Calculations of random alloys with GreenALM

Introduction to hands-on workshop

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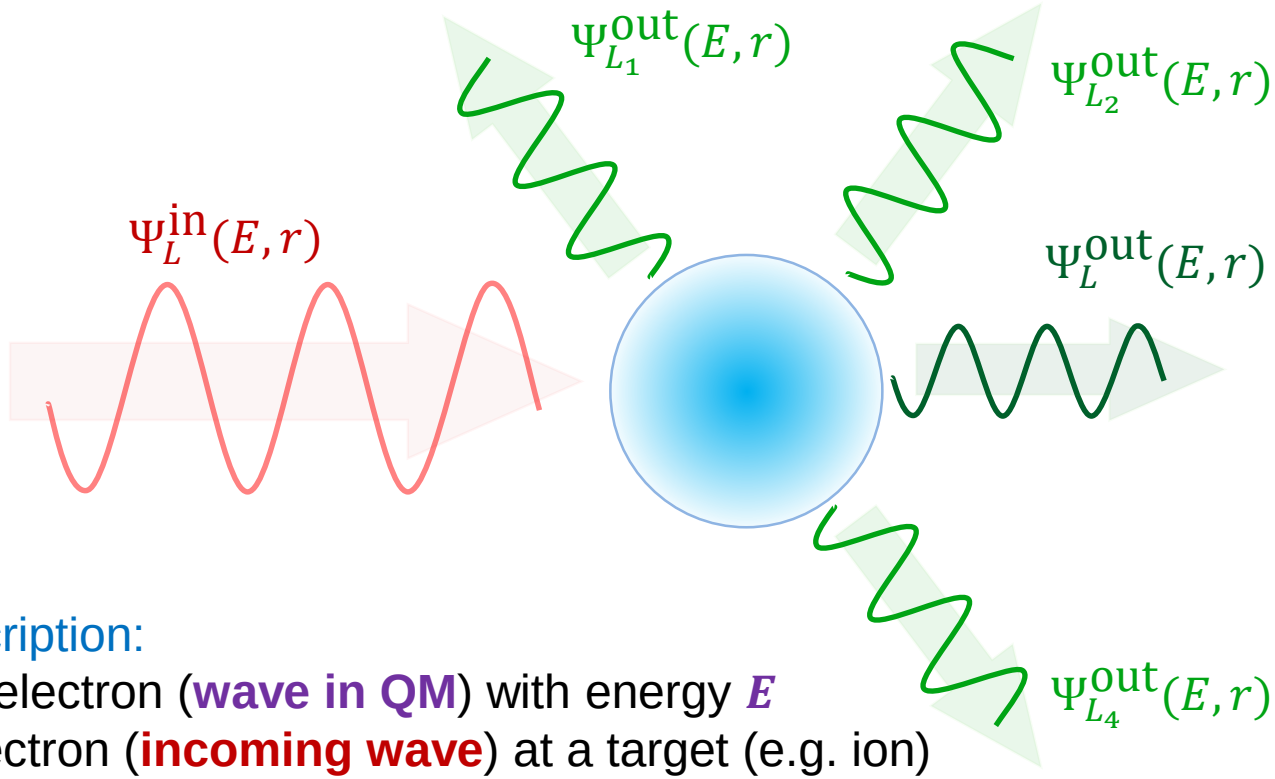
Green's Function-based for alloys

Density Functional Theory (**DFT**)
Kohn-Sham approach → **one-electron** Schrödinger equation (**SE**)

