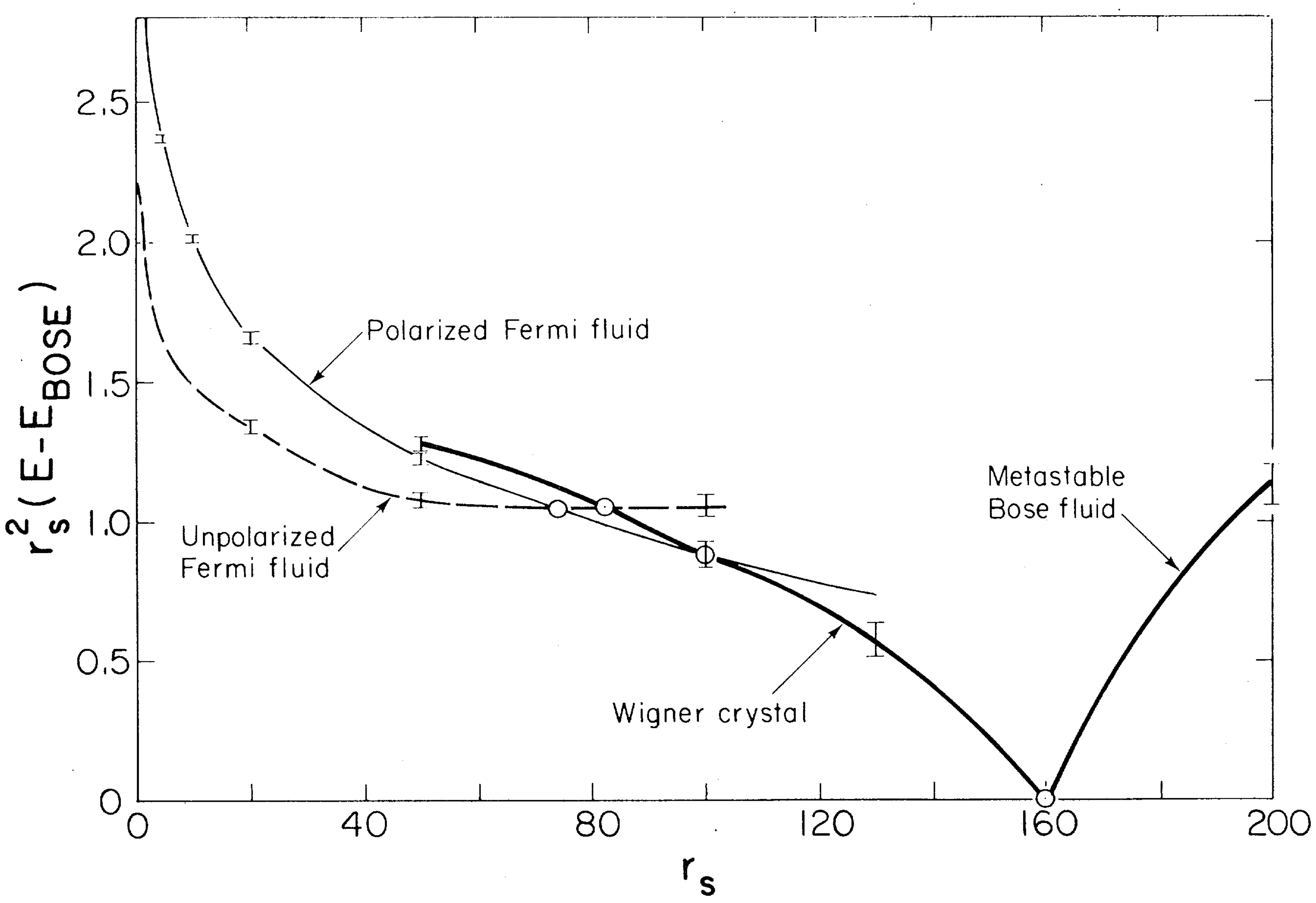
Hohenberg-Kohn theorem

Hohenberg-Kohn theorem applied to non-interacting electrons

$$\begin{tikzcd}
V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] & \varrho_0(\mathbf{r}) \arrow[l, Rightarrow] \arrow[r, Leftrightarrow, "\textbf{Kohn-Sham}"] & \varrho_0(\mathbf{r}) \arrow[r, Rightarrow] & V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] \\
\Psi_i(\mathbf{r}_1, \dots \mathbf{r}_N) \arrow[r, Rightarrow] & \Psi_0(\mathbf{r}_1, \dots \mathbf{r}_N) \arrow[u, Rightarrow] & \varphi_{i=1,N}(\mathbf{r}) \arrow[u, Rightarrow] & \varphi_i(\mathbf{r}) \arrow[l, Rightarrow]
\end{tikzcd}$$

$$\begin{aligned}
E[\{\varphi_i(\mathbf{r})\}] &= \sum_{i=1}^{N} -\frac{1}{2}\int \varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})d^3r + E_{\mathrm{H}}[\rho(\mathbf{r})] + E_{\mathrm{xc}}[\rho(\mathbf{r})] + \int V_{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r \\
&= \sum_{i=1}^{N} \epsilon_i - V_{\mathrm{H}}[\rho(\mathbf{r})] + E_{\mathrm{xc}}[\rho(\mathbf{r})] - \int \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}\rho(\mathbf{r})d^3r
\end{aligned}$$

The Local Density Approximation



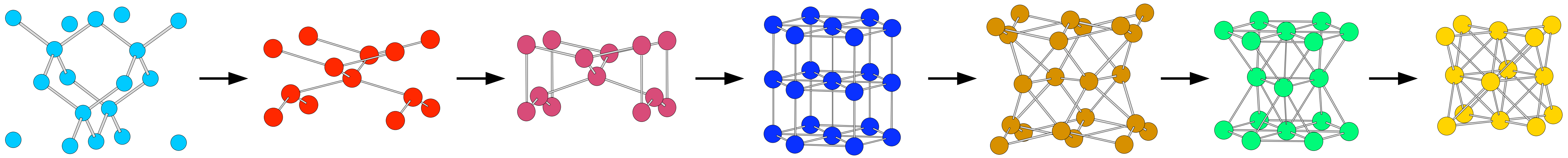
D. M. Ceperley and B. J. Alder, “Ground State of the Electron Gas by a Stochastic Method” Phys. Rev. Lett. 45, 566 (1980). http://link.aps.org/abstract/PRL/v45/p566

The Phases of Silicon

Under pressure Si displays 11 crystal phases

- LDA correctly predicts the energetic order of all these phases

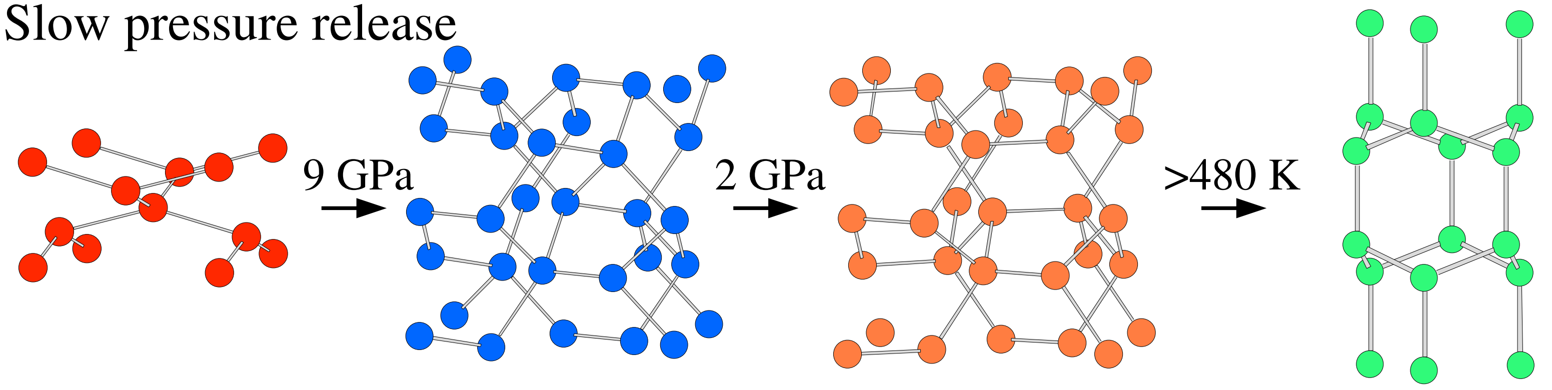
Compression



Si(I) diamond
Z=4
→ 11 GPa →
Si(II) β−tin
Z=6
→ 13 GPa →
Si(XI) Imma
Z=6
→ 16 GPa →
Si(V) hexagonal
Z=8
→ 36 GPa →
Si(VI) orthorhombic
Z=10
→ 42 GPa →
Si(VII) hcp
Z=12
→ 79 GPa →
Si(X) fcc
Z=12

