

# Lecture on First-principles Computations (10): Pseudopotential Plane-Wave Method

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# Solving the Kohn-Sham equation iteratively

$$n_{in}(\mathbf{r}) = n_{trial}(\mathbf{r})$$

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left( -\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

$$n_{out}(\mathbf{r}) = \sum_{l=1}^N |\phi_l(\mathbf{r})|^2$$

$$n_{out}(\mathbf{r}) = n_{in}(\mathbf{r})?$$

yes

exit

no

$$n_{in}^{new} = \alpha n_{out} + (1 - \alpha) n_{in}$$

Simple linear mixing here;  
More sophisticated mixing scheme exists.

# Single-particle Schrödinger equation in a periodic potential

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The key is to solve the single-particle Schrödinger Eq.

$$\left( -\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

Consider a periodic potential:  $V_{eff}(\mathbf{r}) = V_{eff}(\mathbf{r} + \mathbf{R})$

The eigenstates are Bloch orbitals

$$\left( -\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \phi_{l\mathbf{k}}(\mathbf{r}) = \epsilon_{l\mathbf{k}} \phi_{l\mathbf{k}}(\mathbf{r})$$

$$\phi_{l\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \phi_{l\mathbf{k}}(\mathbf{r})$$

# Plane waves as basis functions

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$$\left( -\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \phi_{l\mathbf{k}}(\mathbf{r}) = \epsilon_{l\mathbf{k}} \phi_{l\mathbf{k}}(\mathbf{r})$$

Plane waves:  $|\mathbf{p}\rangle = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{p}\cdot\mathbf{r}}, \langle \mathbf{p} | \mathbf{p}' \rangle = \delta_{\mathbf{p}\mathbf{p}'}$

$$\left( -\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

$$\phi_{l\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{l,\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad V_{eff}(\mathbf{r}) = \sum_{\mathbf{G}} V_{eff}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

The Hamiltonian matrix:

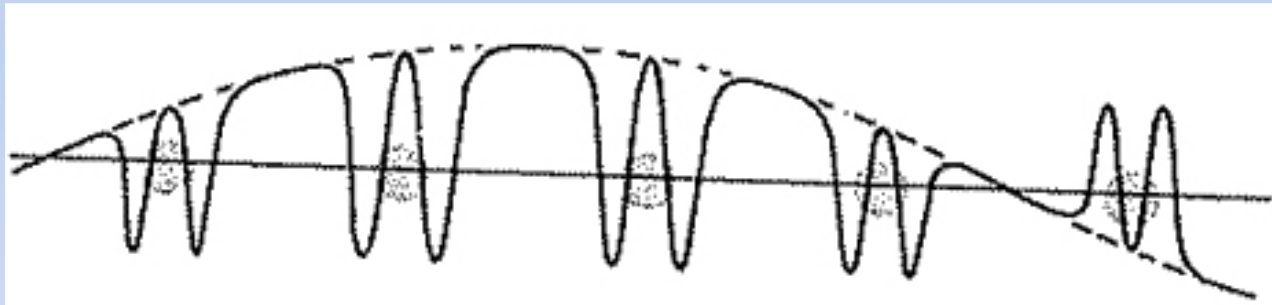
$$\langle \mathbf{k} + \mathbf{G} | -\frac{\nabla^2}{2m} + V_{eff} | \mathbf{k} + \mathbf{G}' \rangle = \frac{(\mathbf{k} + \mathbf{G})^2}{2m} \delta_{\mathbf{G}\mathbf{G}'} + V_{eff}(\mathbf{G} - \mathbf{G}')$$

# Problem: the wave functions oscillates strongly around the nuclei

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## Observation:

Due to the presence of core electrons, **the valence electron wave function oscillates strongly near the nuclei** (and orthogonalized to the core electrons).