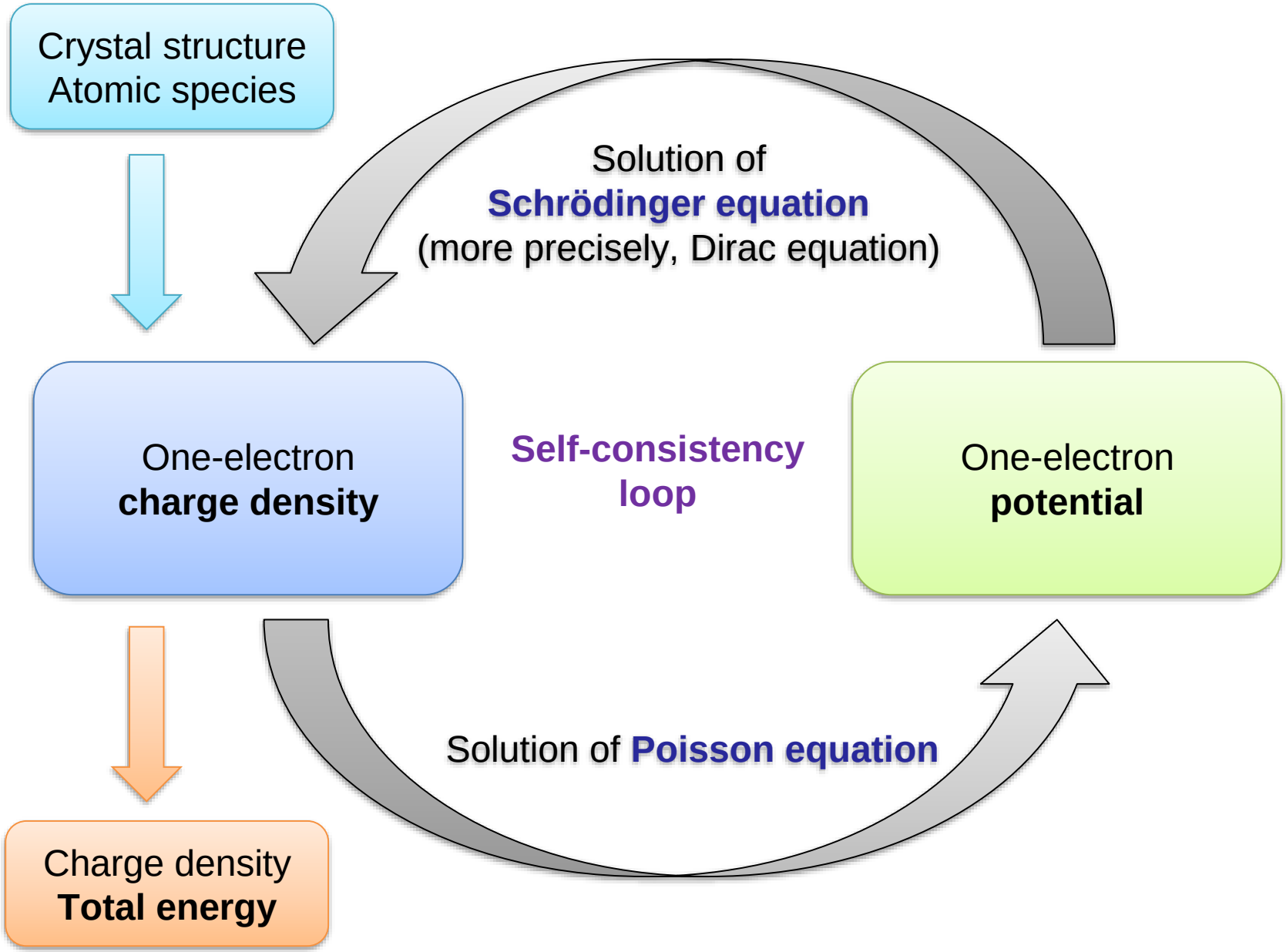


Alternative description:

- Consider an electron (**wave in QM**) with energy ***E***
- Shoot the electron (**incoming wave**) at a target (e.g. ion)
- See how it scatters (**outgoing wave**)
- Moving electron is described by **SE**