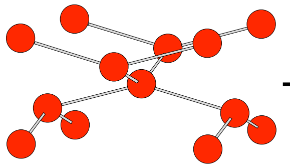
Decompression

Slow pressure release



Si(II) β−tin
Z=6
→ 9 GPa →
Si(XII) R8
Z=4
→ 2 GPa →
Si(III) BC−8
Z=4
→ >480 K →
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

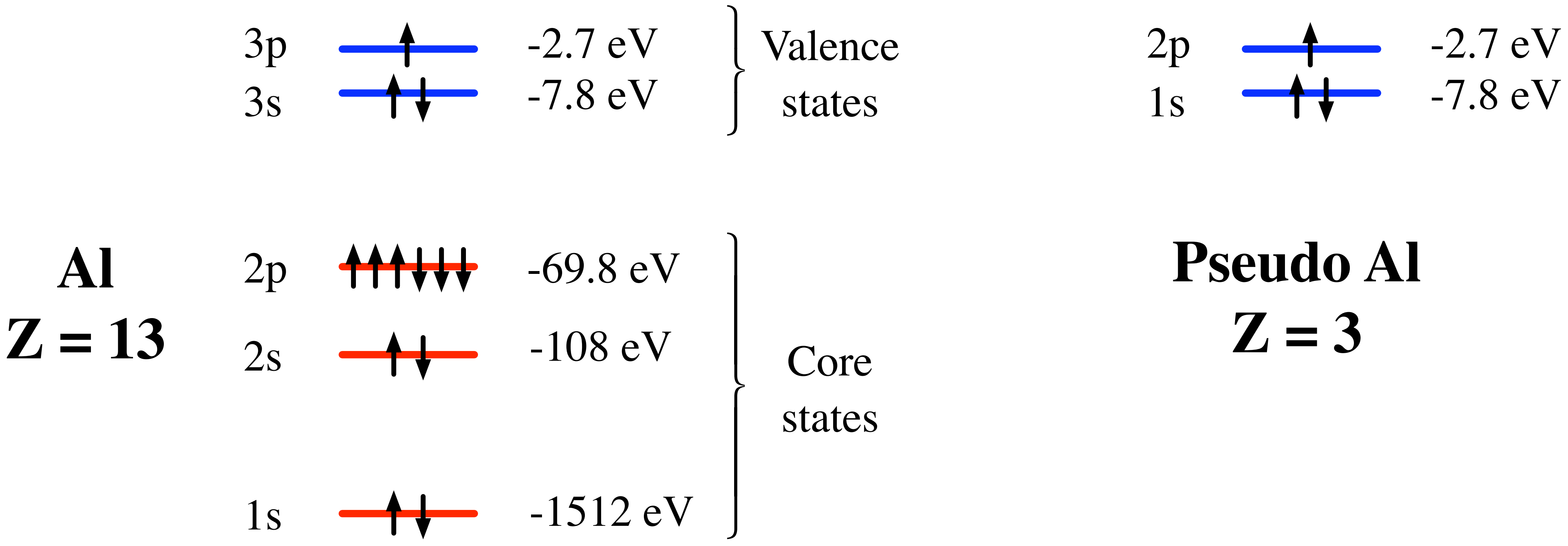
Density Functional Theory in Practice

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



3p -2.7 eV

3s -7.8 eV

Valence states

2p -69.8 eV

2s -108 eV

1s -1512 eV

Core states

Al
Z = 13

2p -2.7 eV

1s -7.8 eV

Pseudo Al
Z = 3

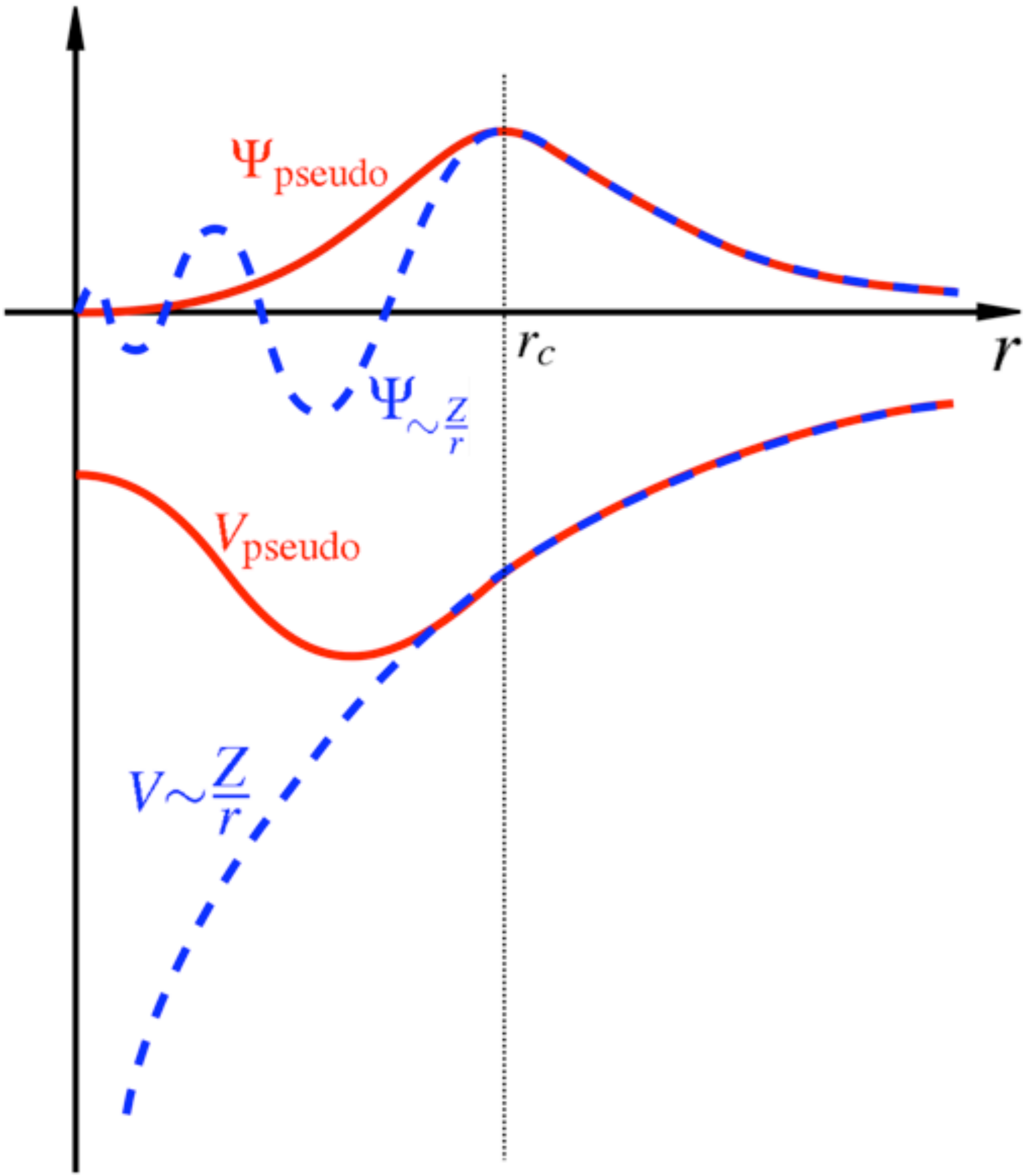
$$\boxed{\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}\right]\varphi_i = \epsilon_i\,\varphi_i}$$

