Brief Quantum Mechanics (QM) Review

- **QM results:** ***Utilization of***

The Schrödinger Equation

(time independent; see next slide) describes electrons.

- Solutions to the **Schrödinger Equation** result in ***quantized*** (discrete) **energy levels** for electrons.

Quantum Mechanics (QM)

- **The Schrödinger Equation:**

(**time independent**)

$$H\psi = E\psi$$

(this is a differential operator eigenvalue equation)

H ≡ Hamiltonian operator for the system

E ≡ Energy eigenvalues

(allowed energies)

ψ ≡ Wavefunction

Particles are QM waves!

- **The Schrödinger Equation:**

$$H\psi = E\psi$$

- ***Particles are QM waves!***

$$|\psi|^2 \equiv \text{probability density}$$

$$|\psi|^2\, d^3r \equiv \text{Probability that an electron is in differential volume } d^3r$$

- ψ is a function of ***ALL*** coordinates of ***ALL*** particles in the problem!

Electrons in Periodic Crystalline Materials

Reduction to one Electron Problem

Hamiltonian for a Perfect, Periodic Crystal

N_e electrons, N_n nuclei; N_e , $N_n \sim 10^{23}$ (huge!)

Notation: **i** = electron; **j** = nucleus

- The general, the ***many-body*** ***Classical*** Hamiltonian:

(Gaussian units!)

$$H = H_e + H_n + H_{e\text{-}n}$$

H_e = Pure Electronic Energy = **KE(e^-) + PE(e^- - e^-)**

$$H_e = \sum_i (p_i)^2/(2m_i) + (½)\sum_i \sum_{i'} [e^2/|r_i - r_{i'}|] \quad (i \neq i')$$

H_n = Pure Nuclear Energy = **KE(n) + PE(n- n)**

$$H_n = \sum_j (P_j)^2/(2M_j) + (½)\sum_j \sum_{j'} [Z_j Z_{j'} e^2/|R_j - R_{j'}|] \ (j \neq j')$$

$H_{e\text{-}n}$ = Electron-Nuclear Interaction Energy = **PE(e^- - n)**

$$H_{e\text{-}n} = - \sum_i \sum_j [Z_j e^2/|r_i - R_j|]$$

Lower case **r, p, m**: Electron position, momentum, mass

Upper case **R, P, M**: Nuclear position, momentum, mass

- **The Classical**, ***Many-Body*** **Hamiltonian**:

$$H = H_e + H_n + H_{e-n}$$

- ***Three Approximations***, rigorously justified in many advanced texts (QM & SS), after a lot of work, reduce the complexity of the problem significantly. This gives:

⇒ **For electronic properties calculations**

(bandstructures, etc.) **H** is reduced to a

One Electron Hamiltonian!

One Electron Hamiltonian!

- This is the usual ***Starting Point*** (with no proof) for ***ALL*** elementary SS physics texts (including Kittel's book) !
- What follows is a brief outline of these approximations. Details left to the student!

Approximation #1:

Separate electrons into 2 types:

Core Electrons &

Valence Electrons

- **Core Electrons:** Those in *filled*, inner shells of the atoms. Play ***NO*** role in determining the electronic properties of the solid!

Example:

The **Si** ***free atom*** **electronic configuration:**

Core Electrons = $1s^2 2s^2 2p^6$ (filled shells!)

Localized around the nuclei & play *NO* role in the bonding.

⇒ Lump the core shells with the **Nuclei** ≡ **Ions**

(in $\sum_i$, include only the valence electrons)

Core Shells + Nucleus ≡ Ion Core

$$\Rightarrow H_{e\text{-}n} \rightarrow\rightarrow H_{e\text{-}i}\,,\; H_n \rightarrow\rightarrow H_i$$

Valence Electrons

- Those in the ***unfilled***, outer shells of the free atoms. These determine the electronic properties of the solid and take part in the bonding!

***Example*:**

The **Si** *free atom* **electron configuration:**

$$1s^2 2s^2 2p^6 3s^2 3p^2$$

Valence Electrons = $3s^2 3p^2$

(unfilled shells!)

- In the solid, these hybridize with electrons on neighbor atoms. This forms strong covalent bonds with the 4 **Si** nearest-neighbors in the **Si** lattice.