Computationally expensive and harder to implement

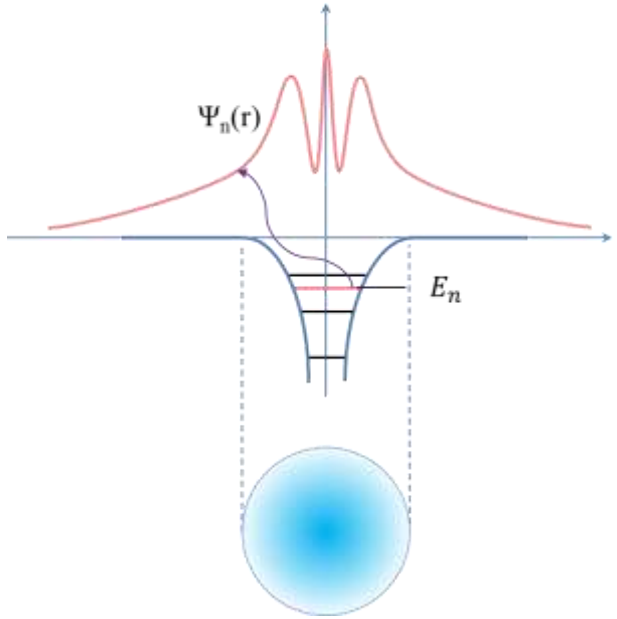
Kohn-Sham scheme in practice



Methods to solve Kohn-Sham equations

Hamiltonian-based:

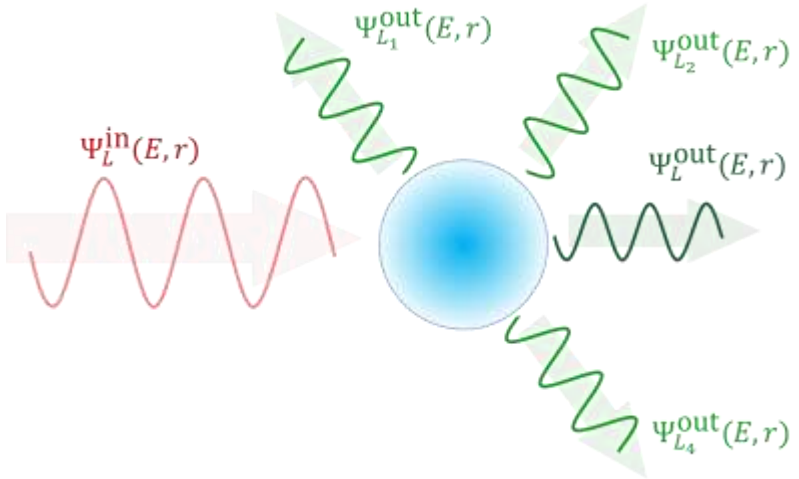
- Energy-independent basis
- Wave-functions
- Describes stationary states



- **Easy** to implement
- Only for **periodic** (or **periodized**) systems

Green's function (**GF**)-based:

