DENSITY-FUNCTIONAL PRACTICE: PLANE AND SIMPLE

Two ways of looking at it

Minimization (non-linear) of the functional

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^\star(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\ d\mathbf{r} + E_H[n(\mathbf{r})] +$$

$$+E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})\ d\mathbf{r}$$

Solution (SCF) of the Euler-Lagrange eqs.

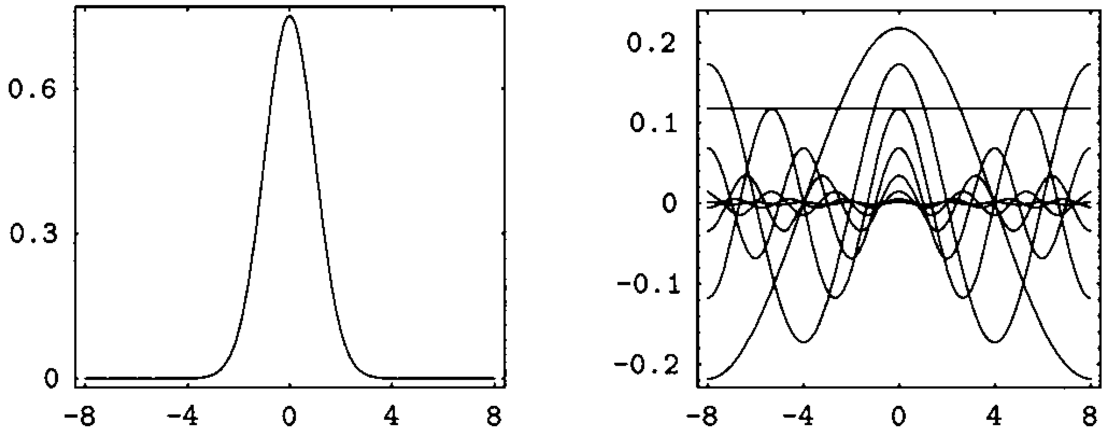
$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \hat{H}_{KS}\ \psi_i(\mathbf{r}) = \epsilon_i\ \psi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ d\mathbf{r}', \qquad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

How do we solve these sets of one-particle differential equations that come from Hartree, Hartree-Fock, or density-functional theory?

Solution: expansion in a basis

$$\left|\psi\right\rangle = \sum_{n=1,k} c_n \left|\varphi_n\right\rangle$$



Differential equation ⇒ linear algebra

$$\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$$

$$\left|\psi\right\rangle = \sum_{n=1,k} c_n \left|\varphi_n\right\rangle \qquad \left\{\left|\varphi_n\right\rangle\right\} \text{ orthogonal}$$

$$\left\langle\varphi_m\right|\hat{H}\left|\psi\right\rangle = E\left\langle\varphi_m\middle|\psi\right\rangle$$

$$\sum_{n=1,k} c_n \left\langle\varphi_m\right|\hat{H}\left|\varphi_n\right\rangle = Ec_m$$

Matrix Formulation

$$\sum_{n=1,k} H_{mn} c_n = E c_m$$

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

Matrix Formulation

$$\det\begin{pmatrix} H_{11}-E & \ldots\ldots & & H_{1k} \\ . & H_{22}-E & & . \\ . & & & . \\ . & & & . \\ H_{k1} & \ldots\ldots & & H_{kk}-E \end{pmatrix} = 0$$

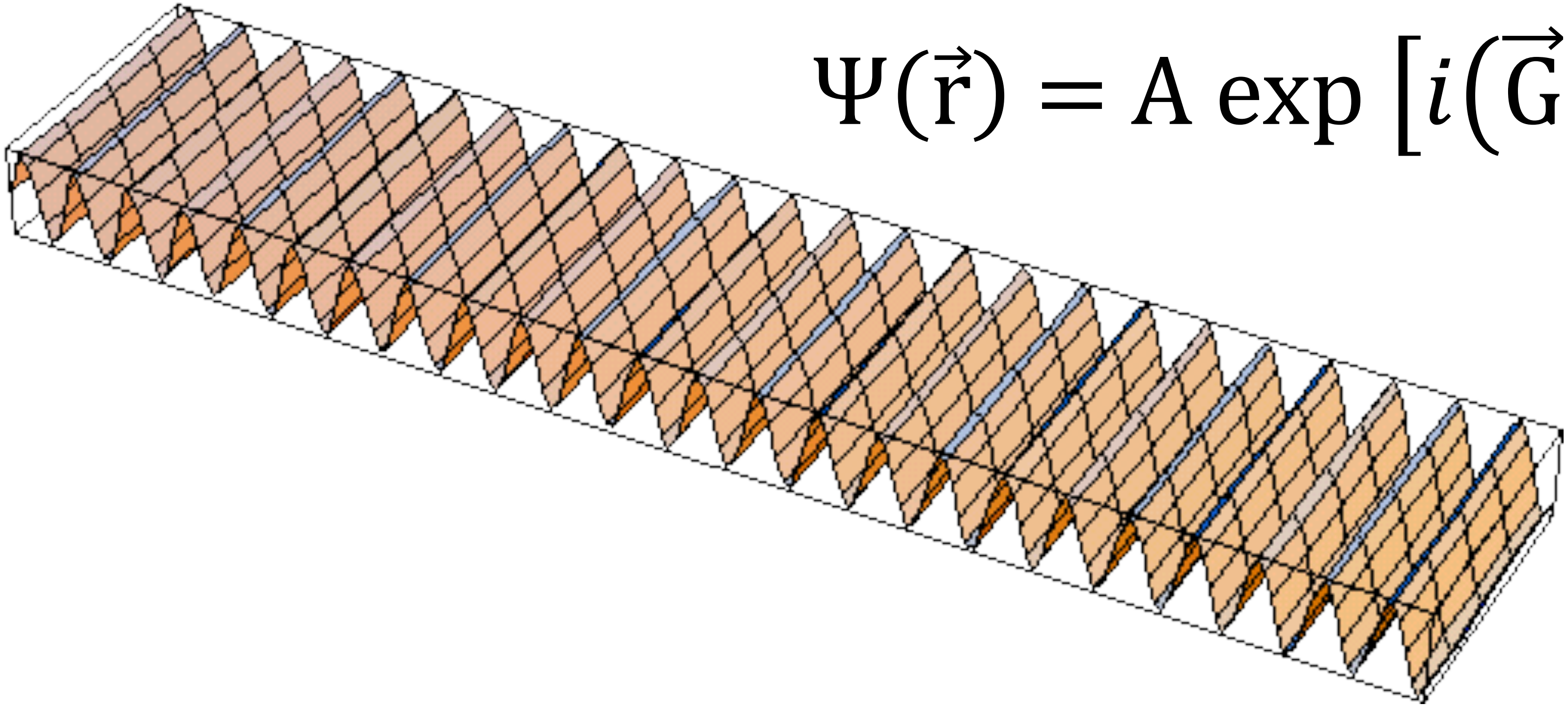
What choice for a basis ?

- For molecules: often atomic orbitals, or localized functions as Gaussians
- For solids, periodic functions such as sines and cosines (plane waves)

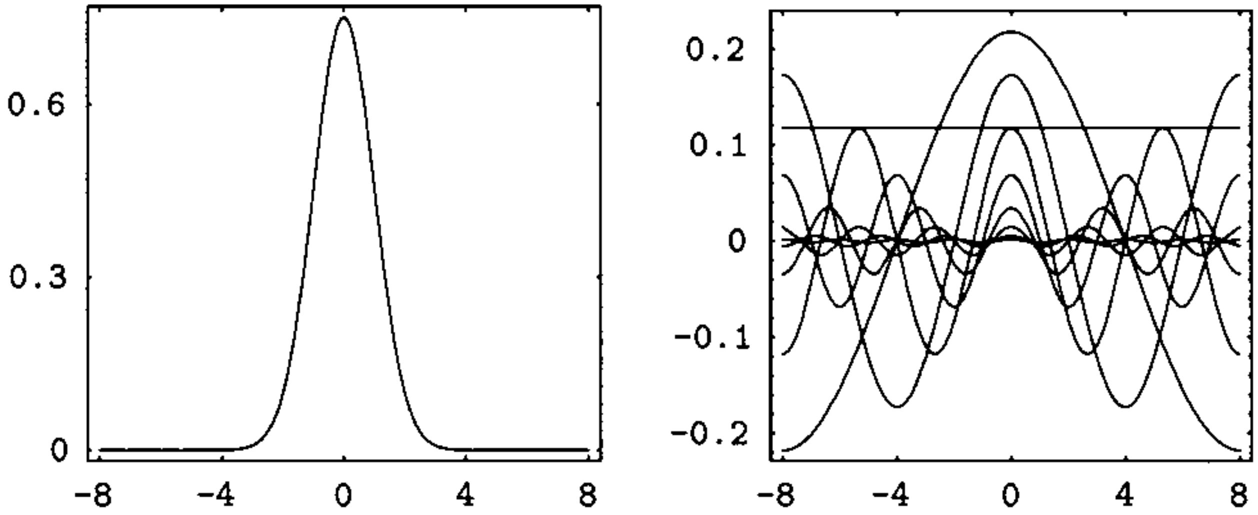
What are plane waves, and why?

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) = E\,\Psi(\vec{r})$$

$$\Psi(\vec{r}) = A\exp\left[i\left(\vec{G}\cdot\vec{r}\right)\right]$$

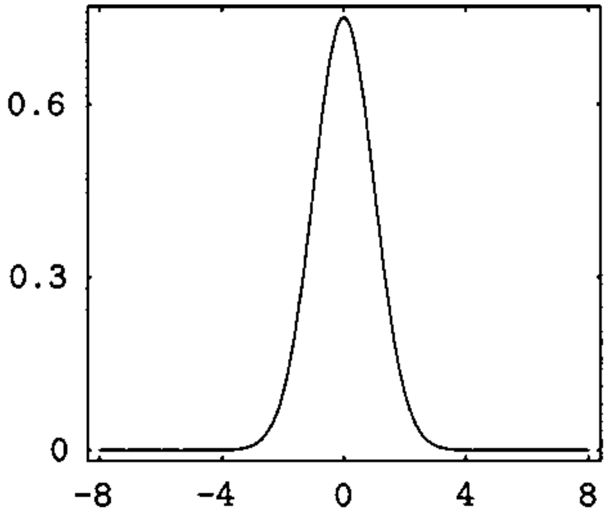


The set of eigenfunctions of a Hermitian operator is complete

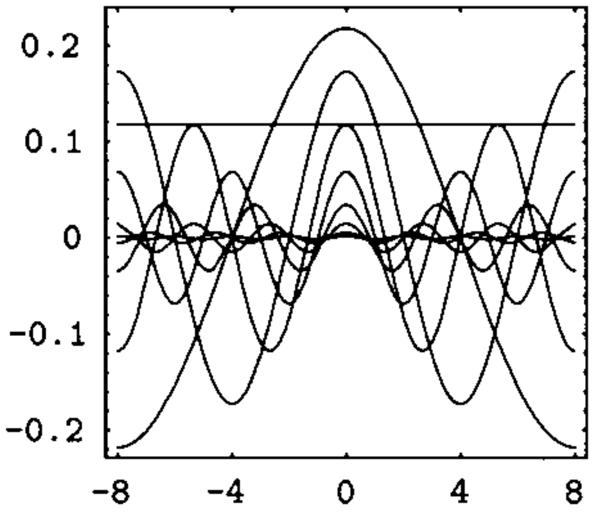


(a) (b)

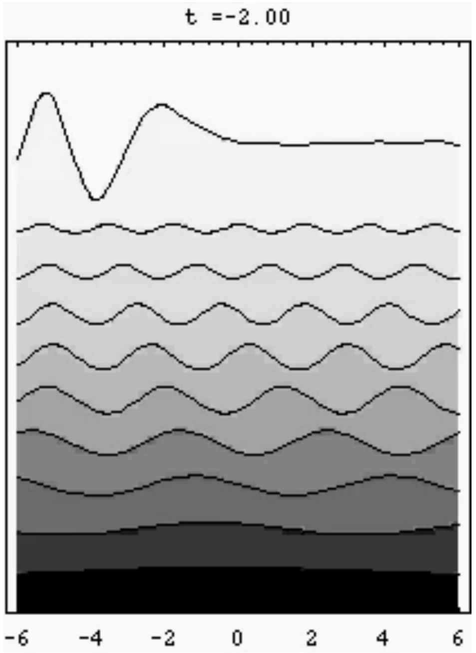
The set of eigenfunctions of a Hermitian operator is complete



(a)



(b)



Relation with Bravais lattices

- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.