Approximation #2:

The Born-Oppenheimer (Adiabatic) Approximation

Separates electron & ion motions.

- ***Separates*** **the electron & ion motions.**
- Rigorous proof needs many body QM.

Qualitative (semi-quantitative)

Justification: The ratio of the electron & ion masses is of the order:

$$(m_e/M_i) \sim 10^{-3} \; (<< 1)$$

(or smaller!)

$\Rightarrow$ Classically, the massive ions move much slower than the very small mass electrons!

Typical ionic vibrational frequencies: $\upsilon_i \sim 10^{13}\ s^{-1}$

$\Rightarrow$ The time scale of the ion motion is: $t_i \sim 10^{-13}$ s

- Electronic motion occurs at energies of about a bandgap:

$$E_g = h\upsilon_e = \hbar\omega \sim 1\ eV \Rightarrow \upsilon_e \sim 10^{15}\ s^{-1} \Rightarrow t_e \sim 10^{-15}\ s$$

- So, classically,

The electrons respond to the ion motion

~ instantaneously!

$\Rightarrow$ As far as the electrons are concerned, the ions are ~ stationary!

$\Rightarrow$ *In the electron Hamiltonian, H_e, the ions can be treated as ≈ stationary!*

The Large Mass Ions

cannot follow the rapid, detailed motion of

The Small Mass Electrons.

⇒ The Ions ~ see an *Average Electron Potential!*

⇒ *In the ion Hamiltonian, H_i, the electrons can be treated in an average way!*

(As in Chs. 4 & 5 in Kittel on Lattice Vibrations)

Implementation: Born-Oppenheimer (Adiabatic) Approximation

- Write the vibrating ion coordinates as

$R_j = R_{jo} + \delta R_j$, R_{jo} = equilibrium ion positions

δR_j = (small) deviation from the equilibrium positions

- The many body electron-ion Hamiltonian is (schematic!):

$$H_{e-i} \sim = H_{e-i}(r_i,R_{jo}) + H_{e-i}(r_i,\delta R_j)$$

- The ***New* many body Hamiltonian** in this approximation :

$$H = H_e(r_i) + H_{e-i}(r_i,R_{jo}) + H_i(R_j) + H_{e-i}(r_i,\delta R_j) \quad (1)$$

(neglect the last 2 terms in the band calculations) **or**

$H = H_E$ **[1st 2 terms of (1)]** $+ H_I$ **[2nd 2 terms of (1)]**

Here, H_E = **Electron Part** (gives the energy bands)

H_I = **Ion Part** (gives the phonons in Chs. 4 & 5)

Summary: Born-Oppenheimer Approx.

⇒ For electronic properties (bands), this allows us to focus on ***the electronic part*** of the many-body Hamiltonian:

$$H_E = H_e(r_i) + H_{e\text{-}i}(r_i,R_{jo})$$

(schematic):

$H_e(r_i)$ = electron kinetic energy + electron-electron (Coulomb) repulsion

$H_{e\text{-}i}(r_i,R_{jo})$ = electron (Coulomb) attraction to the ***STATIONARY*** ions.

Summary:

Born-Oppenheimer Approximation:

⇒ For calculations of electronic properties (bands), ***the vibrating ion part***, $\mathbf{H_I}$ of the many-body Hamiltonian ***can be neglected.***

Born-Oppenheimer Approximation

⇒ ***Focus on the electronic part*** of **H**:

$$\mathbf{H_E = H_e(r_i) + H_{e-i}(r_i,R_{jo})}$$

$$\mathbf{H_E = \sum_i (p_i)^2/(2m_i) + (\tfrac{1}{2})\sum_i\sum_{i'}[e^2/|r_i - r_{i'}|]}$$

$$\mathbf{- \sum_i\sum_j [Z_j e^2/|r_i - R_{jo}|] \ (i \neq i')}$$

- ***NOTE!*** So far, the Hamiltonian is still classical!

We want to do Quantum Mechanics!

⇒ Replace each electron momentum with its quantum operator: $\mathbf{p_i} \equiv \mathbf{-i\hbar\nabla_i}$ (everywhere in $\mathbf{H_E}$!)