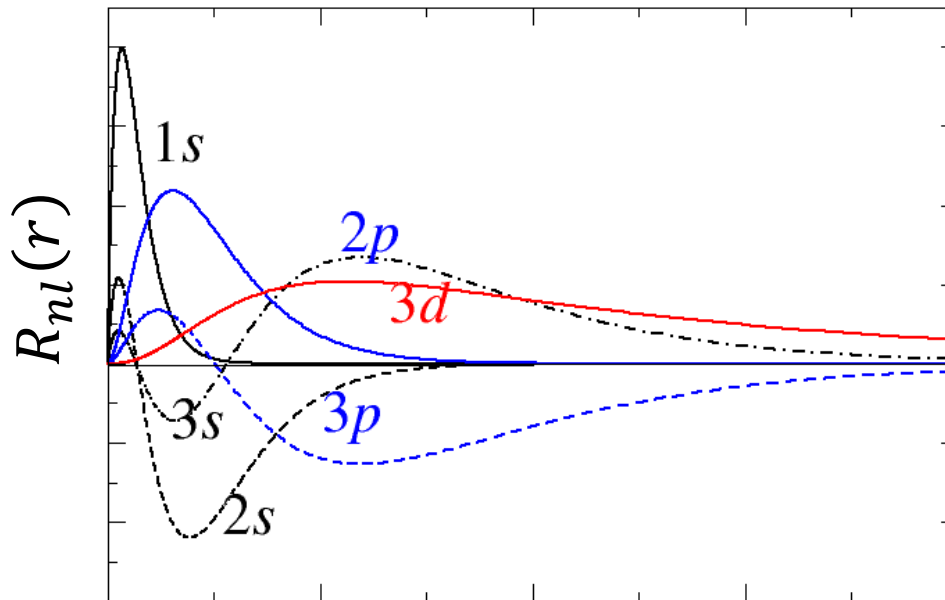
## Consequence:

**Prohibitively large amount of plane waves are needed to represent the wave function, (for heavy elements) not practical!**

# Consider a spherical atom ...

$$\left( -\frac{\nabla^2}{2m} - \frac{Z}{r} + V_{Hxc}(r) \right) \phi_{nlm}(\mathbf{r}) = \epsilon_{nl} \phi_{nlm}(\mathbf{r})$$

$$\phi_{nlm}(\mathbf{r}) = \frac{R_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$



# Orthogonalized plane wave (OPW) method

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Herring (1940)

$$\chi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \left[ e^{i\mathbf{p}\cdot\mathbf{r}} - \sum_j \langle u_j | \mathbf{p} \rangle u_j(\mathbf{r}) \right]$$

$$\langle u_j | p \rangle = \frac{1}{\sqrt{\Omega}} \int d\mathbf{r} u_j(\mathbf{r}) e^{i\mathbf{p}\cdot\mathbf{r}}, \quad \langle u_j | u_{j'} \rangle = \delta_{jj'}$$

$$\langle \chi_p | \chi_p \rangle = 1 - \sum_j |\langle u_j | p \rangle|^2$$

Using  $\chi_p(\mathbf{r})$  to expand the valence eigenfunctions of the atoms, the required number of basis functions can be significantly reduced. The local orbitals  $u_j(\mathbf{r})$  are usually chosen as the core orbitals of the atom.

# Applying the OPW method to atoms

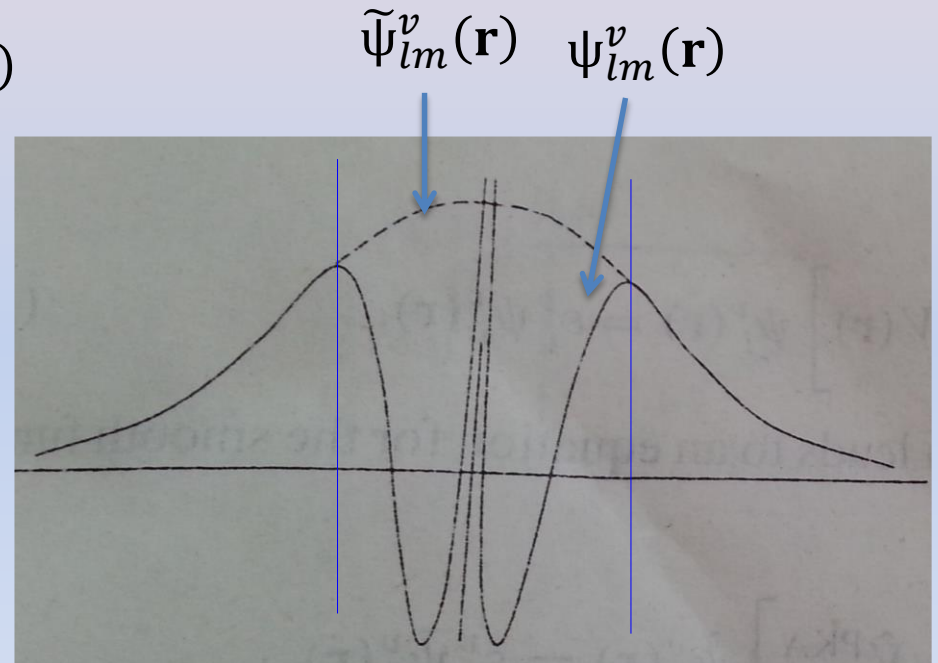
Expressing the valence states of the atom as:

$$\psi_{lm}^v(\mathbf{r}) = \tilde{\Psi}_{lm}^v(\mathbf{r}) + \sum_j b_{lmj} u_{lmj}(\mathbf{r})$$

$$\psi_{lm}^v(\mathbf{r}) = \int d\mathbf{p} c_{lm}(\mathbf{p}) \chi_{\mathbf{p}}(\mathbf{r})$$

$$\tilde{\Psi}_{lm}^v(\mathbf{r}) = \int d\mathbf{p} c_{lm}(\mathbf{p}) e^{i\mathbf{p}\cdot\mathbf{r}}$$

$$b_{lmj} = \int d\mathbf{p} c_{lm}(\mathbf{p}) \langle u_j | \mathbf{p} \rangle$$



The true physical valence wave function is split into a smooth part plus a local oscillating part.



# The PKA (Phillips & Kleinman, Antoncik) transform

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Choose the core states as the projector function  $u_{lmj}(\mathbf{r})$

$$u_{lmj}(\mathbf{r}) = \psi_{lmj}^c(\mathbf{r}), \quad \hat{H}\psi_{lmj}^c(\mathbf{r}) = \epsilon_{lj}^c \psi_{lmj}^c(\mathbf{r})$$

Inserting  $\psi_{lm}^v(\mathbf{r}) = \tilde{\Psi}_{lm}^v(\mathbf{r}) + \sum_j b_{lmj} \psi_{lmj}^c(\mathbf{r})$

$$\left( -\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \psi_{lm}^v(\mathbf{r}) = \epsilon_l^v \psi_{lm}^v(\mathbf{r})$$



$$\left( -\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) + \hat{V}^R \right) \tilde{\Psi}_{lm}^v(\mathbf{r}) = \epsilon_l^v \tilde{\Psi}_{lm}^v(\mathbf{r})$$

$$\hat{V}^R \tilde{\Psi}_{lm}^v(\mathbf{r}) = \sum_j (\epsilon_{lj}^c - \epsilon_l^v) b_{lmj} \psi_{lmj}^c(\mathbf{r}), \quad b_{lmj} = \langle \psi_{lmj}^c | \tilde{\Psi}_{lm}^v \rangle$$

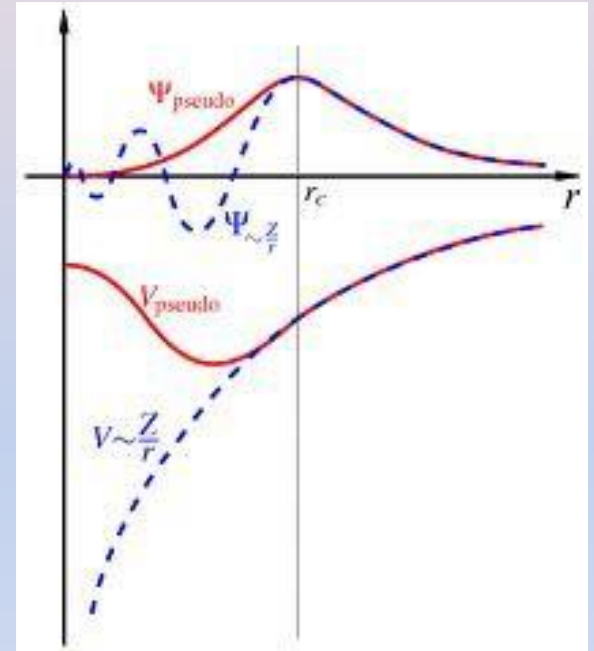
# The concept of pseudopotential

$$\hat{V}^{\text{PKA}} = \hat{V}_{\text{eff}} + \hat{V}^R$$

## The cancellation theorem:

$\hat{V}^R$  is repulsive and cancels the  $-Z/r$  part in  $\hat{V}_{\text{eff}}$  close to the nucleus.  $\hat{V}^{\text{PKA}}$  is much weaker than  $\hat{V}_{\text{eff}}$ .