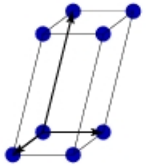
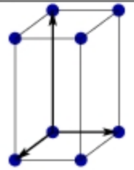
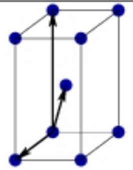
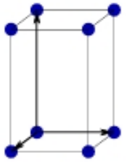
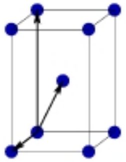
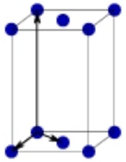
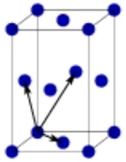
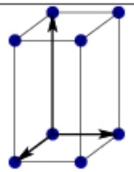
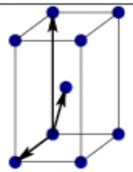
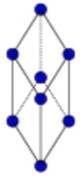
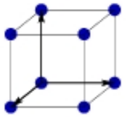
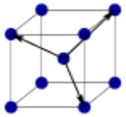
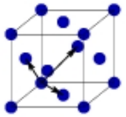
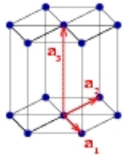
$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \quad \text{l,m and n integers}$$

$$\vec{a}_1,\ \vec{a}_2 \text{ and } \vec{a}_3 \text{ primitive lattice vectors}$$

- 14 Bravais lattices exist in 3 dimensions (1848)

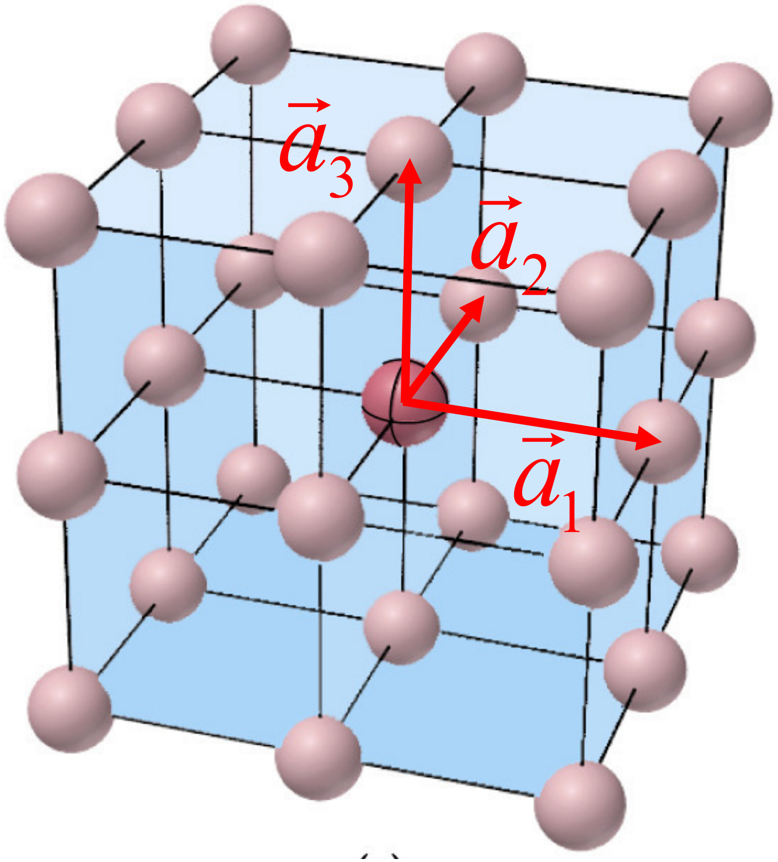
4 Lattice types

7 Crystal classes

14 Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Reciprocal lattice (I)

- Let's start with a Bravais lattice, defined in terms of its primitive lattice vectors…



$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

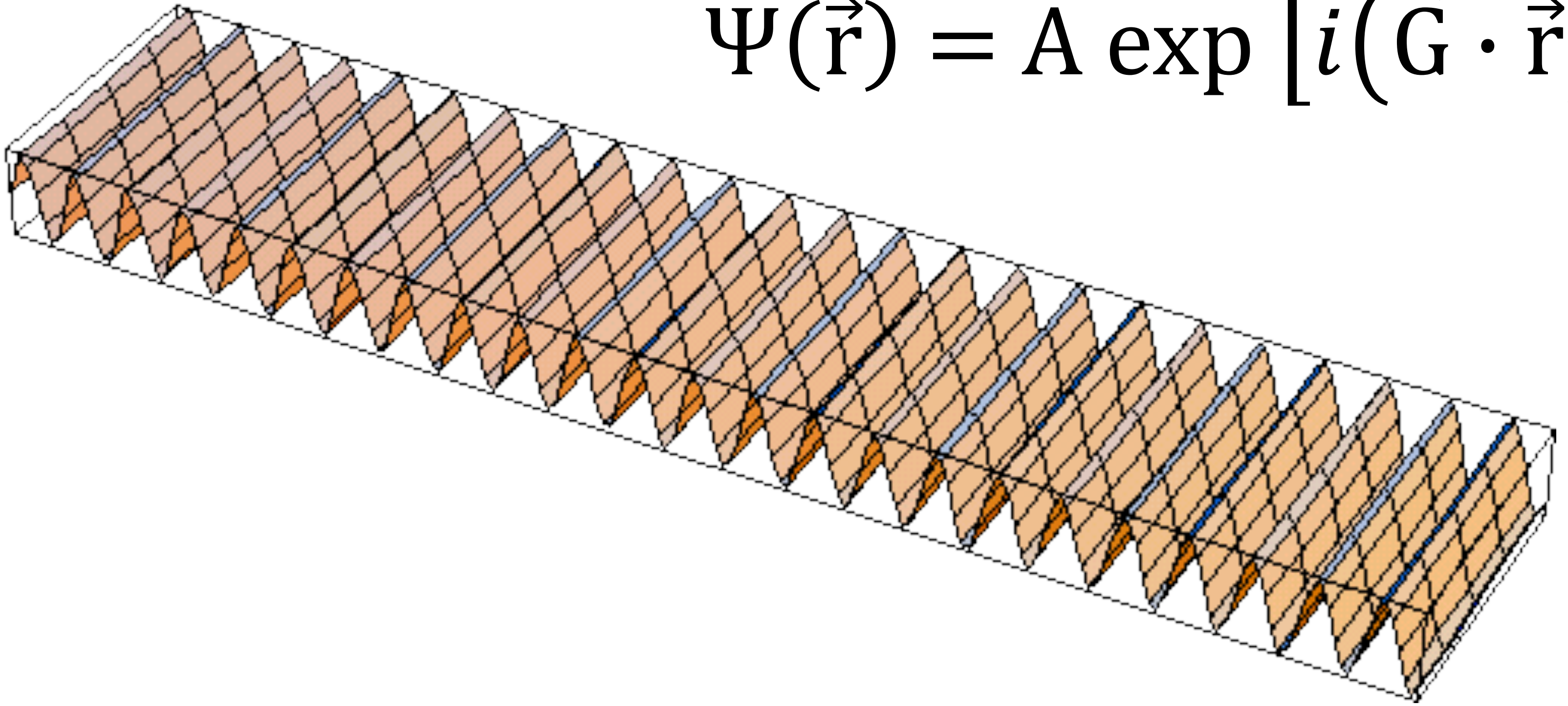
l, m, n integer numbers

$$\vec{R} = (l, m, n)$$

Reciprocal lattice (II)

- …and then let’s take a plane wave

$$\Psi(\vec{\mathrm{r}}) = \mathrm{A}\exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right]$$



Reciprocal lattice (III)

- What are the wavevectors for which our plane wave has the same amplitude at all lattice points ?

$$\exp[i(\vec{G}\cdot\vec{r})] = \exp[i(\vec{G}\cdot(\vec{r}+\vec{R}))]$$

$$\exp[i(\vec{G}\cdot\vec{R})] = 1$$

$$\exp[i(\vec{G}\cdot(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3))] = 1$$

$\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ define the primitive unit cell

$$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

$\vec{G}_1$, $\vec{G}_2$ and $\vec{G}_3$ define the reciprocal space Brillouin Zone

Reciprocal lattice (IV)

$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$ n integer is satisfied by

$\vec{G} = h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3$ with h, i, j integers,

provided $\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}$ $\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}$ $\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}$

$\vec{G} = \left(h, i, j\right)$ are the reciprocal-lattice vectors

Examples of reciprocal lattices

Direct lattice	Reciprocal lattice
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
Orthorhombic	Orthorhombic

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}$$

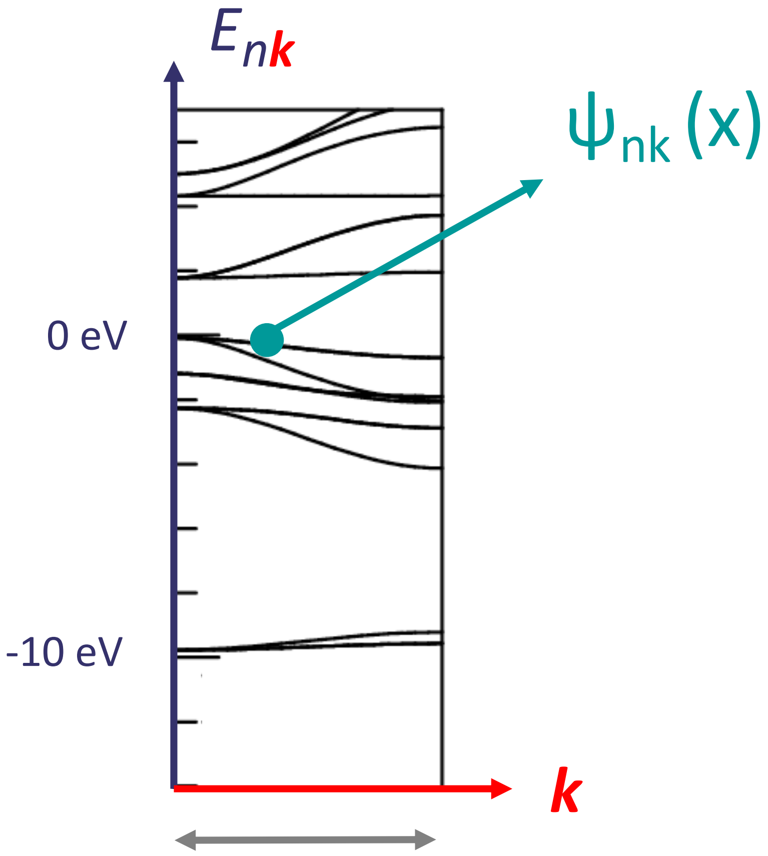
Bloch Theorem

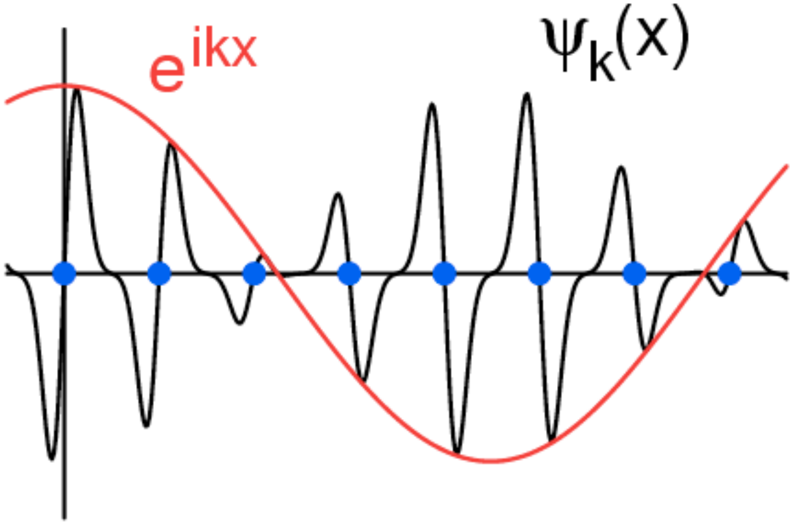
$$[\,\hat{H}\,,\;\hat{T}_{\mathrm{R}}\,] \;=\; 0 \quad\Rightarrow\quad \Psi_{n\mathbf{k}}(\mathbf{r}) \;=\; u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}}$$

- *n*, ***k*** are the quantum numbers (band index *n* and crystal momentum ***k***)
- *u* is periodic (same periodicity as Hamiltonian)

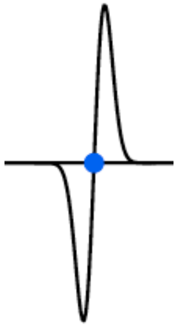
Bands and Bloch Theorem

Bloch wavefunction





Ingredient:
Atomic
wavefunction



From Bloch Theorem…

$$\psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})\exp\left(i\vec{k}\cdot\vec{r}\right)$$

...to expansion in a basis

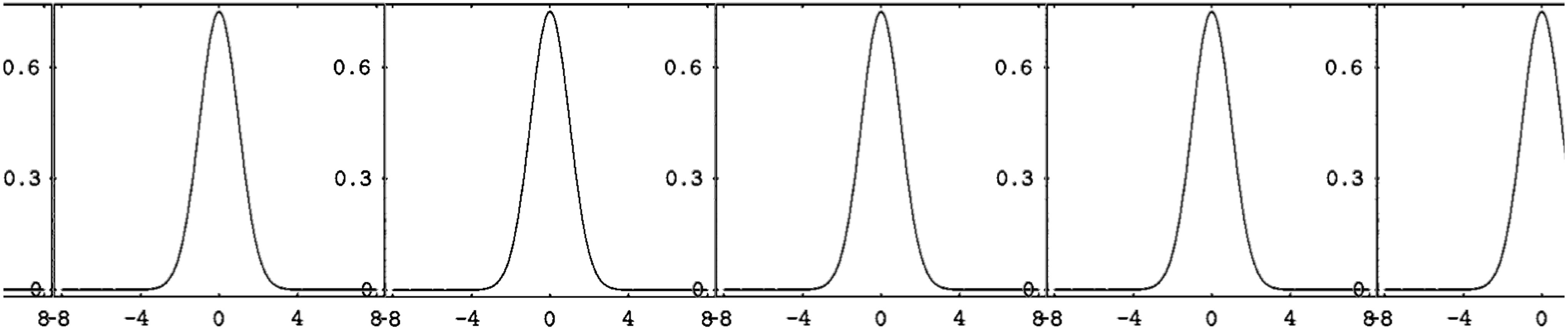
$$\psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})\exp\left(i\vec{k}\cdot\vec{r}\right)$$

periodic u is expanded in planewaves, labeled according to the reciprocal lattice vectors