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

Pseudopotentials

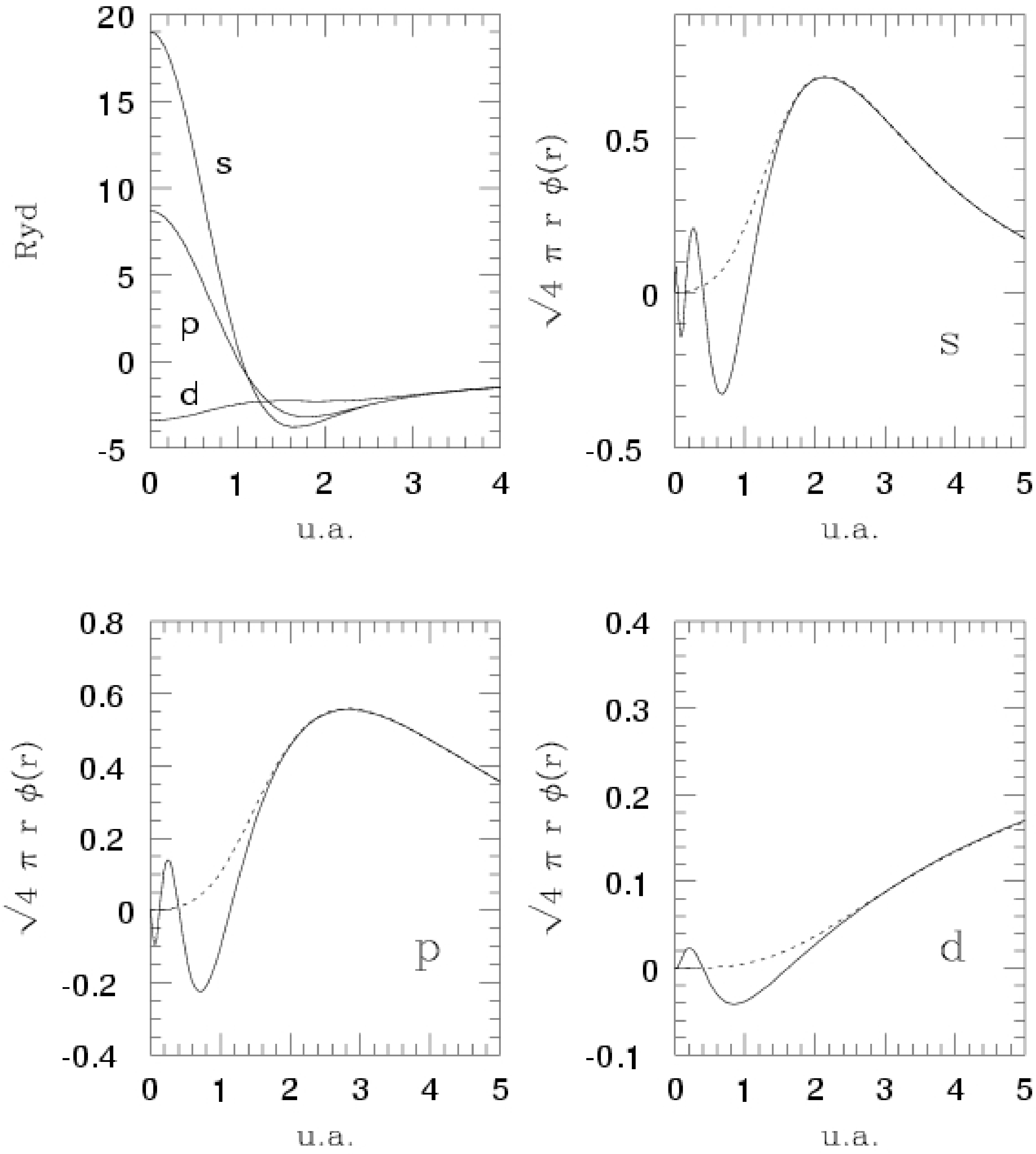
The pseudopotential and the wave function

- 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



Non-Local Pseudopotentials

- Electron states with different angular momenta scatter differently from the core
- States that have shell below them with same angular momentum feel stronger repulsion due to orthogonality constraint



Basis Set Choices and Convergence

Basis set choices

- Real potential and wave function are shown in blue
- For molecules: often atomic orbitals, or localized functions like Gaussians
- For solids, periodic functions such as sines and cosines (plane waves)
- Use of Bloch theorem for periodic solids

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

⇒ Remember the importance of *k*-point sampling

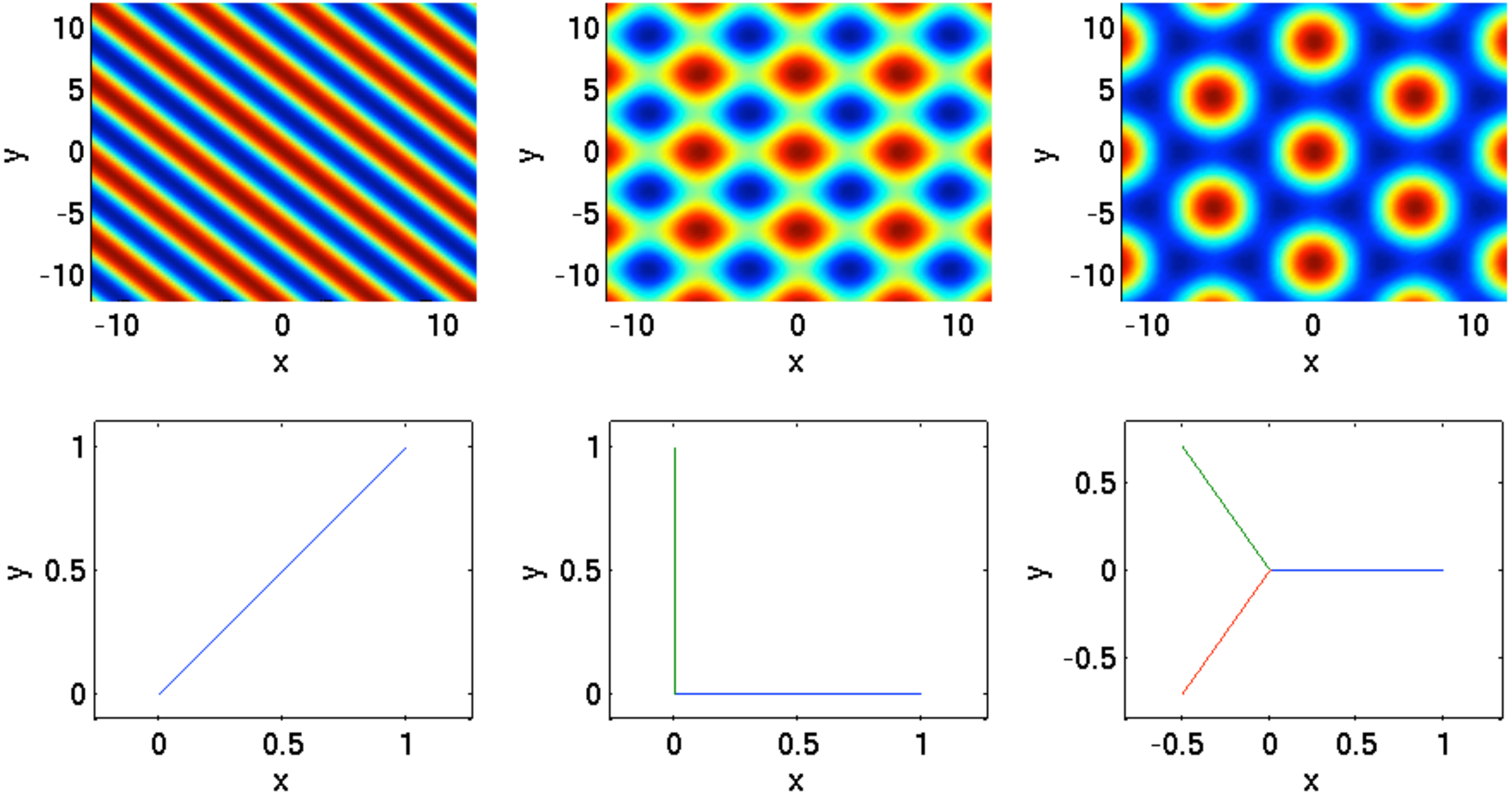
Convergence

- Increase size of basis set to approach completeness

Plane Wave Basis Set

- Superposition of plane waves to represent orbitals

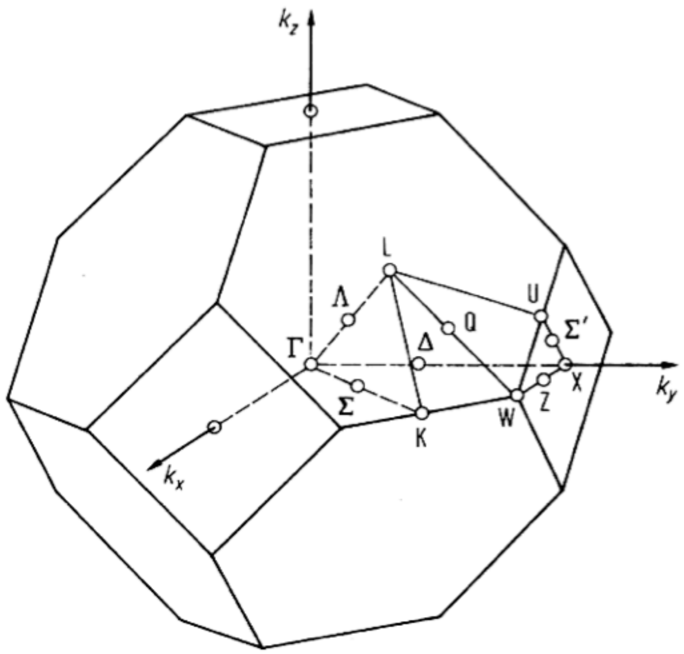
$$u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}| \leq G_{\max}} c_{nk}(\mathbf{G}) \, \exp(i\, \mathbf{G} \cdot \mathbf{r})$$

