

# Quick Review on Quantum Mechanics

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# About Me...

- Education and Work Experience
- Materials Theory and Modeling Group
  - Computational modeling: DFT, TDDFT, MD, Phase field microstructure modeling, machine learning
  - Projects:
    - Molecular quantum materials for quantum information applications
    - Low-dimensional materials for electronic applications
    - Nuclear materials and sensors

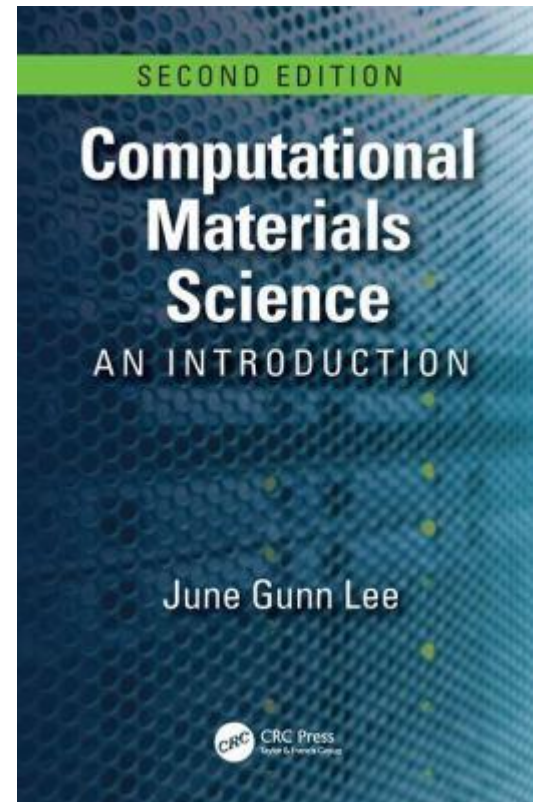
# Learning Outcomes

Understand some key quantum mechanical concepts, such as

- Electrons
- Schrödinger equation
- Hamiltonian  $\hat{H}$
- Energy
- Wave function

Main Textbook:

June Gunn Lee, *Computational Materials Science An Introduction*, CRC Press Taylor & Francis Group, Boca Raton, FL, USA, either 1st or 2nd edition.

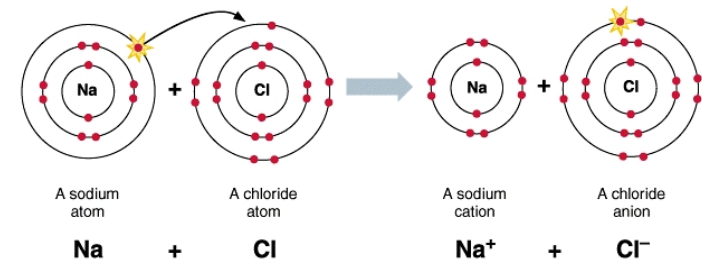
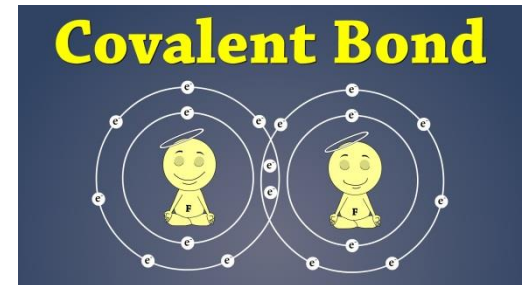
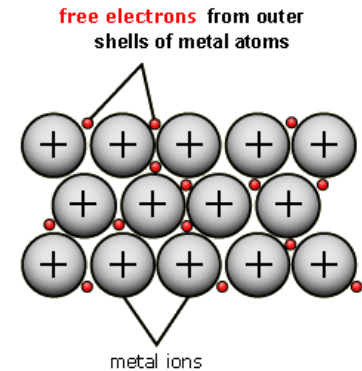


# Why Quantum Mechanics?

- A key controlling factor for the behavior of a material is the type of bonding between atoms, metallic, covalent, ionic etc.

## Metallic? Covalent? Ionic?

- Metallic: A delocalized sea of electrons
- Covalent: Localized electronic distribution between atoms
- Ionic: Strong electrostatic interactions between ions (e.g., electrons transferred from one atom to another)
- A fundamental description of bonding requires a calculation of the electronic distributions.
- Method is called **electronic structure method / first-principles method / *ab-initio* method**.
- Governing law is quantum mechanics.
- Amplify the subatomic phenomena into some form of signal that we can observe macroscopically.
- Nuclei and electrons are treated as point-like particles in terms of mass, charges, positions, etc.



