From Atoms to Materials: Predictive Theory and Simulations

Week 1: Quantum Mechanics and Electronic Structure

Lecture 1.3: Basic Quantum Mechanics of Electronic Structure

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Quantum mechanics in 5 postulates

1. The state of electrons is determined by their wave function

$\Psi(r,t)$ We will focus on equilibrium properties: WF does not depend on time → $\Psi(r)$

2. Physical observables ↔ linear operators
   Mathematical objects that act on functions

Position: $\vec{r}$

Momentum: $\vec{p} = \frac{\hbar}{i}\vec{\nabla} = \frac{\hbar}{i}\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$

Quantum mechanics in 5 postulates

3. Average results of measurements is given by

$$\langle O \rangle = \int \Psi^*(r) \hat{O} \Psi(r) d^3r$$

Example:

$$\langle \vec{r} \rangle = \int \Psi(\vec{r}) \vec{r} \Psi(\vec{r}) d^3r = \int \vec{r} \left| \Psi(\vec{r}) \right|^2 d^3r$$

$\left| \Psi(\vec{r}) \right|^2$ Probability density of electron being in volume d^3r around r

Quantum mechanics in 5 postulates

4. The equilibrium wave function can be obtained from the Schrödinger equation:

Hamiltonian operator

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

Energy

$$\bar{\bar{M}} \cdot \bar{V} = \lambda \bar{V}$$

ψ_n , E_n

5. Pauli's exclusion principle

- Two electrons maximum per orbital
- Electrons in one orbital must have different spin

The Hamiltonian operator

- *H* is the operator for the total energy of the system
- We can write it using the two operators we just learned
- For hydrogen the Hamiltonian operator contains two terms:
  - Kinetic energy:

$$K = \frac{|\vec{p}|^2}{2m} = -\frac{\hbar^2}{2m}\vec{\nabla}\cdot\vec{\nabla} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$\vec{\nabla}\cdot\vec{\nabla} = \nabla^2$$

  - Potential energy:

$$V = -\frac{e^2}{|\vec{r}|}$$

The Born Oppenheimer Hamiltonian

- Any material is a collection of electrons and nuclei
  - N_e electrons at positions r_i
  - N_n nuclei at positions R_i and charge Z_i
- Born Oppenheimer approximation
  - Massive nuclei are classical and fixed in space

$$H = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i}^{N_n} \sum_{j}^{N_e} \frac{e^2 Z_i}{\left|\vec{r}_j - \vec{R}_i\right|} + \sum_{i<j}^{N_n} \frac{e^2 Z_i Z_j}{\left|\vec{R}_i - \vec{R}_j\right|} + \sum_{i<j}^{N_e} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|}$$

KE

e-n interaction

n-n interaction

e-e interaction

Electronic structure and ionic dynamics

$$H_{ele}\psi\left(\{\vec{r}_i\}\right) = E\psi\left(\{\vec{r}_i\}\right)$$

- Hamiltonian and wave function depend parametrically on ionic positions
- Eigenvalue (energy) then depends on the ionic positions

$$H_{ele}\left(\{\vec{r}_i\};\{\vec{R}_i\}\right)\psi\left(\{\vec{r}_i\};\{\vec{R}_i\}\right) = E\left(\{\vec{R}_i\}\right)\psi\left(\{\vec{r}_i\};\{\vec{R}_i\}\right)$$

- Classical dynamics of ions is then governed by this energy:

$$H_{ions}\left(\{\vec{R}_i\},\{\vec{P}_i\}\right) = E\left(\{\vec{R}_i\}\right) + \sum_{i=1}^{N_n}\frac{\left|\vec{P}_i\right|^2}{2M_i}$$

- $\dot{\vec{R}}_i = \dfrac{\vec{P}_i}{M_i}$
- $\dot{\vec{P}}_i = \vec{F}_i = -\vec{\nabla}_{R_i} E\left(\{\vec{R}_i\}\right)$

Properties of the Schrodinger Eq. and WF's

The Schrödinger equation

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

A family of solutions

$$E_n \qquad \psi_n(\vec{r})$$

Eigenvalues need to be real, so Hamiltonian is an hermitian operator

Wavefunctions are normal to one another

$$\int_{-\infty}^{\infty} \psi_n(\vec{r})\,\psi_m(\vec{r})\,d^3r = \delta_{nm}$$

Equivalent to eigenvalue problem

$$A\vec{x} = \lambda\vec{x}$$

A family of solutions

$$\lambda_n \qquad \vec{x}_n$$

Symmetric matrices have real eigenvalues

Eigenvectors are normal to one another

$$\vec{x}_n\vec{x}_m = \sum_{i=1}^{N} x_{n,i}x_{m,i} = \delta_{ij}$$

Nodal theorem

- The ground state wavefunction (lower energy) has no nodes (except at domain boundaries)

- The more nodes a wavefunction has, the higher its energy