- Energy-dependent basis
- Scattering waves (in, out)
- Response to perturbation



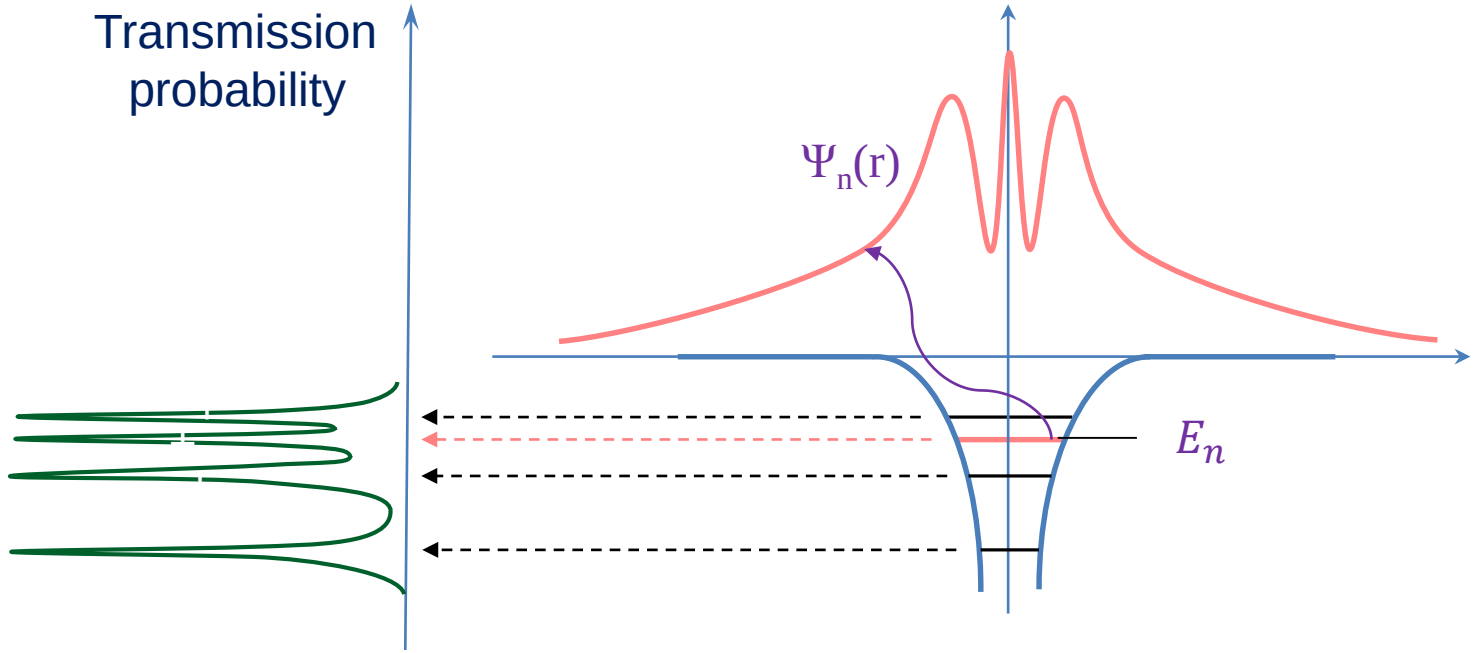
- Heavy: **Difficult** to implement
- **Arbitrary perturbation** on top of a **periodic** system

