SPRING COLLEGE ON
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY

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"The plane-wave pseudo-potential method"
(PW - I)

presented by:

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Outline of lesson 1:

- extended periodic systems (crystals): direct and reciprocal lattice, unit cell, Brillouin Zone
- the plane waves basis set
- localized basis sets versus plane waves
- the concept of pseudopotential
- empirical pseudopotentials (Cohen-Bergstresser)
- less-empirical pseudopotentials (Appelbaum-Hamann)

We are going to deal with *infinite perfect crystals*, having translation symmetry. A perfect crystal is described in terms of

- a **unit cell** that is periodically repeated
- a **basis** of atomic positions $\mathbf{d}_i$ in the unit cell
- a **lattice** of translational vectors $\mathbf{R} = n_1\mathbf{R}_1 + n_2\mathbf{R}_2 + n_3\mathbf{R}_3$
- a **reciprocal lattice** of vectors $\mathbf{G}$ such that $\mathbf{G} \cdot \mathbf{R} = 2\pi l$, with l an integer. Such conditions hold if $\mathbf{G} = m_1\mathbf{G}_1 + m_2\mathbf{G}_2 + m_3\mathbf{G}_3$ with $\mathbf{G}_i \cdot \mathbf{R}_j = 2\pi\delta_{ij}$.

The one-electron states $\psi(\mathbf{r})$ of a perfect crystal Hamiltonian $H = T + V$ are described by a **band index** i and a **wave vector** $\mathbf{k}$.

It is convenient to consider the *thermodynamic limit*: a slab of crystal composed of $N = N_1 N_2 N_3$ unit cells, $N \to \infty$, obeying Periodic Boundary Conditions:

$$\psi(\mathbf{r} + N_1 \mathbf{R}_1) = \psi(\mathbf{r} + N_2 \mathbf{R}_2) = \psi(\mathbf{r} + N_3 \mathbf{R}_3) = \psi(\mathbf{r}).$$

There are N wave vectors $\mathbf{k}$ in the unit cell for the reciprocal lattice, called the **Brillouin Zone** (BZ). The one-electron states (energy bands) can be written as

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

where $u_{\mathbf{k}}(\mathbf{r})$ is translationally invariant:

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$$

How to solve $H\psi = \epsilon\psi$?

Expand ψ in some suitable basis set $\{\phi_i\}$ as

$$\psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r}).$$

For an orthonormal basis set, solve

$$\sum_j (H_{ij} - \epsilon\delta_{ij})c_j = 0$$

where the *matrix elements* $H_{ij} = \langle\phi_i|H|\phi_j\rangle$. For a non-orthonormal basis set, solve:

$$\sum_j (H_{ij} - \epsilon S_{ij})c_j$$

where $S_{ij} = \langle\phi_i|\phi_j\rangle$ (*overlap matrix*).

Most popular basis sets:

- **Localized** basis sets: Bloch sums of atomic-like wavefunctions centered on atoms
    - Linear Combinations of Atomic Orbitals (LCAO)
    - Gaussian-type Orbitals (GTO)
    - Linearized Muffin-Tin Orbitals (LMTO)
- **Delocalized** basis sets:
    - Plane Waves (PW)
- **Mixed** basis sets:
    - Linearized Augmented Plane Waves (LAPW)
    - Projector Augmented Plane Waves (PAW)

Bloch sum:

$$\phi_{\mathbf{k}} = \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{r} - \mathbf{R})$$

PW basis set

A PW basis set for states of vector $\mathbf{k}$ is defined as

$$\langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle = \frac{1}{\sqrt{N\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \qquad \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \leq E_{cut}$$

Ω is the unit cell volume, $N\Omega$ the crystal volume, E_{cut} is a cutoff on the kinetic energy of PW.

The PW basis set is *orthonormal*:

$$\langle \mathbf{k} + \mathbf{G} | \mathbf{k} + \mathbf{G}' \rangle = \delta_{\mathbf{G}\mathbf{G}'}$$

and *complete* for $E_{cut} \rightarrow \infty$.

The components on a PW basis set are the *Fourier transform*:

$$|\psi\rangle = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} |\mathbf{k} + \mathbf{G}\rangle$$

$$c_{\mathbf{k}+\mathbf{G}} = \langle \mathbf{k} + \mathbf{G} | \psi \rangle = \frac{1}{\sqrt{N\Omega}} \int \psi(\mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} d\mathbf{r} = \widetilde{\psi}(\mathbf{k} + \mathbf{G}).$$

Advantages and disadvantages of various basis sets

- Localized basis sets:
  - + fast convergence with respect to basis set size (just a few functions per atom needed)
  - − difficult to evaluate convergence quality (no systematic way to improve convergence)
  - − difficult to use (two- and three-center integrals)
  - − difficult to calculate forces (*Pulay forces*)

- Plane Waves:
  - − slow convergence with respect to basis set size (many more PW than localized functions needed)
  - + easy to evaluate convergence quality (just increase cutoff)
  - + easy to use (Fourier transform)
  - + easy to calculate forces (no Pulay forces)

Are PW a practical basis set for electronic structure calculations? Not really!