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# Different Computational Modeling Methods

- **Quantum Mechanics (QM)**

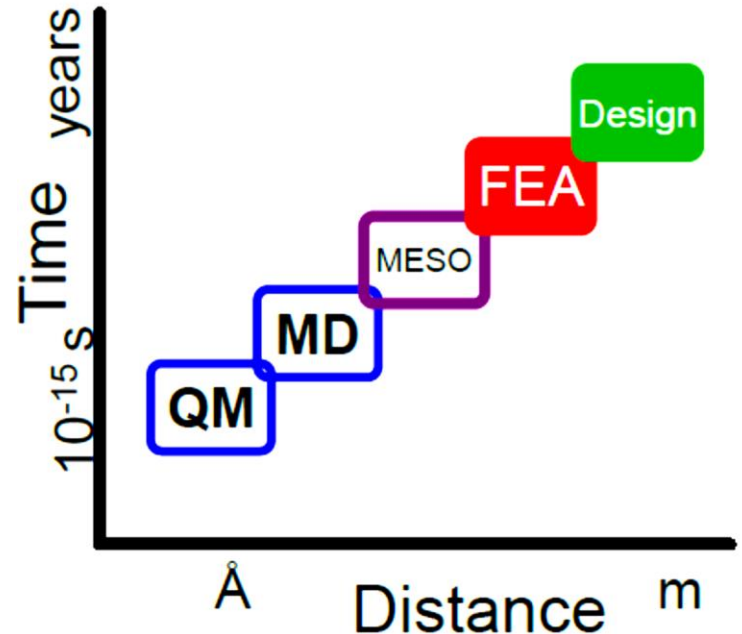
- First-principles quantum simulation
- Electronic degrees of freedom, interactions, bonding, energy estimation
- Schrödinger equation, wave functions

- **Molecular Dynamics (MD)**

- Atomistic modeling
- Forces between the particles and potential energy defined by molecular mechanics force fields.

- **Mesoscale to Continuum**

- Phase field simulation: Thermodynamics-based approach to model phase changes and evolving microstructures in materials
- Finite element approach: Partial differential equation solver for use to simulate structural responses.



# Schrödinger Equation

**Schrödinger equation** - The basis for all quantum mechanical calculations of the electronic structure of a material.

$$\hat{H}\Psi(r_i, r_I, t) = E\Psi(r_i, r_I, t)$$

- Solve the equation for wave function  $\Psi$
- $\hat{H}$ : Hamiltonian operator
- $E$ : System energy
- $r_i$ : Coordinates of the electron
- $r_I$ : Coordinates of the nucleus
- $t$ : Time
- Describe the energy of the electrons and nuclei in a material.

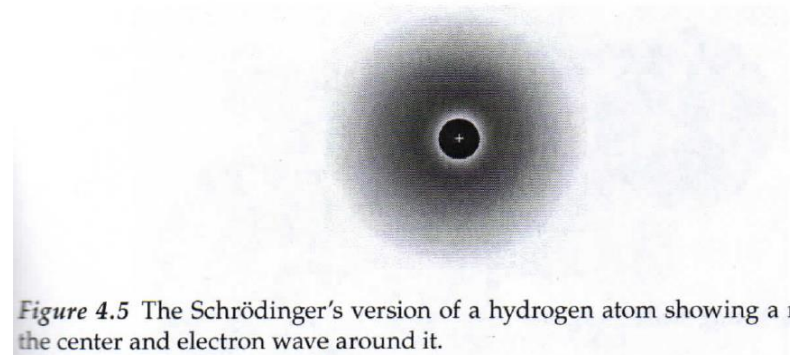


Figure 4.5 The Schrödinger's version of a hydrogen atom showing a nucleus at the center and electron wave around it.