Connection to Hamiltonian Formalism

Equivalent for simple systems

Green's function based

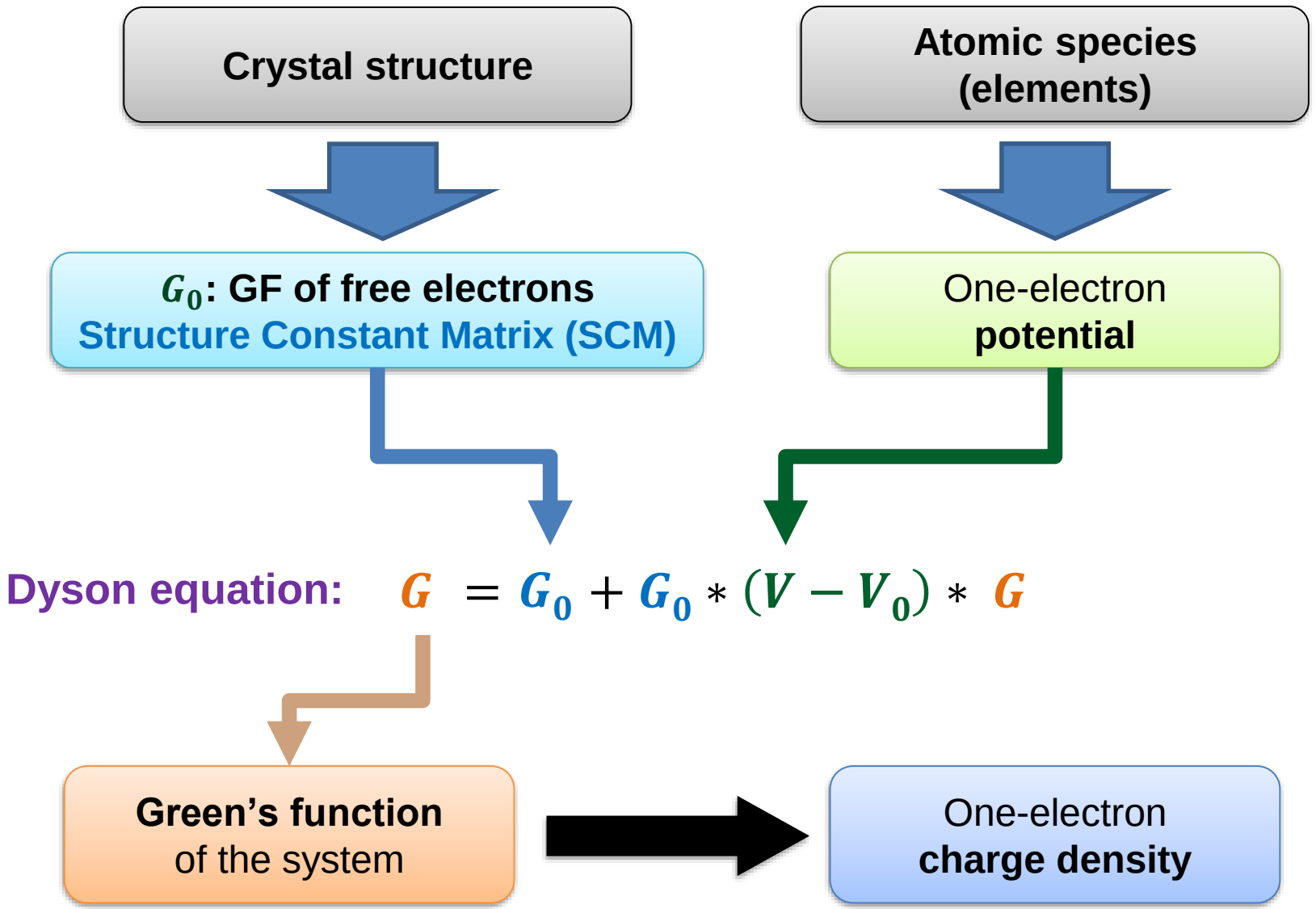
Hamiltonian based



Stationary states Ψ_n appear as **resonances** of **transmission probability** at energies E_n

However, **GF** can describe more **general systems** (e.g. disordered). Examples later

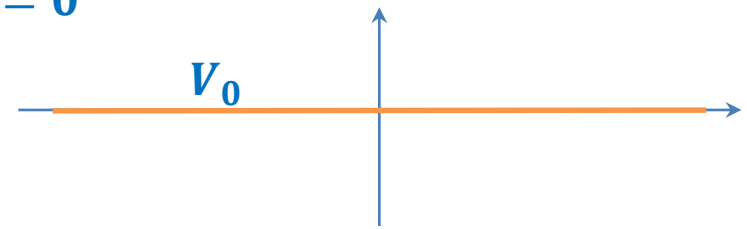
Solution of Schrödinger Equation using GFs



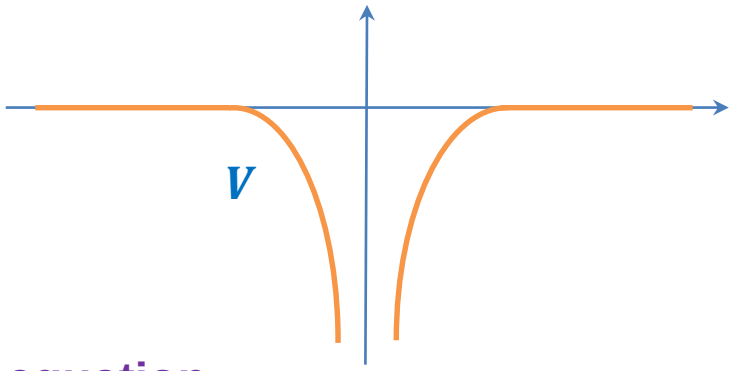
Green's Functions of the Perturbed System

GF approach: describes response to **arbitrary perturbations**

Reference system: e.g. free electrons $V_0 = 0$
GF: G_0 − **easy** to calculate



Perturbed system: e.g. ionic potential V
GF: G − **difficult** to calculate directly



