PHYS 551 Lecture #27

Title: Tight-Binding

Now that we have shown that $\psi(\vec{k},\vec{r}) = \Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\phi_A(\vec{r}-\vec{R})$ satisfies the Bloch condition, all that remains is to grind through the Schrödinger equation. While the "short-hand" formalism is compact, it may be useful to do the calculation explicitly. First, the wave-function $\psi(\vec{k},\vec{r})$ must be normalized. Thus

$$\begin{aligned}\int \psi^*\psi\, dV &= 1 \\ &= |\Gamma|^2 \sum_R \sum_{R'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \int \phi_A^*(\vec{r}-\vec{R}')\phi_A(\vec{r}-\vec{R})dV\end{aligned}$$

Now for each $\vec{R}'$, the sum over $\vec{R}$ *must* be the same since the crystal has the same distribution of neighbors for all sites. Thus, choose $\vec{R}'$=0 and scale by N, for the number of sites.

$$\int \psi^*\psi\, dV = 1 = N|\Gamma|^2 \sum_R e^{i\vec{k}\cdot\vec{R}} \int \phi_A^*(\vec{r})\phi_A(\vec{r}-\vec{R})\, dV$$

Let us definite a function, (the overlap integral)

$$B(\vec{R}) \equiv \int \phi_A^*(\vec{r})\phi_A(\vec{r}-\vec{R})dV$$

Now

$$1 = N|\Gamma|^2 \sum_R e^{i\vec{k}\cdot\vec{R}} B(\vec{R})$$

So

$$|\Gamma| = \left[N\sum_R e^{i\vec{k}\cdot\vec{R}} B(\vec{R})\right]^{-1/2} \quad \text{and} \quad B(0) = 1$$

(this is just the $\phi_A^*\phi_A$ term)

Since atomic orbitals have exponential decays far from the atom, $B(\vec{R})_{\vec{R}\neq 0} << B(0)$ and so we can assume $B(\vec{R}\neq 0) \approx 0$.

Now substitute $\psi(k,r)$ into the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(\vec{r})\psi = E(\vec{k})\psi$$

or

$$
\begin{aligned}
-\frac{\hbar}{2m}\Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\nabla^2\phi_A(\vec{r}-\vec{R}) &+ U(\vec{r})\Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\phi_A(\vec{r}-\vec{R}) \\
&= E(k)\Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\phi_A(\vec{r}-\vec{R})
\end{aligned}
$$

Notice that ϕ_A already satisfies the Schrödinger equation. So:

$$
\begin{aligned}
\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\left[E_a - U_a(\vec{r}-\vec{R})\right]\phi_A(\vec{r}-\vec{R}) &+ U(\vec{r})\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\phi_A(\vec{r}-\vec{R}) \\
&= E(k)\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\phi_A(\vec{r}-\vec{R})
\end{aligned}
$$

Grouping terms gives:

$$
\begin{aligned}
\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}[U(\vec{r}) - U_a(\vec{r} &- \vec{R})]\phi_A(\vec{r}-\vec{R}) \\
&= (E(\vec{k}) - E_a)\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\phi_A(\vec{r}-\vec{R})
\end{aligned}
$$

Now multiply by ψ^* and integrate:

$$
\begin{aligned}
\sum_{\vec{R}'}\sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\int & dV\left[U(\vec{r}) - U_A(\vec{r}-\vec{R})\right]\phi_A^*(\vec{r}-\vec{R}')\phi_A(\vec{r}-\vec{R}) = \\
(RHS) &= (E(\vec{k}) - E_a)\sum_{R'}\sum_{R}\int dV e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\phi_A^*(\vec{r}-\vec{R}')\phi_A(\vec{r}-\vec{R})
\end{aligned}
$$

Now we can again set $\vec{R}' = 0$ and substitute N for the right hand side.

$$
RHS = (E(\vec{k}) - E_a)N\sum_{R} e^{i\vec{k}\cdot\vec{R}}\int dV\phi_A^*(\vec{r})\phi_A(\vec{r}-\vec{R})
$$

$$
RHS = (E(\vec{k}) - E_a)|\Gamma|^{-2}
$$

So,

$$
E(\vec{k}) = E_a + |\Gamma|^2\left[N\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\int dV[U(\vec{r}) - U_A(\vec{r}-\vec{R})]\phi_A^*(\vec{r})\phi_A(\vec{r}-\vec{R})\right]
$$

Let $A(\vec{R}) \equiv -\int dV\,\phi_a^*(\vec{r})[U(\vec{r}) - U_A(\vec{r}-\vec{R})]\phi_a(\vec{r}-\vec{R})$

And now

$$E(\vec{k}) = E_A - N|\Gamma|^2 \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} A(\vec{R})$$

