Electron in the presence of two ions.

Consider an electron in one dimension in the presence of two positive ions. There are two levels of crude approximations to this:

**Crudest:** double infinite well

![Diagram of infinite well](image1)

**Better:** double finite well

![Diagram of finite well](image2)

The energies can be determined exactly. The two lowest energy eigenfunctions are:

- \( \psi_{\text{sym}}(x) \)
- \( \psi_{\text{antisym}} \)

The energy is:

\[
E_n = \frac{\hbar^2 n^2}{2ma^2}
\]

where \( n = 1, 2, 3, \ldots \)

The energies have to be obtained by numerical solution. The two lowest energy eigenfunctions are:

- \( \psi_{\text{sym}} \)
- \( \psi_{\text{antisym}} \)

Energy needs to be calculated numerically.
One can compare the energy for a single finite well to that of the states for a double finite well.

**Example:** Consider wells of width $a$. For a single well, the energy is:

<table>
<thead>
<tr>
<th>Level</th>
<th>Infinite</th>
<th>Finite with $V_0=100$  ( \frac{\hbar^2 \pi^2}{2ma^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n=1$</td>
<td>(\frac{\hbar^2 \pi^2}{2ma^2})</td>
<td>(\frac{\hbar^2 \pi^2}{2ma^2}) 0.883722</td>
</tr>
<tr>
<td>$n=2$</td>
<td>(4\frac{\hbar^2 \pi^2}{2ma^2})</td>
<td>(\frac{\hbar^2 \pi^2}{2ma^2}) 3.5329722</td>
</tr>
</tbody>
</table>

Now for double wells whose $b = 0.1a$ (energies in units of $\frac{\hbar^2 \pi^2}{2ma^2}$):

<table>
<thead>
<tr>
<th>Level</th>
<th>Infinite</th>
<th>Finite with $V_0=100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n=1$ symmetric</td>
<td>1</td>
<td>0.87892 (\text{difference}) 0.00918</td>
</tr>
<tr>
<td>$n=1$ antisym</td>
<td>1</td>
<td>0.88816</td>
</tr>
<tr>
<td>$n=2$ symmetric</td>
<td>4</td>
<td>3.5132 (\text{difference}) 0.0380</td>
</tr>
<tr>
<td>$n=2$ antisymmetric</td>
<td>4</td>
<td>3.5512</td>
</tr>
</tbody>
</table>

Observe that there is no change with the infinite square wells other than that there are two states per energy level. For the finite square well, there are two distinct energy levels for each $n$. Also notice that the splitting increases as $n$ increases.
One can plot the energy levels:

Single

\[
\begin{align*}
3.532972 & \quad \text{anti} \quad \{ n=2 \} \\
0.88392 & \quad \text{sym} \quad \{ n=1 \}
\end{align*}
\]

Double

\[
\begin{align*}
3.5512 & \quad \text{anti} \quad \{ n=2 \} \\
3.5132 & \quad \text{sym} \quad \{ n=1 \}
\end{align*}
\]

Now consider three ions. In the crudest approximation there are three distinct orthogonal states, each with the same energy.

A similar situation applies when the wells are finite, except that the three states have distinct energies:

\[
\begin{align*}
\text{single well} & \quad \text{3 wells} \\
n=2 & \quad \{ n=2 \} \\
n=1 & \quad \{ n=1 \}
\end{align*}
\]

\[
\text{symmetric} \quad \text{symmetric} \quad \text{antisymmetric}
\]
Increasing the number of wells increases the splitting. Thus $n=1$ splits into a band of many, closely spaced levels. Similarly $n=2$ splits but with a larger range than $n=1$. This is the origin of energy bands.

**Energy Eigenstates in a Periodic Potential.**

In general a three dimensional lattice of ions interacts with electrons via a potential $V(\vec{r})$. However, there is one crucial requirement:

$V(\vec{r})$ must be invariant under shifts in $\vec{r}$ by any lattice vector. So

$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

where $\vec{R}$ is any lattice vector.