Instead, we can use the **Dyson equation**

$$G = G_0 + G_0 * (V - V_0) * G$$

Nonlinear equation for G: can be solved numerically

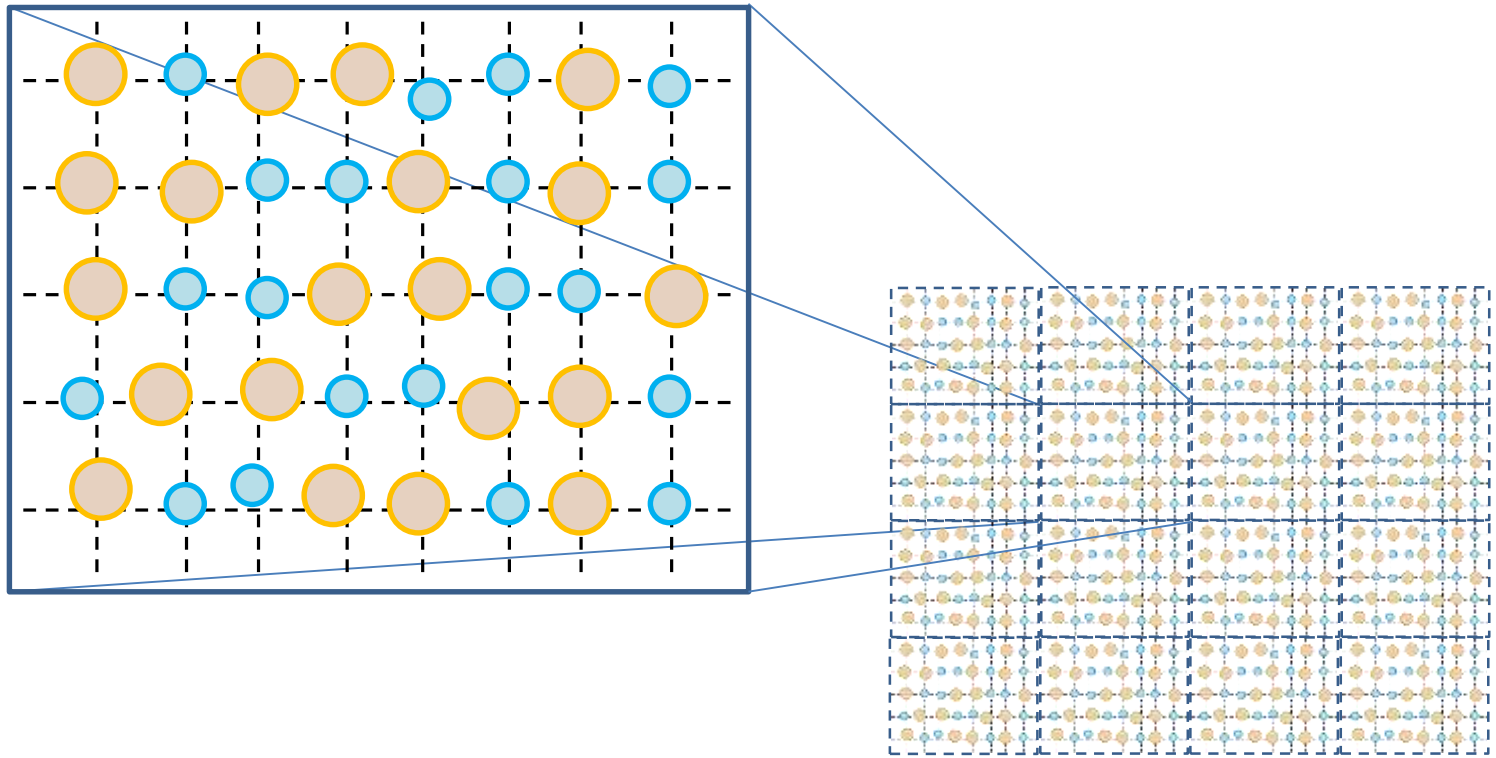
Description of alloys

Four methods available:

- **Conventional supercell** methodology (as used in, say, VASP)
- Coherent potential approximation (**CPA**)
- **Non-local** CPA (**NL-CPA**)
- Locally self-consistent Green's function (**LSGF**)

Supercell Approach to alloy modeling

Periodization: **Supercell** approach



\+ Works both for **Hamiltonian** and **GF** methods

— An **approximation**: E.g., residual resistivity ρ_0 is zero (infinite lifetime)!