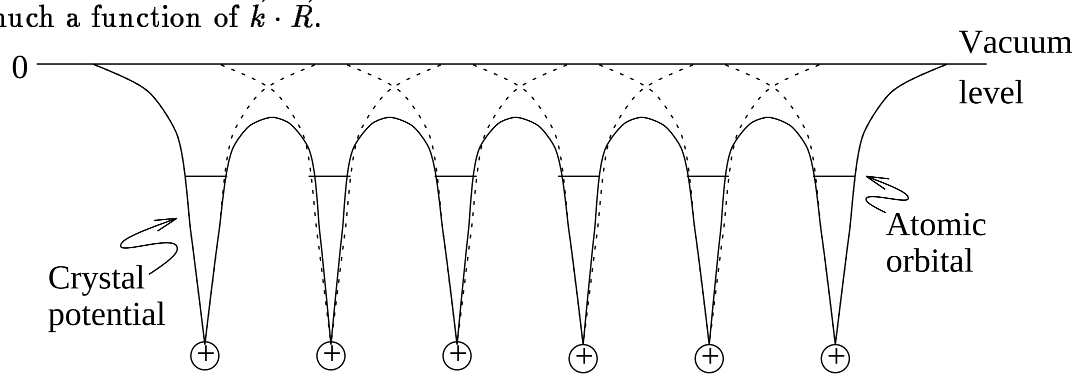
or (assuming $B(0) \approx 0$ and $B(\vec{R} \neq 0) = 0$)

$$\boxed{E(\vec{k}) = E_A - \frac{\sum_R e^{i\vec{k}\cdot\vec{R}} A(\vec{R})}{\sum_R e^{i\vec{k}\cdot\vec{R}} B(\vec{R})} \approx E_A - \sum_R e^{i\vec{k}\cdot\vec{R}} A(\vec{R})}$$

$$\text{If } \vec{R} = 0, \quad E(\vec{k}) = E_A - \underbrace{\int dV\,\phi_a^*(\vec{r})[U_A(\vec{r}) - U(\vec{r})]\phi_a(\vec{r})}_{\alpha} - \sum_{R}^{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} A(\vec{R})$$

Notice: Since $U_A(\vec{r}) > U(\vec{r})$, α is POSITIVE and thus the energy is lowered! Also notice the lack of E($\vec{k}$) dependence in the first two terms. In order to observe the dispersion, we must include at least one more term.

The A($\vec{R} \neq 0$) are once again overlap integrals. The sign of A($\vec{R} \neq 0$) $e^{i\vec{k}\cdot\vec{R}}$ is very much a function of $\vec{k} \cdot \vec{R}$.



Examining $\vec{k} = 0$: $e^{i\vec{k}\cdot\vec{R}} = 1 \qquad A(\vec{R}) > 0$!

$$E(0) = E_A - \alpha - \sum_{R}^{R\neq 0} A(\vec{R}), \text{ Energy is at a maximum}$$

$$\vec{k} \cdot \vec{R} = \pi \quad e^{i\vec{k}\cdot\vec{R}} = -1$$

$$E(0) = E_A - \alpha + \sum_{R}^{R\neq 0} A(\vec{R}), \text{ Energy is at a maximum}$$

Thus the crystal has formed a band; small orbital overlaps give “weak” dispersion, large overlaps give “strong” dispersion.

EXAMPLE: Tight-Binding in a cubic lattice with a one atom basis. Assume $\phi_A(\vec{R})$ is real and s-like. Also assume $A(\vec{R})$ is zero except at nearest neighbors, $\pm a\hat{x}, \pm a\hat{y}, \pm a\hat{z}$. Since the wave-function is spherically symmetric $A(\vec{R})$ has the same magnitude for all neighbor pairs. Let $A(\vec{R}) \equiv A$

So

$$E(\vec{k}) = E_a - \alpha - A\left[e^{ik_x \cdot a} + e^{-ik_x \cdot a} + e^{ik_y \cdot a} + e^{-ik_y \cdot a} + e^{ik_z \cdot a} + e^{-ik_z \cdot a}\right]$$

$$E(\vec{k}) = E_a - \alpha - 2A\left[cos\ k_y a + cos\ k_y a + cos\ k_z a\right]$$

At $k = 0,\ E(0) = E_a - \alpha - 6A$

At $k = \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right),\ E\left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right) = E_a - \alpha + 6A$

Thus the band-width (top to bottom) $= 12A$

If $|\vec{k}|$ small, then

$$cos\ k_x a \approx 1 - \frac{(k_x a)^2}{2}, ...$$

so

$$E(k) \approx E_a - \alpha - 2A\left[3 - \frac{a^2}{2}(k_x^2 + k_y^2 + k_z^2)\right]$$

$$E(k) \approx E_a - \alpha - 6A + Aa^2k^2 \quad \propto k^2$$

Typically $Aa^2 < \frac{\hbar^2}{2m_e}$, so the electrons behave as if they were extremely massive

$$\boxed{\frac{1}{m^*} = \frac{2Aa^2}{\hbar^2}} \quad |\vec{k}| \text{ small, near zone center}$$