From elementary Fourier analysis: length scale $\delta \longrightarrow$ Fourier components up to $q \sim 2\pi/\delta$. In a solid, this means $\sim 4\pi(2\pi/\delta)^3/3\Omega_{BZ}$ PW (Ω_{BZ} = volume of the BZ).
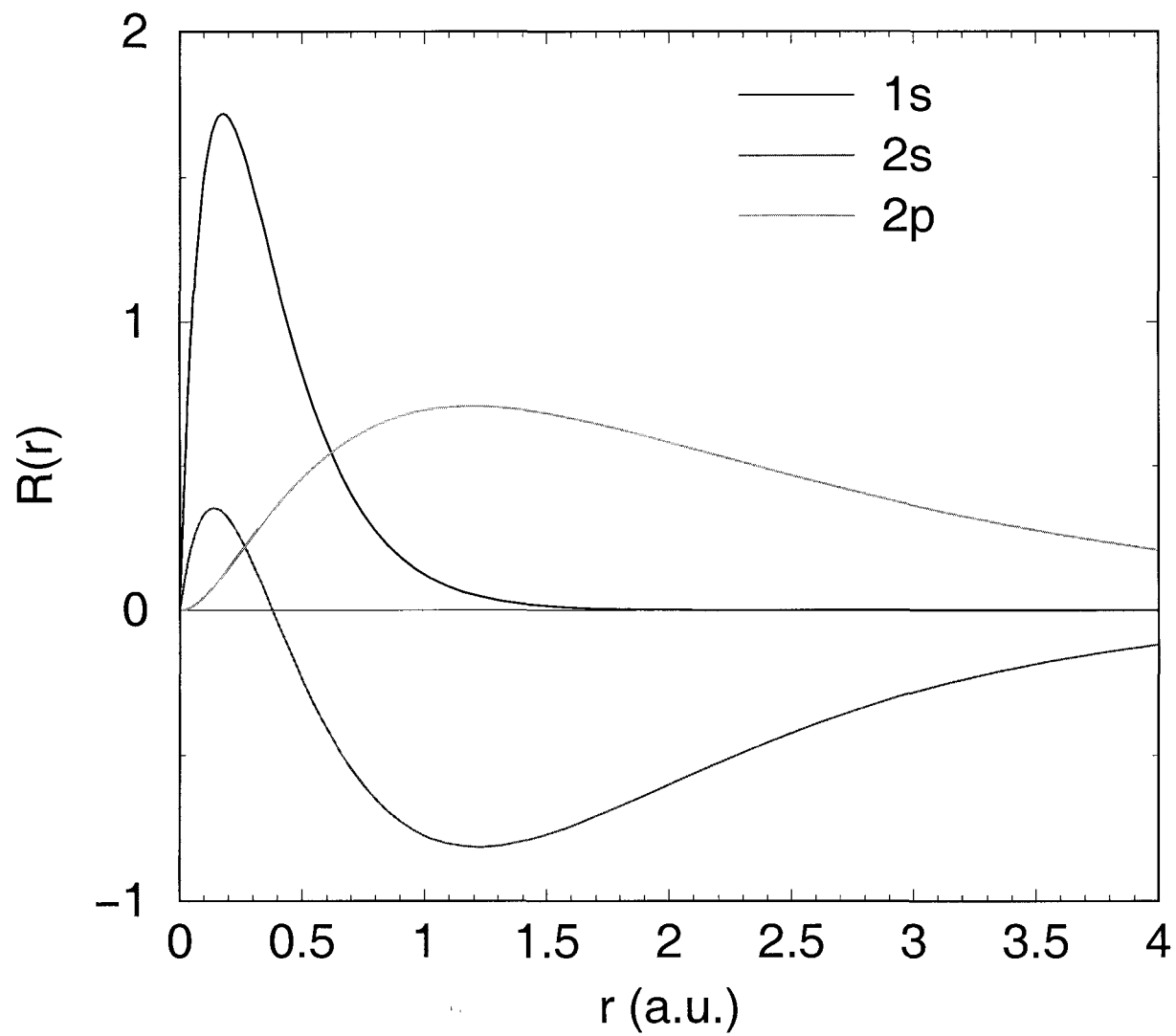
Estimate for diamond: $1s$ wavefunction has $\delta \simeq 0.1$ a.u., $\Omega = (2\pi)^3/(a_0^3/4)$ with lattice parameter $a_0 = 6.74$ a.u. $\longrightarrow 250,000$ PW!

Need to:

- get rid of core states
- get rid of orthogonality wiggles close to the nucleus

Solution: **Pseudopotentials**

C 1s2 2s2 2p2

Pseudopotential (PP): a smooth effective potential that reproduces the effect of the nucleus plus core states on valence states.

Early *empirical* PPs: fitted to some known experimental data (band gaps, ionization potentials, etc.). A classical example: Cohen-Bergstresser PPs for diamond and zincblende semiconductors.