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$

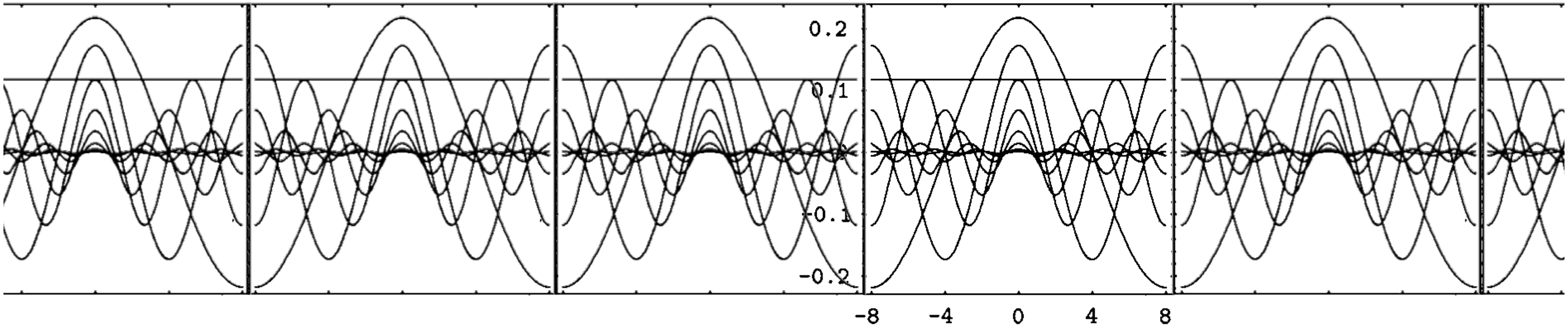
…to expansion in a basis

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$

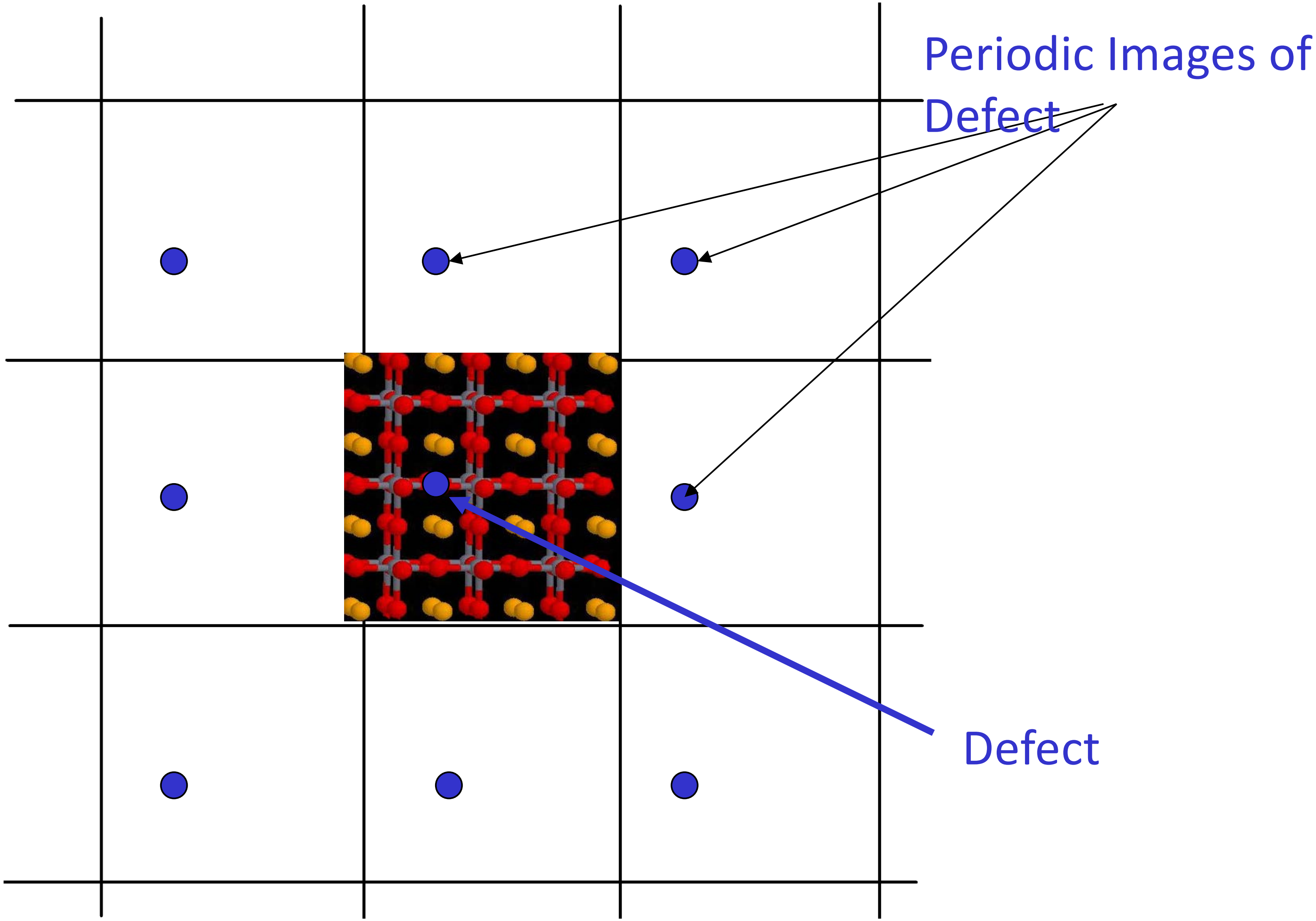


…to expansion in a basis

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\,\vec{G}\cdot\vec{r})$$



For isolated/non periodic systems we use a supercell

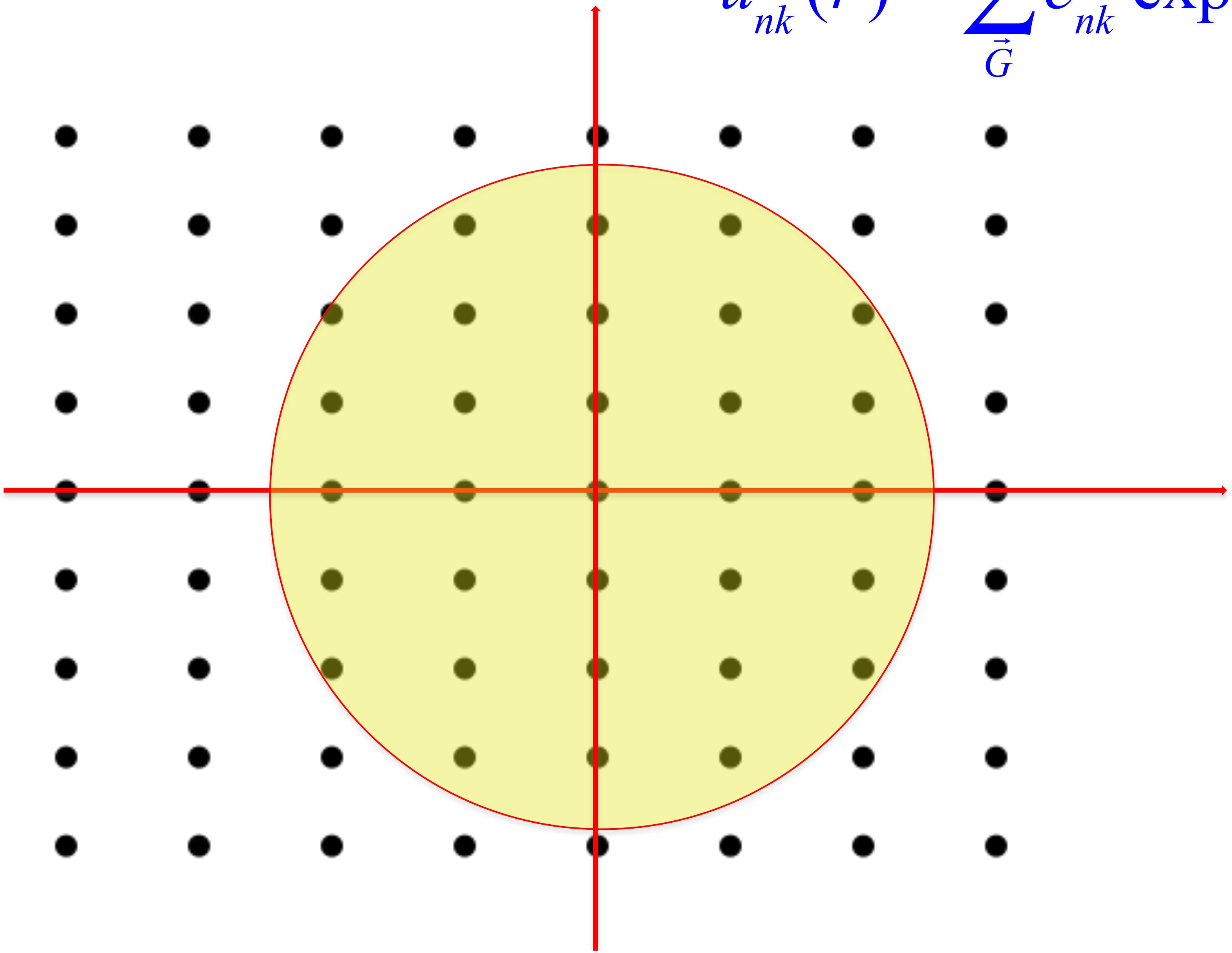


Periodic Images of Defect

Defect

Plane wave expansion

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$



Plane wave expansion

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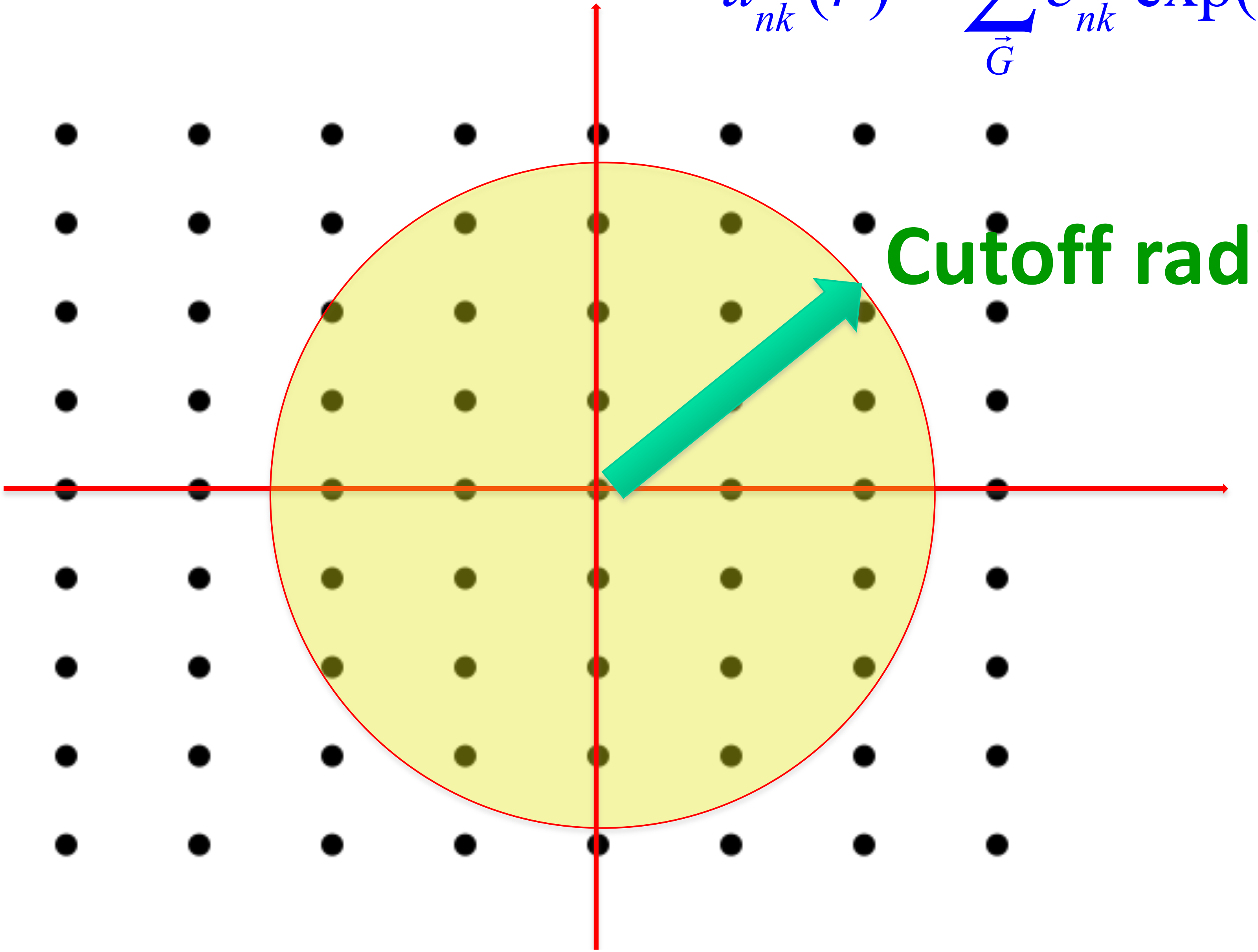
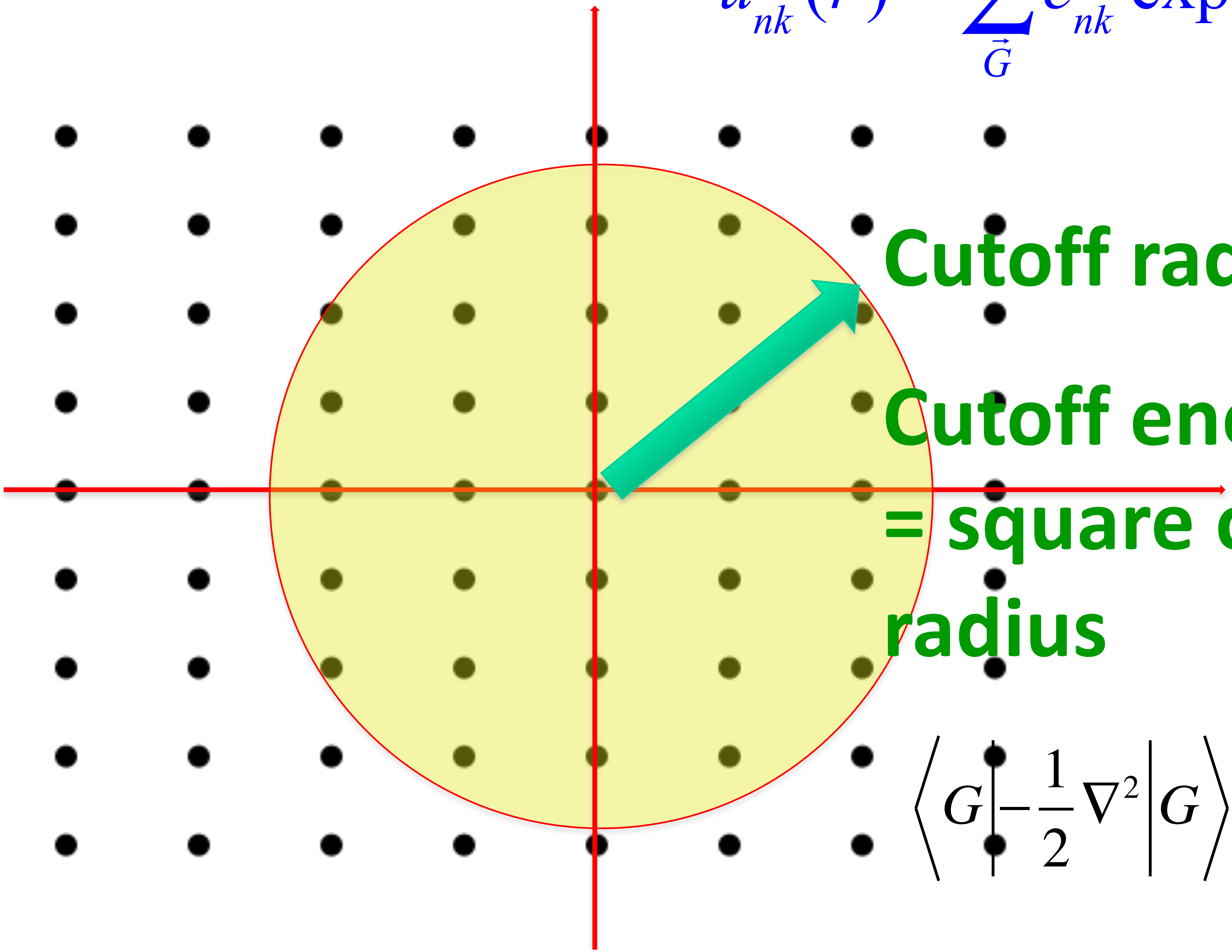