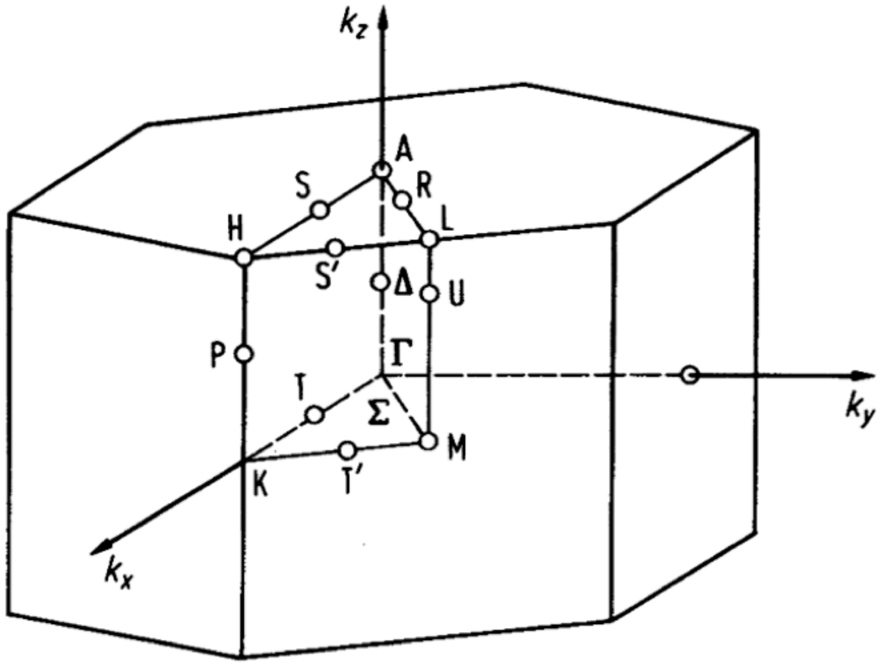


Band structure of crystals (1)

Bloch states and Brilloin zones

- Crystal structures defined by Bravais lattice $\{\mathbf{a}_i\}$ and basis
- Periodic density ⇒ *Bloch theorem* $$\psi(\mathbf{r}+\mathbf{R}) = \psi(\mathbf{r}) \cdot \exp\left(i\mathbf{k}\cdot\mathbf{r}\right)$$
- Fourier transformation $$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \cdot \exp\left(i\mathbf{G}\cdot\mathbf{r}\right)$$
- *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



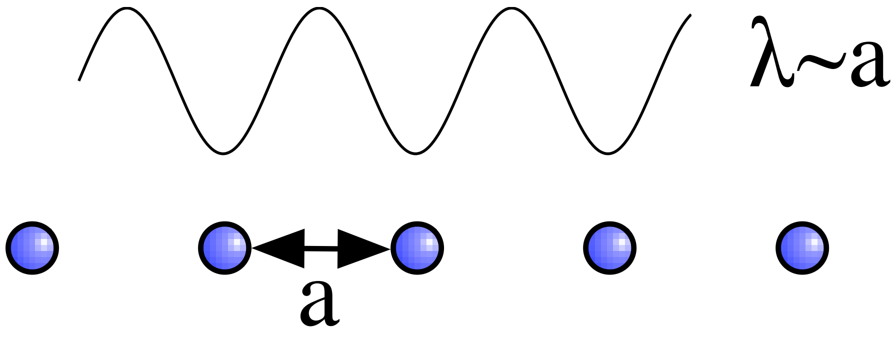


Band structure of crystals (2)

Diffraction picture for origin of the energy gap

- Start with a 1D crystal and consider diffraction of electron wave

$$\begin{aligned} n\lambda &= 2d\cdot\sin\theta \quad \text{with} \quad d=a \;\; \text{and} \;\; \sin\theta = 1 \\ n\lambda &= 2a \\ k &= \frac{2\pi}{\lambda} \\ k &= \frac{n\pi}{a} \end{aligned}$$



- Take lowest order (n = 1) and consider incident and reflected electron wave

$$\psi_i = e^{ikx} = e^{i\frac{\pi}{a}\cdot x} \quad \text{and} \quad \psi_r = e^{-i\frac{\pi}{a}\cdot x}$$

- Total wave function for electrons with diffracted wave length

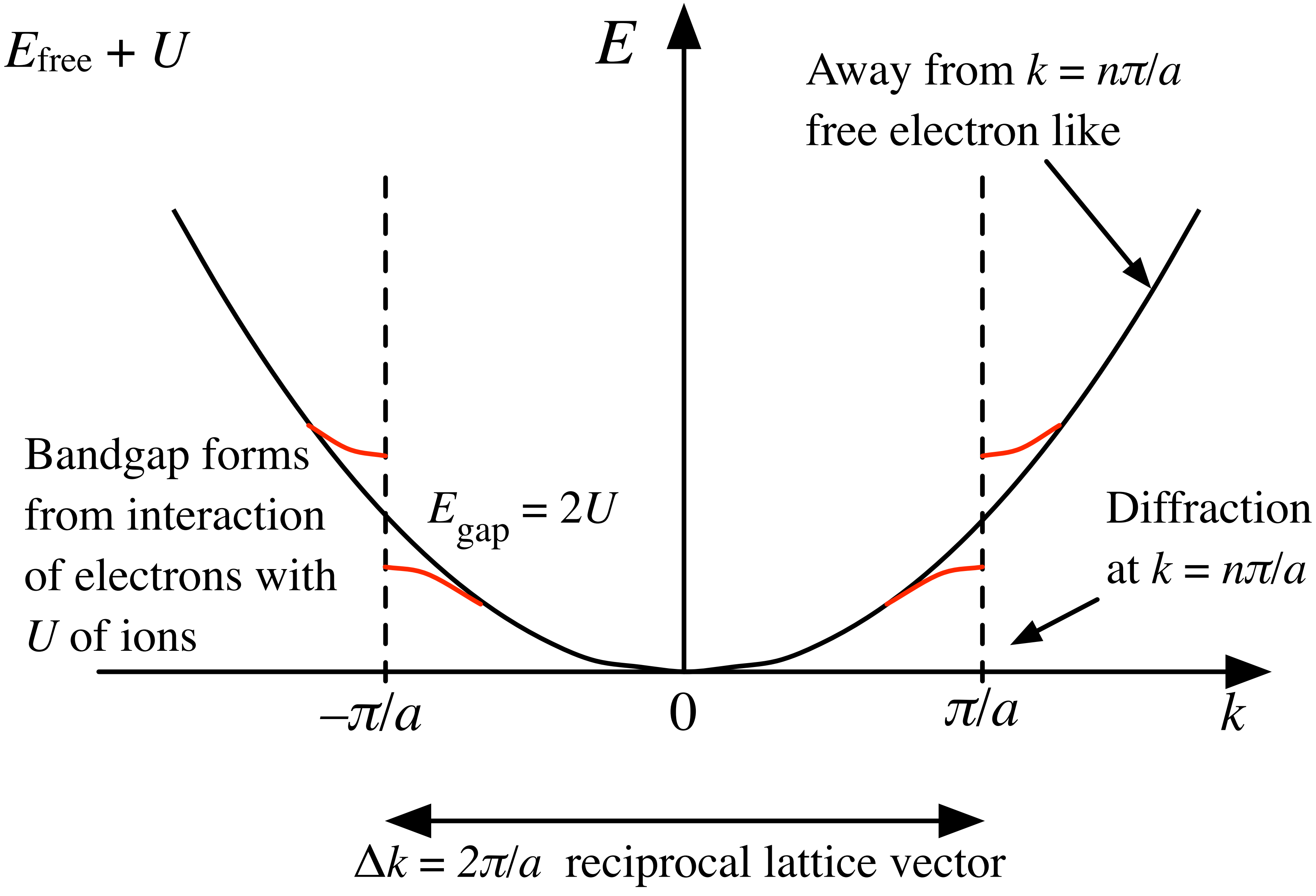
$$\psi = \psi_i \pm \psi_r \quad \Rightarrow \quad \psi_+ = \psi_i + \psi_r = 2\cos\frac{\pi x}{a} \quad \text{and} \quad \psi_- = \psi_i - \psi_r = 2\sin\frac{\pi x}{a}$$

- Only two solutions for $k = \pi/a$: Electron density on atoms or between
- No traveling wave solution

Band structure of crystals (3)

Diffraction picture for origin of the energy gap

- If ion potential is a weak perturbation U, the electrons near diffraction condition have two possible solutions
  - Electron density between ions: $E = E_{\text{free}} - U$
  - Electron density on ions: $E = E_{\text{free}} + U$
  - Near diffraction condition energy is parabolic in k, $E \propto k^2$
  - Electron near diffraction conditions are not free
  - Their properties can still be described as "free" with an *effective mass* m^*