Cohen-Bergstresser PPs are given as a few Fourier components $V(G)$ of the crystal potential for the fcc lattice. The band structure is obtained by diagonalizing $H = T + V$ on a small PW basis set:

$$\langle \mathbf{k} + \mathbf{G} | T + V | \mathbf{k} + \mathbf{G}' \rangle = -\frac{\hbar^2}{2m}(\mathbf{k} + \mathbf{G})^2 \delta_{\mathbf{G}\mathbf{G}'} + \sum_{\mu} S_{\mu}(\mathbf{G} - \mathbf{G}') V_{\mu}(\mathbf{G} - \mathbf{G}')$$

Simple and useful but little more than a parameterization of the band structure.

Kinetic energy in PW:

$$\langle \mathbf{k} + \mathbf{G} | - \frac{\hbar^2 \nabla^2}{2m} | \mathbf{k} + \mathbf{G}' \rangle \quad = \quad -\frac{\hbar^2}{2m} \frac{1}{N\Omega} \int e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \nabla^2 e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} d\mathbf{r}$$

$$= \quad \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2 \delta_{\mathbf{GG}'}$$

Potential energy in PW:

$$V(\mathbf{r}) = \sum_{\mu \in cell} \sum_{\mathbf{R}} V_\mu(\mathbf{r} - \mathbf{d}_\mu - \mathbf{R})$$

$$\langle \mathbf{k} + \mathbf{G} | V | \mathbf{k} + \mathbf{G}' \rangle \quad = \quad \frac{1}{N\Omega} \int e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \sum_{\mu} \sum_{\mathbf{R}} V_\mu(\mathbf{r} - \mathbf{d}_\mu - \mathbf{R}) e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} d\mathbf{r}$$

$$= \quad \sum_{\mu} e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{d}_\mu} \frac{1}{N\Omega} \sum_{\mathbf{R}} \int V_\mu(\mathbf{r} - \mathbf{R}) e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} d\mathbf{r}$$

$$= \quad \sum_{\mu} S_\mu(\mathbf{G} - \mathbf{G}') V_\mu(\mathbf{G} - \mathbf{G}')$$

where $S_\mu(\mathbf{G})$ is the *structure factor*:

$$S_\mu(\mathbf{G}) = \sum_{\mathbf{d}_i \in cell}^{type\ \mu} e^{-i\mathbf{G}\cdot\mathbf{d}_i}$$

containing structural information; $V_\mu(\mathbf{G})$ is the *Fourier transform* of the atomic potential for atom of type μ

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

If the potential has spherical symmetry, $V(\mathbf{r}) = V(r)$, then:

$$V(\mathbf{G}) = V(G) = \frac{4\pi}{\Omega} \int r^2 V(r) \frac{\sin(Gr)}{G} dr.$$

Early *atomic* , *transferrable PPs* for self-consistent calculations: Silicon by Appelbaum and Hamann (1973)

$$V(r) = -e^2 \int \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + (v_1 + v_2 r^2)e^{-\alpha r^2}$$

where:

$$n_0(\mathbf{r}) = Z_v \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} e^{-\alpha r^2}$$

is assumed to be the ionic electron (pseudo) charge-density distribution (Z_v = number of valence electrons). May also be written as

$$V(r) = -Z_v e^2 \frac{\text{erf}(\sqrt{\alpha} r)}{r} + (v_1 + v_2 r^2)e^{-\alpha r^2}$$

Able to reproduce the band structure of crystalline Si, but also useful in other calculations. Still lacking a first-principle derivation.

Fourier transform for Appelbaum-Hamann PP:

$$V(G) = \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} V(r) d\mathbf{r} = -\frac{4\pi Z_v e^2}{\Omega G^2} e^{-\frac{G^2}{4\alpha}} + \frac{1}{\Omega}\left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}}\left[v_1 + \frac{v_2}{\alpha}\left(\frac{3}{2} - \frac{G^2}{4\alpha}\right)\right]e^{-\frac{G^2}{4\alpha}}.$$

The $G = 0$ term is divergent, but its divergence is compensated by the divergence in the Hartree term:

$$\langle \mathbf{k} + \mathbf{G}|V_H|\mathbf{k} + \mathbf{G}'\rangle = \frac{1}{N\Omega} \int e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} V_H(\mathbf{r}) d\mathbf{r} = 4\pi e^2 \frac{n(\mathbf{G})}{G^2}$$

where $n(\mathbf{r})$ is the self-consistent charge,

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

Note that $n(\mathbf{G} = 0) = (\sum Z_v)/\Omega$. Consider the case of one atom per unit cell for simplicity:

$$\lim_{G\to 0}\left(\frac{4\pi Z_v e^2}{\Omega G^2} + V(G)\right) = \frac{\pi e^2 Z_v}{\Omega \alpha} + \frac{1}{\Omega}\left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}}\left(v_1 + \frac{3}{2}\frac{v_2}{\alpha}\right).$$