Plane wave expansion

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$



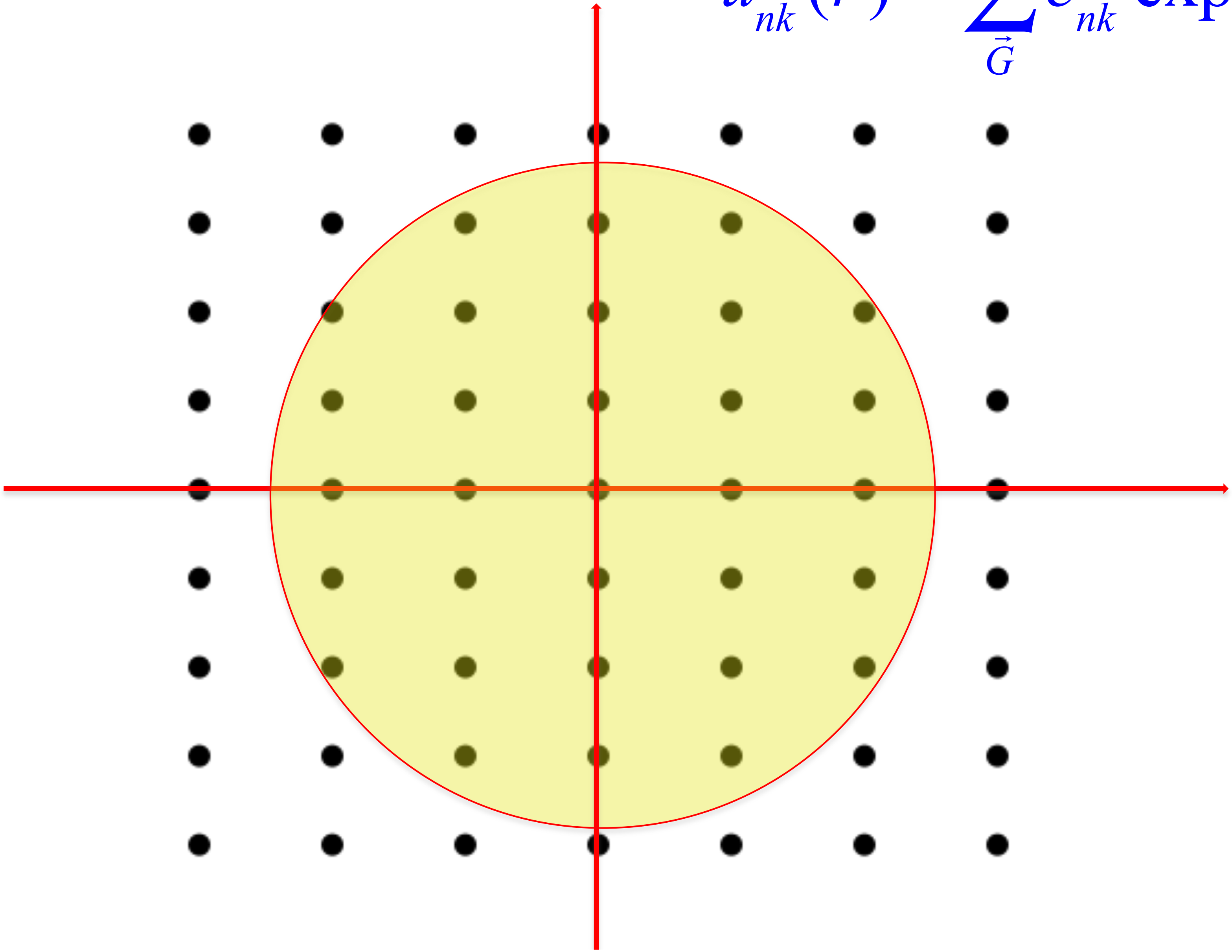
Cutoff radius

Cutoff energy = square of radius

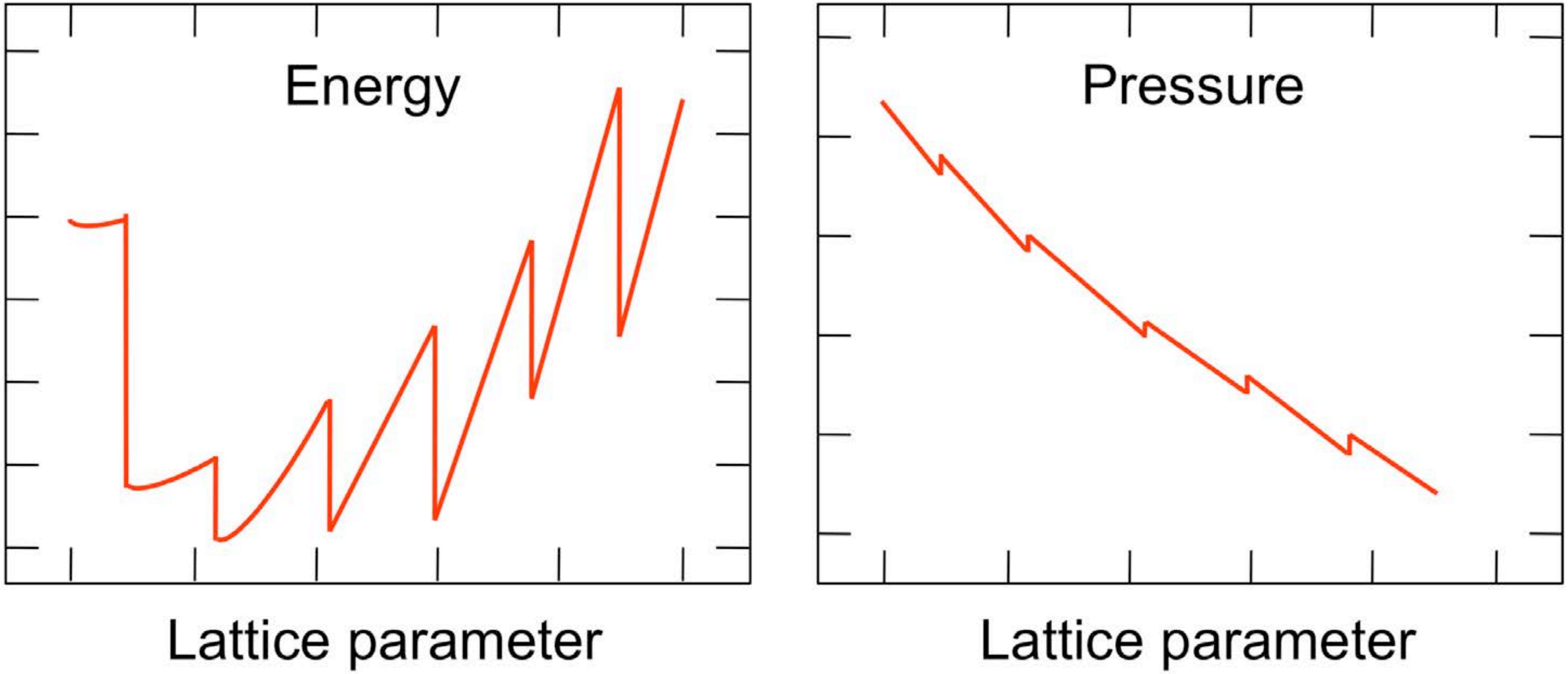
$$\left\langle G \middle| -\frac{1}{2}\nabla^2 \middle| G \right\rangle = \frac{1}{2}G^2$$

What happens if the volume changes?

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$



(Exaggerated view)



Courtesy of X. Gonze, 2017

Derivatives are easy!
(Poisson equation)

In real space:

$$\nabla^2 \mathbf{V}(\vec{\mathbf{r}}) = -4\,\pi\,\mathbf{n}(\vec{\mathbf{r}})$$

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In real space:

$$\boldsymbol{\nabla}^2 \mathbf{V}(\vec{\mathbf{r}}) = -4\,\boldsymbol{\pi}\,\mathbf{n}(\vec{\mathbf{r}})$$

Let's try to get the $V_{\vec{\mathrm{G}}}$ reciprocal-space coefficients from the $n_{\vec{\mathrm{G}}}$

$$\mathrm{n}(\vec{\mathrm{r}}) = \sum_{\vec{\mathrm{G}}} n_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}} \cdot \vec{\mathrm{r}}\right)\right]$$
$$\mathrm{V}(\vec{\mathrm{r}}) = \sum_{\vec{\mathrm{G}}} V_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}} \cdot \vec{\mathrm{r}}\right)\right]$$

Derivatives are easy!
(Poisson equation)

$$\mathrm{n}(\vec{\mathrm{r}}) = \sum_{\vec{\mathrm{G}}} n_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right]$$

$$\Updownarrow$$

$$n_{\vec{\mathrm{G}}} = \frac{1}{V}\int \mathrm{n}(\vec{\mathrm{r}})\exp\left[-i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right]$$

Derivatives are easy!
(Poisson equation)

No Pulay terms:

$$\vec{\nabla}\, \mathbf{V}(\vec{\mathbf{r}}) = \sum_{\vec{G}} i\, \vec{G}\, V_{\vec{G}} \exp\left[i\left(\vec{G} \cdot \vec{r}\right)\right]$$

$$\mathrm{V}(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} \exp\left[i\left(\vec{G} \cdot \vec{r}\right)\right]$$

Derivatives are easy!
(Poisson equation)

No Pulay terms:

$$\nabla^2 \mathbf{V}(\vec{\mathrm{r}}) = \sum_{\vec{\mathrm{G}}} -\left\|\vec{\mathrm{G}}\right\|^2 V_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}} \cdot \vec{\mathrm{r}}\right)\right]$$

$$\mathrm{V}(\vec{\mathrm{r}}) = \sum_{\vec{\mathrm{G}}} V_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}} \cdot \vec{\mathrm{r}}\right)\right]$$