# Simplifying the Problem

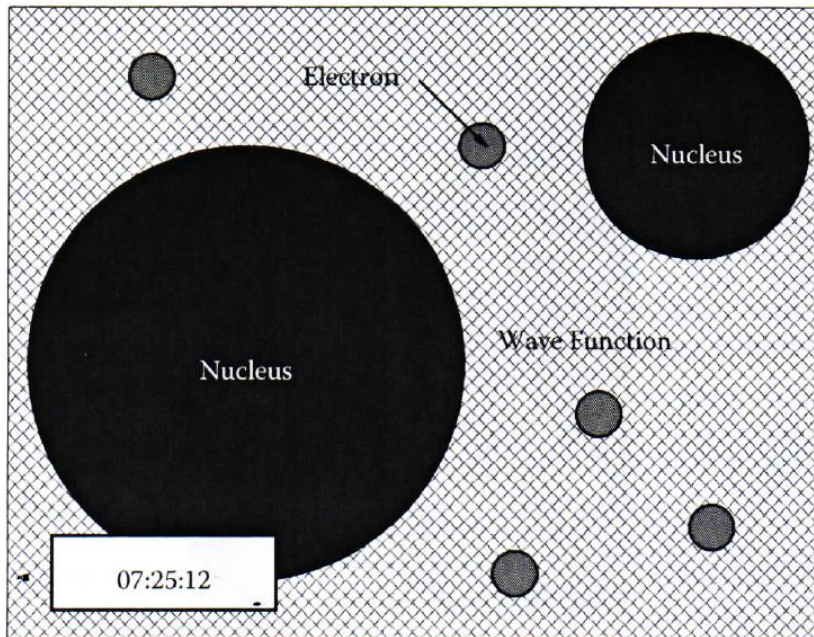


Figure 4.7 Schematic of the Schrödinger model for an  $n$ -electron system.

$$\hat{H}\Psi(r_i, r_I, t) = E\Psi(r_i, r_I, t)$$

- Entities including nuclei, electrons and time variable are active participants in the model **via the wave functions (as fine meshes)**.
- Schrödinger equation can only be solved for one-hydrogen-atom (only one electron) system.
- For other  $n$ -electron systems, too complex!

# Applying Approximations

Forget gravity, relativity and time

Outcomes:

- Electron's mass is too small, and its speed is much slower than that of light.
- Incorporate relativistic effects in the construction of pseudopotentials
- Only consider the ground-state energy of electrons
- Calculate time-independent Schrödinger equation



# Applying Approximations

Forget nuclei and spin, because nuclei are far more massive than electrons.

Outcomes:

- Freeze the positions of nuclei (not variables, but parameters from the electron's view)
- Decouple nuclear and electronic dynamics – Born-Oppenheimer approximation
- Total energy of an atom

$$E_{atom} = E_{nucleus} + E_{electron}$$

- Spin variable can be switched on or off.

# Time-Independent Electronic Wave Equation (i.e., Time-Independent Schrödinger Equation)

Original equation:

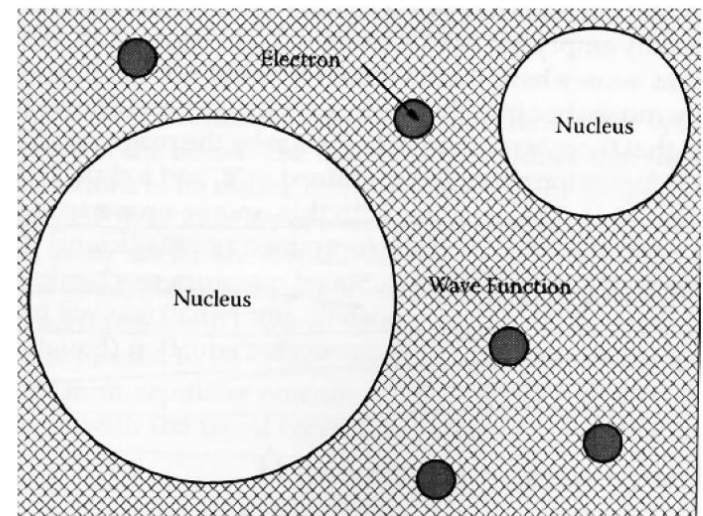
$$\hat{H}\Psi(r_i, r_I, t) = E\Psi(r_i, r_I, t)$$

↓ After the approximations

$$\hat{H}(r) \Psi(r) = E\Psi(r)$$

- $\hat{H}$ : Hamiltonian energy operator
- Wave function  $\Psi$
- $E$ : Total energy of the system
- $r$ : Electronic coordinates

All nuclei are fixed, and the time variable is no longer active.



The Schrödinger model for a n-electron system after the Born-Oppenheimer Approximation. The wave functions are drawn as fine meshes.