**Example**: Consider a one dimensional lattice with spacing $a$. Then for a Coulomb interaction

Clearly $V(x+a) = V(x)$

$V(x+2a) = V(x)$

$V(x-a) = V(x)$
We expect that this will have implications for the wave functions corresponding to energy eigenstates. These satisfy the time-independent Schrödinger equation:

\[-\frac{\hbar^2}{2m} \nabla^2 \Psi(x) + V(x) \Psi(x) = E \Psi(x)\]  

What are the implications of the fact that \( V(x) = V(x+a) \)?

Consider a one-dimensional potential with lattice constant \( a \). Then:

\[-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) = E \Psi(x)\]

Now let \( x' \) be defined as:

\[x' = x - a.\]

\[\Rightarrow x = x' + a.\]

Now:

\[\frac{d \Psi(x)}{dx} = \frac{d \Psi(x'+a)}{dx} = \frac{dx'}{dx} \frac{d \Psi(x'+a)}{dx'} = \frac{d \Psi(x'+a)}{dx'}\]

Thus:

\[-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x'+a)}{dx'^2} + V(x'+a) \Psi(x'+a) = E \Psi(x'+a)\]

\[\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2 \Psi(x'+a)}{dx'^2} + V(x') \Psi(x'+a) = E \Psi(x'+a).\]

But we can drop the prime (it just labels the variable). Thus:

\[-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x+a)}{dx^2} + V(x) \Psi(x+a) = E \Psi(x+a)\]
So, now we have shown that

\[ \psi(x) \text{ is an eigenstate with energy } E \]
\[ \Rightarrow \psi(x+a) \text{ is an eigenstate with energy } E. \]

But we can iterate this to give:

\[ \psi(x) \text{ is an eigenstate with energy } E \]
\[ \Rightarrow \psi(x+na) \text{ is an eigenstate with energy } E \]

where \( n \) is any integer.

Finally we can translate this as:

\[ \psi(\vec{r}) \text{ is an eigenstate with energy } E \]
\[ \Rightarrow \psi(\vec{r}+\vec{R}) \text{ is an eigenstate with energy } E \]

provided \( \vec{R} \) is a lattice vector.

Thus each energy level is vastly degenerate:

<table>
<thead>
<tr>
<th>Energy</th>
<th>Wavefunctions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_2 )</td>
<td>( \psi_2(\vec{r}+\vec{R}) ) for all lattice vectors ( \vec{R} )</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>( \psi_1(\vec{r}+\vec{R}) ) for all lattice vectors ( \vec{R} )</td>
</tr>
</tbody>
</table>
Next, we aim to relate \( \Psi(\vec{R}) \) to \( \Psi(\vec{R} + \vec{R'}) \). Such a relationship reflects purely geometrical considerations. There is also some choice in the wavefunction \( \Psi(\vec{R}) \) which can simplify the arguments. General mathematical considerations regarding symmetries in quantum mechanics imply that we can always find \( \Psi(\vec{R}) \) such that

\[
\Psi(\vec{R} + \vec{R'}) = c(\vec{R}) \Psi(\vec{R})
\]

where \( |c(\vec{R})| = 1 \).

**Exercise:** Show that \( c(\vec{R} + \vec{R'}) = c(\vec{R}) c(\vec{R'}) \) for all lattice vectors \( \vec{R}, \vec{R'} \)

**Answer:**
\[
\Psi(\vec{R} + \vec{R'}) = c(\vec{R} + \vec{R'}) \Psi(\vec{R}) = c(\vec{R}) c(\vec{R'}) \Psi(\vec{R})
\]

\[
\Rightarrow c(\vec{R} + \vec{R'}) = c(\vec{R}) c(\vec{R'}) = c(\vec{R}) c(\vec{R'})
\]