Derivatives are easy!
(Poisson equation)

$$\sum_{\vec{\mathrm{G}}} \left\|\vec{\mathrm{G}}\right\|^2 V_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right] = \mathbf{4}\,\boldsymbol{\pi} \sum_{\vec{\mathrm{G}}} n_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right]$$

Derivatives are easy!
(Poisson equation)

$$\sum_{\vec{\mathrm{G}}} \left\|\vec{\mathrm{G}}\right\|^2 V_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right] = 4\,\boldsymbol{\pi} \sum_{\vec{\mathrm{G}}} n_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right]$$

$$\boldsymbol{V_{\vec{\mathrm{G}}} = 4\,\pi\,\frac{n_{\vec{\mathrm{G}}}}{\left\|\vec{\mathrm{G}}\right\|^2}}$$

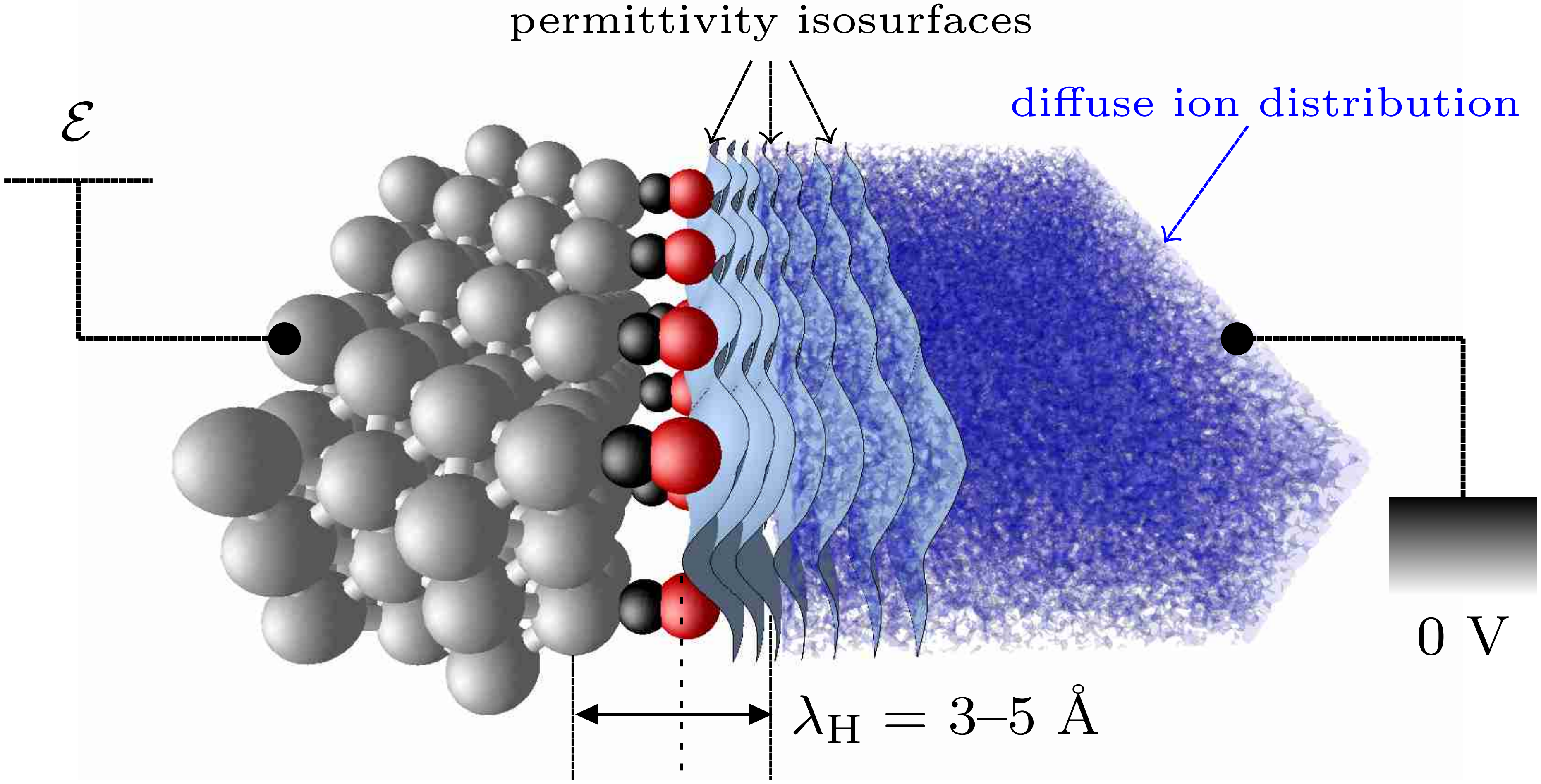
Derivatives are easy!
(Poisson equation)

$$\sum_{\vec{\mathrm{G}}} \left\|\vec{\mathrm{G}}\right\|^2 V_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right] = 4\,\boldsymbol{\pi} \sum_{\vec{\mathrm{G}}} n_{\vec{\mathrm{G}}} \exp\left[i\left(\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}\right)\right]$$

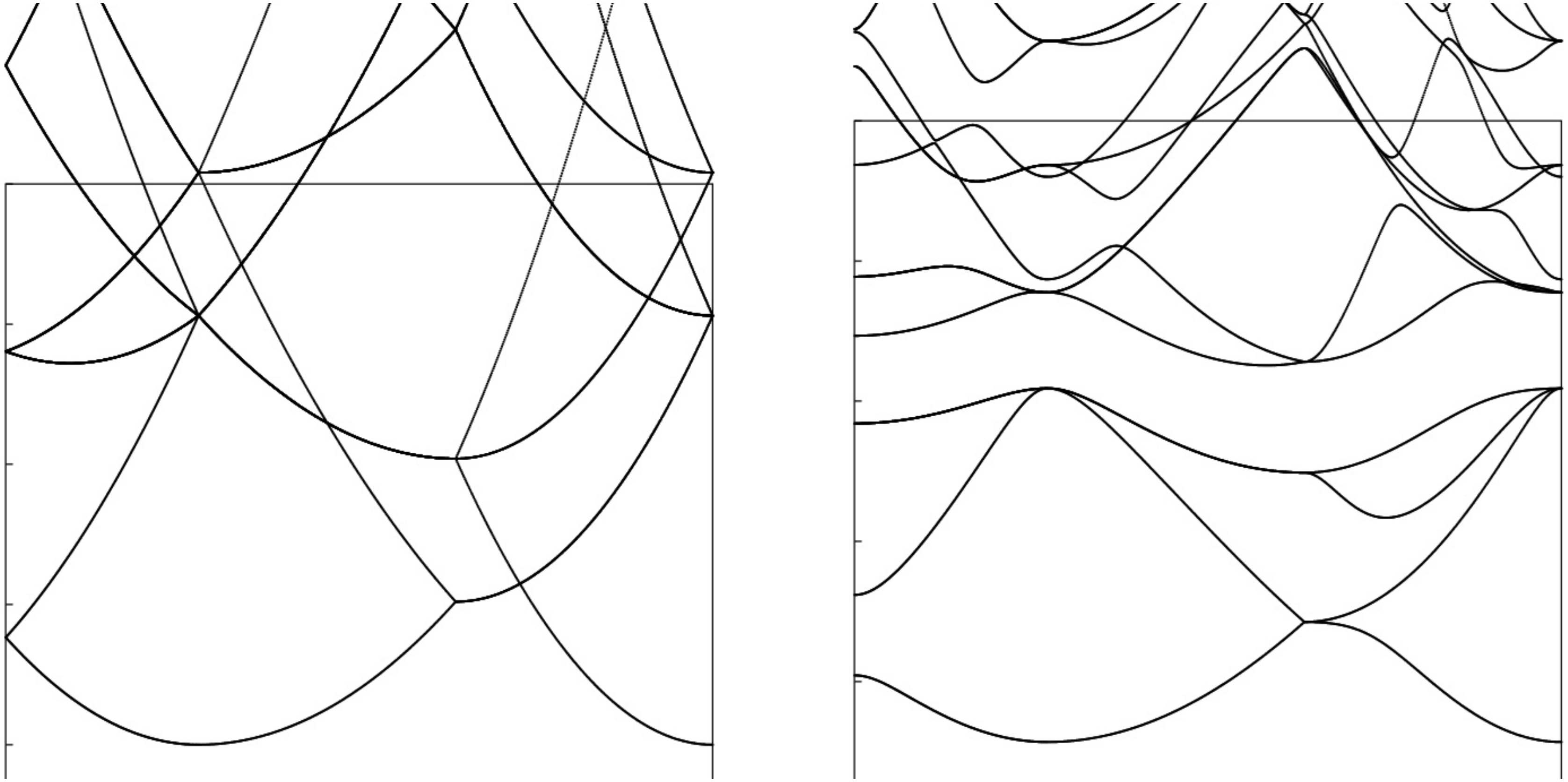
$$\boldsymbol{V_{\vec{\mathrm{G}}} = 4\,\pi\,\frac{n_{\vec{\mathrm{G}}}}{\left\|\vec{\mathrm{G}}\right\|^2}}$$

$$\mathbf{V}(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{G}}} \boldsymbol{V_{\vec{\mathbf{G}}}} \,\mathbf{exp}\left[\boldsymbol{i}\left(\vec{\mathbf{G}}\cdot\vec{\mathbf{r}}\right)\right]$$

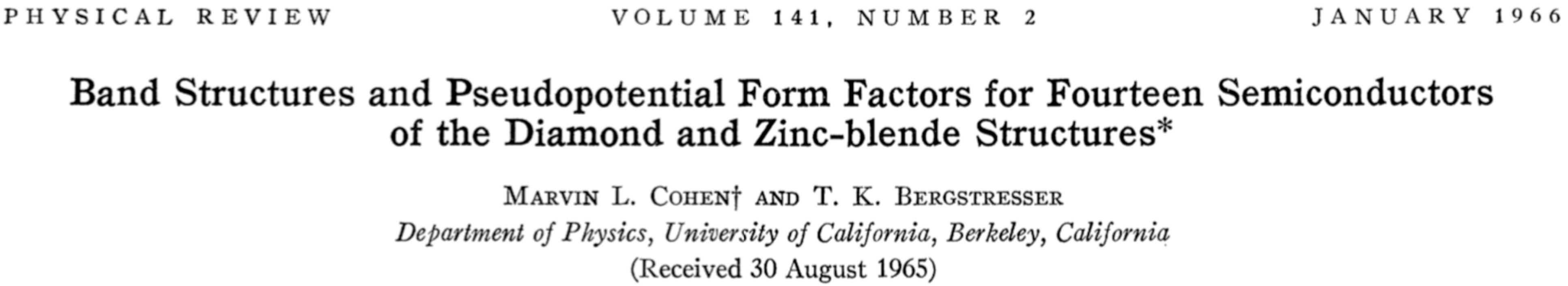
First-principles simulations in realistic electrochemical environments



Free electron gas vs. silicon



Cohen and Bergstresser



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Band Structures and Pseudopotential Form Factors for Fourteen Semiconductors of the Diamond and Zinc-blende Structures*

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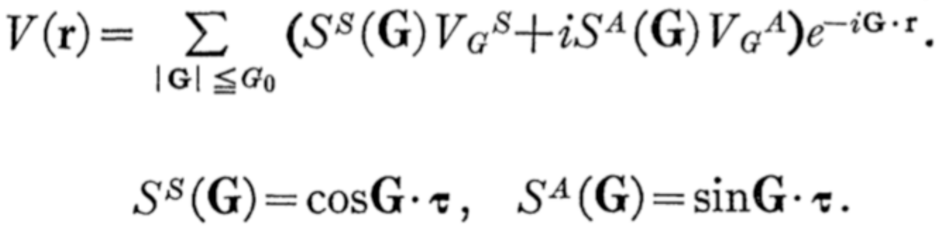
(Received 30 August 1965)



$$V(\mathbf{r})=\sum_{|\mathbf{G}|\leqq G_0}(S^S(\mathbf{G})V_G{}^S+iS^A(\mathbf{G})V_G{}^A)e^{-i\mathbf{G}\cdot\mathbf{r}}.$$

$$S^S(\mathbf{G})=\cos\mathbf{G}\cdot\boldsymbol{\tau}\,,\quad S^A(\mathbf{G})=\sin\mathbf{G}\cdot\boldsymbol{\tau}\,.$$