Away from $k = n\pi/a$ free electron like

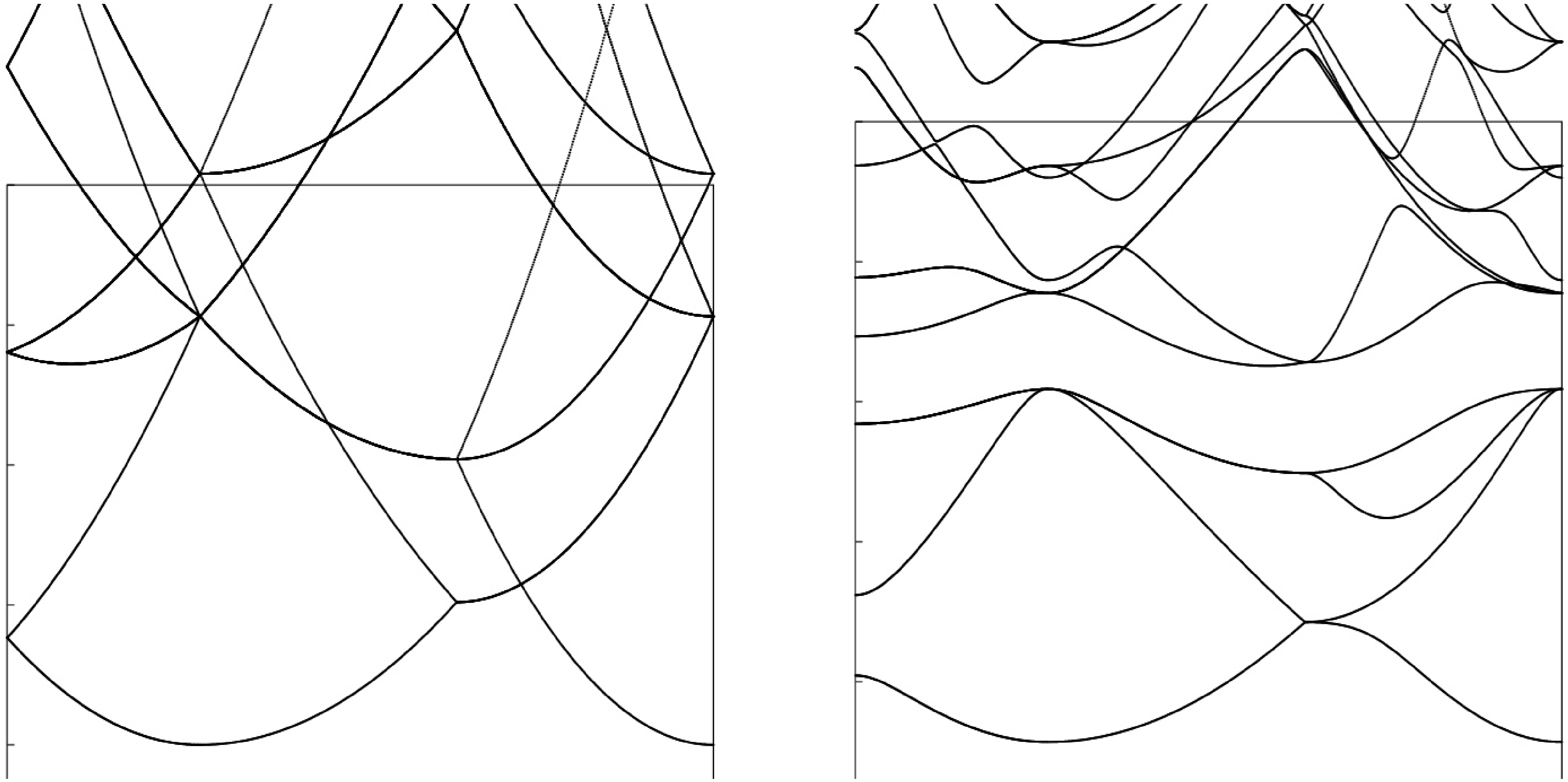
Bandgap forms from interaction of electrons with U of ions

