Molecular wave functions

Lowest energy is \( k = 0 \).

\[
|\Psi_{k=0}\rangle = A \sum_{\ell=1}^{N} e^{i\ell a} |\ell\rangle = A \left[ |1\rangle + |2\rangle + |3\rangle + |4\rangle + \cdots \right]
\]

"Envelope" is constant.

\[
|\Psi_{k=0}\rangle = A \sum_{\ell=1}^{N} e^{i\ell a} |\ell\rangle
\]

Highest energy is \( k = \pi/a \).

\[
|\Psi_{k=\pi/a}\rangle = A \sum_{\ell=1}^{N} e^{i\ell a} |\ell\rangle = A \left[ |1\rangle - |2\rangle + |3\rangle - |4\rangle + \cdots \right]
\]

"Envelope" with wavelength \( \lambda = 2a \).

Others are complex. e.g. \( k = \pi/2a \).

\[
|\Psi_{k=\pi/2a}\rangle = A \sum_{\ell=1}^{N} e^{i\ell a} |\ell\rangle = A \left[ |1\rangle + |2\rangle - |3\rangle - |4\rangle + \cdots \right] + iA \left[ |1\rangle - |3\rangle + |5\rangle + \cdots \right]
\]

\[
|\Psi_{k=\pi/2a}\rangle = A \sum_{\ell=1}^{N} e^{i\ell a} |\ell\rangle = A \left[ |1\rangle - |3\rangle + |5\rangle - \cdots \right] + iA \left[ |2\rangle - |4\rangle + |6\rangle + \cdots \right]
\]

\[
Re \ |\Psi_{k=\pi/2a}\rangle
\]

Im \ |\Psi_{k=\pi/2a}\rangle

Non-zero only on even wells.
\[ A = \frac{2\pi}{k} \] is the wavelength of the envelope modulating the sequence of wavefunctions. 

\[ \tilde{k} \] is called the "crystal momentum."

Despite the tight-binding approximation, electrons are free to move throughout the metal!

To understand conductors vs. insulators, look at many-electron systems - soon.

**Bloch's theorem**

A periodic potential obeys \( V(x + a) = V(x) \) for some spacing \( a \).

\[
V(x) \\
\hline
\begin{array}{c}
\text{a} \\
\end{array}
\]

Define translation operator \( T_a : T_a \psi(x) = \psi(x + a) \).

Now \( [T_a, V(x)] \psi(x) \triangleq T_a (V(x) \psi(x)) - V(x) T_a \psi(x) \)

\[
= (V(x + a) - V(x)) \psi(x + a)
\]

For periodic potential, \( [T_a, V(x)] = 0 \)

\( \rightarrow [T_a, H] = 0 \). Compatible!

Can choose simultaneous eigenvectors:

\( H \psi(x) = E \psi(x) \) and \( T_a \psi(x) = \psi(x + a) = \lambda \psi(x) \).

Note if \( \psi = e^{iKx} \), \( \psi(x + a) = e^{iK(a + x)} = e^{iK(x + a)} \).
Can multiply $e^{ikx}$ by periodic $u(x)$. So Bloch's theorem says for periodic potentials,

$$u(x) = e^{ikx} u(x) \quad \text{with} \quad u(x+n) = u(x) \text{ periodic.}$$

Alternate statement of theorem: for energy eigenstate,

$$u(x+n) = e^{ikx} u(x).$$

For periodic boundary conditions,

$$u(x+Na) = u(x) \Rightarrow e^{iNKa} = 1$$

$$|K = \frac{2\pi n}{Na}|, \quad n \in \mathbb{Z}.$$ 

Trivial limiting case: $V=0$ (it's periodic!)

Then $u = \text{const}$, $u(x) = e^{ikx}$ (plane wave)

$K$ is envelope modulating periodic function, as before.

Probability density doesn't see envelope:

$$\rho(x) = |u(x)|^2 = |u(x)|^2.$$

Prob current $J = \frac{hK}{m} |u|^2$

Crystal momentum gives probability flow.