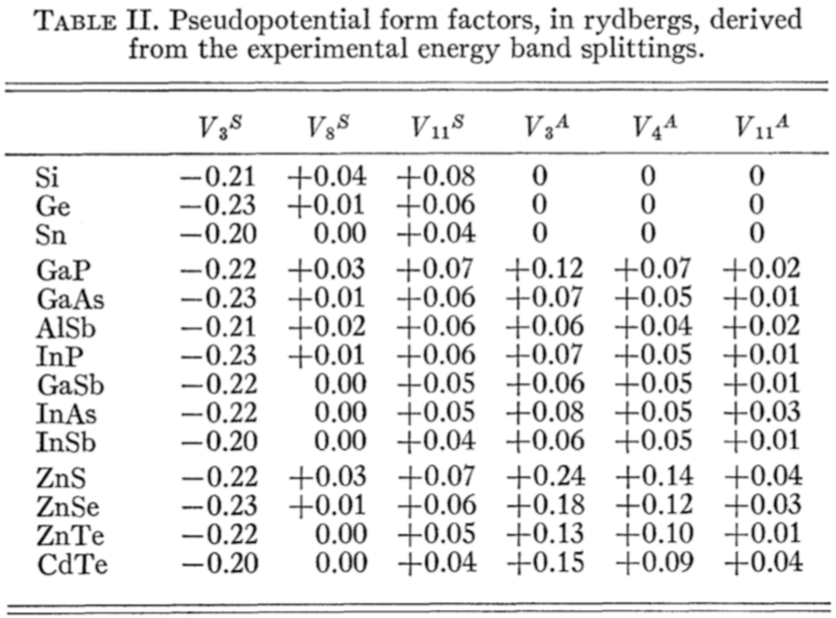
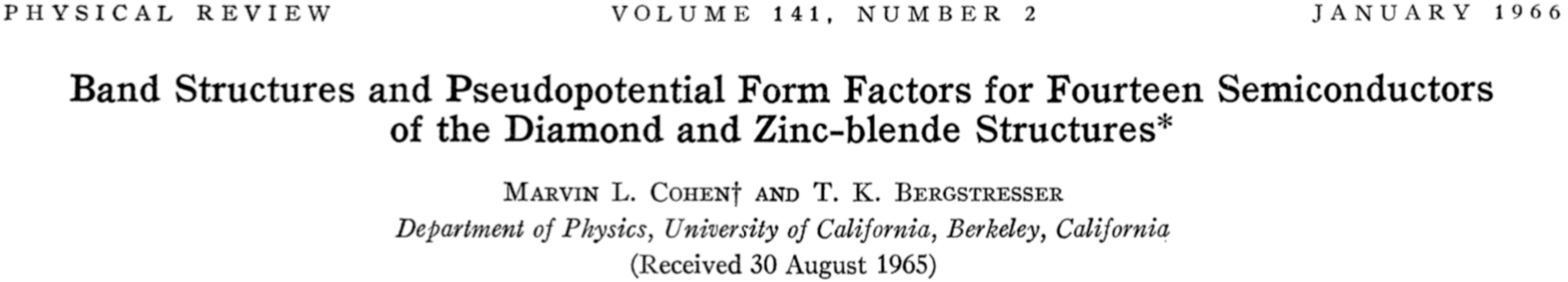


TABLE II. Pseudopotential form factors, in rydbergs, derived from the experimental energy band splittings.

	$V_3{}^S$	$V_8{}^S$	$V_{11}{}^S$	$V_3{}^A$	$V_4{}^A$	$V_{11}{}^A$
Si	−0.21	+0.04	+0.08	0	0	0
Ge	−0.23	+0.01	+0.06	0	0	0
Sn	−0.20	0.00	+0.04	0	0	0
GaP	−0.22	+0.03	+0.07	+0.12	+0.07	+0.02
GaAs	−0.23	+0.01	+0.06	+0.07	+0.05	+0.01
AlSb	−0.21	+0.02	+0.06	+0.06	+0.04	+0.02
InP	−0.23	+0.01	+0.06	+0.07	+0.05	+0.01
GaSb	−0.22	0.00	+0.05	+0.06	+0.05	+0.01
InAs	−0.22	0.00	+0.05	+0.08	+0.05	+0.03
InSb	−0.20	0.00	+0.04	+0.06	+0.05	+0.01
ZnS	−0.22	+0.03	+0.07	+0.24	+0.14	+0.04
ZnSe	−0.23	+0.01	+0.06	+0.18	+0.12	+0.03
ZnTe	−0.22	0.00	+0.05	+0.13	+0.10	+0.01
CdTe	−0.20	0.00	+0.04	+0.15	+0.09	+0.04

Cohen and Bergstresser



PHYSICAL REVIEW VOLUME 141, NUMBER 2 JANUARY 1966

Band Structures and Pseudopotential Form Factors for Fourteen Semiconductors of the Diamond and Zinc-blende Structures*

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(Received 30 August 1965)

$$\left\langle G\left|-\frac{1}{2}\nabla^2\right|G'\right\rangle = \int dr\,\exp(-iGr)\left[-\frac{1}{2}\nabla^2\right]\exp(iG'r) = \frac{1}{2}G^2\delta_{G,G'}$$

$$\left\langle G\middle|V(r)\middle|G'\right\rangle = \int dr\,\exp(-iGr)V(r)\exp(iG'r) = V(G-G')$$

Cohen and Bergstresser

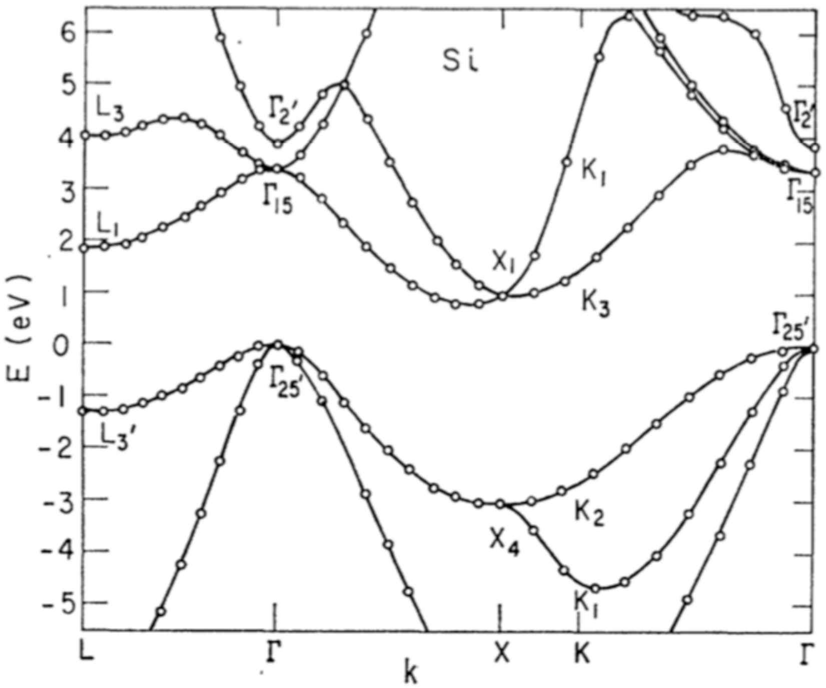


FIG. 1. Band structure of Si.

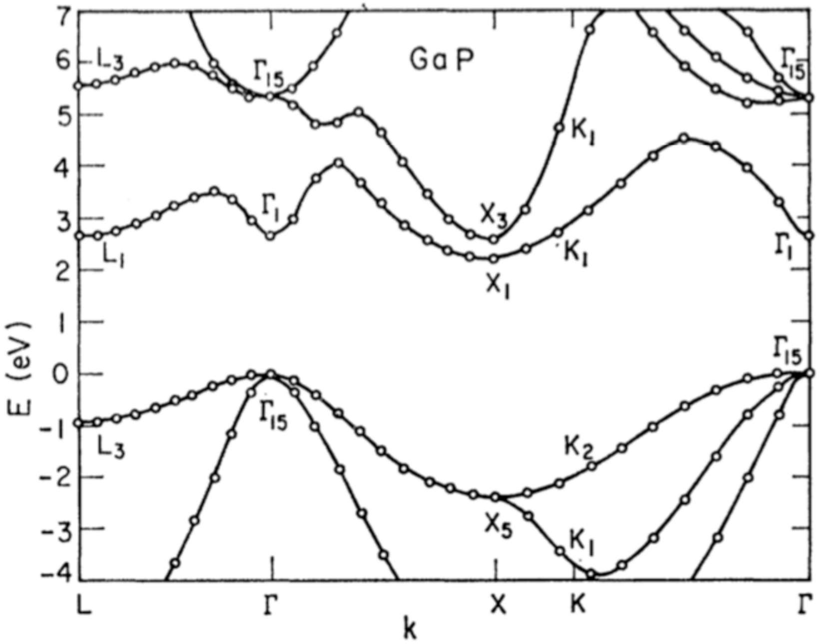
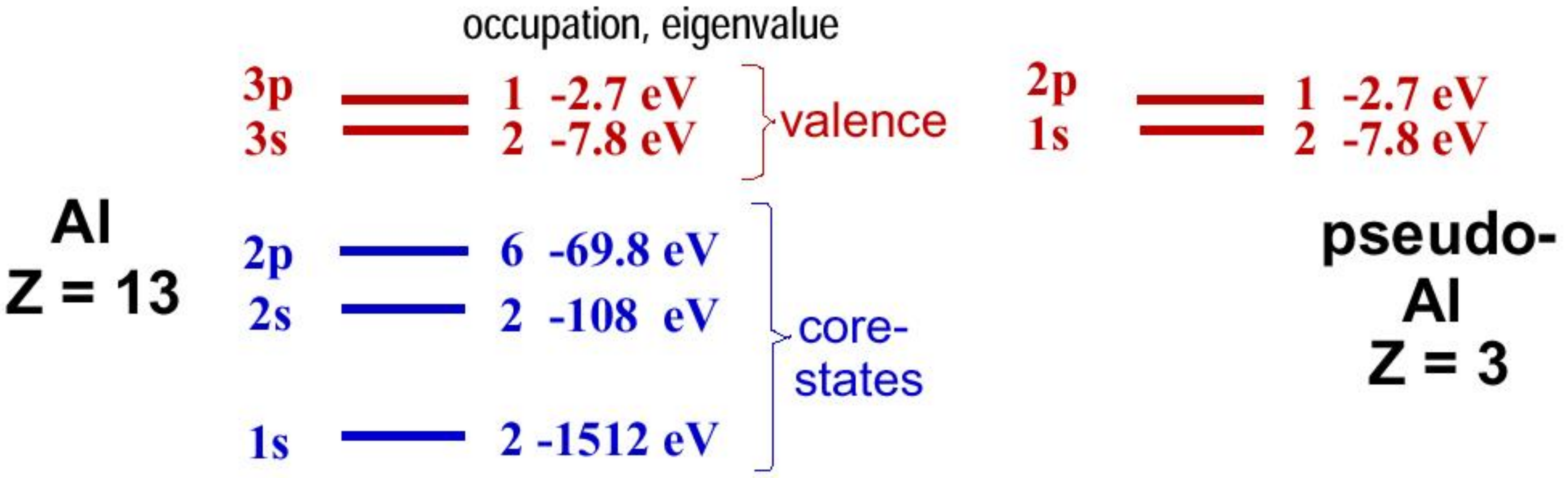


FIG. 4. Band structure of GaP.

Pseudopotentials (I)

- Electrons in the inner shells do not contribute to valence bonding – so they are frozen in the state they have in an isolated atom
- Releasing the frozen core does not add any linear term to the energy (von Barth and Gelatt, 1980)

Pseudopotentials (II)



occupation, eigenvalue

Al
Z = 13

3p 1 -2.7 eV
3s 2 -7.8 eV
valence

2p 6 -69.8 eV
2s 2 -108 eV
1s 2 -1512 eV
core-states

2p 1 -2.7 eV
1s 2 -7.8 eV

pseudo-Al
Z = 3

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}\right)\psi_j = \varepsilon_j \psi_j$$

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}^{(\mathrm{ps})}\right)\psi_j^{(\mathrm{ps})} = \varepsilon_j \psi_j^{(\mathrm{ps})}$$

From Eckhard Pehlke lecture notes – Fritz-Haber Institut
http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/pehlke1.pdf

Pseudopotentials (III)

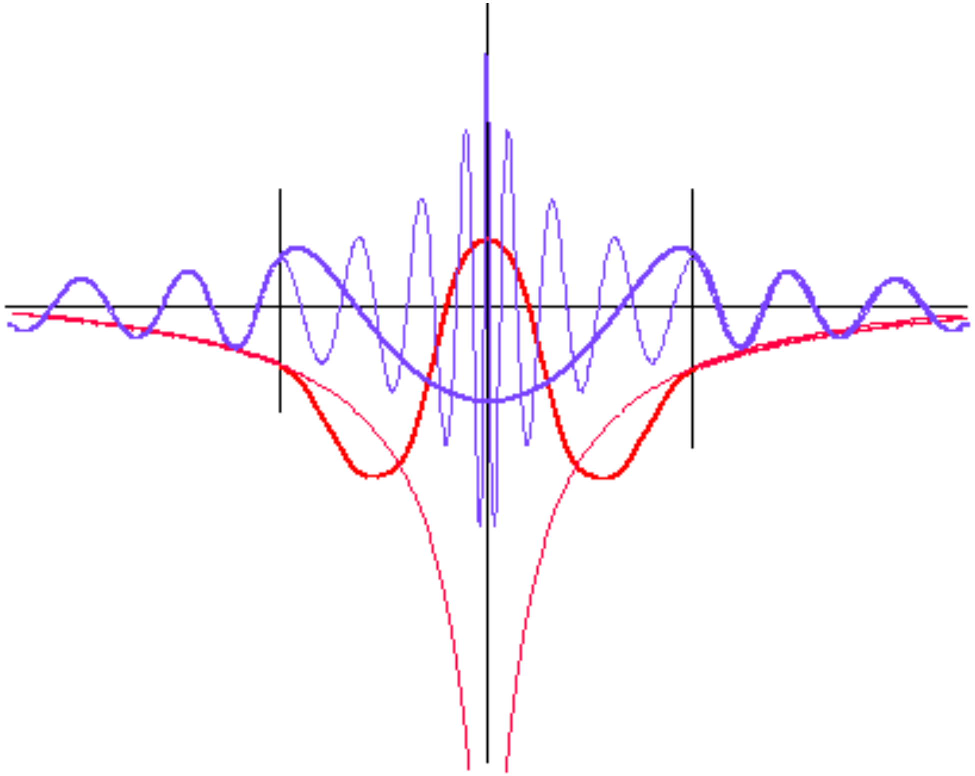


Figure 2.3: A schematic representation of the potentials (red lines) and wavefunctions (blue lines) for an atom. The real potential and wavefunction are shown with thin lines, while the pseudopotential and wavefunction are shown in thick lines. Outside the cutoff region (vertical black lines) the two are identical. *Picture courtesy of Chris Goringe.*