Diffraction at $k = n\pi/a$

$\Delta k = 2\pi/a$ reciprocal lattice vector

Band Structure: Free Electron Gas and Si

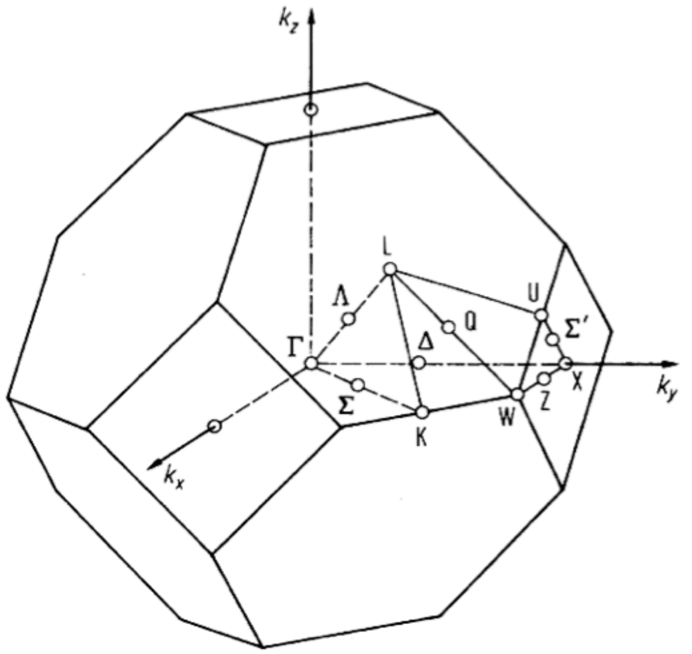
Free electron gas　　　　Silicon

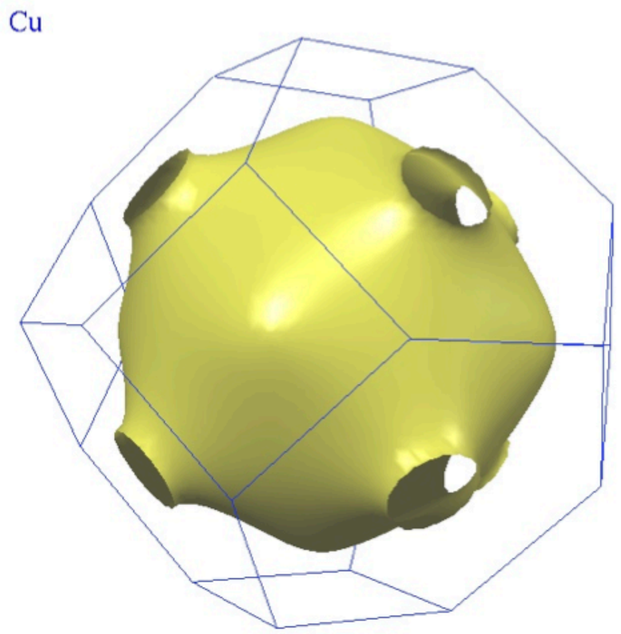


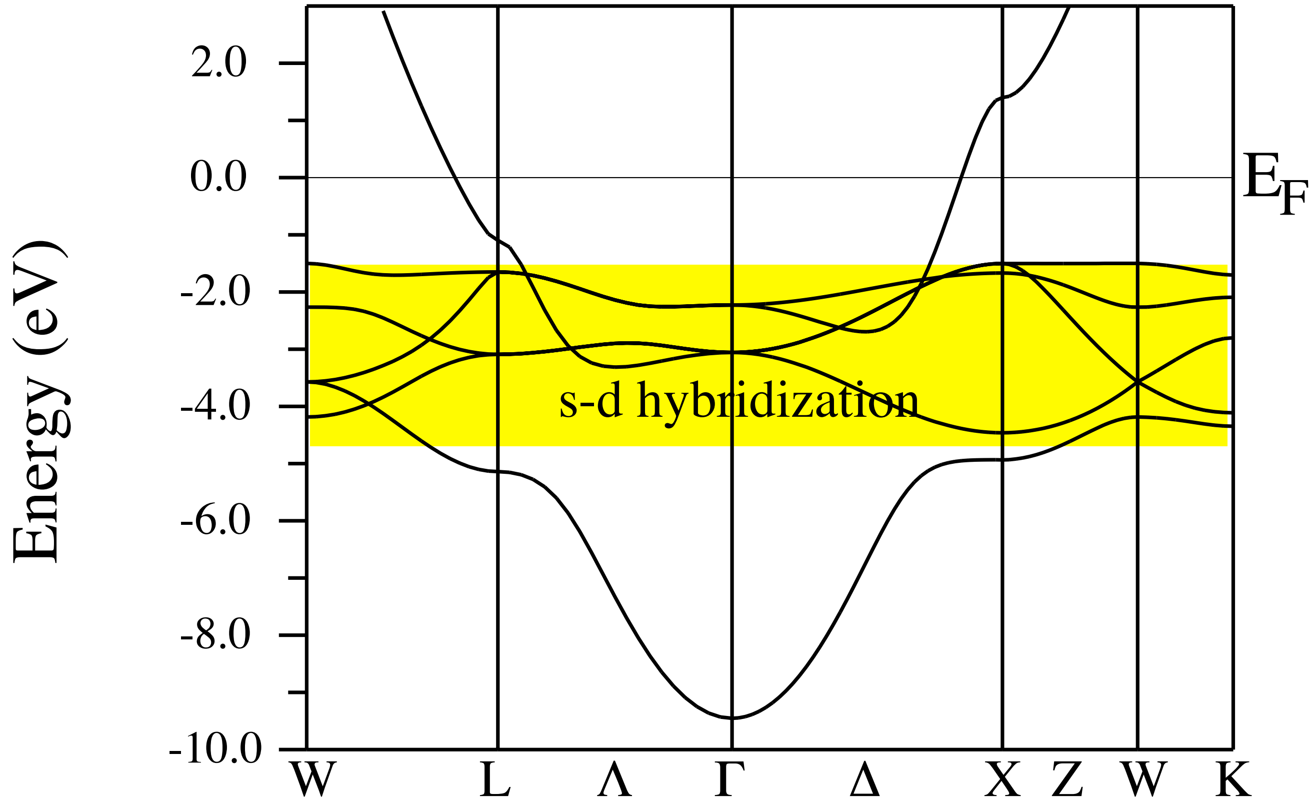
$$E = \frac{\hbar^2 k^2}{2m} \quad \text{and} \quad \varphi(\mathbf{r}) = \exp(i\,\mathbf{k}\cdot\mathbf{r})$$

Example of metallic band structure: Cu

- Copper: Band structure calculated with Wien2k

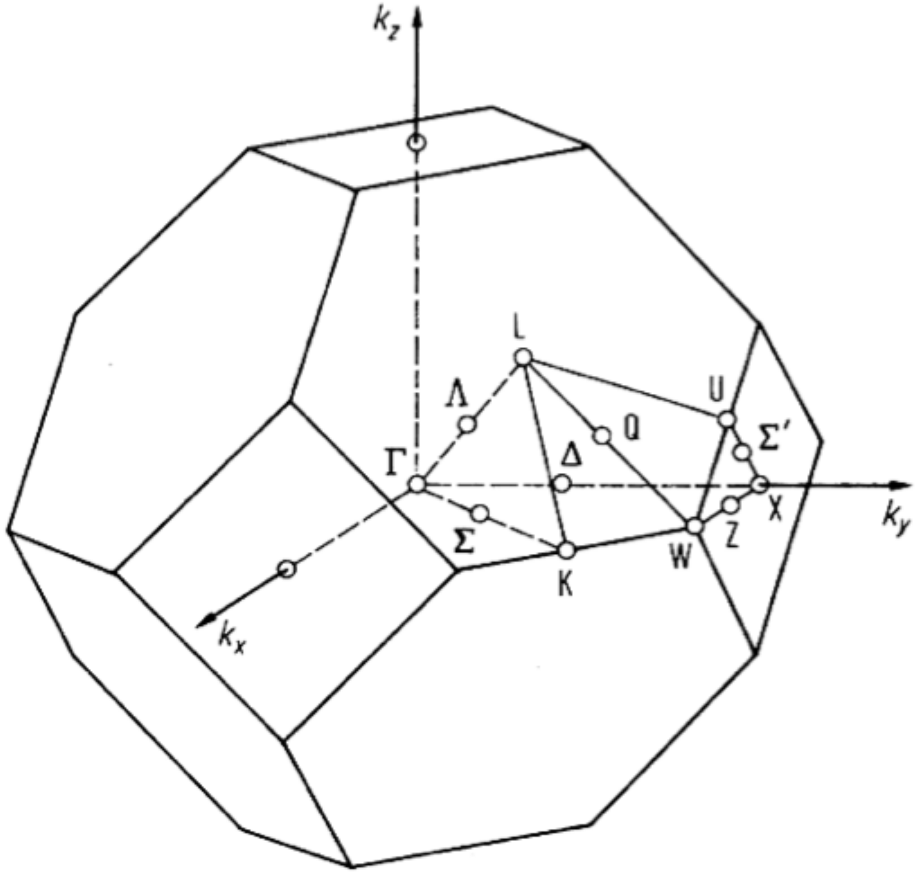




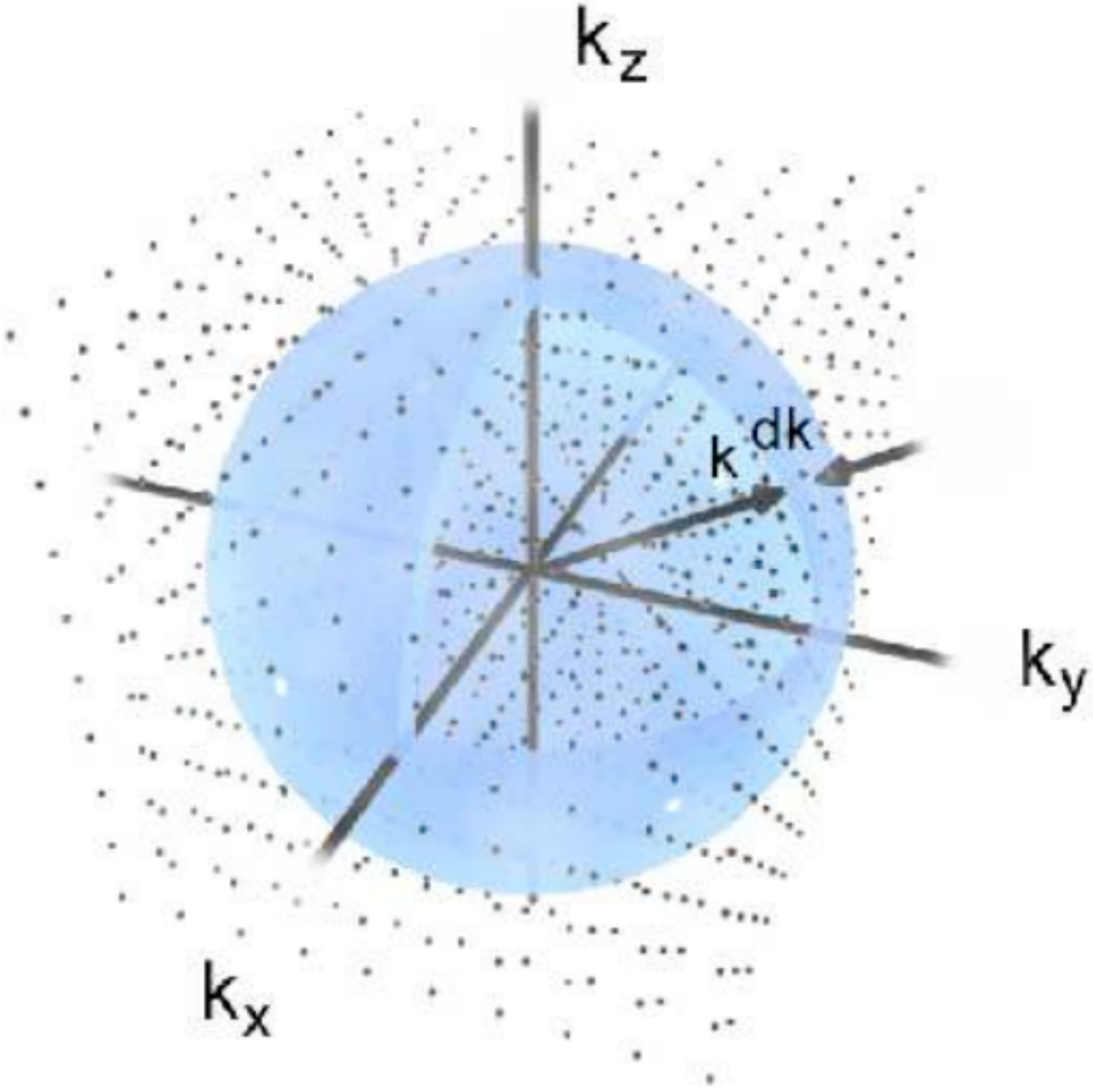


- *Nearly free electron s*-band dominates at low and high energies
- Electron near diffraction conditions have different effective mass
- *Hybridization* between *nearly-free s* and *atomic-like d* orbitals at intermediate energies
- Necking of Fermi surface in [111] directions ⇒ *Hume-Rothery stabilization*