$\hat{V}^{\text{PKA}}$  is not very smooth, and can be replaced by much simpler “model pseudopotentials”.



Pseudopotential is not unique!

# Advantage of the pseudopotential approach

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- In contrast to the PKA approach, the pseudopotential can be chosen at will, and does not depend on the pseudowavefunctions. Hence the pseudofunctions can be made orthonormal to each other.

$$\langle \tilde{\Psi}_i^{PS} | \tilde{\Psi}_j^{PS} \rangle = \delta_{ij}$$

- By doing ab initio calculations on atoms, and imposing conditions like “norm-conservation”, one can get highly accurate, transferable pseudopotentials that can be used in other chemical environments (molecules, solids, ...)

# Requirement for “good” pseudopotentials

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Hamann, Schluter, Chiang (1979)

- [1.] All-electron and pseudo valence eigenvalues agree for the chosen atomic reference configuration.
- [2.] All-electron and pseudo valence wavefunctions agree beyond a chosen core radius  $R_c$ .
- [3.] The logarithmic derivatives of the all-electron and pseudo wavefunctions agree at  $R_c$ .
- [4.] The integrated charge inside  $R_c$  for each wavefunctions agrees (**norm-conservation**).
- [5.] **The energy derivatives of the logarithmic derivatives** of the all-electron and pseudo wavefunction agree at  $R_c$ .

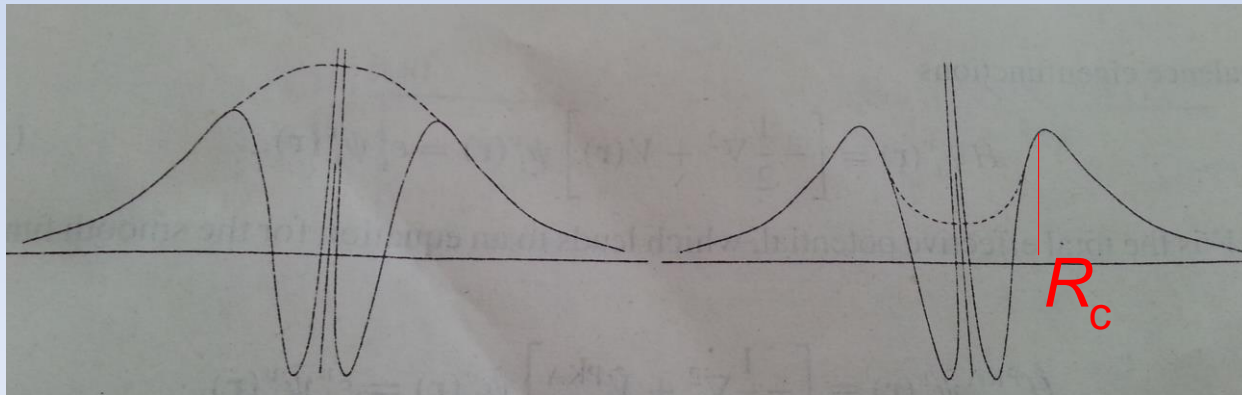
# Requirement for “good” pseudopotentials

Logarithmic derivative:

$$D_l(\epsilon, r) = \frac{r\psi'_l(\epsilon, r)}{\psi_l(\epsilon, r)} = r \frac{d}{dr} \ln \psi_l(\epsilon, r)$$

Norm conservation:  $Q_l = \int_0^{R_c} dr r^2 |\psi_l^{PS}(\mathbf{r})|^2 = \int_0^{R_c} dr r^2 |\psi_l^{AE}(\mathbf{r})|^2$

$\rightarrow \left[ \frac{dD_l^{PS}(\epsilon, r)}{d\epsilon} \right]_{R_c} = \left[ \frac{dD_l^{AE}(\epsilon, r)}{d\epsilon} \right]_{R_c}$  (Important for transferability !)