Norm-conserving pseudopotentials

- Real and pseudo valence eigenvalues agree for a chosen atomic configuration
- Real and pseudo wavefunctions agree beyond a core radius
- The integral of real and pseudo charge from 0 to a distance greater than core radius agree
- The logarithmic derivatives of the real and pseudo wavefunctions, and their first energy derivatives, agree for distances greater than the core radius

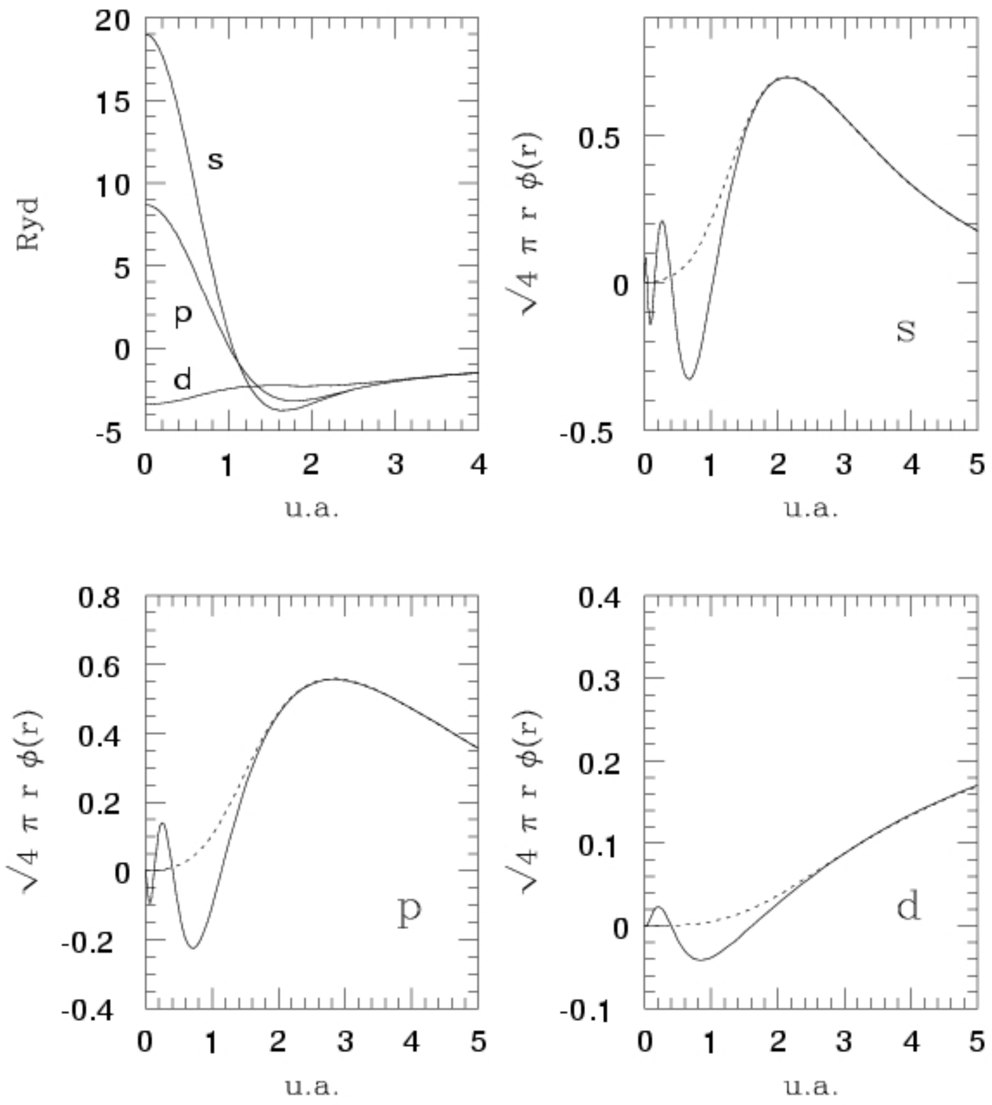
Norm-conserving pseudopotentials

- $\epsilon_l^{ps} = \epsilon_l^{ae}$
- $\phi_l^{ps}(r)$ is nodeless
- $\phi_l^{ps}(r) = \phi_l^{ae}(r)$ for $r > r_c$
- $\int_{r<r_c} |\phi_l^{ps}(r)|^2 r^2 dr = \int_{r<r_c} |\phi_l^{ae}(r)|^2 r^2 dr$

Non-local, norm conserving

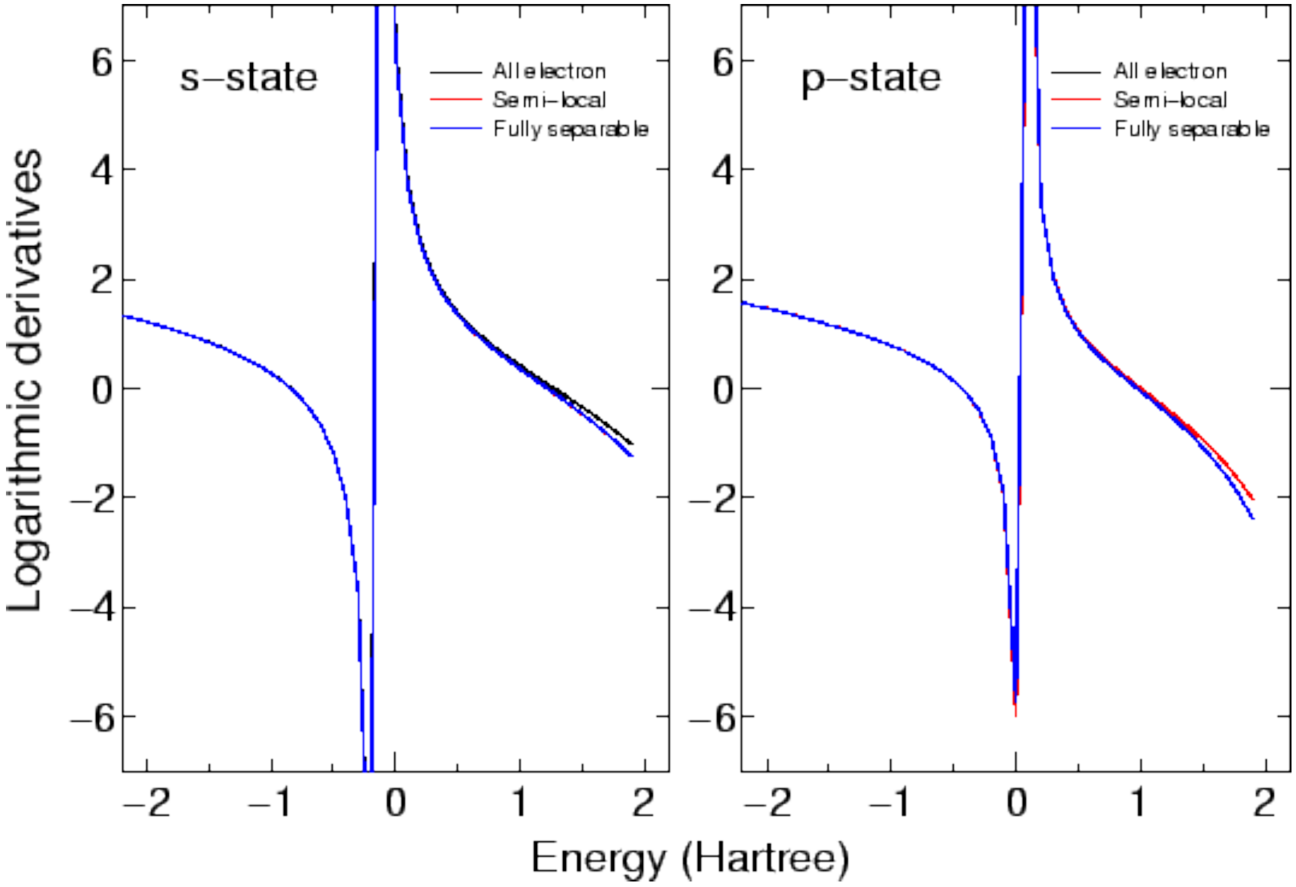
Different **angular momenta** scatter differently from the core (states that have shell below them with same angular momentum are repelled more)

Non-local PP



Logarithmic derivatives

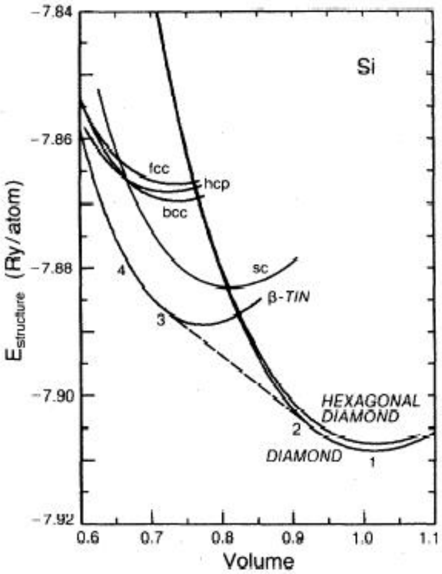
$$\frac{d}{dr}\ln u_l\left(E,r\right)$$



Momentum-space formalism for the total energy of solids

J Ihm, Alex Zunger and Marvin L Cohen†

Department of Physics, University of California and Materials and Molecular Research
Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, USA

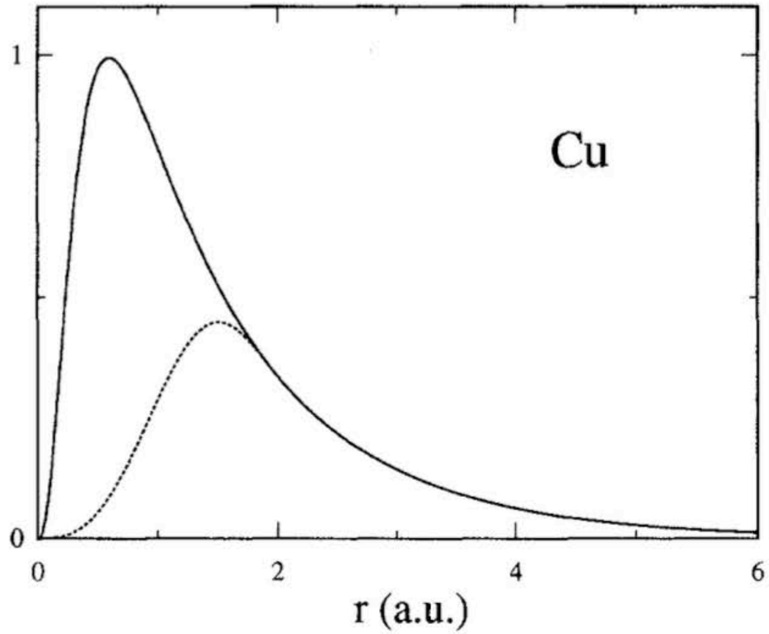


Yin and Cohen,
PRL 1980, PRB 1982

Pseudopotentials that work: From H to Pu

G. B. Bachelet, D. R. Hamann, and M. Schlüter
Phys. Rev. B **26**, 4199 – Published 15 October 1982; Erratum Phys. Rev. B **29**, 2309 (1984)

Note on ultrasoft pseudopotentials



3d pseudo- and all-electron orbitals for Cu (Laasonen et al, Phys. Rev. B 47, 10142 (1993))

$$\hat{V}_{US} \equiv V_{loc}(r) + \sum_{lm} D_{lm} |\beta_l\rangle\langle\beta_m|$$

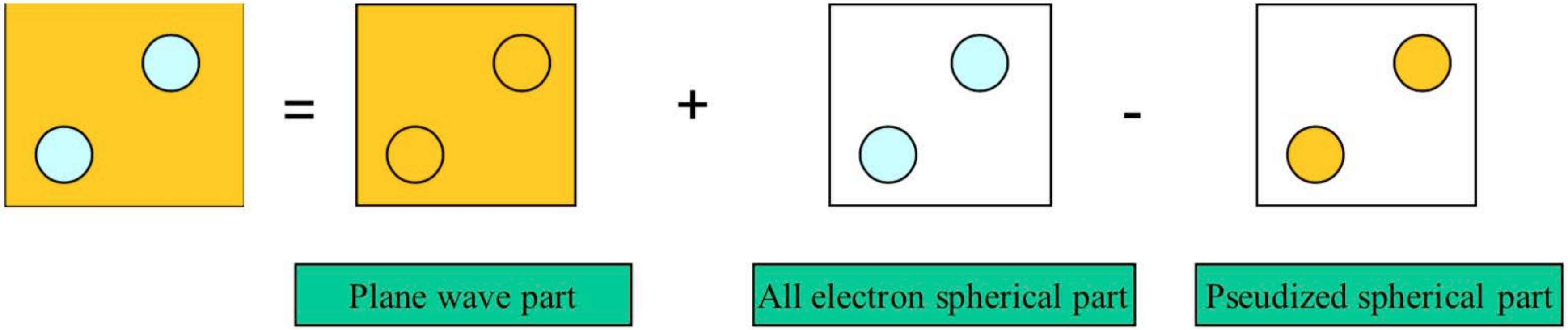
$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 + \sum_i \sum_{lm} \langle\psi_i|\beta_l\rangle Q_{lm}(\mathbf{r}) \langle\beta_m|\psi_i\rangle$$