# Hamiltonian Energy Operator $\hat{H}$

$$\hat{H}(r) \Psi(r) = E\Psi(r)$$

A sum of all energy terms:

$$\hat{H} = E_I^{kin} + E_i^{kin} + U_{Ii} + U_{ij} + U_{IJ}$$

After Born-Oppenheimer approximation (freeze nuclei):

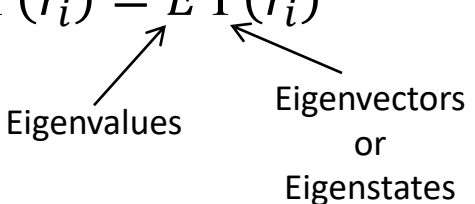
$$\hat{H} = E_i^{kin} + U_{Ii} + U_{ij}$$

- Capital index  $I$  refers to nucleus while lowercase  $i$  is electron

$$\hat{H} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_I^N \sum_i^n \frac{Z_I}{|r_{Ii}|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|}$$

# Electronic Wave Equation (or Schrödinger Equation)

$$\left[ -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_I^N \sum_i^n \frac{Z_I}{|r_{Ii}|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|} \right] \Psi(r_i) = E \Psi(r_i)$$


  
Eigenvalues      Eigenvectors  
                         or  
                         Eigenstates

QM concerns:

- Wavelengths  $\lambda$
- Wave vectors  $k$  (k points in electronic band structure)
- Wave functions of electrons  $\Psi$

Not all wavelike functions can be qualified as a wave function in QM, but only special ones.

- We want the result is a multiple of the original wave function.

# Characteristics of Wave Functions

## ★ How to choose a wavelike function for $\Psi$ ?

- $\Psi$  should be **continuous, square integrable** (due to  $\nabla^2$ ), and **single valued for all coordinates** to fit into the Schrödinger equation.
- The real physical meaning of  $\Psi$  can be realized only when it is **squared as  $|\Psi|^2$** .
- Each  $\Psi$  must be **orthogonal** with other wave functions in a given system to ensure distinct physical states (1s, 2s, 2p...) of its own corresponding to its unique eigenvalue.
- The probability of finding an electron must add up to unity (**normalized**).  
Therefore

$$\int \psi_i \psi_j dr = \begin{cases} 0, & \text{if } i \neq j, \text{ orthogonality} \\ 1, & \text{if } i = j, \text{ normality} \end{cases}$$

- $\Psi$  must be **antisymmetric** with respect to the exchange of any pair of electron coordinates. Pauli's principle: no two electrons of the same spin can occupy the same orbital.

**All info required to define a quantum state is contained in  $\psi_i$**

Solving the Schrödinger equation of the system  $\Rightarrow$  A set of wave functions  $\{\psi_i(r)\}$  as solutions (one solution per each electron  $i$ )

# Plane Wave

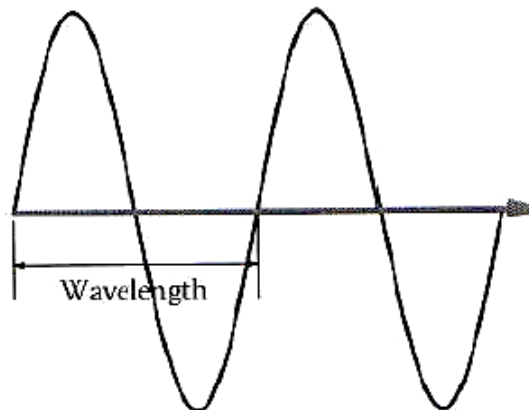
- One basic wave function is plane wave (PW).
- It propagates perpendicularly to wave fronts with a constant frequency in one direction.
- Simplest, frequently used for solids

$$\phi_{PW}(x) = \cos(kx) + i\sin(kx) = \exp(ikx)$$

$$\text{Wavelength } \lambda = 2\pi/k$$

The eigenvalue after double differentiation ( $\nabla^2$ ) is  $-k^2$ .

Free electrons travel this way, and valence electrons in metals do similarly.