What one should know when modeling alloys with supercells

Total energy of a random alloy:

$$E = \sum_P V_P \xi_P \,, P \;-\; \text{clusters (pairs, triangles, etc.)}$$

$$\xi_P = \langle p_i p_j \cdots p_k \rangle_{ijk \in P} - \text{correlation functions}$$

If you model your alloy with a supercell there is an error:

$$\delta E = \sum_P V_P \delta \xi_P \,,$$

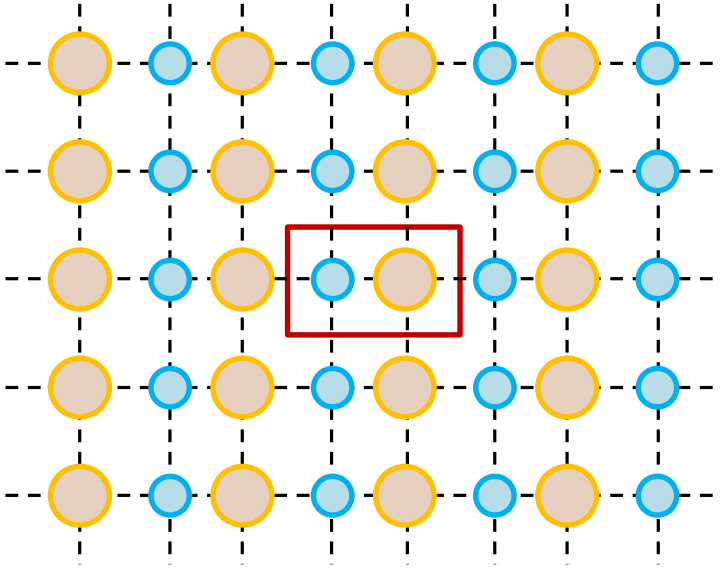
where

$\delta \xi_P$ – deviations of correlation functions

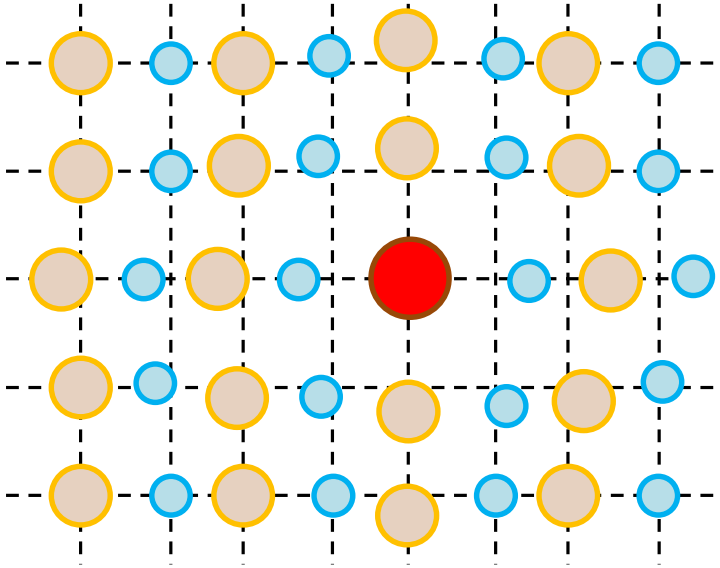
If V_P are large and $\delta \xi_P$ are non-zero, you might get a very large error

Green's function approach to alloy modeling

Reference system: **Periodic (V_0)**
GF G_0 is easy to calculate



Distorted system: consider as **perturbation ΔV**



Solve **Dyson equation** to get G : $G = G_0 + G_0 * \Delta V * G$

\+ Can only be implemented within **GF-based** methodology

\+ If applied to **disordered alloys**: gives **finite ρ_0** (and lifetime)

What to be aware of as a DFT-code user?

Atomic units are used:

- Length: **1 au** ≈ 0.529 Å, **1 Å** $= 10^{-10}$ m
- Energy: **1 Ry** ≈ 13.6 eV, **1 eV** $\approx 1.6 \cdot 10^{-19}$ J

- Know your **cut-offs**:
  - Number of ***k*-points** in the BZ
  - or plane-wave : depends on the **basis set** (see below)
- Which **XC** term to use
- For magnetic systems: Which **magnetic state** to use