Lecture 12

AE Electron Band Theory II

Tight binding band

Question

- Consider a 1D crystal of Hydrogen with 2 atoms under B.v.K. BC – This is equivalent to hydrogen molecule. The Hamiltonian is given by H = KE + V_1 + V_2. Consider 1s orbitals at |1> and |2>. Ignoring <1|2>, solve for the band structure for this problem, and plot ω versus k.
- Repeat the above for the 4 atom case.
- Make an intelligent guess for 8 atoms.

Simple and Useful Picture

- Of the two terms in V, consider only the 2nd term (we will call this –t), ignoring the 1st term, which tends to be smaller than the 1st term ("Wannier orbital"). Only in this case, the normalization factor of the bonding or anti-bonding wave function is $1/\sqrt{2}$.
- Consider a macroscopic 1D crystal consisting of $N = 2^M$ hydrogen atoms – one can consider bonding and anti-bonding of 2, 4, 6, 8, atoms in succession.
- N degenerate 1s orbitals split into states forming an "energy band" of width = $2(t+t/2+t/4+\ldots) = 4t$
- For $t > 0$, then the lowest energy state = $1/\sqrt{N}\,(|0\rangle+|1\rangle+\ldots|N-1\rangle)$ while the highest energy state = $1/\sqrt{N}\,(|0\rangle-|1\rangle+|2\rangle-|3\rangle+\ldots|N-1\rangle)$. I.e., the lowest energy has $k=0$ while the highest energy has $k=\pi/a$.

Motivation for Tight Binding Method

- “Standard” View of Bloch’s Theorem

Form 2 of Bloch Theorem [Bragg diffraction

$$\psi_{n\vec{k}}(\vec{x}) = \sum_{\vec{G}} C_n(\vec{G}) \exp\left[i(\vec{k}+\vec{G})\cdot\vec{x}\right]$$

- Alternative View of Bloch’s Theorem

Form 4 of Bloch Theorem [Modulated local wave function

$$\psi_{n\vec{k}}(\vec{x}) = \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R})\underset{\substack{\uparrow\\ \text{Wannier Orbital}}}{\phi_n(\vec{x}-\vec{R})}$$

$$\phi_n(\vec{r}-\vec{R}) = \frac{1}{V_{BZ}} \int_{BZ} d\vec{k} e^{-i\vec{R}\cdot\vec{k}} \psi_{n\vec{k}}(\vec{r})$$

Tight Binding Method

(aka LCAO method, linear combination of atomic orbital)

- Another way of introducing the electron band concept, complimentary to the free electron view discussed so far
- Start from the atomic orbitals and construct electron bands by bonding and anti-bonding
- Equivalent to the free electron + crystal potential view
- Useful to think in terms of tight binding when orbitals are localized tightly around atomic cores (e.g. *d* or *f* orbitals in TM or RE ions) while it is useful to think in terms of free electron like band when orbitals are extended (e.g. *s* or *p* orbitals)

Principle of Tight Binding Method

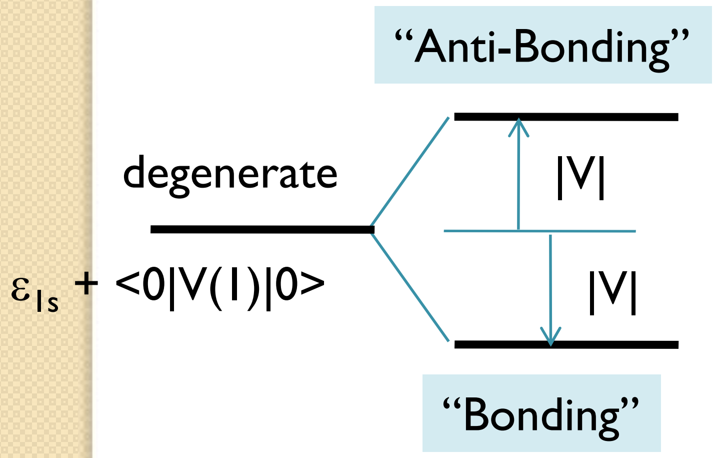
- Construct Wannier function from atomic orbitals
- To be precise in general, we need an infinite number of atomic orbitals
- Approximately, though, one can take a few atomic orbitals
- By choice, the matrix to diagonalize for each k has dimensions N x N, where N = sum of the number of atomic orbitals considered per each atom of the primitive basis

Practical Tight Binding Method

Fit the observed or the calculated band structure in order to encapsulate physics in simple terms

Simple Example of Tight Binding Method

- Consider only 1s orbitals for 1D crystal of hydrogen (hypothetical crystal – actually useful "toy model" for investigating transition metal or rare earth compounds)
- First consider a hydrogen molecule



"Anti-Bonding"

degenerate

ε_{1s} + <0|V(1)|0>

|V|

|V|

"Bonding"

V real negative

|0> -|1>

|0> +|1>

|0> : 1s wave function on one hydrogen atom

|1>: 1s wave function on the other hydrogen atom

V: Off-diagonal element of Hamiltonian

V = ε_{1s} <0|1> + <0|V(1)|1>

V(1) = Coulomb potential from proton of hydrogen 1

Simple and Useful Picture

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Actual Solution of the 1s Tight Binding Model in 1D

$\varepsilon_k = \varepsilon_{1s} - 2\beta - 2t \cos(ka)$

$\beta = -\langle 0| V(1) |0\rangle$

$t = -\langle 0|V(1)|1\rangle$

$\langle 0|1\rangle$ is approximated as 0

This form is consistent with the consideration of the previous slide.

Bare Bone Tight Binding of H 1s

$H = T + V$ V: periodic pot.

$$|\psi\rangle = \sum_n e^{ikna} |n\rangle$$

$\langle n|H|n\rangle \equiv \varepsilon$ (throw in atomic energy -2β and so on)

$\langle m|H|n\rangle = -t$ if $m - n = \pm 1$

(keep nearest neighbor only)

t is called a "hopping" matrix element

$\langle m|n\rangle = \delta_{mn}$ (somewhat of a over-simplification but an often-used approx)

$$H\,|\psi\rangle = \varepsilon_k\,|\psi\rangle$$

$$\Downarrow \qquad\qquad \Rightarrow$$

$$\langle m|H|\psi\rangle \qquad\qquad e^{ikna}\,\varepsilon_k$$

$$\boxed{\varepsilon_k = \varepsilon - 2t\cos ka}$$