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Lec. 1. Introduction to the course

~~A review~~ Introduction to materials from the perspective of their electronic structure.

Electronic Structure: The distribution of electrons in a mat in space, ~~and~~ across subsystems in the material, over energy eigenvalues or windows, etc.

Why is this important? – All properties of materials ultima emerge from the way the electrons are distributed & the w they respond to external stimuli. So any investigation into th electronic structure is tantamount to probing the microsco origins of material properties & phenomena.

Having said that, it might often seem quite excessive to answer every question about materials by invoking the electronic str This is because, the solution of the electronic structure is a quantum mechanical problem often required tedious computation & sometimes being impossible. Other "coarse-grained" metho such as FEManalysis, force-field based MD, phase-field modeling, effe Hamiltonians, etc. are often employed to understand more macroscopic phenomena in materials.

This course will, however, focus on a bottom-up approach starting from the electrons. An outline of problem can be given as follows: What is the ground ~~electronic~~ state of a system of atom and electrons under given external conditions?

If there are L atoms and N electrons then we can write

$$\hat{H} = \sum_{I=1}^{L} -\frac{\nabla_I^2}{2M_I} + \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} + V_{II} + \sum_{i=1}^{N}\sum_{I=1}^{L} -\frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \sum_{i<j} \frac{1}{r_{ij}}$$

This is converted to an electronic problem at fixed nuclei

$$\hat{H}_e = -\sum_{i=1}^{L} \frac{\nabla_i^2}{2} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{I,i} \frac{-Z_I}{|\vec{r}_i - \vec{R}_I|} \quad \text{— (2)}$$

Clamped Nuclear problem. $\Leftarrow$ $\hat{H}_e(\vec{R}_I)\, \psi_n(\vec{r}; \vec{R}_I) = E_n(\vec{R}_I)\, \psi_n(\vec{r}; \vec{R}_I)$ — (3)

$$\therefore \hat{H} = \underbrace{\sum_{I=1}^{L} -\frac{\nabla_I^2}{2M_I}}_{\hat{T}_I} + \hat{H}_{el}(\vec{R}_I) + \underbrace{\sum_{I<J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}}_{\hat{V}_{IJ}} \quad \text{— (4)}$$

Now we ~~expand the instantaneous wf. make this ansatz~~ as : $\Psi(\vec{r}, \vec{R}, t) = \sum_{n=0}^{\infty} \chi_n(\vec{R}, t)\, \psi_n(\vec{r}; \vec{R})$

$$\hat{H}\, \Psi(\vec{r}, \vec{R}, t) = i \frac{\partial}{\partial t} \Psi(\vec{r}, \vec{R}, t)$$

$$\text{LHS} = \sum_{n=0}^{\infty} \left(\hat{T}_I + \hat{V}_{IJ} + \hat{H}_{el} \right) \chi_n(\vec{R}, t)\, \psi_n(\vec{r}; \vec{R}) \quad \text{— (5)}$$

$$= \sum_{n=0}^{\infty} \Big\{ \psi_n(\vec{r}; \vec{R})\, \hat{T}_I\, \chi_n(\vec{R}, t) + \hat{W}_n(\vec{r}, \vec{R})\, \chi_n(\vec{R}, t) + \psi_n E_n(\vec{R})\, \chi_n(\vec{R}, t) \Big\}$$

Consider $\nabla_I \left(\chi_n(\vec{R}, t)\, \psi_n(\vec{r}; \vec{R}) \right)$

$$= \psi_n(\vec{r}; \vec{R})\, \nabla_I \chi_n(\vec{R}, t) + \chi_n(\vec{R}, t)\, \nabla_I \psi(\vec{r}; \vec{R})$$

$$\Rightarrow \vec{\nabla}_I \cdot \nabla_I \left(\chi_n(\vec{R}, t)\, \psi_n(\vec{r}; \vec{R}) \right)$$

$$= \left(\nabla_I \psi_n(\vec{r}; \vec{R}) \right) \cdot \left(\nabla_I \chi_n(\vec{R}, t) \right) + \psi_n(\vec{r}; \vec{R})\, \nabla_I^2 \chi_n$$

$$+ \left(\nabla_I \chi_n(\vec{R}, t) \right) \cdot \left(\nabla_I \psi_n(\vec{r}; \vec{R}) \right) + \chi_n(\vec{R}, t)\, \nabla_I^2 \psi_n$$

$$= \left(\nabla_I^2 \psi_n(\vec{r}; \vec{R}) + 2 \left(\nabla_I \psi_n(\vec{r}; \vec{R}) \right) \cdot \nabla_I \right) \chi_n(\vec{R}, t) + \psi_n(\vec{r}; \vec{R})\, \nabla_I^2 \chi_n$$