Note on projector augmented wave (PAW)

$$\Psi = T\tilde{\Psi} \qquad T = 1 + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i |$$

Explicitly,

$$\Psi = \tilde{\Psi} + \sum_R \left(|\Psi_R^1\rangle - |\tilde{\Psi}_R^1\rangle \right)$$



Plane wave part

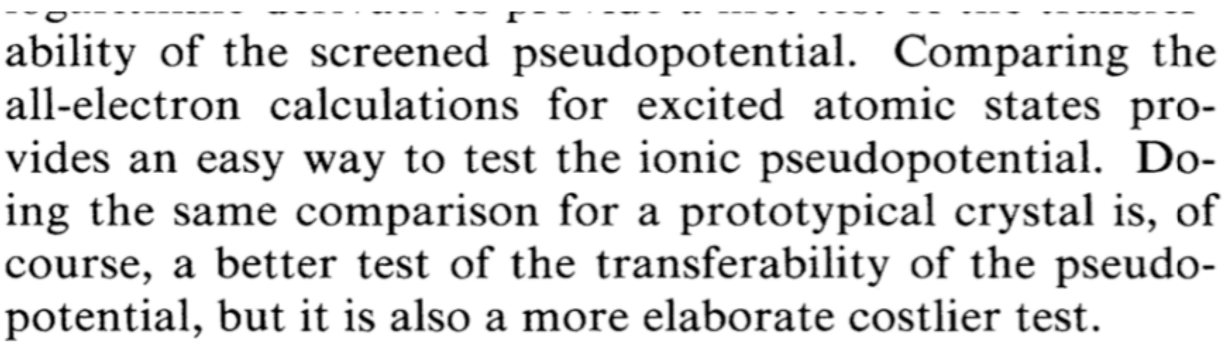
All electron spherical part

Pseudized spherical part

$$|\Psi_R^1\rangle = \sum_{i \in R} |\phi_i\rangle \langle \tilde{p}_i | \tilde{\Psi}\rangle \qquad |\tilde{\Psi}_R^1\rangle = \sum_{i \in R} |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi}\rangle$$

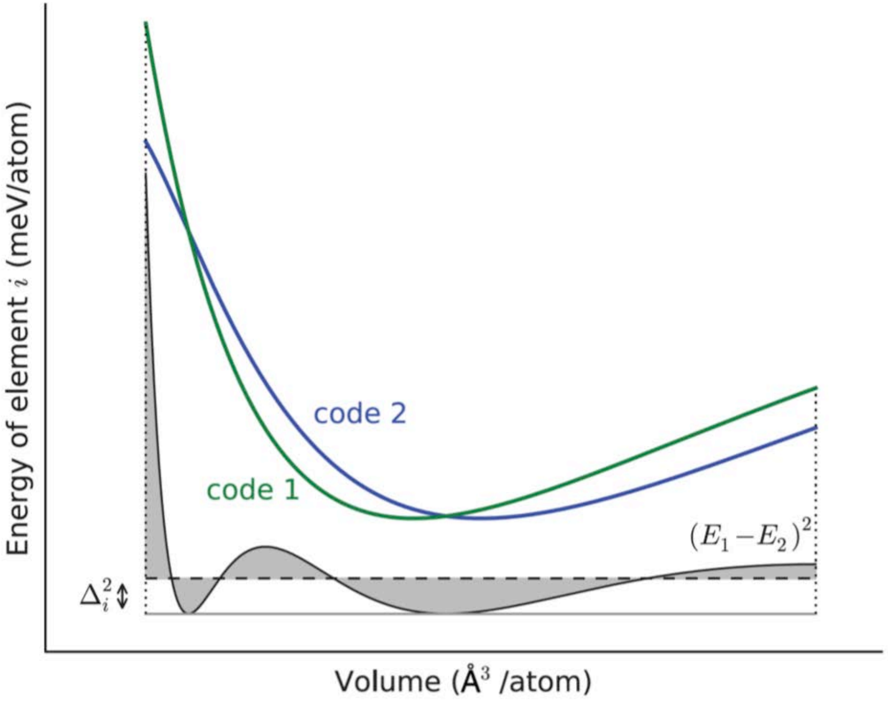
Courtesy of X. Gonze, 2017

From the atom to the solid

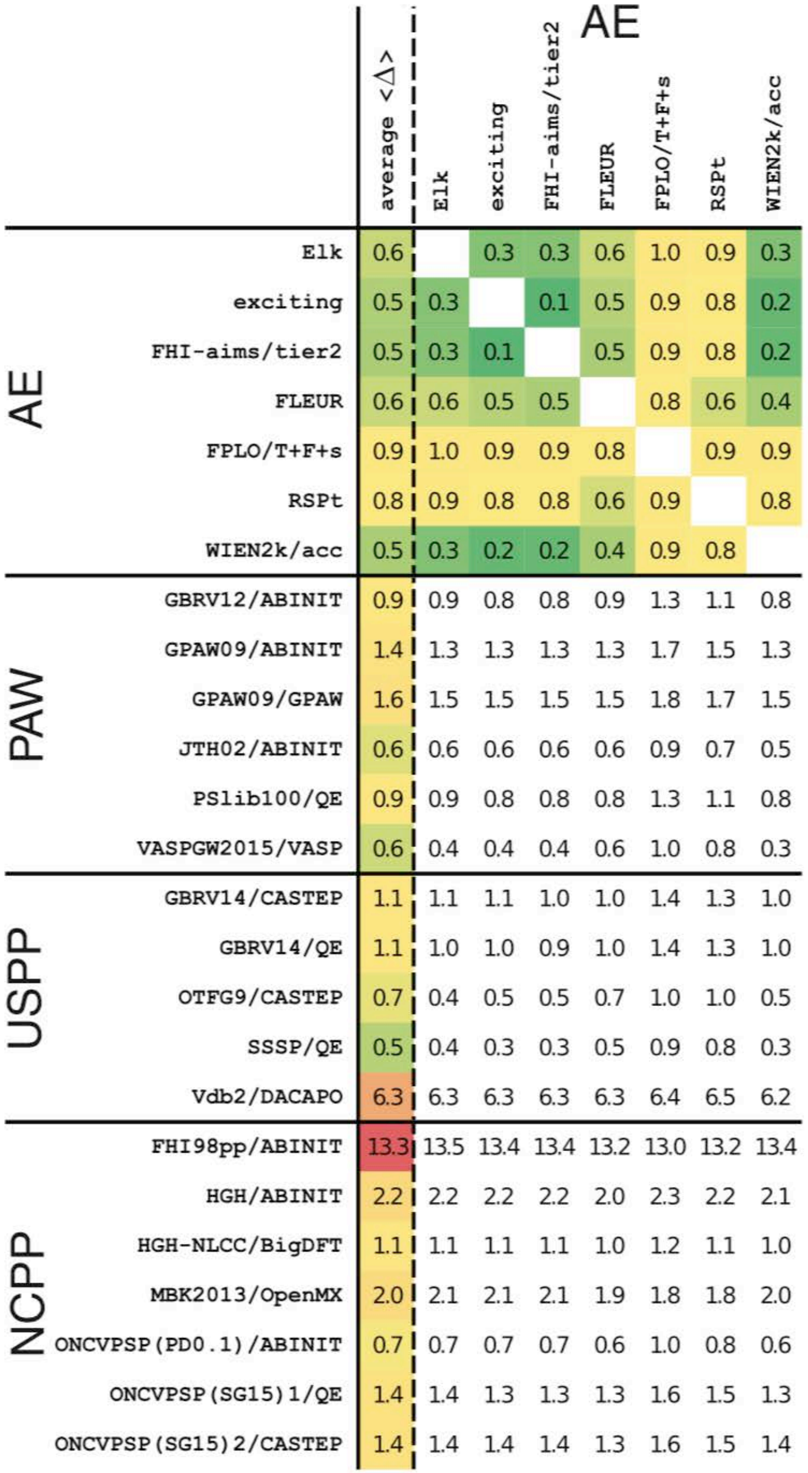


ability of the screened pseudopotential. Comparing the all-electron calculations for excited atomic states provides an easy way to test the ionic pseudopotential. Doing the same comparison for a prototypical crystal is, of course, a better test of the transferability of the pseudopotential, but it is also a more elaborate costlier test.

Cottenier Delta test

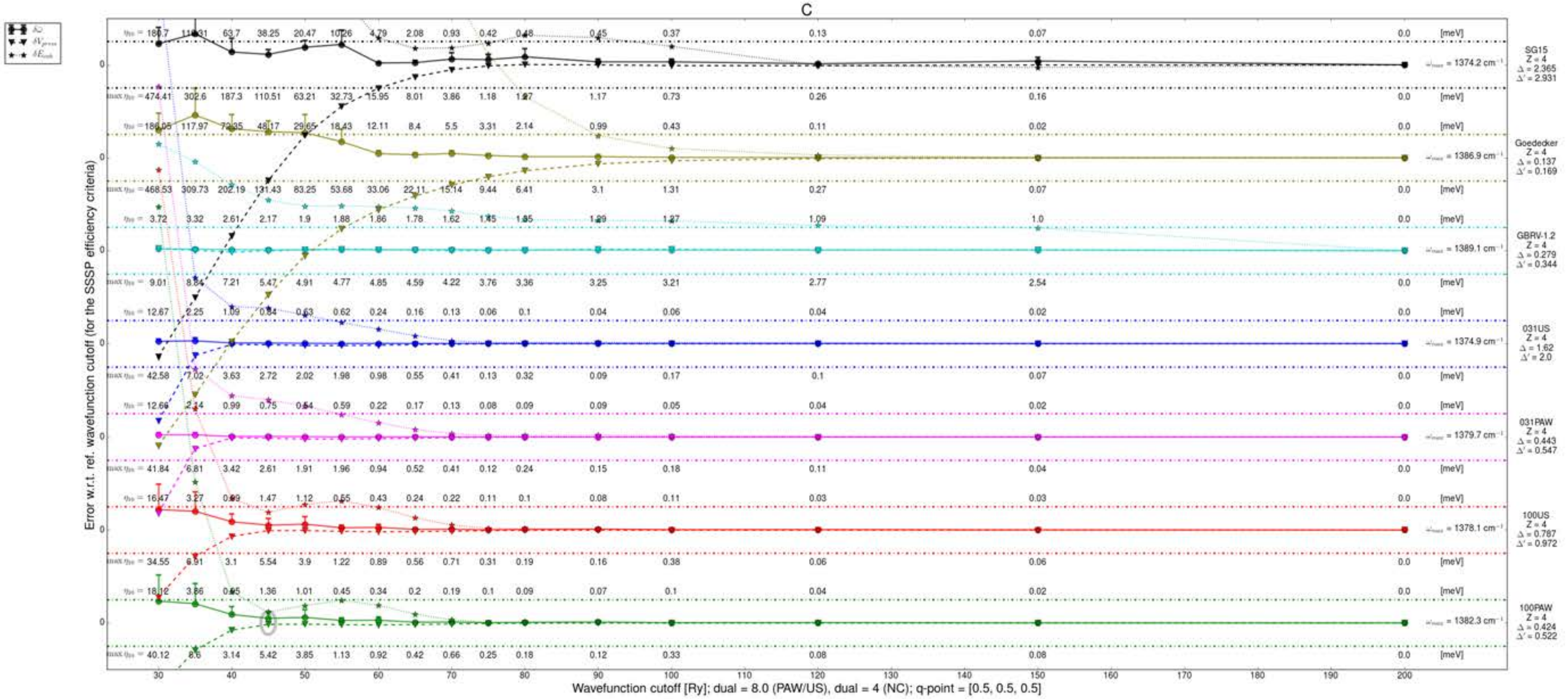


Science 351, aad3000 (2016)



			AE						
		average <Δ>	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3
USPP	GBRV14/CASTEP	1.1	1.1	1.1	1.0	1.0	1.4	1.3	1.0
	GBRV14/QE	1.1	1.0	1.0	0.9	1.0	1.4	1.3	1.0
	OTFG9/CASTEP	0.7	0.4	0.5	0.5	0.7	1.0	1.0	0.5
	SSSP/QE	0.5	0.4	0.3	0.3	0.5	0.9	0.8	0.3
	Vdb2/DACAPO	6.3	6.3	6.3	6.3	6.3	6.4	6.5	6.2
NCPP	FHI98pp/ABINIT	13.3	13.5	13.4	13.4	13.2	13.0	13.2	13.4
	HGH/ABINIT	2.2	2.2	2.2	2.2	2.0	2.3	2.2	2.1
	HGH-NLCC/BigDFT	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.0
	MBK2013/OpenMX	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0
	ONCVPSP(PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
	ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
	ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

https://www.materialscloud.org/sssp



The plane waves basis set

- Systematic improvement of completeness/resolution
- Huge number of basis elements – only possible because of pseudopotentials
- Allows for easy evaluation of gradients and Laplacian
- Kinetic energy in reciprocal space, potential in real space
- Basis set does not depend on atomic positions: there are no Pulay terms in the forces

To learn more:

- Feliciano Giustino (OUP) or Richard Martin (CUP) electronic-structure books. Readings on Moodle.

- 2005 MIT Class on Atomistic Modeling of Materials
  https://ocw.mit.edu/3-320S05
- 2009 ICMR Summer School on Materials Modelling and 2017 ICTP HPC and high-throughput materials modeling
  http://materialscloud.org/learn

QUESTIONS?