# $L$ -dependent norm-conserving pseudopotential

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- Do all-electron atomic calculations at a given configuration, obtain the all-electron (AE) wave function  $\psi_l^{AE}(r)$ .
- Construct pseudopotential and wave function  $\tilde{V}_l(r), \tilde{\psi}_l^{PS}(r)$  to reproduce  $\psi_l^{AE}$  beyond  $R_c$ .
- Unscreening:  $V_l^{\text{Ion}}(r) = \tilde{V}_l(r) - V_{\text{Hxc}}^{\text{PS}}(r)$

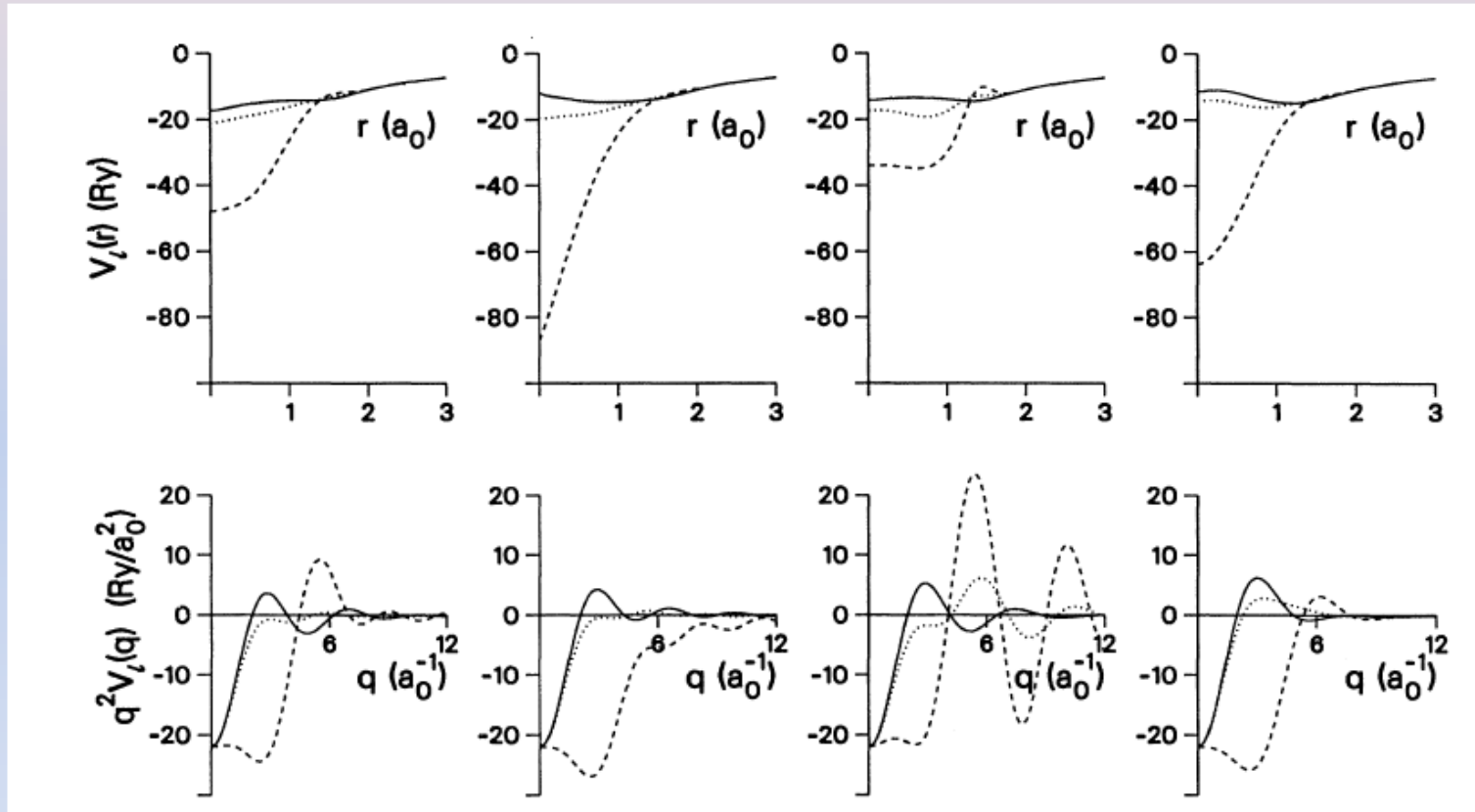


Pseudopotential due to valence electrons

- Semilocal form (SL):  $V_l^{\text{Ion}}(r) = V_{\text{local}}(r) + \delta V_l(r)$

$$\hat{V}_{SL} = V_{\text{local}}(r) + \sum_{lm} |Y_{lm}\rangle \delta V_l(r) \langle Y_{lm}|$$

# Different pseudopotentials exist ...



Troullier-Martins

Kerker

HSC

Vanderbilt

# Separable pseudopotential operators

$$\hat{V}_{SL} = V_{local}(r) + \sum_{lm} |Y_{lm}\rangle \delta V_l(r) \langle Y_{lm}|$$

Computationally inefficient!