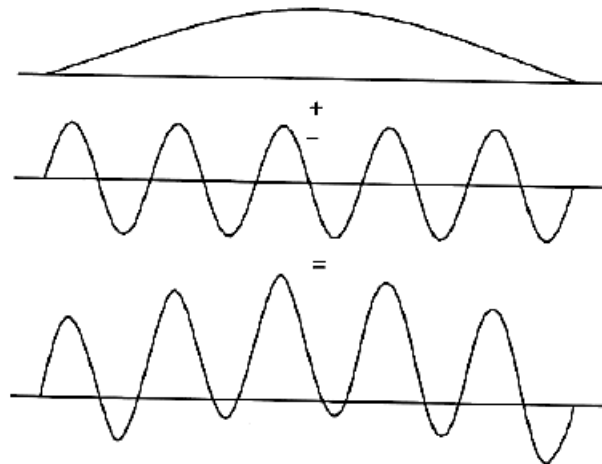


# Special Properties of Waves and Electrons

- Superposition principle of waves

Interference takes place when two PW meet each other and diffraction takes place between waves and solid lattice.

One PW plus another PW depends on how their phases match each other. If two waves are completely out of phase, that will be no wave.



- Indistinguishability of electrons

No way to notice when two electrons have switched their positions. A wave function describing two electrons must have a symmetric probability distribution:



$$|\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2$$

# Energy

$$\left[ -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_I^N \sum_i^n \frac{Z_I}{|r_{Ii}|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|} \right] \Psi(r_i) = E \Psi(r_i)$$

$E$  is the eigenvalue of  $\hat{H}$  associated with the wave function,  $\Psi$ .

What important information can  $E$  provide to us?

- Various ground-state energies over possible positions of nuclei  A potential energy surface in which each point represents a structural configuration.  Global minimum can tell us the most stable structure (lattice parameters, bond lengths, bond angles, cohesive energies, defect formation energies etc.) – **Geometry Optimization**
- The energy difference between one point to another provides us the barrier energy between two configuration. For example, estimation of activation energy.
- Ground-state energy

In quantum mechanics, there is only one ground-state energy in a given system under given conditions, and any energy lower than this value does not exist.

- The ground-state configuration is the starting point for a variety of other calculations, e.g. band structure, density of states, and thermodynamic quantities.



# Challenges & Solutions

- Solve Schrödinger equation for  $n$ -electron systems
- $n$ -electron systems – “many-body problem”

Dealing with  $n$  electrons that interact with all other electrons at the same time is too complex to solve numerically.

**We need various levels of approximations!**

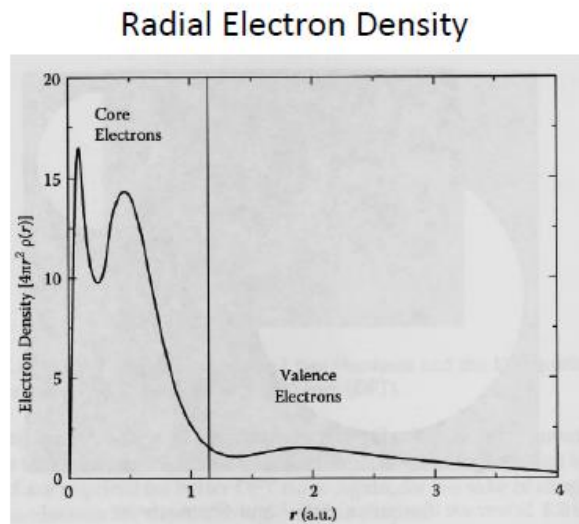
- Density function theory – Implement electron density, energy functional, Kohn-Sham equation (new form of Schrödinger equation)

# Density Functional Theory – Electron Density

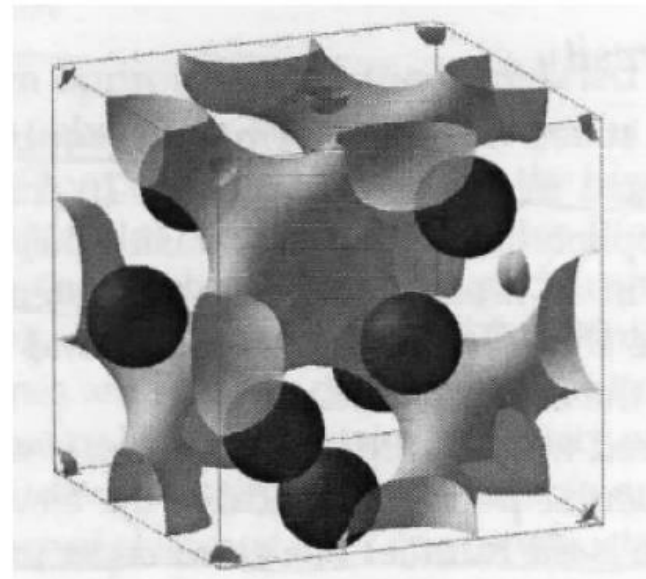
What are wave function  $\Psi(r)$  and electron density  $\rho(x)$ ?