$\hat{W}_n$

$\therefore$ (5) becomes :

$$\sum_{n=0}^{\infty} \Big\{ \psi_n(\vec{r}; \vec{R})\, \hat{T}_I\, \chi_n(\vec{R}, t) + \hat{W}_n(\vec{r}; \vec{R})\, \chi_n(\vec{R}, t) + U_n(\vec{R})\, \chi_n(\vec{R}, t) \Big\}$$

RHS = $\psi_n(\vec{r}; \vec{R})\, i \frac{\partial \chi_n(\vec{R}, t)}{\partial t}$ — (6)

$$= \left(\nabla_I^2 \psi_n(\vec{r};\vec{R}) + 2\underbrace{\left(\nabla_I \psi_n(\vec{r};\vec{R})\right)}_{\hat{W}_n} \cdot \nabla_I \right) \chi_n(\vec{R},t) + \psi_n(\vec{r};\vec{R}) \nabla_I^2 \chi_n(\vec{R},t)$$

∴ (5) becomes:

$$\sum_{n=0}^{\infty} \left\{ \psi_n(\vec{r};\vec{R}) \hat{T}_I \chi_n(\vec{R},t) + \hat{W}_n(\vec{r};\vec{R}) \chi_n(\vec{R},t) + U_n(\vec{R}) \chi_n(\vec{R},t) \right\}$$

$$\text{RHS} = \psi_n(\vec{r};\vec{R})\, i \frac{\partial \chi_n(\vec{R},t)}{\partial t} \quad \text{— (6)}$$

multiplying both sides by $\psi_m^*(\vec{r};\vec{R})$ and integrating over $d^3\vec{r}$ we get:

$$i \frac{\partial \chi_m(\vec{R},t)}{\partial t} = \left\{ \hat{T}_I + U_m(\vec{R}) \right\} \chi_m(\vec{R},t) + \sum_{n=0}^{\infty} \hat{D}_{mn}(\vec{R}) \chi_n(\vec{R},t) \quad \text{— (7)}$$

where $\hat{D}_{mn}(\vec{R}) \equiv \sum_{I=1}^{L} \left\{ \langle \psi_m | -\frac{\nabla_I^2}{2M_I} | \psi_n \rangle + \langle \psi_m | -\frac{\nabla_I}{M_I} | \psi_n \rangle \cdot \nabla_I \right\}$

→ called the non adiabatic coupling term.

Both terms are neglected due to large M_I and we get the Born-Oppenheimer Approximation.

$$i \frac{\partial \chi_m(\vec{R},t)}{\partial t} = \left\{ \hat{T}_I + U_m(\vec{R}) \right\} \chi_m(\vec{R},t) \quad \text{— (8)}$$

$U_m(\vec{R})$ ⟶ potential energy surface arising from the m^{th} electronic state.

(8) ⇒ if a system starts out in the m^{th} state ($\chi_n = \delta_{mn}$) then it will continue in that state. Note that this is also of the adiabatic theorem.

Since nuclei are heavier, the quantum problem of nucleis indicated in (8) is often just treated classically. Nuclei move under the potential energy $U_0(\vec{R})$ (ground state potential energy) classically.

Eq. of motion: $M_I \frac{d^2 \vec{R}_I}{dt^2} = -\nabla_I U_0(\vec{R}_I)$ — (9)

The equilibrium structure of the system is obtained by setting LHS of (9) to 0. This defines $\vec{R}_{eq}$: $\nabla_I U_0(R)\Big|_{R_{eq}} = 0$ → (10)

This is, in the field, also called the equilibrium or optimized geometry. We will be, for the most part, interested in the electronic structure for the equilibrium geometry. i.e.

$$\hat{H}_{el}(\vec{R}_{eq})\, \psi_n(\vec{r}; \vec{R}_{eq}) = E_n(\vec{R}_{eq})\, \psi_n(\vec{r}; \vec{R}_{eq}) \quad \text{— (11)}$$

ψ_n is actually a many-electron wavefunction and usually (11) is intractable. The essential difficulty arises due to the e-e repulsion term. We will generally write:

$$\hat{H}_{el} = \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^{N} V_{ext}(\vec{r}_i) \quad \text{— (12)}$$

where $V_{ext}(\vec{r}_i) = \sum_{I=1}^{L} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|}$ — (13)

In the first method of solving (11) we will assume the e-e repulsion is zero.