**Exercise:** Suppose that \( \vec{a}_1, \vec{a}_2, \vec{a}_3 \) are lattice vectors. Then \( \vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \)

Show that

\[
c(\vec{R}) = c(\vec{a}_1)^{n_1} c(\vec{a}_2)^{n_2} c(\vec{a}_3)^{n_3}
\]

**Answer:** This follows from the previous exercise.

Now since \( |c(\vec{a}_i)| = 1 \) we have
\[
c(\vec{a}_1) = e^{i x_1 2\pi}
\]
\[
c(\vec{a}_2) = e^{i x_2 2\pi}
\]
\[
c(\vec{a}_3) = e^{i x_3 2\pi}
\]

where \( x_1, x_2, x_3 \) are real. Thus:

\[
c(\vec{R}) = e^{i 2\pi (n_1 x_1 + n_2 x_2 + n_3 x_3)}
\]
But

\[ 2\pi \left( n_1 x_1 + n_2 x_2 + n_3 x_3 \right) = \mathbf{R} \cdot (\mathbf{a}_1^* + \mathbf{a}_2^* + \mathbf{a}_3^*) \]

where \( \mathbf{a}_i^* \) are the reciprocal lattice vectors. Letting \( \mathbf{E} = x_1 \mathbf{a}_1^* + x_2 \mathbf{a}_2^* + x_3 \mathbf{a}_3^* \)
we get:

\[ c(\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \]

and finally this gives:

\[ \Psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \Psi(\mathbf{r}) \quad - (3) \]

where \( \mathbf{R} \) is any lattice vector. This is one form of Bloch's theorem.

Notice that \( e^{i\mathbf{k} \cdot \mathbf{R}} \) is a global phase factor. Thus the physical predictions will not be altered by transla
ing through \( \mathbf{R} \), since \( |\Psi(\mathbf{r})|^2 \)
will be unaltered.

Example: One dimension: Let \( \Psi(x) = e^{ikx} \sin \left( \frac{2\pi x}{a} \right) \) where \( a \) is the
lattice constant. Verify that this satisfies (3), plot \( |\Psi(w)|^2 \) vs \( x \)
and \( |\Psi(x+na)|^2 \) vs \( x \).

Answer: \( \mathbf{r} + \mathbf{R} \sim x + na \) for any integer \( n \). Then:

\[ \Psi(x+na) = e^{ikx} e^{i nak} \sin \left( \frac{2\pi}{a} (x+na) \right) \]

\[ = e^{ikx} e^{i nak} \sin \left( \frac{2\pi x}{a} \right) \]

\[ = e^{i nak} \Psi(x) \]

\[ \sim e^{i\mathbf{k} \cdot \mathbf{R}} \]
Then \( |\psi(x)|^2 = \sin^2 \left( \frac{2\pi x}{a} \right) \)

\[ |\psi(x+a)|^2 = \sin^2 \left( \frac{2\pi x}{a} \right) \]

give the same probability densities.

Now, we can define:

\[ u(\vec{r}) = e^{-i\vec{k} \cdot \vec{r}} \psi(\vec{r}) \] \hspace{1cm} -(4)

Then

\[ u(\vec{r} + \vec{R}) = e^{-i\vec{k} \cdot \vec{R}} e^{-i\vec{k} \cdot \vec{r}} \psi(\vec{r} + \vec{R}) \]

\[ = e^{-i\vec{k} \cdot \vec{r}} \psi(\vec{r}) = u(\vec{r}) \]

Thus we arrive at Bloch's theorem:

In a periodic potential \( V(\vec{r} + \vec{R}) = V(\vec{r}) \) for any lattice vector \( \vec{R} \), the energy eigenstates have form:

\[ \psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u(\vec{r}) \] \hspace{1cm} -(5)

where \( u(\vec{r} + \vec{R}) = u(\vec{r}) \) for all lattice vectors.