- All information required to define a quantum state is contained in the wave function  $\Psi(r)$ .
- The electron density  $\rho(r)$  decides everything in an  $n$ -electron quantum system.  $\rho(r)$  in an  $n$ -electron system is the number of electrons per unit volume at a given point  $r$ .

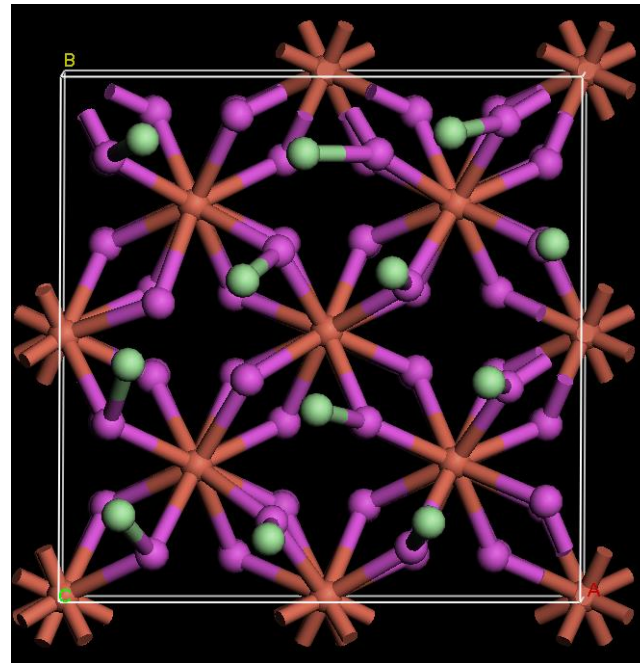
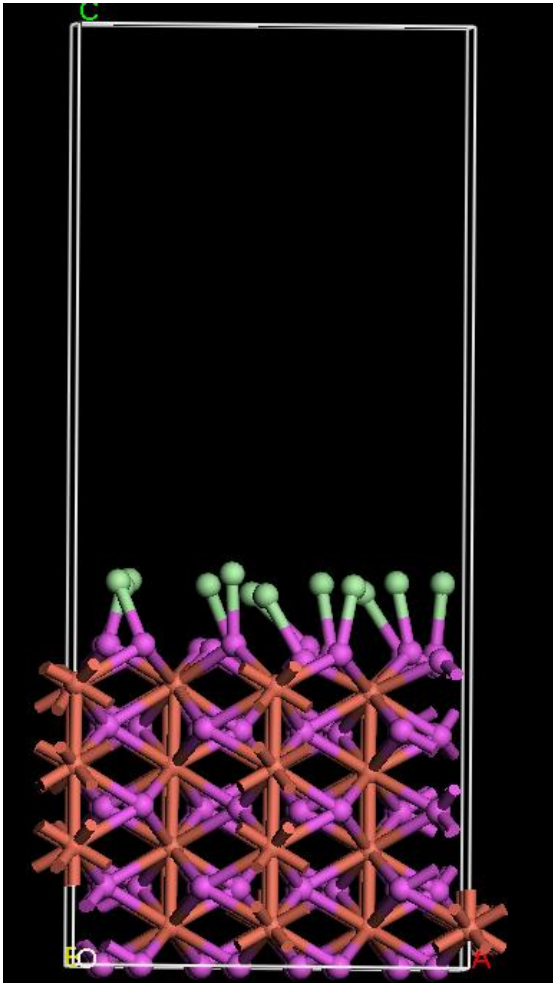
Electron density of an Si atom:



Isosurface of Electron Densities in an Si Bulk

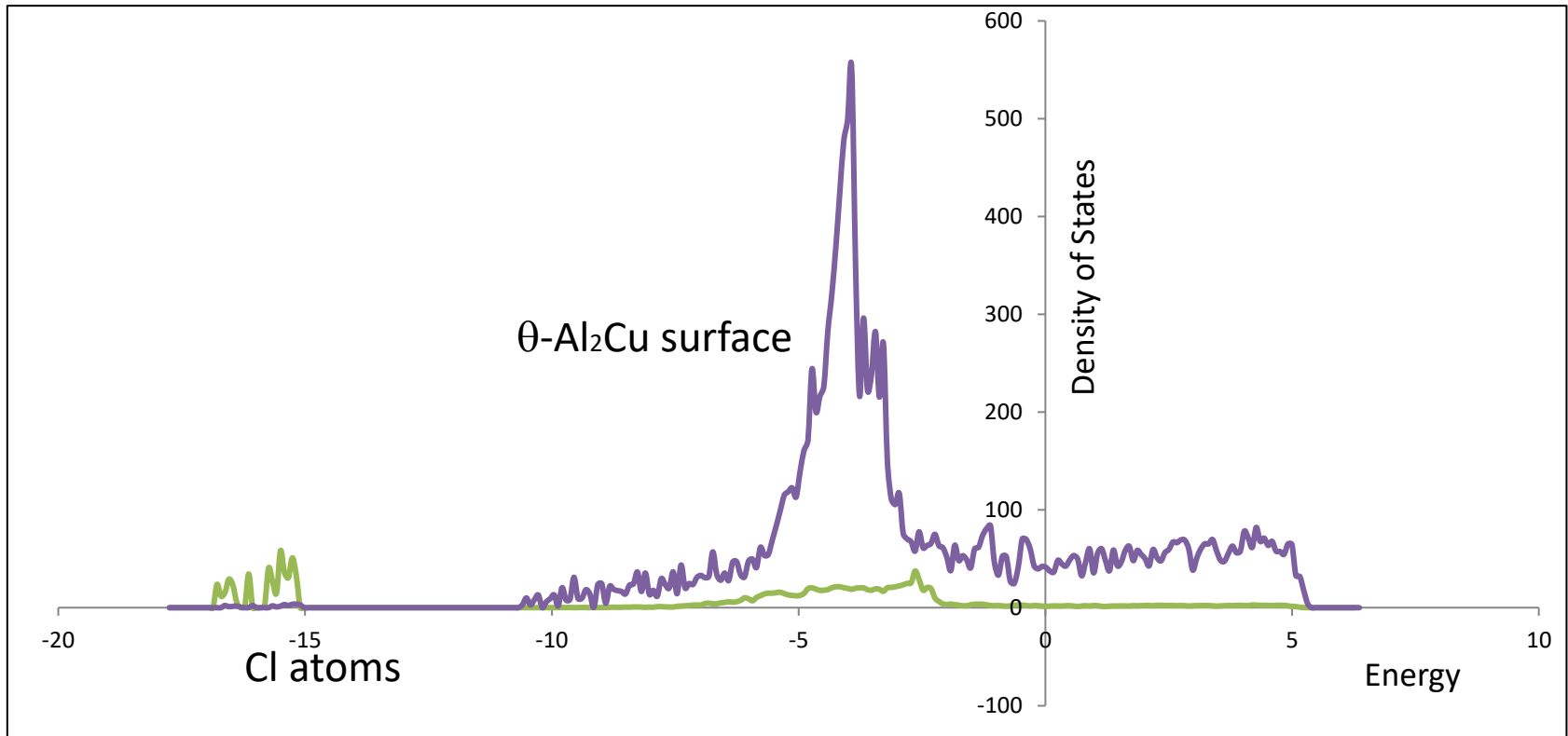


# $\theta$ -Al<sub>2</sub>Cu (001) Surface Reactions with Cl<sup>-</sup> ions (Al Alloy Corrosion Project)



- Slight lattice distortion:  
(12.044, 12.123, 28.618, 90.29°, 90.18°, 89.76°)
- Each Cl ion forms a bond with a Al atom individually.  
 $Cl^- \rightarrow Cl(ads) + e^-$
- Where does  $e^-$  go?

# Determine Cl-Al Bonds (LDOS)



- Bonds include ionic and covalent aspects.
- No electrons accumulate in the valence band of Cl near the Fermi energy = 0.
- Aluminum of the  $\theta$ -Al<sub>2</sub>Cu surface gain electrons from chloride.

In the DFT scheme, assume that the electrons do not interact with one another (one-electron approach).

$$\rho(r) = 2 \sum_i^{occ} |\phi_i(r)|^2$$

$\phi_i(r)$  represent the so-called KS orbitals in a noninteracting reference system.