Integrating the Brillouin zone



asca



- Large real-space Wigner-Seitz cell => small Brillouin Zone (few k-points rqd)
- Small real-space Wigner-Seitz cell => large Brillouin Zone (many k-points rqd)

http://voh.chem.ucla.edu/vohtar/winter05/classes/115B/pdf/DFT_notes_Cocula_Carter.pdf

k-points

- The wavefunction (and energy) of each electron depends on both its quantum number *n* and its position *k* within the Brillouin Zone

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

- 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**)

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

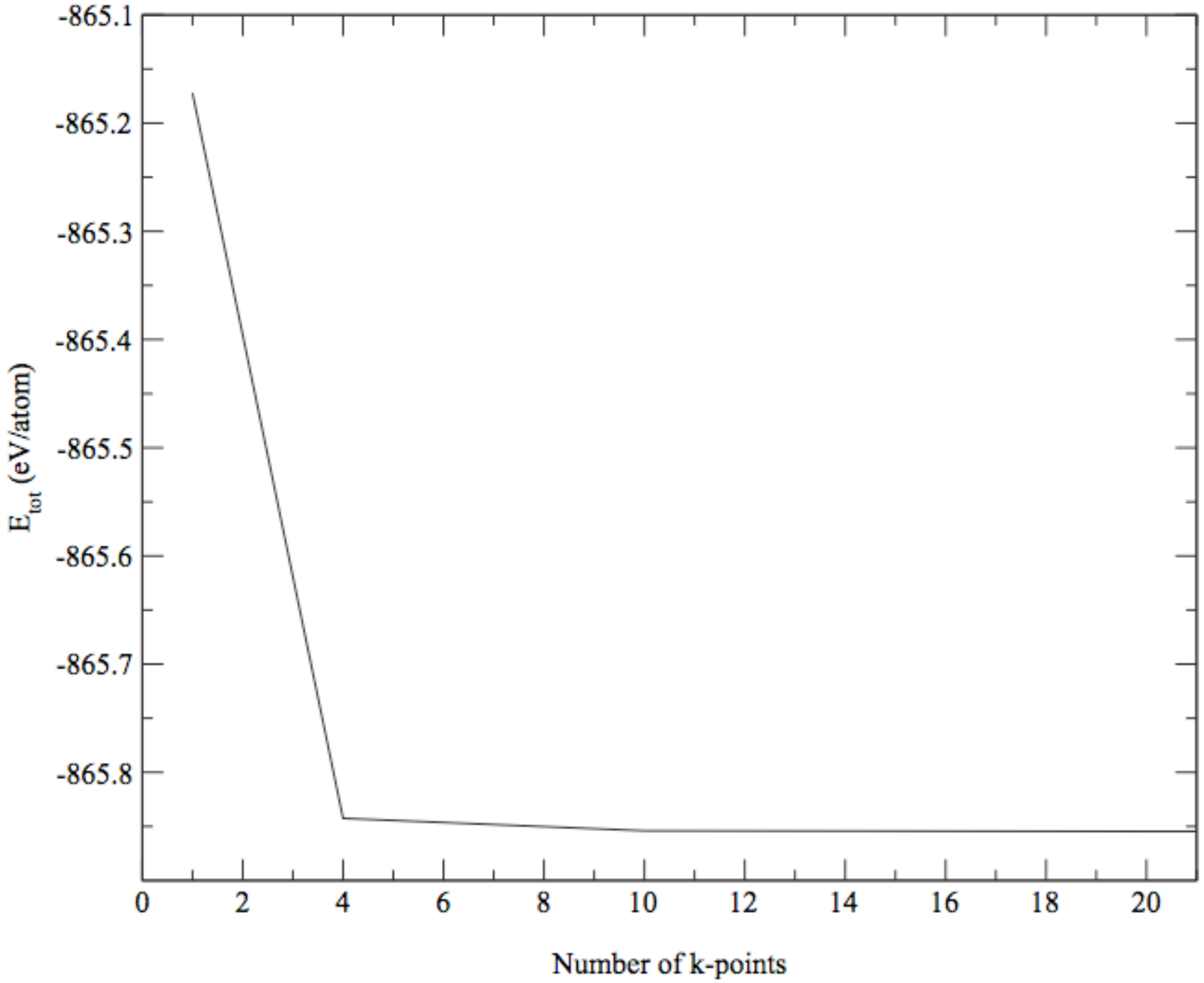
k-points + smearing

- The integration occurs over **occupied** electron states: energy ≤ Fermi energy
- At $T = 0$, equivalent to adding a step (Heaviside H) function:

$$\rho(\mathbf{r}) = \sum_n \frac{V_{\text{cell}}}{(2\pi)^3} \int_{1\text{BZ}} H(E_{\text{F}} - \varepsilon_{n,\mathbf{k}}) |\psi_{n,\mathbf{k}}|^2 d^3\mathbf{k}$$

- For a material with a band gap (no Fermi surface), no problem.
- For a *metal*, **huge** problem: this Heaviside function is **not smooth**
- **Solution:** replace Heaviside function with a smooth function. **Smearing.**
  - Fermi-Dirac occupancy at a *finite, artificial temperature*
  - Integral of a Gaussian centered at Fermi energy, with a finite width
  - Polynomial expansion (Methfessel-Paxton)
- **N.B.:** there is *another solution* called tetrahedron method for integrating *without smoothing*; however, it can have some issues that make it less than desirable for our purposes.

k-points



http://voh.chem.ucla.edu/vohtar/winter05/classes/115B/pdf/DFT_notes_Cocula_Carter.pdf

