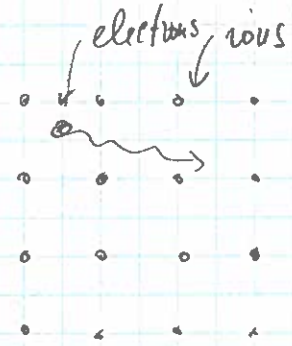
LECTURE 1: SOLIDS AS INERACTING QUANTUM MANY-BODY SYSTEMS



Solid = electrons + crystalline lattice

"Condensed Matter theory of everything:"

$$\left.\begin{aligned} H = & \sum_i \frac{P_i^2}{2M} + \frac{(Ze)^2}{2}\sum_{i,i'} \frac{1}{|\vec{R}_i - \vec{R}_{i'}|} && \leftarrow \text{ions} \\ & + \sum_j \frac{p_j^2}{2m} + \frac{e^2}{2}\sum_{j,j'} \frac{1}{|\vec{r}_j - \vec{r}_{j'}|} && \leftarrow \text{electrons} \\ & - Ze^2 \sum_{i,j} \frac{1}{|\vec{R}_i - \vec{r}_j|} && \leftarrow \text{el-ion interaction} \end{aligned}\right\} \quad (1)$$

- this is an INTRACTABLE problem in general
  - $N=1$ is hydrogen atom (easy)
  - $N = 2-100$ – chemistry of atoms (tractable using approximations)
  - $N \sim 10^{23}$ – theory of solids

Key issue: Enormous size of the Hilbert space of $N \sim 10^{23}$ particles.

To estimate this size consider a simple problem of $N \sim 10^{23}$ spins (up ↑ or down ↓). The Hilbert space size is $2^N = 2^{10^{23}} \simeq 10^{10^{23}/3}$!!! For comparison the # of atoms

earth $\sim 3.8 \times 10^{50}$

sun $\sim 1.2 \times 10^{57}$

universe $\sim 1.3 \times 10^{79}$

$\Rightarrow$ Drastic approximations are required to make progress in any description of solids.

The Born-Oppenheimer approximation

- originally developed as a description of molecules
- based on the observation that $m \ll M$, namely $\frac{m}{M} \sim 10^{-3} - 10^{-5}$
  $\rightarrow$ electrons will move much <u>faster</u> than ions

One can deduce that $v_{ion} \sim \left(\frac{m}{M}\right)^{2/4} v_F \sim 10^{-2} - 10^{-3} v_F$

also $v_F \sim 3 \times 10^6 \, m/s \sim 10^{-2} c$ (non-relativistic)

- We explore the consequences of $v_{ion} \ll v_F$ for the solution of the Schrödinger eq.:

$$H \Psi(\vec{r}, \vec{R}) = E \Psi(\vec{r}, \vec{R}) \tag{2}$$

where $\vec{r} = \{\vec{r}_j\}$ and $\vec{R} = \{\vec{R}_i\}$ as shorthand notation.

Make an ansatz: $\Psi(\vec{r}, \vec{R}) = \sum_n \phi_n(\vec{R}) \Psi_{e,n}(\vec{r}, \vec{R})$ (3)

where $\Psi_{e,n}$ are solutions to the electron problem at fixed ion positions:

$$(T_e + V_{ee} + V_{ei}) \Psi_{en} = E_{e,n} \Psi_{e,n} \tag{4}$$

The full Schr. eq. now reads

$$(T_i + T_e + V_{ii} + V_{ee} + V_{ei}) \Psi = E \Psi \tag{5}$$

$$\rightarrow \quad (T_i + V_{ii}) \Psi + \sum_n \phi_n \underbrace{(T_e + V_{ee} + V_{ei}) \Psi_{e,n}}_{E_{e,n} \Psi_{e,n}} = E \Psi$$

- multiply by $\Psi^*_{e,m}(\vec{r}, \vec{R})$ and integrate (over $\vec{r}$)

$$\sum_n \int d\vec{r} \, \Psi^*_{e,m}(\vec{r}, \vec{R}) \, T_i \, \phi_n(\vec{R}) \, \Psi_{e,n}(\vec{r}, \vec{R}) + (V_{ii} + E_{e,m}(\vec{R}) - E) \, \phi_m(\vec{R}) = 0 \tag{6}$$

(we used orthonormality of $\Psi_{e,n}$)

The first term now requires attention

$$\sum_i \langle em | \frac{P_i^2}{2M} \phi_n(\vec{R}) | en \rangle = -\frac{\hbar^2}{2M} \sum_i \int d\vec{r}\, \Psi^*_{e,m}(\vec{r},\vec{R}) \Big[\underbrace{(\nabla^2_{R_i} \phi_n(\vec{R}))}_{①}$$

$$+ \underbrace{2(\vec{\nabla}_{R_i} \phi_n(\vec{R})) \cdot \vec{\nabla}_{R_i}}_{②} + \underbrace{\phi_n(\vec{R}) \nabla^2_{R_i}}_{③} \Big] \Psi_{e,n}(\vec{r},\vec{R}) \qquad (7)$$

- the first term in the integral can again be evaluated based on orthonormality.
- If we for a moment NEGLECT the other two terms we get:

$$\boxed{\left[T_i + V_{ii} + E_{e,n}(\vec{R}) \right] \phi_n(\vec{R}) = E_n \phi_n(\vec{R}) \qquad (8)}$$

"effective ionic potential"

<u>The upshot</u> Eqs. (4) and (8) constitute the B-O approximation.

(i) We solve Eq. (4) for FIXED ionic positions, obtain $E_{e,n}(\vec{R})$

(ii) Given $E_{e,n}(\vec{R})$ we solve Eq. (8) to obtain E_n and $\phi_n(\vec{R})$

In this way electron and ion motions have been <u>decoupled</u> and are only connected via eff. ionic potential $E_{e,n}(\vec{R})$.

We must still demonstrate that the two terms neglected in Eq. (7) make negligible contributions. One can show that the corresponding integrals go as

① $\sim \left(\frac{m}{M}\right)^{1/2} \varepsilon_F$ $\Rightarrow$ thus ② and ③ are indeed small compared to ①.

② $\sim \left(\frac{m}{M}\right)^{3/4} \varepsilon_F$ ③ $\sim \left(\frac{m}{M}\right) \varepsilon_F$

- Illustrate this on term ③:

Consider $$\frac{\hbar^2}{2m}\nabla_R^2 \Psi_{e,n}(\vec{r},\vec{R}) \approx \frac{\hbar^2}{2m}\nabla_r^2 \Psi_{e,n}(\vec{r},\vec{R}) \qquad (9)$$
$$\simeq \varepsilon_F \Psi_{e,n}(\vec{r},\vec{R})$$

- the first equality holds because $\Psi_{e,n}$ is a function of differences $(\vec{r}-\vec{R})$.

Hence we have

$$\frac{\hbar^2}{2M}\nabla_R^2 \Psi_{e,n} \approx \left(\frac{m}{M}\right)\varepsilon_F \Psi_{en} \qquad (10)$$

- Estimates for ① and ② can be done in a similar fashion.