Integral of  $\rho(r)$  over  $r$ ?

$$\int \rho(r) dr = n \quad \text{The total number of electrons } n$$

If we know the electron density of an atom, we can add up all the overlapping electron densities of atoms to roughly generate the electron density for a solid made of those atoms.

What information can we get from the electron density in a system?

Wave function  $\Psi$ , orbitals  $\phi_i$ , the total number of electrons  $n$ , but it is also directly related to potentials, energies, and thus all properties.

# Kohn-Sham Approach

$$\left[ -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_I^N \sum_i^n \frac{Z_I}{|r_{Ii}|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|} \right] \Psi(r_i) = E \Psi(r_i)$$

- A major difficulty is the last term, the coupled interactions between  $n$  electrons.
- The last term contains various interactions that are difficult to formulate in calculable equations.

Kohn-Sham method:

- Map the  $n$ -electron system (interacting) on the one-electron system (noninteracting) under the given external energy.

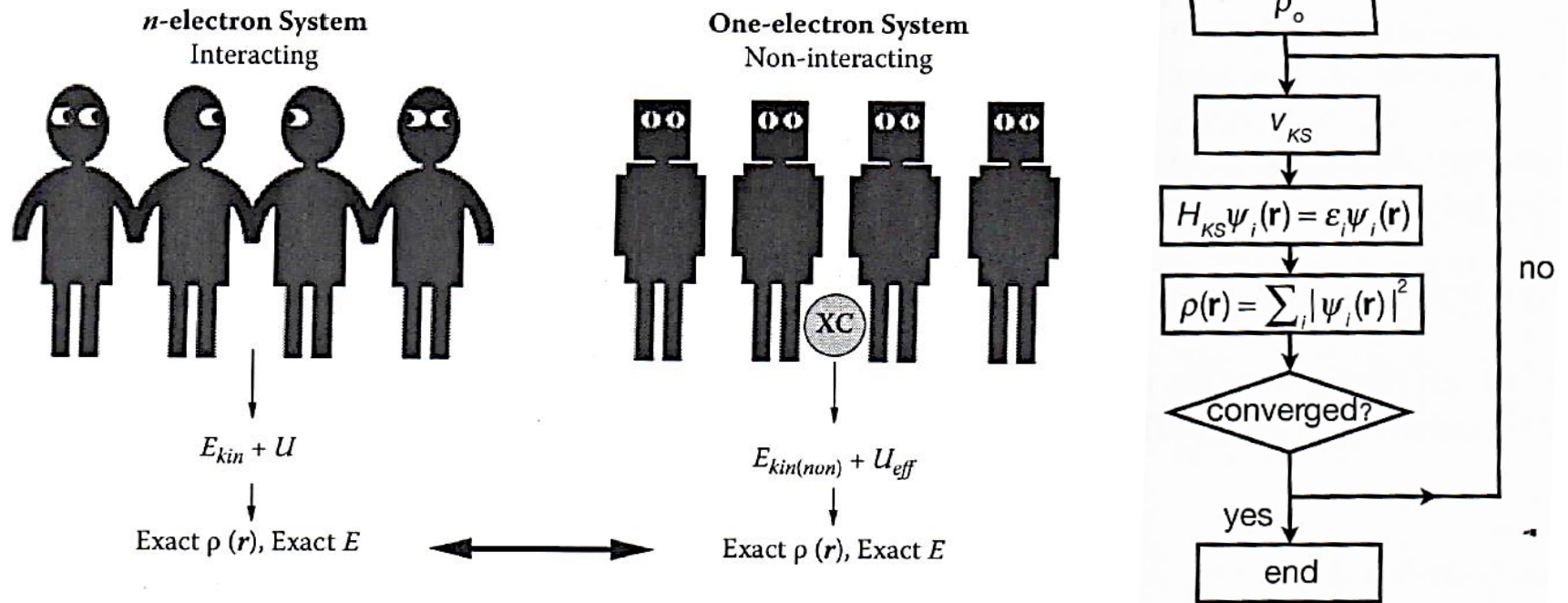


Figure 5.7 Schematic of the Kohn-Sham ansatz.

The corresponding Hamiltonian is

$$\hat{H}_{KS} = E_{kin}^{non} + U_{ext} + U_H + U_{xc} = -\frac{1}{2} \nabla^2 + U_{eff}$$

$U_{eff}$  manipulates the ground-state electron density of the noninteracting system to be identical with that of the true interacting system.