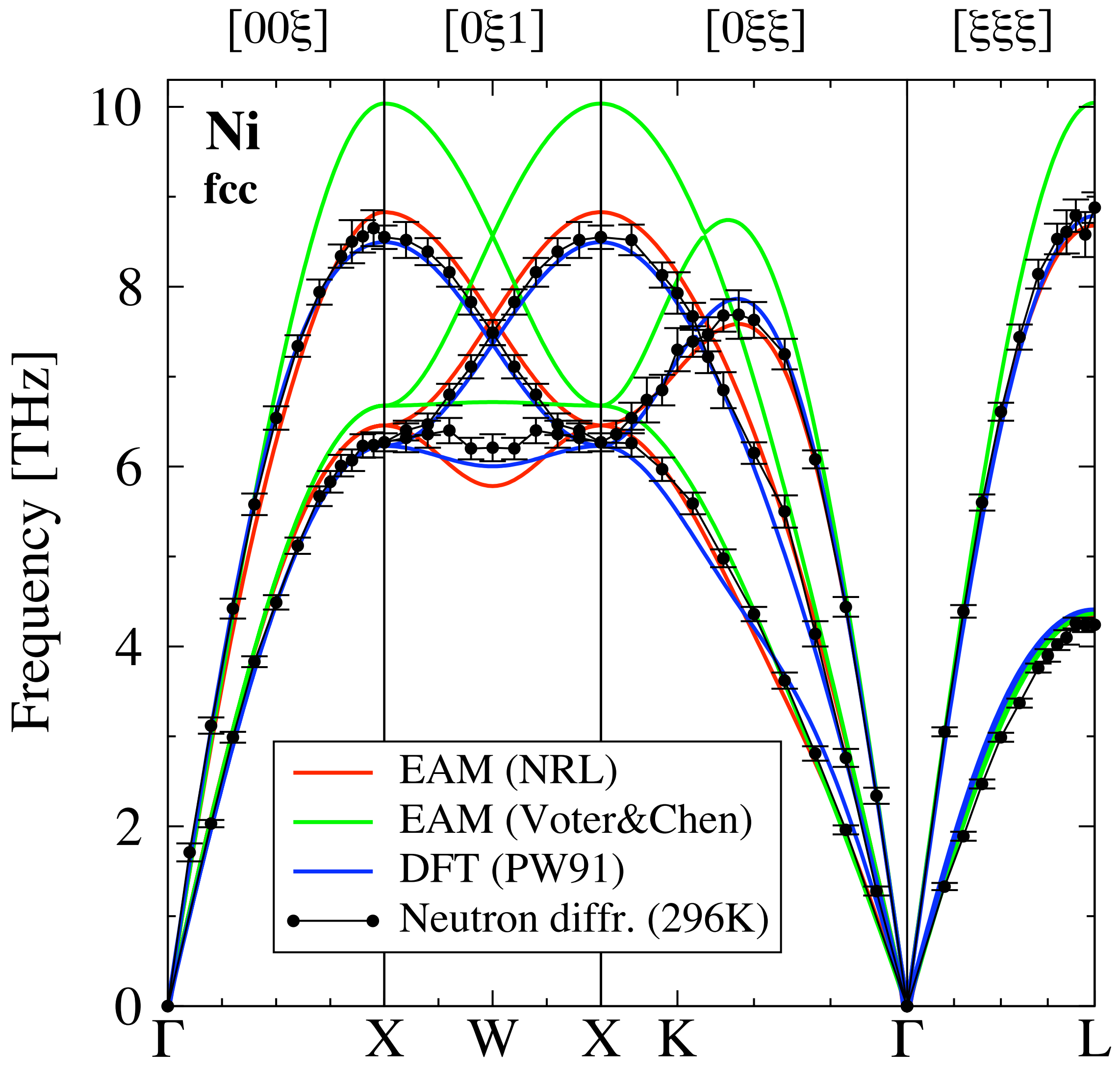
Successes and Failures of DFT

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

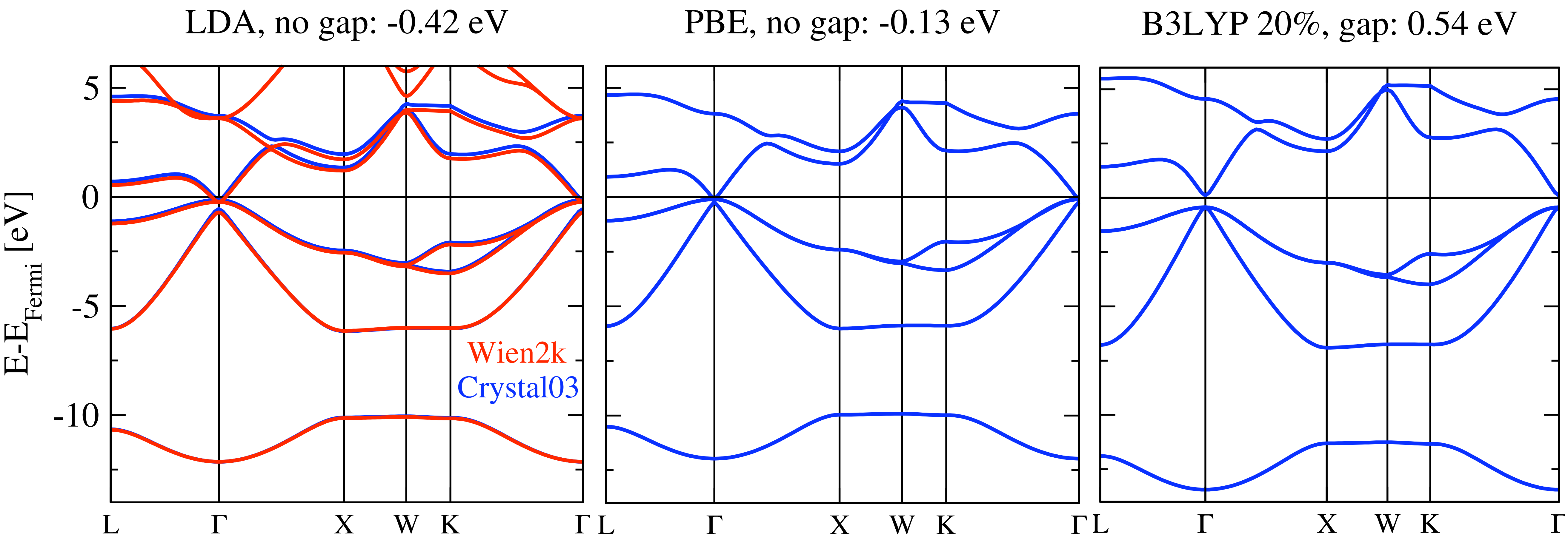
- In many cases such as for metals, vacancy and interstitial energies are highly accurate (within 0.1 eV)
- In some cases such as interstitial defects in silicon, DFT is too low by about 1 eV predicting a 3–3.5 eV formation energy instead of the 4.5 eV of experiments and QMC [Phys. Rev. B 74, 121102(R)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

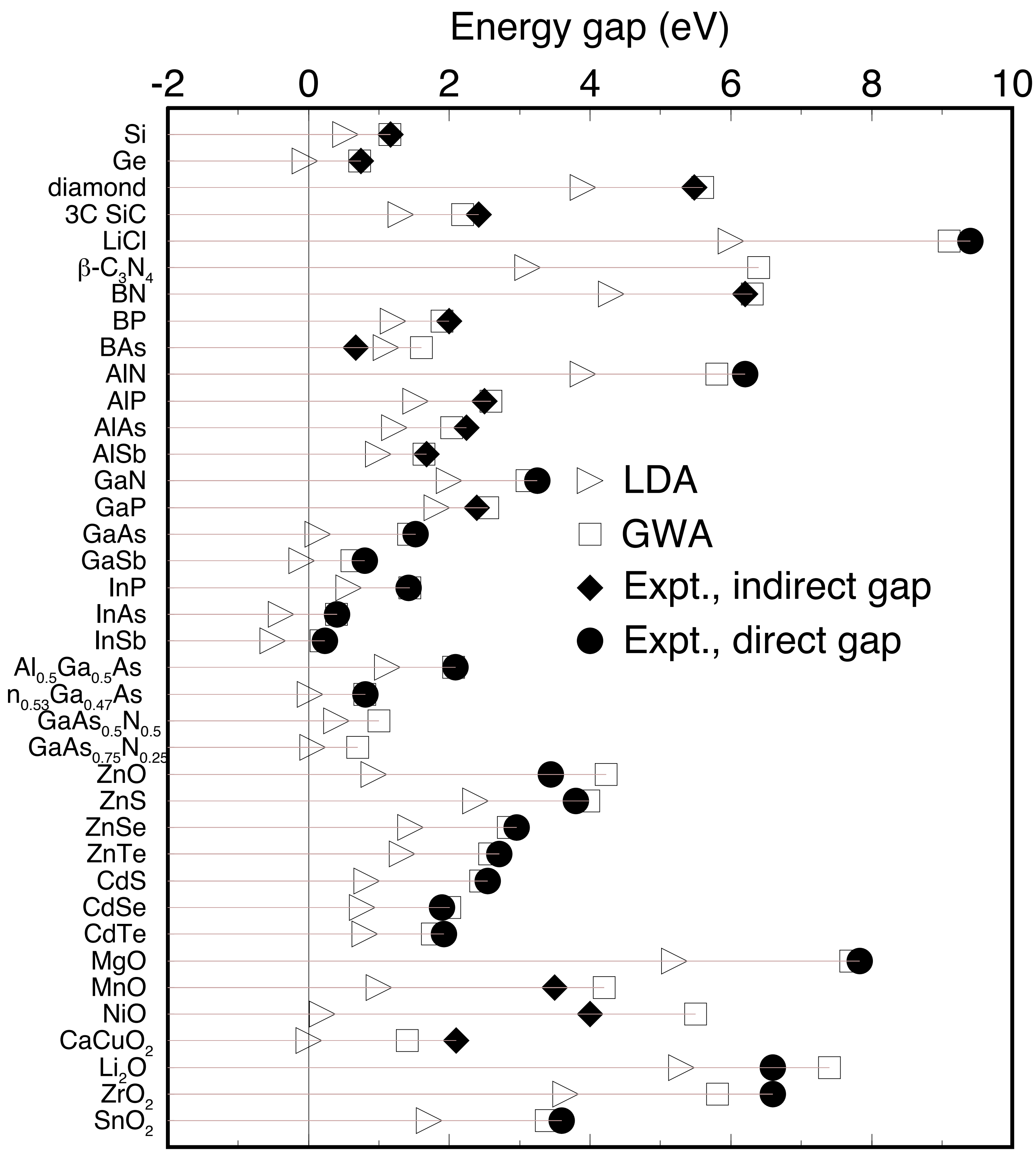
B3LYP 20%, gap: 0.54 eV

- 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.

“Parameters” of a DFT calculation

What do you need to know to *reproduce* a calculation?

- **Software:** what code was used?
    - VASP, QuantumEspresso, Gaussian, Wien2k, …
- **Exchange-correlation potential:** LDA, GGA, MetaGGA, Hybrid, …
- **Basis functions:** what type and how many?
    - Type: Planewaves, linear combination of atomic orbital / Gaussians, APW
    - How many is often characterized by a “cutoff”
- **Brillouin zone integration:** how dense and what method?
    - K-point density inversely proportional to size of cell
    - Smearing to convert discrete grid into continuous integral *or* interpolation
- **Treatment of atomic cores:** pseudopotential / PAW / all-electron
    - If PP or PAW, what electrons are in the core vs. valence?
    - Can control the number of basis functions needed
- **Self-consistency parameters:** convergence (and error) in results
    - Energy change in SCF loop (accuracy of energy, wavefunctions, forces, stresses)
    - Force or energy criterion for optimization
- **Optional other parameters:** DFT+U, GW, etc.
    - “Beyond DFT” methods can introduce new parameters