To Calculate Electronic Properties:

Solve the Schrödinger Equation with $\mathbf{H_E}$

(this is still a many electron problem!)

Approximation #3: The Mean Field or *One Electron* Approximation

Approximation #3: The Mean Field or *One Electron* Approximation

- For **H_E**: Make the

Mean Field Approximation

⇒ ***Every electron experiences the SAME average potential***

due to all other electrons (Coulomb repulsion) plus all ions (Coulomb attraction).

- The **N** electron Hamiltonian **H_E** is then ***replaced by***

N ***IDENTICAL*** one-electron Hamiltonians:

$$\mathbf{H_{1e} = (p)^2/(2m_o) + V(r)}$$

One Electron Approximation:

⇒ The many electron Hamiltonian is replaced by a one electron Hamiltonian:

$$H_{1e} = (p)^2/(2m_o) + V(r)$$

- Do Quantum Mechanics ⇒ $p \equiv -i\hbar\nabla$
- **V(r)** ≡ **Effective Potential** ≡ Average potential of one electron interacting with all others + all the ions

  V(r) is periodic & has the lattice symmetry!
- Given **V(r),** solve the

One Electron Schrödinger Equation:

$$H_{1e}\psi_n = E_n\psi_n$$

n = eigenvalue label (band index), ψ_n = one electron wavefunction

- The ***Primary Justification*** of the one-electron approximation is that

It explains VOLUMES of data

on electronic properties of

all types of solids

(metals, semiconductors & insulators!).

NOTE!

- There are some (specialized) data for which an explanation requires the many body **H**.

But, ***MOST*** data needs only the one electron **H**!

The **One-electron Approximation:**

- What about **spin effects?** These are neglected in $\mathbf{H_E}$. *Spin can be included!* (Also, we need the **Pauli Exclusion Principle:** Requires quantum field theory!)
- **Spin-orbit coupling?** This is neglected in $\mathbf{H_E}$. ***Spin-orbit coupling can be included.*** (Relativistic corrections are needed.)
- The **One-electron Approximation:** Is used ***without discussion or justification*** in *~ALL* elementary SS physics texts!

A Rigorous Justification: Is found in Hartree & Hartree-Fock theory of many electron QM. Also, in the **Local Density Approximation (LDA) to** ***Density Functional Theory.***

The Bandstructure Problem

- *Begin with* the one-electron Hamiltonian:

$$H_{1e} = (p)^2/(2m_o) + V(r)$$

p ≡ **-iħ∇**, **V(r)** ≡ Periodic Effective Potential

- *Solve* the one-electron Schrödinger Equation:

$$H_{1e}\psi_n(r) = E_n\psi_n(r)$$

In general, this is still a very complicated, highly computational problem!

The **Bandstructure Problem**

(Many people's careers over many years!)

- Start with the 1 e^- Hamiltonian:

$$H_{1e} = -(i\hbar\nabla)^2/(2m_o) + V(r)$$

- **Step 1:** Determine the effective periodic potential **V(r)**
- **Step 2:** Solve the one-electron Schrödinger Equation:

$$H_{1e}\psi_n(r) = E_n\psi_n(r)$$

A complex, sophisticated, highly computational problem!

- There are ***many schemes, methods, & theories to do this!***
- We'll give a brief overview of only a few!

- The 1 e^- Hamiltonian is:

$$H_{1e} = -(i\hbar\nabla)^2/(2m_o) + V(r)$$

- ***Note!!*** Knowing the form of the effective periodic potential **V(r)** is itself a ***difficult problem!***
- However, we can go a long way towards understanding ***the physics*** behind the nature of bandstructures without specifying **V(r)**!

We can ***USE SYMMETRY!***

- **Group Theory** ≡ A math tool which does this in detail.

$V(r) \equiv$ Periodic Crystal Potential.

- Has all of the symmetries of the crystal lattice!

Translational Symmetry

Rotational Symmetry

Reflection Symmetry

- The most important symmetry is

Translational Symmetry.

- Using this considerably reduces the complexities of bandstructure calculations!
- We will illustrate bandstructure calculations with some model calculations first. Then, we will discuss real bandstructures.