➔ Nonlocal (NL) separable potential

Reference  
atomic pseudofunction

$$\hat{V}_{NL} = V_{local}(r) + \sum_{lm} \frac{|\psi_{lm}^{PS} \delta V_l\rangle \langle \delta V_l \psi_{lm}^{PS}|}{\langle \psi_{lm}^{PS} | \delta V_l | \psi_{lm}^{PS} \rangle}$$

$$\langle \psi_i | \delta \hat{V}_{NL} | \psi_j \rangle = \sum_{lm} \frac{\langle \psi_i | \psi_{lm}^{PS} \delta V_l \rangle \langle \delta V_l \psi_{lm}^{PS} | \psi_j \rangle}{\langle \psi_{lm}^{PS} | \delta V_l | \psi_{lm}^{PS} \rangle}$$

Kleinman & Bylander (1982)

The coupling between  $\psi_i, \psi_j$  are removed;

three-center integrals become two-center integrals !



# Calculations with plane-wave basis sets

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- Plane waves are the most natural basis for periodic systems

$$\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}=0}^{G_{cut}} c_{n,\mathbf{G}}(\mathbf{k}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

kinetic energy of plane waves:

$$E^{kin} = -\frac{\hbar^2 \nabla^2}{2m} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m}$$

$$E_{cut}^{kin} = \hbar^2 \frac{|\mathbf{k} + \mathbf{G}_{cut}|^2}{2m}$$

The energy cutoff in plane-wave expansion determines the resolution that the wave function in the unit cell can be described.

# The Hamiltonian matrix within plane basis

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The Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2 \nabla^2}{2m} + \hat{V}_{local}^{Ion} + \hat{V}_{NL}^{Ion} + \hat{V}_H + \hat{V}_{xc} = -\frac{\hbar^2 \nabla^2}{2m} + \hat{V}_{local} + \hat{V}_{NL}^{Ion} + \hat{V}_H$$

The Hamiltonian matrix:

$$\langle \mathbf{k} + \mathbf{G} | \hat{H} | \mathbf{k} + \mathbf{G}' \rangle = \frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m} \delta_{\mathbf{G}, \mathbf{G}'} + V_{local}(\mathbf{G} - \mathbf{G}') + \frac{4\pi n(\mathbf{G} - \mathbf{G}')}{|\mathbf{G} - \mathbf{G}'|^2} + V_{\mathbf{G}, \mathbf{G}'}^{NL}(\mathbf{k})$$

$$V_{local}(\mathbf{G}) = \frac{1}{\sqrt{\Omega}} \int d\mathbf{r} V_{local}(\mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$n(\mathbf{G}) = \frac{1}{\sqrt{\Omega}} \int d\mathbf{r} n(\mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$V_{\mathbf{G}, \mathbf{G}'}^{NL}(\mathbf{k}) = \sum_{a, l, m} \langle \mathbf{k} + \mathbf{G} | p_{alm} \rangle V_{alm} \langle p_{alm} | \mathbf{k} + \mathbf{G}' \rangle$$

 Projector function

# Solving the Hamiltonian

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Even under the pseudopotential approximation, the number of plane waves are very many (a few hundreds per atom).

$$H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \langle \mathbf{k} + \mathbf{G} | \hat{H} | \mathbf{k} + \mathbf{G}' \rangle$$

The Hamiltonian matrix is a big matrix, and a full diagonalization of the matrix is not practical. The standard way to solve the Hamiltonian is **iterative diagonalization**.

Standard algorithms for iterative diagonalization include:

- Davidson algorithm
- Conjugate gradient method

# Computer codes

- Ab-initio

<http://www.abinit.org/>

- Quantum Espresso

<http://www.quantum-espresso.org/>